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PROGRESS SERIES

METAL PHYSICS

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PROGRESS IN METAL PHYSICS

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Editors

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FOREWORD

THE newer branches of science generally develop at the points of contact of the older disciplines and in the fringe areas between science and technology; the union between physics and metallurgy has been particularly fruitful and has resulted in the growth of the now distinct study of Metal Physics. Because of the hybrid pedigree of this new branch of science, original publications relating to it are appearing in a very large number of different journals, and because of its recent origin it is sometimes difficult to digest the new material as it appears.

Experience in the more rapidly developing branches of science has shown that no individual can read, appraise and assimilate all the papers that are of interest to him, and it is found that the necessary perspective on a topic can usually be most efficiently realized by the aid of a review prepared by someone who is himself active in that particular field. The purpose of the series, of which this is the fifth volume, is to provide such reviews in the general area of the Physics of Metals. It is the hope of the Editors that all the significant aspects of the subject will be discussed and that those that are advancing rapidly will be reviewed at appropriate intervals.

B. CHALMERS and R. KING

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1

THE FRACTURE OF METALS

N. J. Petch

THE basic problem in fracture is to find some factor that will account for the order of magnitude difference between the theoretical, and the observed strengths of real solids.

The theoretical strength, first estimated from the molecular attraction term in the Van der Waals equation, is most readily obtained from the surface energy (POLANYI,⁽¹⁾ OROWAN,⁽²⁾ SEITZ and READ⁽³⁾). Fig. 1

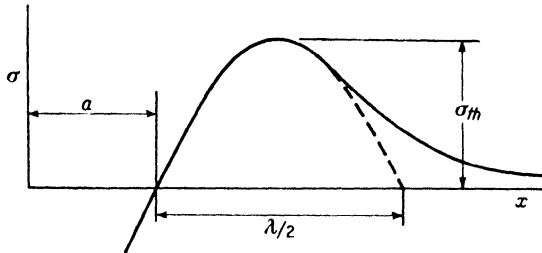


Fig. 1. The interatomic force as a function of spacing

shows how the cohesive force between atoms varies with their separation and the initial part of this curve can be approximately represented by

$$\sigma = \sigma_{th} \sin (2\pi x/\lambda) \quad . \quad . \quad . \quad (1)$$

where σ_{th} is the maximum stress that must be applied to pull the atoms apart (the theoretical strength).

The work done per unit area during fracture is then approximately given by

$$\int_0^{\lambda/2} \sigma_{th} \sin (2\pi x/\lambda) \cdot dx = \lambda \sigma_{th} / \pi$$

This work appears after fracture as the surface energy $2S$ of the two new surfaces produced. Thus,

$$\sigma_{th} = 2\pi S/\lambda \quad . \quad . \quad . \quad (2)$$

For the initial part of the curve, HOOKE'S law gives

$$\sigma = Ex/a$$

where E is Young's Modulus, and, since $\cos (2\pi x/\lambda) \sim 1$ in this part,

$$d\sigma/dx = 2\pi \sigma_{th}/\lambda$$

Therefore,

$$2\pi\sigma_{th}/\lambda = E/a$$

and in equation (2)

$$\sigma_{th} = \left(\frac{ES}{a}\right)^{\frac{1}{2}} \quad . \quad . \quad . \quad (3)$$

Common values of E , S and a are 10^{11} dynes/cm², 10^3 ergs/cm² and 3×10^{-8} cm., and in equation (3) these values give

$$\sigma_{th} = 10^{11} \text{ dynes/cm}^2 \text{ (} 10^6 \text{ lb/in.}^2 \text{)}$$

More detailed calculations on ionic crystals indicate substantially similar values (ZWICKY,⁽⁴⁾ BORN and FURTH⁽⁵⁾). These theoretical strengths are about 10–1000 times greater than the observed values.

The existence of this divergence is really apparent in brittle solids without calculation. HOOKE'S law holds up to fracture, whereas there would be considerable deviation from this if the theoretical strength were approached (Fig. 1); also, the strain at fracture would greatly exceed the observed values of less than 1 per cent.

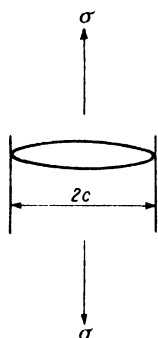


Fig. 2. The Griffith crack

THE GRIFFITH THEORY

The attempt to bridge the gap between the theoretical and observed strengths dates from the classical work of GRIFFITH⁽⁶⁾ (1920, 1924) on the fracture of glass. He postulated the presence of cracks at which there is a stress concentration of sufficient magnitude that the theoretical strength can be generated locally from quite low mean stresses.

GRIFFITH considered the case of a flat plate of uniform thickness containing a crack of elliptical cross-section and width $2c$ (Fig. 2) that extended right through the plate, and for the formulation of his theory he used an energy argument.

The INGLIS⁽⁷⁾ solution for the stresses and strains around such a crack when subjected to a principal tensile stress σ normal to the plane of the crack (the other principal stresses then lying in this plane) was used to calculate the strain energy due to the presence of the crack. This term is negative, since there is a relief of strain energy.

For plane stress (thin plates),

$$\text{strain energy} = -\pi c^2 \sigma^2 / E$$

per unit plate thickness.*

* ZENER⁽⁸⁾ has given a simple estimate of this. The strain energy will be relieved in a volume that is approximately that generated by revolution of the crack. This gives $-\pi c^2 \sigma^2 / 2E$.

The corresponding surface energy associated with the crack is

$$\text{surface energy} = 4cS$$

The crack will spread under the influence of the tensile stress only if the decrease in strain energy is greater than the increase in surface energy. Thus, the equilibrium size of the crack under σ is given by

$$\begin{aligned} \frac{d}{dc} (4cS - \pi c^2 \sigma^2 / E) &= 0 \\ 4S - 2\pi \sigma^2 c / E &= 0 \end{aligned}$$

Hence,

$$\sigma = \left(\frac{2ES}{\pi c} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (4)$$

The crack can spread if this stress is exceeded, so equation (4) gives the fracture stress σ_c in the presence of the crack.

It will be noticed that c increases as the crack spreads, so that the stress required to maintain spreading decreases.

The corresponding expression for plane strain (thick plate) is

$$\sigma_c = \left(\frac{2ES}{(1 - \nu^2)\pi c} \right)^{\frac{1}{2}}$$

where ν is Poisson's ratio.

SACK⁽⁹⁾ has extended this treatment to a very flat, oblate ellipsoidal crack (a penny shape) and the expression obtained for the fracture stress,

$$\sigma_c = \left(\frac{\pi ES}{2(1 - \nu^2)c} \right)^{\frac{1}{2}} .$$

only differs from GRIFFITH'S by a numerical factor.

The strength of a body containing a crack can also be treated directly in terms of the stresses.^{(6), (10)} The highest tensile stress (which occurs at the end of the major axis) is given by

$$\sigma_{\max} = 2\sigma \left(\frac{c}{\rho} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (5)$$

where ρ is the radius of curvature at the end of the crack (INGLIS⁽⁷⁾). The value of ρ for the sharpest possible crack will be of the order of magnitude of the atomic spacing a . Substituting a for ρ in equation (5) and using the theoretical strength from equation (3), the fracture strength is obtained as

$$\sigma_c = \left(\frac{ES}{4c} \right)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (6)$$

ELLIOTT⁽¹¹⁾ has given a more detailed treatment in terms of the inter-atomic forces and actual atomic positions at the edge of the crack, but

again the results only differ from those of GRIFFITH and SACK by small numerical factors.

Thus, there is agreement on the form of the expression that gives the strength of a body containing a crack when that body behaves elastically up to fracture. Comparison with the observed strength of glasses containing artificial cracks is satisfactory.⁽⁸⁾

Table 1 gives the size of the cracks required to explain some observed strengths as calculated from equation (4). It will be seen that for glass and strong polycrystalline metals the crack width is quite small, a few thousand atoms,

TABLE 1
The Size of the Griffith Cracks

<i>Material</i>	σ_c <i>dynes/cm²</i>	<i>S</i> <i>ergs/cm²</i>	<i>E</i> <i>dynes/cm²</i>	<i>c</i> <i>cm</i>
Glass . .	1.8×10^9	210	6.2×10^{11}	2.6×10^{-5}
Fe*† . .	7×10^9	1220	20.5×10^{11}	7.8×10^{-5}
Zn*† . .	1.8×10^7	800	3.5×10^{11}	0.55
NaCl*† . .	2.2×10^7	150	4.9×10^{11}	0.10

but that weak single crystals require large cracks.

THE PHYSICAL NATURE OF THE GRIFFITH CRACKS IN GLASSES

Freshly drawn glass fibres have strengths that approach the theoretical value. GRIFFITH obtained 220,000–900,000 lb/in.² in potash glass fibres of up to 0.02 in. diameter when they were tested within a few seconds of drawing. The strength diminished on standing until after a few hours it reached a steady value that varied between 20,000 and 500,000 lb/in.² as the diameter varied between 0.04 and 0.00013 in.

GRIFFITH suggested that the random molecular configuration existing at the high temperature of drawing was replaced by an ordered configuration during the spontaneous weakening at room temperature and that the local stresses arising from this transformation possibly exceeded the theoretical strength, so producing actual cracks. A concurrent volume change supported the idea of a configurational change.

ANDEREGG⁽¹²⁾ has reported the absence of this spontaneous weakening in the glasses examined by him. However, his measurements were made "within a very few minutes" of preparation and it seems possible that he may have missed the initial fall in strength since his results agree closely with GRIFFITH's steady values (Fig. 3). ANDEREGG did observe a fall in strength (250,000 down to 50,000 lb/in.²) with soda-lime glasses (but not with chemically more-resistant glasses) after alternate

* cleavage fractures, † polycrystalline, ‡ single crystals.

spraying with moisture and drying, and this is consistent with the enlargement of surface cracks by chemical attack.

GRIFFITH found that fused silica only showed spontaneous weakening when it was impure and even then to a lesser degree than glass; however, a weakening did take place on contact with other bodies and he suggested that actual surface cracks were produced under the high stresses set up in a perfectly elastic body by point contact.

An ingenious experiment that has a bearing on the nature of the Griffith cracks is due to OROWAN.⁽¹³⁾ The strength of mica cleavage

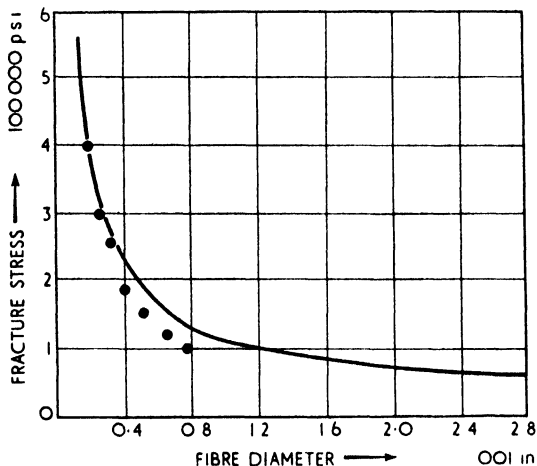


Fig. 3. The relationship between the strength of a glass fibre and its diameter. GRIFFITH⁽⁶⁾ —; ANDEREGG⁽¹²⁾ •

plates, normally about 5×10^4 lb/in.², is increased tenfold to near the theoretical value when test grips are used that leave the edges stress free. This suggests that the normal strength is determined by the damage done to the edges during cleavage. The classical experiments by JOFFÉ,⁽¹⁴⁾ showing the greatly increased strength of rock salt when tested in water, must also be mentioned. These have been interpreted in terms of the removal of surface cracks by solution, but the effect is not entirely simple (SCHMID and BOAS⁽¹⁵⁾).

The toughening of commercial glass articles by the creation of surface compressive stresses indicates that the Griffith cracks are principally located at the surface.

Although there is no definite proof, on the basis of these various observations it seems quite possible that the Griffith cracks in brittle, elastic materials are actual cracks, mainly associated with the surface.

It is understandable that there is no direct visual evidence of the existence of these cracks, since they may be very shallow (10^{-5} cm in

glass) and the separation of the two surfaces may be of atomic dimensions. However, ANDRADE and TSIEN⁽¹⁶⁾ have found that etching glass in sodium vapour develops lines that are possibly associated with Griffith cracks, because freshly drawn specimens give few lines, whereas the number is greatly increased on etching after standing (Plate I). Also, if silver is spluttered on to glass and then heated, coagulation takes place along lines that may be Griffith cracks (ANDRADE and MARTINDALE⁽¹⁷⁾). LAD⁽¹⁸⁾ has made a similar observation on NaCl.

THE TYPES OF METALLIC FRACTURE

The fracture of metals is more complicated than that of completely brittle materials because a number of phenomenologically different fracture mechanisms can occur, and there is also the distinction that fracture is normally preceded by plastic deformation.

The fracture of single crystals of hexagonal magnesium is associated with shear and has been described as shear fracture.⁽¹⁵⁾ Slip takes place on one set of planes and it is eventually replaced by fracture along the same planes, and this fracture may jump from one glide plane to another, so that a rough stepped surface is produced that is oblique to the tension (Plate I). When the initial inclination of the glide plane to the applied stress is less than $\sim 12^\circ$, the fracture passes more or less transversely through the crystal or along a twin plane.

With single crystals of zinc and cadmium, basal glide may be limited by the onset of twinning on (1012) and secondary basal glide then develops in the twins. This produces necking, which continues until the crystal is drawn down to a wedge, and final separation takes place along a line.⁽¹⁵⁾ In this case, the whole process is one of glide and twinning; there is no distinct fracture stage (Plate I).

With cubic metal crystals (Cu,⁽²⁰⁾ Al⁽²¹⁾) glide on one set of planes is eventually succeeded by secondary glide on another set; necking takes place, the crystals draw down to a double wedge, and again there is no definite fracture stage.

At low temperatures, single crystals may fracture by cleavage, producing a bright smooth surface (Plate I). In this case, definite crystallographic planes are involved and these are listed in Table 2 for the principal metals that show cleavage. No f.c.c. metals are known to fracture in this way.

Thus, single metal crystals may fracture by a process associated with shear, by complete glide without a separate fracture stage or by cleavage.

In the tensile testing of polycrystalline metals of moderate ductility (Cu, Al, mild steel), there is first plastic deformation, which is followed by necking, and then fracture eventually begins at the centre of the neck. An increase of strain is necessary to propagate the fracture, and

THE FRACTURE OF METALS

TABLE 2

Cleavage Planes in Crystals⁽¹⁶⁾

<i>Material</i>	<i>Lattice Type</i>	<i>Cleavage Plane</i>	<i>Critical Normal Stress, kg/mm²</i>	<i>Temperature °C</i>	<i>Reference (Normal Stress)</i>
Fe	b.c.c.	(001)	27.6	— 185	(22)
W	„				
Mg	c.p.h.	(0001), (10 $\bar{1}$ 1) (10 $\bar{1}$ 2), (10 $\bar{1}$ 0)			
Zn	„	(0001)	0.18–0.20	— 185	(23) (24)
Bi	rhombohedral-body-centred	(111)	{ 0.32 0.29	+ 20, — 80	(25)
		(11 $\bar{1}$)	0.69	+ 20	(26)
Sb	„	(11 $\bar{1}$)	0.66	+ 20	(26)
		(111), (110)			
As	„	(111), (110)			
Te	Hexagonal	(10 $\bar{1}$ 0)	0.43	+ 20	(27)
NaCl	f.c.c.	(100)	0.22	+ 20	(28)
CaF ₂	fluorite type	(111)	1.5–2.4	+ 20	(29)

the crack gradually opens during this strain and extends in a direction at right angles to the tension (Plate I). Eventually, the mechanism changes and final separation is by shear, thus producing the well-known “cup and cone.” The initial part of this fracture has a matt or fibrous appearance and is variously referred to as a “ductile,” “plastic” or “fibrous” fracture. In it, the crack passes irregularly through the grains. Sometimes there is no fibrous part and fracture takes place entirely by shear at about 45° to the tension. This may occur in cylindrical specimens of magnesium and cold-worked steel, and it is often favoured in plate and sheet specimens, where the strain is two-dimensional.

Some polycrystalline metals (fine-grained Zn, Pb, Au) are sufficiently ductile that cylindrical specimens can draw down to a point and there is no separate fracture stage. In other cases, this complete glide may be possible if thin sheets are used, or if the tensile test is carried out under a superimposed hydrostatic compression.

At low temperatures, the metals that fracture by cleavage in the single crystal state may also cleave in the polycrystalline state. In contrast to plastic fracture, no obvious increase in strain is necessary for crack propagation. Rather similar, are the intercrystalline fractures that may occur at room temperature if there are composition peculiarities at the grain boundaries (“overheating” in steel, temper brittleness).

Heating above room temperature serves merely to increase the ductility of single crystals without altering their fracture mechanism, but with polycrystalline metals at high-temperatures and slow strain rates (creep conditions) fracture becomes intercrystalline.

Under alternating stress, single, and polycrystalline specimens may eventually fracture, although the maximum stress applied is much below that required under static load (fatigue fracture).

The combination of corrosive conditions with a stress affects fracture. With a static stress, cracks arise that are normally intercrystalline (stress-corrosion); with an alternating stress, fatigue failure is accelerated (corrosion-fatigue).

It is apparent that there is a formidable variety in the mechanisms by which metals may fracture.

THE CRITERIA FOR FRACTURE IN METALS

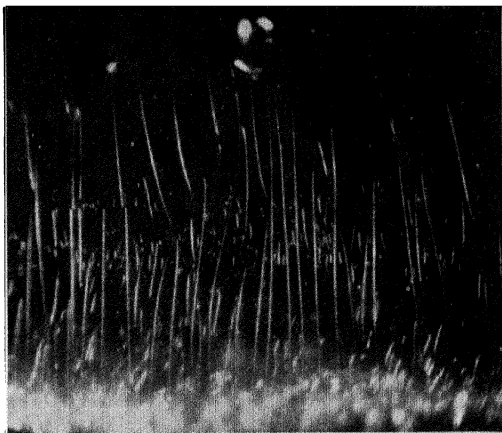
Single Crystals

The shear fracture of magnesium single crystals appears to be determined by a critical shear stress.⁽¹⁵⁾

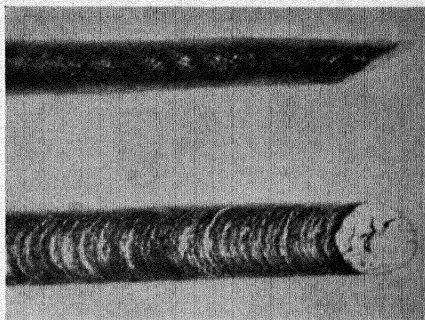
SOHNCKE's law⁽³⁰⁾ (1869), which was based on measurements on rock salt crystals, states that the condition for the cleavage of single crystals is a critical stress normal to the cleavage plane. This does not appear to be exactly true for rock salt crystals and it has not been confirmed in the case of melt-grown KCl or KBr.⁽¹⁵⁾ In the case of metals, SCHMID^{(25), (27), (31)} has found the normal stress law to be obeyed for Bi, Te and Zn over the range of orientation in which there is no change in the indices of the cleavage plane (Fig. 4 and Table 2). Particularly in the case of Zn, some uncertainty arises in the measurements from the varying amounts of strain prior to fracture. The applicability of the law to Zn has recently been denied (GREENOUGH and DERUYTTERRE⁽³²⁾).

Polycrystals

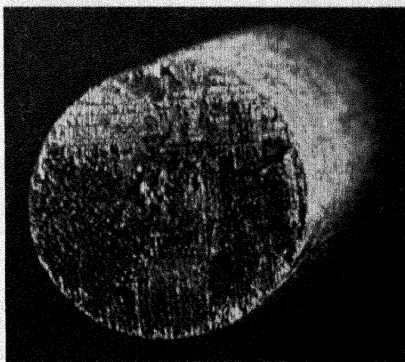
Consideration of the criteria for the fracture of polycrystals dates from the work of LUDWIK⁽³³⁾ (1923), who suggested that the yield stress Y and a critical tensile stress S' were involved (Fig. 5). He assumed that both Y and S' increase with strain, but that Y increases more rapidly and fracture results when Y and S' intersect. Any factor that alters the yield curve may alter the strain at the intersection and so may produce a change from ductility to brittleness. This hypothesis was modified by DAVIDENKOV⁽³⁴⁾ (1936) who pointed out that brittle (cleavage) fracture is phenomenologically distinct from plastic (fibrous) fracture and he therefore suggested the existence of two critical stresses (Fig. 5); S' then refers to cleavage fracture (the cleavage strength) and S refers to plastic fracture and has a negative slope.



(a)



(b)



(c)

Plate I (a) Cracks developed perpendicular to the length in a glass tube etched by sodium vapour,⁽¹⁶⁾ (b) shear fracture in magnesium,⁽¹⁵⁾ (c) cleavage in α -Fe⁽¹⁵⁾

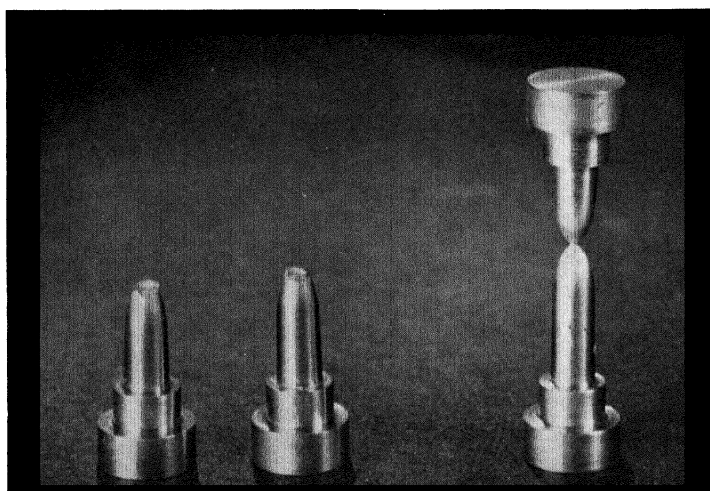
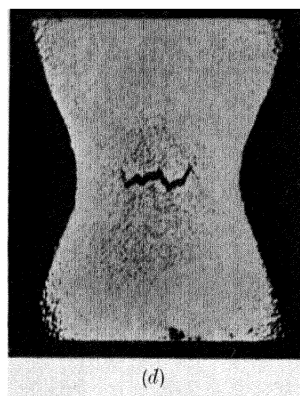


Plate I. (d) Section through the neck of an Al specimen, showing the development of a plastic fracture,⁽⁶⁸⁾ (e) the influence of hydrostatic pressure on ductility⁽⁴¹⁾

THE FRACTURE OF METALS

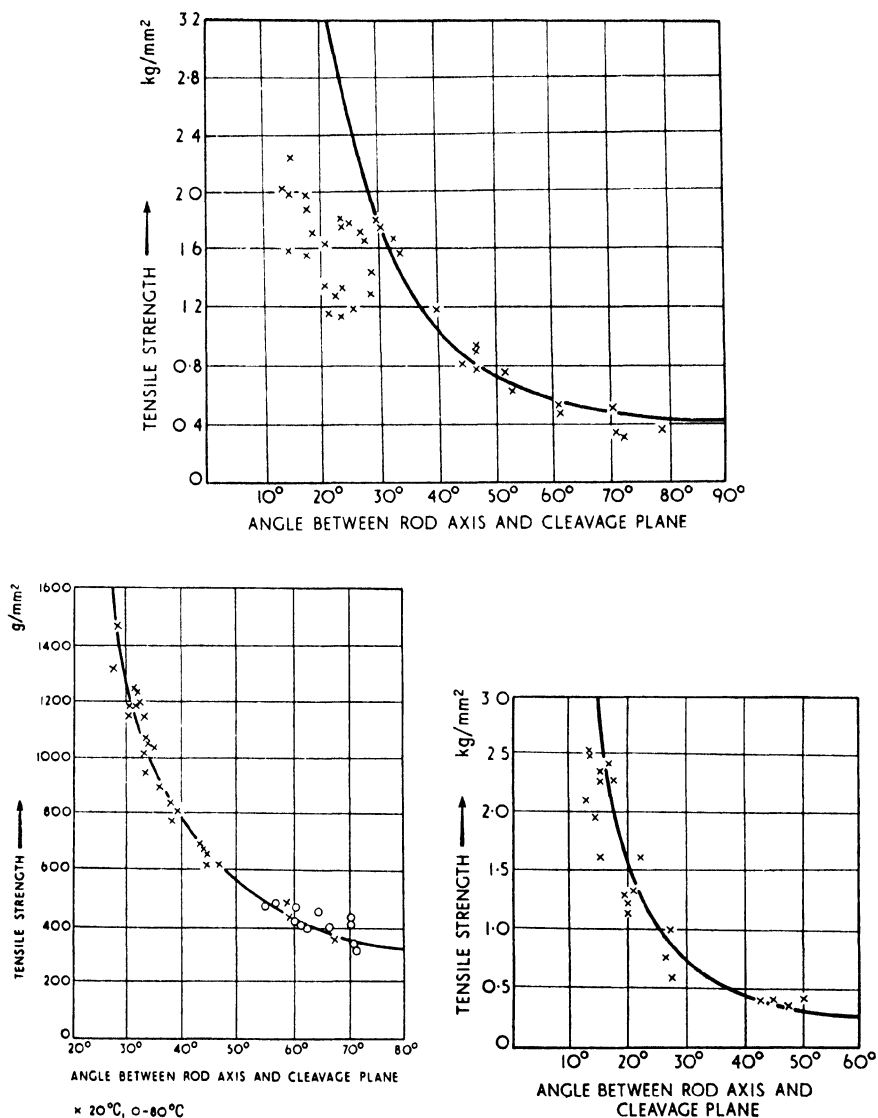


Fig. 4. The cleavage strength of single crystals, (a) $\text{Te}^{(27)}$, (b) $\text{Bi}^{(25)}$, (c) $\text{Zn}^{(23), (31)}$. The points are experimental, the curves are for the constant normal stress law

This supposition of a critical tensile stress for plastic fracture has been opposed (OROWAN, NYE and CAIRNS,⁽³⁵⁾ OROWAN⁽²⁾) on the grounds that a plastic crack in a tensile test piece does not suddenly run across, as in the Griffith-type fracture of glass; instead, once started, a continual increase of strain is necessary to propagate the crack and this propagation can be arrested at any time by arresting the strain. Since this additional plastic deformation at the crack is necessary, a plastic yield condition (which is approximately a critical shear stress, not a critical tensile stress) must be involved and plastic fracture

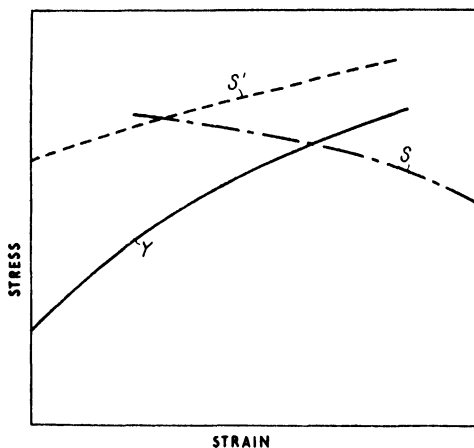


Fig. 5. The Ludwik-Davidenkov criteria of fracture

cannot generally obey a critical tensile criterion. On the other hand, the shear stress cannot alone be a sufficient condition for fracture, because shear stresses higher than those produced in a tensile test can occur in rolling or drawing. That a tensile stress criterion is incorrect for plastic fracture is also shown by experiments on thin discs of soft metal joined over the whole of their flat surfaces to rods of hard metal. This sandwich test-piece can withstand axial tensile stresses a number of times greater than can a test-piece made solely from the soft metal.^{(35), (40)}

Cleavage in polycrystals appears to be simpler, and the assumption of a critical tensile criterion is widely accepted and has been successful in explaining a number of phenomena. However, it remains an assumption and requires some analysis. It seems a reasonable idea that the fracture of a perfect elastic solid under simple tension should involve a critical tensile stress (as assumed in the calculation of the theoretical strength) and that for real elastic solids (glass) the local attainment of the theoretical critical tension should be necessary. It then seems a reasonable possibility that local generation of the theoretical tension is also the condition for cleavage, since cleavage is the nearest that a metal gets to

elastic fracture. Whether this criterion for the local, concentrated stresses means a critical tension when the unconcentrated, applied stresses are considered, or whether the criterion becomes a critical applied shear stress, will depend upon the physical nature of the stress concentrator (the Griffith crack), as will be discussed later in greater detail. At present, it is sufficient to notice that the experimental evidence

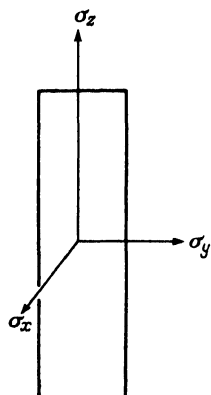


Fig. 6. Triaxial stress

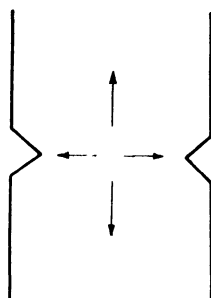


Fig. 7. Stresses in a notch

(ZENER,⁽³⁶⁾ MCADAM⁽³⁷⁾) suggests that shear stresses are involved in the cleavage strength, and this disagrees with the assumption of a critical tensile stress criterion.

More progress has been made in the understanding of cleavage than of the other types of fracture, and for this reason it will be considered in detail in this review.

The Influence of the Stress System

The nature of this system, whether uni-, bi- or tri-axial, has a considerable effect on fracture. At the same time, the axial yield stress is affected, and it is convenient to begin with a consideration of this second feature. In Fig. 6, the greatest shear stress is half the greatest difference between the tensile stresses, say $(\sigma_z - \sigma_x)/2$, so that replacement of a uniaxial tension by a triaxial tension will reduce the shear stress produced by a given σ_z , and the latter will have to be raised, if the same shear stress is to be maintained. Thus, since yielding depends approximately upon a critical shear stress, transverse tension raises the axial yield stress, whereas transverse compression lowers it. Such tension most commonly occurs because of a notch (Fig. 7). Yielding in the notch produces a lateral contraction that is opposed by the unyielding metal outside, so generating the transverse tension, and solution of this plasticity problem shows that the axial yield stress can

be raised in this way to $\sim 3y$, where y is the yield stress under uniaxial tension (PRANDTL,⁽³⁸⁾ HILL⁽³⁹⁾). Transverse compression can arise in forming operations such as rolling and wire drawing.

When the axial yield stress is raised by a notch, plastic fracture occurs at a higher axial stress, but at a lower strain, implying a lower shear stress (MCADAM,⁽³⁷⁾ OROWAN⁽⁴⁰⁾). Conversely, when the axial yield stress is lowered by transverse compression, fracture occurs at a lower axial stress, but at a higher strain, implying a higher shear stress. The higher strain in this second case is very well demonstrated by BRIDGMAN's experiments⁽⁴¹⁾ (Plate I) in which extremely high ductilities are obtained when a tensile test is carried out with a superimposed hydrostatic compression. The sandwich test-piece with a soft disc between hard supports resembles a notched specimen since opposition to yielding generates transverse tensile stresses, so the measurements with this test-piece illustrate the raised axial stress for fracture. Since the criteria for plastic fracture are still uncertain, these effects cannot be fully explained.

Transverse tensile stresses are produced in the common tensile test when a neck forms, since this is equivalent to a notch, and the magnitude of these stresses influences fracture. Thus, thin sheet specimens, which cannot support a stress normal to the surface, favour greater ductility than do the normal test pieces.

A point of extreme importance in the metallurgy of mild steel, is that cleavage fracture can arise in a notch, particularly if the temperature is lowered. This is commonly attributed to the triaxial tension. Cleavage does not occur in a normal tensile test at room temperature, because the steel yields and then fractures by a plastic mechanism before the cleavage strength can be attained, but it is widely assumed that, when the axial yield stress is raised in a notch, the cleavage strength is unaffected, so cleavage can then occur. However, the experimental evidence suggests that the cleavage strength is also raised by transverse tension, so that some reconsideration of this action of the notch is necessary, and this will be discussed later.

THE GRIFFITH CRACKS IN METALS

Since cleavage in metals is possibly a Griffith-type fracture, the question of the physical nature of the Griffith cracks that can be effective is of extreme interest.

In a thoroughly annealed metal, actual cracks of the Griffith form should close up and disappear. Regeneration of the cracks by the local stresses arising, for example, from mechanical contact, which is possible in elastic bodies, is not likely where plastic deformation can occur, so it appears probable that the Griffith cracks in metals are of a different nature from those in glass.

A possible source might be flat platelet precipitates, at which cracks develop on the application of a stress because of low adhesion between the precipitate and matrix and because of differences in their elastic and plastic properties. It appears quite probable that there are fractures, particularly some intercrystalline ones, in which precipitates do act in this way, but it is doubtful whether they can supply a general explanation of the Griffith cracks in metals, because, for instance, the low cleavage strength of very pure zinc single crystals would require the presence of large precipitates (Table 1).

Some recent work relative to this question began from the well-known observation that coarse-grained metals are more prone to cleavage fracture than are fine-grained ones and involved a study of the depen-

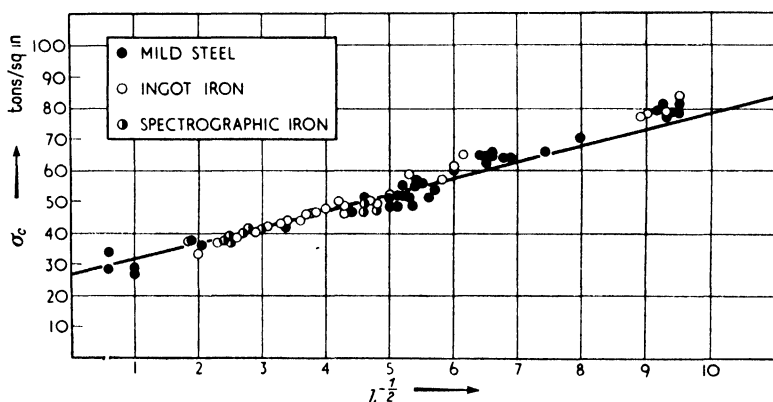


Fig. 8. The dependence of the cleavage strength of ferrite at -196°C on grain size⁽⁴²⁾

dence of cleavage strength upon grain size (PETCH⁽⁴²⁾). Using mild steel, ingot iron and electrolytic iron, it was found that the cleavage strength σ_c was related to the grain diameter l by

$$\sigma_c = \sigma_0 + kl^{-\frac{1}{2}} \quad \dots \quad (7)$$

where σ_0 and k are constants (Fig. 8). The cleavage strengths were obtained from the fracture stresses in liquid nitrogen. Depending upon the grain size, various amounts of plastic deformation prior to the fracture were observed and some allowance for this was necessary, since the cleavage strength is altered by plastic strain. To make the results directly comparable at the various grain sizes, a correction to zero deformation was carried out, using the pre-strain/cleavage strength curves determined by McADAM, GEIL and MEBS⁽³⁷⁾ and equation (7) refers to this zero deformation state. The correction was zero or quite small over much of the grain size range used.

A theory of this cleavage strength : grain size relationship can be

obtained if the Griffith cracks are identified with glide planes in which dislocation movement has been held up by grain boundary blockage. Essentially, the idea is that a concentrated stress will be produced by the blocked dislocations and this may be relieved by yielding during the initial plastic deformation, but, after sufficient strain-hardening, cleavage may become easier than yielding.

ZENER,⁽⁸⁾ who first considered glide planes as stress-concentrators, thought in terms of the concentration due to relaxation of the shear stress along the glide plane by viscous flow. More recently, the stresses directly due to the dislocations have been considered. ESHELBY, FRANK and NABARRO⁽⁴³⁾ have calculated the positions taken up by the dislocations in an array of like dislocations that is pressed against an obstacle and they have obtained the shear stresses that result. KOEHLER⁽⁴⁴⁾ has used these dislocation positions to calculate the tensile stresses and this calculation can be extended to give the cleavage strength: grain size relationship (PETCH⁽⁴²⁾).

Let the dislocations be numbered 0, 1, 2, 3 . . . i . . . $(n - i)$, starting with the dislocation nearest the obstacle and taking it as the origin of coordinates. The dislocations are located along the plus x axis and an applied shear stress τ tends to drive them towards the origin.

The position of the i^{th} dislocation is given approximately by

$$x_i = \frac{(\pi i)^2 D}{8n\tau}$$

where $D = \mu b/2\pi(1 - \nu)$ and μ , b , and ν are the rigidity modulus, Burgers vector and Poisson's ratio respectively.⁽⁴³⁾

The normal stresses at a general point (x, y) due to a positive edge dislocation at the origin are

$$\sigma_x = -Dy \frac{(3x^2 + y^2)}{(x^2 + y^2)^2} \quad . \quad . \quad . \quad (8)$$

$$\sigma_y = Dy \frac{(x^2 - y^2)}{(x^2 + y^2)^2} \quad . \quad . \quad . \quad (9)$$

The value of σ_x at (x, y) due to the array of blocked dislocations can be obtained directly by summation of the stresses due to the individual dislocations. Thus, along the y axis,

$$\sigma_x = -Dy \sum_{i=0}^{n-1} \frac{3 \left(\frac{(\pi i)^2 D}{8n\tau} \right)^2 + y^2}{\left\{ \left(\frac{(\pi i)^2 D}{8n\tau} \right)^2 + y^2 \right\}^2}$$

Putting $y = y_1 \left(\frac{\pi i}{8n\tau} \right)$

$$\sigma_x = \frac{-8n\tau}{\pi^2} \cdot y_1 \sum_{i=0}^{n-1} \frac{3i^4 + y_1^2}{(i^4 + y_1^2)^2}$$

The maximum value of σ_x will occur at a particular y_1 value and then

$$\sigma_x(\max) = \alpha n \tau \quad . \quad . \quad . \quad . \quad (10)$$

where α is a constant.

Along the y axis itself, $\sigma_x(\max) = \infty$ at $y = 0$, but this is merely the value of σ_x at the centre of the first dislocation and due to itself as given by equation (8), which in fact cannot be applied right up to the dislocation. The effect of the array of dislocations, as distinct from the single dislocation, is brought out by consideration of the stress on lines parallel to the y axis. Since the only difference from the above calculation is an alteration in x for each dislocation, $\sigma_x(\max)$ will be given in each case by an expression of the same form as equation (10). The expressions for $\sigma_y(\max)$ will be similar. Thus, tensile stresses are produced in the region ahead of the blocked dislocations that are of the form

$$\sigma = \alpha n \tau \quad . \quad . \quad . \quad . \quad (11)$$

To extend this into a cleavage strength : grain size relationship,⁽⁴²⁾ a connection between n and the grain size is required. This can be obtained by the following argument. The dislocations initially present within a crystal can probably move at small stresses, lower than the conventional yield point, but they cannot pass beyond the confines of the grain boundary. On the glide planes that contain a Frank-Read⁽⁴⁵⁾ source, there will be dislocation multiplication, which will continue until stifled by the interaction with the accumulated dislocations. There will then be an array of n positive dislocations pressing against the grain boundary at one end of the glide plane and n negative dislocations pressing against the boundary at the other end of the glide plane and the largest value of n will arise in grains with a source at the centre. This maximum n can be calculated from the condition that the length of the array of n like dislocations under a shear stress τ must be equal to half the grain diameter.

Once yielding has taken place, dislocations are probably produced in the region of stress concentration at the end of the glide planes that contain a Frank-Read source, and these dislocations will spread across the grain (FRANK⁽⁴⁶⁾). In doing so, they may start other sources to operate within the second grain, and presumably the maximum number of like dislocations in an array will again arise from a source operating near the centre of the crystal and will be determined by the semi-diameter.

The calculation by ESHELBY, FRANK and NABARRO shows that the length L of an array of n -like dislocations under a shear stress τ is given by

$$L = \frac{2nD}{\tau}.$$

With L equal to grain $l/2$

$$n = \frac{l\tau}{4D}$$

Substituting in equation (11),

$$\sigma = \frac{\alpha l \tau^2}{4D} \quad . \quad . \quad . \quad (12)$$

So far, it has been assumed that the positions of the dislocations within the array are determined solely by the interaction between their own stress fields and by τ . In real crystals, however, there will probably be an internal stress τ_0 acting in opposition to the applied shear stress and representing the frictional resistance of solute atoms and precipitates to the movement of the dislocations through the crystal.

Then, from equation (12)

$$\sigma = \frac{\alpha}{2D} (\tau - \tau_0)^2 l$$

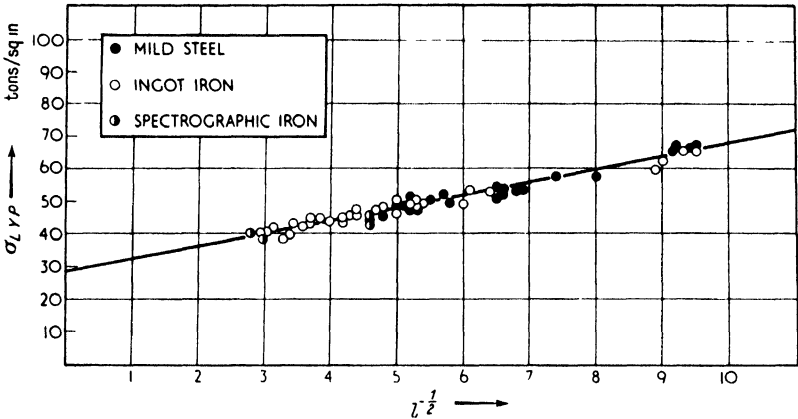


Fig. 9. The dependence of the lower yield point of ferrite at -196°C on grain size⁽⁴²⁾

In terms of the applied tensile stress σ^* corresponding to τ and the tensile stress σ_0 corresponding to τ_0 ,

$$\sigma \propto (\sigma^* - \sigma_0)^2 l$$

Fracture results when σ reaches the theoretical cleavage strength $\sigma_{t.c.s.}$ and the applied stress σ^* then becomes equal to the cleavage strength σ_c . Thus,

$$\sigma_{t.c.s.} \propto (\sigma_c - \sigma_0)^2 l$$

If this is rearranged with $\sigma_{t.c.s.}$ constant,

$$\sigma_c = \sigma_0 + k l^{-1/2} \quad . \quad . \quad . \quad (13)$$

where k is a constant.

Thus, the assumption that the Griffith cracks can be identified with slip planes in which dislocations are held up at a grain boundary and

that the concentrated tensile stresses are produced by the arrays of blocked dislocations leads to a cleavage strength : grain size relationship that is in agreement with experimental observation.

Fig. 9 shows that the dependence of the lower yield point $\sigma_{l.y.p.}$ upon the grain-size of these ferrites at -196°C is of the form

$$\sigma_{l.y.p.} = \sigma_0 + k \cdot l^{-1/2}$$

This is in agreement with HALL'S⁽⁴⁷⁾ room-temperature measurements. The value of σ_0 is common for both the cleavage strength, and the yield point equations. This similarity between cleaving and yielding is to be

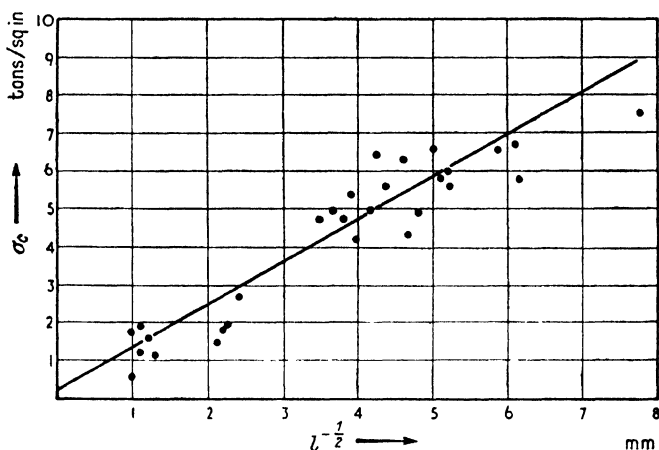


Fig. 10. The dependence of the cleavage strength of Zn at -196°C on grain size⁽⁴⁸⁾

expected if the Griffith cracks can be identified with blocked glide planes, because the lower yield point, which represents the propagation of a Luder's line, involves the yielding of one grain under the influence of a glide plane in a neighbouring grain. Thus, the yield point depends upon the shear stresses due to the blocked dislocations, whereas cleavage depends upon the normal stresses.

In this theory of the Griffith cracks in plastic solids, the cleavage strength of the polycrystalline aggregate depends upon the grain size (which determines the stress concentration factor), the theoretical strength in the grain boundary region (which may be affected by composition and by solute atom adsorption at the grain boundary) and by the internal stress τ_0 . Nominal single crystals will always contain some boundary at which dislocation blockage can take place.

Atomic slip is not the sole mechanism of plastic deformation; twinning and kinking may also occur and these may be additional sources of Griffith cracks. Normally, the stresses ahead of a blocked twin in a metal are relieved by some non-twinning plastic deformation (twin

accommodation), but the blockage of a twin in calcite, for instance, produces cleavage and it may well be that cleavage arises in metals, if twin accommodation becomes difficult. Stress concentration by twins or by slip bands probably leads to fairly similar cleavage strength : grain size relationships. Twinning may also produce tensile stresses across the twin plane and so make this a particularly easy path for fracture. Such fracture is termed "parting" in mineralogy.

According to measurements of PETCH and ZEIN⁽⁴⁸⁾ on the cleavage strength of polycrystalline zinc in liquid nitrogen, the dependence upon grain size is again of the form $\sigma_c = \sigma_0 + kl^{-1/2}$ (Fig. 10), although in this case σ_0 is very small. A distinction from the ferrites is that throughout the grain size range examined there was no indication in the experimental stress-strain curves of any plasticity before fracture.

GRIFFITH-TYPE FRACTURE UNDER BI- AND TRI-AXIAL STRESSES

A treatment has been given by GRIFFITH⁽⁶⁾ (1924) for an elastic solid containing a random distribution of Griffith cracks. The problem

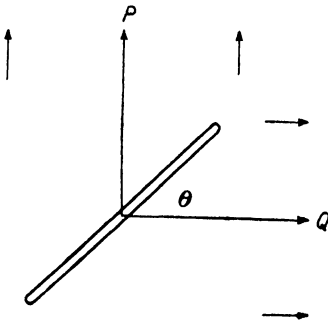


Fig. 11. A Griffith crack under biaxial stress

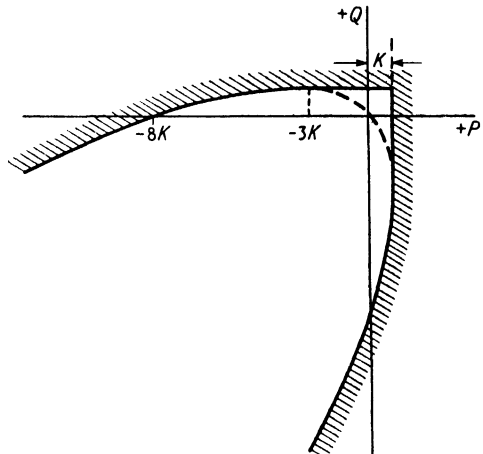


Fig. 12. Griffith-crack fracture under biaxial stress⁽⁴⁰⁾

resolves itself into finding the crack at which the greatest tensile stresses arise under the combined action of the principal stresses P and Q , Fig. 11, and the solution is obtained directly from the Inglis solution for the stress distribution at a crack.

It is found that (a) if $3P + Q > 0$ and $P > Q$, fracture occurs when $P = K$ (the strength for uniaxial stressing); (b) if $3P + Q < 0$ fracture occurs when $(P - Q)^2 + 8K(P + Q) = 0$.

These conditions have been plotted by OROWAN⁽⁴⁰⁾ as shown in Fig. 12: the fracture field lies on the shaded side of the curve.

The plane of fracture is perpendicular to P in (a) and is given in (b) by

$$\cos 2\theta = -\frac{1}{2}(P - Q)/(P + Q) \quad . \quad . \quad . \quad (14)$$

Result (a) shows that tensile or compressive Q stresses transverse to a tension P should have no effect upon fracture provided $P \geq Q$. One consequence is that the strength in tension should be equal to the strength in torsion for brittle solids and this is borne out by cast iron.

For uniaxial compression, (b) shows that the fracture stress is $8K$; that is, the compressive strength is eight times the tensile strength. Experimentally, this is approximately true for cast iron, stone and concrete. Since the fracture surface is at about $\theta = 45^\circ$ (normally it is nearer 55° ; 60° is predicted on equation (14)), it is usually considered in engineering that shear is involved, but on this Griffith theory, fracture takes place under the tensile stresses at the cracks.

Triaxial stresses will have approximately the same effect as biaxial ones since a principal stress perpendicular to P and Q will not be concentrated by the crack.

This treatment of multiaxial stresses is valid for Griffith cracks that are true cracks, and probably these are in fact involved in cast iron (graphite flakes) and in stone, but the treatment cannot be valid if the Griffith cracks are arrays of blocked dislocations, since the concentrated tensile stresses are then controlled by the shear stresses acting on the dislocations. With this type of Griffith crack, the fracture strength will not be independent of the transverse stresses ($Q < P$) as deduced in (a). Instead, transverse tension should raise, and transverse compression should lower, the fracture strength, and this is supported by what experimental evidence there is (MCADAM,⁽³⁷⁾ ZENER⁽³⁶⁾) on the effect of notch-induced, triaxial tension on the cleavage strength of steel.

This conclusion means that some reconsideration of the significance of triaxial stresses in notch-testing is necessary, since it has been widely assumed in this connection that the cleavage strength is independent of transverse stresses and that triaxial tension can raise the yield curve to the cleavage strength. If the condition for both yielding and cleaving is a critical, applied shear stress, triaxial tension cannot bring them closer together. However, it may be that the yield stress is raised in a notch because of the size of the stressed volume. In a steel, the small volume in a notch is not representative of the bulk properties for the nucleation of a Luder's line, so this will hinder the initiation of yielding. This possibility of "elastic super-stressing" when the yielding is localized is supported by experimental evidence (COOK,⁽⁴⁹⁾ MORRISON⁽⁵⁰⁾). Another feature of some importance for raising the yield stress in a notch is the high strain rate that can be developed when the strained volume is small; this will be discussed in the next section.

THE INITIATION AND PROPAGATION OF CLEAVAGE

Strain Rate

It is an old idea that cleavage and brittleness arise from high strain rate (impact), and it is quite true that the increase in yield stress produced in this way will favour the initiation of cleavage, but it is now known that many of the earlier measurements of the effect of strain rate on the yield stress are meaningless, and that, even at the highest rates for which satisfactory measurements have been made, the rise is only a few per cent for copper, aluminium and the later portions of the steel curve, although 30–40 per cent has been obtained on the initial yielding of steel. Consequently, only extremely wide variations in strain rate can be expected to have much effect upon the initiation of cleavage, and this is borne out by experiment.

ROSENTHAL and WOOLSEY⁽⁶⁰⁾ found that a 10^4 -fold increase in strain rate only raised the temperature for the plastic-cleavage transition in the tensile testing of un-notched steel specimens by 20°F. WITTMANN and STEPANOV⁽⁶¹⁾ have obtained an alteration of 90°C from a strain rate variation of 10^6 , and their results agreed with a relationship between the transition temperature T_B and the strain rate V of the form

$$\ln V = k/T_B$$

where k is a constant. Other recent measurements have been made by JONES and WORLEY,⁽⁶²⁾ BUFFUM and JAFFE⁽⁶³⁾ and by RIPLING and BALDWIN.⁽⁶⁴⁾ The very high strain rates required on these figures for any substantial effect on the occurrence of cleavage can be readily produced only if the strain is confined to a very small volume. It has been estimated⁽⁶⁵⁾ that the strain rate at a notch during an impact test is $\sim 10^7$ times that in a normal tensile test, and, at this, the strain rate will contribute appreciably to raising the temperature for the occurrence of cleavage in steel from about -150°C in an un-notched tensile test to about room temperature in a notched impact test.

Velocity

Suppose a Griffith crack spreads from A to B (Fig. 13) in a completely brittle solid. An elastic stress-relaxation will then travel out from AB

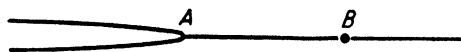


Fig. 13. Griffith-crack propagation

into the volume on either side, and this relaxation will build up a stress concentration at B that will eventually cause the crack to spread farther. The velocity of the crack will depend upon the rate of the elastic stress relaxation, and consequently will be of the order of the velocity of sound. BARSTOW and EDGERTON⁽⁵¹⁾ have observed a crack velocity of

5040 ft/sec. in glass and HUDSON and GREENFIELD⁽⁵²⁾ have observed 3370 ft/sec. for a cleavage fracture in steel. Brittle fractures in ships are in the range 150–4000 ft/sec. (KENNEDY⁽⁵³⁾). The velocity of sound in glass is 16,500–19,000 ft/sec. and in steel 15,500–16,500 ft/sec.

Elastic or Plastic Propagation

A cleavage crack in a metal may travel elastically, as considered above, or it may require some plastic deformation ahead of it. Some experimental evidence suggests the latter. X-ray examination of the surface of a brittle fracture in ship plate has shown the presence of a thin, plastically-deformed layer (OROWAN and CAHN⁽²⁾) and other x-ray evidence of plastic deformation has been obtained by Klier.⁽⁵⁴⁾ The propagation of cleavage from a notch has been found to be associated with the spread of Neumann bands in Si-iron (TIPPER and SULLIVAN⁽⁵⁵⁾) and of Neumann bands and slip bands in mild steel (BAEYERTZ, CRAIG and BUMPS⁽⁵⁶⁾). Even in unnotched specimens there is evidence of localized plasticity at the fracture; thus, in the cleavage of unnotched polycrystalline zinc in liquid nitrogen, the grains remote from the fracture do not show any deformation, whereas a layer a few grains thick immediately adjacent to the fracture is extensively twinned (PETCH and ZEIN⁽⁴⁸⁾).

OROWAN⁽⁴⁰⁾ has suggested that, if the spread of the crack requires any additional plastic deformation, the Griffith expression for the strength must be modified to

$$\sigma = \sqrt{\frac{2Ep}{\pi c}}$$

where p now includes the plastic work associated with unit surface area of the crack. With increasing thickness of the deformed layer, this plastic work will rapidly swamp the surface energy.

It seems possible however that the crack may travel elastically in spite of the evidence of plasticity. Any requirement of plastic deformation ahead of B (Fig. 13) will slow down the crack (the velocity of plastic waves has been treated by VAN KARMAN and DUWEZ⁽⁵⁷⁾), yet the observed velocities of cleavage cracks in steel can be very similar to those in completely brittle solids (glass), suggesting elastic propagation. Also, when the crack velocities are considered, the suppression of the yield in steel by the high strain rate seems possible. According to WOOD and CLARK,⁽⁵⁸⁾ the delay time t for yielding in a steel under a stress σ is given by $t = t_0 e^{-\sigma/\sigma_0}$, where $t_0 = 3.34 \times 10^4$ sec. and $\sigma_0 = 3.64 \times 10^3$ p.s.i. at room temperature. Thus, the delay time is $\sim 10^{-5}$ sec. at twice the normal yield stress and $\sim 10^{-10}$ sec. at three times the normal yield. Assuming that the rise of stress in an element that fractures takes place as the crack travels ~ 0.1 in., the total time for loading the

element is $\sim 10^{-5}$ – 10^{-6} sec. at the observed crack velocities. MOTT⁽⁵⁹⁾ suggests 10^{-9} sec. Since the cleavage strength is two to three times the normal yield stress, it is not impossible on these figures that yielding may be suppressed. However, this refers to slip; twinning seems to have a somewhat shorter delay.

If the crack can travel elastically, the observed plasticity requires explanation. It may be that the propagation of the crack is not preceded, but followed, by plastic deformation. The elastic spreading of a Griffith crack is accompanied by the progressive release of elastic strain energy in excess of that required to form the new surface; consequently a crack that travels elastically can spread beyond B (Fig. 13) without the necessity of waiting for the transference of the complete stress relaxation to B . Thus, such a crack will be followed by a wave of continuing stress relaxation and associated stress concentration that will tend to sustain the stresses after the crack has passed. If sustained long enough, yielding may occur, and this will be helped by the presence of the new free surface produced by the crack. In this way, yielding may follow after the cleavage. ROBERTSON'S experiments, described later, clearly show the lag of the stress relaxation behind the propagation of the crack.

Metallographic evidence from BAEYERTZ, CRAIG and BUMPS⁽⁵⁶⁾ has a bearing on this point. At temperatures near the top of the impact transition range for mild steel, they observed that slip (not twinning) was associated with the cleavage cracks and that some of the latter were curved, suggesting that deformation took place ahead of them. However, at the bottom of the transition range, displacements in some cleavages were observed, suggesting deformation after fracture. At these lower temperatures, twinning replaced slip.

A reasonable conclusion would seem to be that plastic deformation takes place ahead of a cleavage crack near the top of the transition range, but that these cracks can probably travel more or less elastically at the bottom of the range. Some of the observed plasticity may follow, rather than precede the fracture. In KENNEDY'S measurements, the low velocity cracks are probably travelling near the top of the transition range, the high velocity ones, near the bottom.

In a polycrystalline metal, a cleavage plane in one crystal is, of course, skew to a cleavage plane in the next crystal, so some secondary fracture at the grain boundaries is necessary to link the cleavages into a complete fracture. This may contribute some plastic deformation.

The Maintenance of Propagation

The production of a propagating cleavage crack due to localized conditions will not matter in many cases, if the crack cannot continue to propagate under the general stress. This has been emphasized in recent

THE FRACTURE OF METALS

work by ROBERTSON⁽⁶⁷⁾ on ship plate. He points out that the usual notch tests can grade materials into an order of merit with respect to their liability to cleavage fracture, but they do not supply any design data about permissible stresses below which a cleavage crack cannot propagate. In experiments designed to obtain this type of data, 12 in. $\times$ 3 in. specimens were subjected to a uniform tensile stress parallel to the 3 in. length; a temperature gradient was maintained in the 12 in. direction by heating at one end and cooling with liquid nitrogen at the other, and a cleavage crack was started from a saw cut at the cold end by a small explosion. The crack travelled for a certain distance in the direction of the rising temperature and the temperature at which arrest occurred was measured. Some results of this type of measurement are shown in Table 3.

TABLE 3
The Robertson Test

Plate	Material	Stress Transverse to Crack tons/in. ²	Arrest Temp. °C
A	1 in. plate 0.20% C 1.44% Mn	15	12
		13	10
		10	10
		7.5	10
		5	— 36
B	1 in. plate 0.13% C 0.97% Mn	15	— 5
		13.5	— 5
		12	— 42
C	1 in. plate 0.31% C 1.32% Mn	10	20
		7.5	20
		5	— 45
D	$\frac{3}{8}$ in. plate 0.23% C 1.02% Mn	10	8
		7.5	7
		5	— 35
E	$\frac{3}{8}$ in. plate 0.23% C 0.87% Mn	16	— 10
		15	— 20
		10	— 22

These results indicate a sudden drop in the arrest temperature as the stress transverse to the crack is lowered. This strength transition occurs at about 5 tons/in.² for most of the plates, although it is at 12 tons/in.² in *B* and is indefinite in the thin plate *E*. Under stresses below the transition strength, cleavage cracks can only propagate at very low temperatures; when the stress is about the transition strength they

can propagate around room temperature. The arrest temperature above the transition strength is practically independent of the stress.

In this test, the crack will be arrested when, with the rise in temperature, the plastic deformation required for further spread becomes too great to be maintained by the stored elastic energy. Presumably, therefore, there is a close relationship to the transition temperature in impact; at low stresses, the arrest will take place near the bottom of the transition range, but the fracture will continue to higher temperatures under higher stresses.

ROBERTSON's experiments demonstrate very clearly the lag of the complete stress relaxation behind the spread of the crack. An appreciable time after the latter has been arrested, the arrival of general stress relaxation at its head causes extensive yielding and possibly further cracking.

Since the strain-energy is involved, the size of the stressed volume will exert an influence on how far a crack can travel before it is finally arrested. If this volume is limited by the size of the structure, the crack will be arrested more readily in a small, than in a large, structure.

Crack Branching and Curving

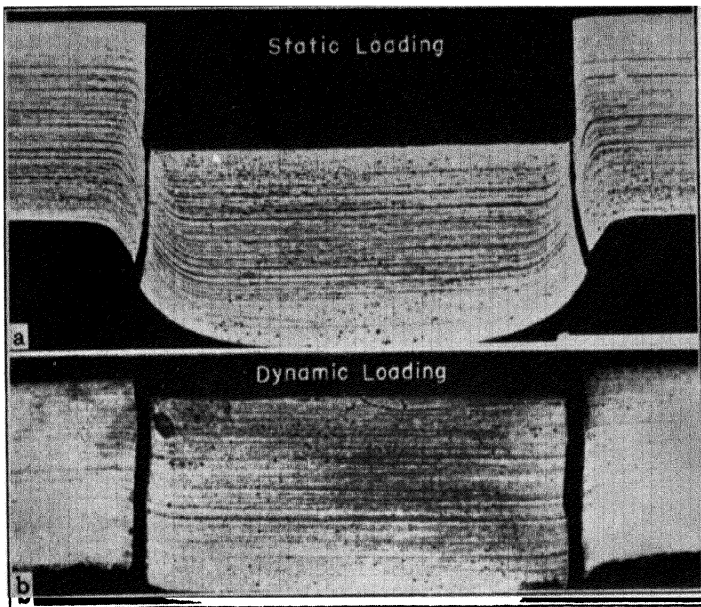
The stresses ahead of a stationary Griffith crack in an elastic medium show that fracture may be expected to occur in the line of the crack, but OROWAN has anticipated that at high velocities the stress field may be modified so that there will be a tendency to turn out of this line and to produce a curved or branching crack. This has been confirmed in a calculation by JOFFÉ.⁽⁶⁶⁾ As the speed increases, the crack may form branches, since nearly equal stresses exist over a wide arc ahead of the crack, and then at still higher speeds, the crack will tend to curve, since the normal to the maximum tensile stress is no longer in line with the crack. The physical occurrence of these effects has been demonstrated by OROWAN in the fracture of cellophane and they are probably relevant to the spicular fracture of glass. In metals, such effects are complicated by the limitation of fracture to the cleavage planes.

METALLURGICAL FEATURES OF CLEAVAGE AND INTERCRYSTALLINE FRACTURE

The Mild Steel Problem

Cleavage fracture is of very great significance in ferrous metallurgy. Since such fracture, once initiated, can propagate at low stresses and with a velocity near that of sound, there are clear possibilities of catastrophic failures, and these have occurred.

The most recent spectacular examples have been in welded ships. Of 5000 American merchant vessels built during the war, more than one fifth had developed cracks in varying degrees by 1946, when most of the



(a)

Plate II. (a) Adiabatic localization of strain⁽³⁸⁾

ships were less than three years old, and by 1951, about 200 had sustained fractures that were classified as serious, while eight tankers and three Liberty ships had broken completely in two.⁽⁶⁹⁾ The significance of welding in this connection lies mainly in the continuity of the structure produced. In discontinuous, riveted construction, a cleavage crack can only run to the edge of the plate, whereas, when continuity is created by welding, the crack can carry on; thus, the interruption of welding by riveting is advantageous. The cracks originate at hatchway corners and other structural discontinuities that act as notches, and it has been found that suitable redesigning to avoid these discontinuities, combined with the use of arrester plates, has brought considerable improvement, so that the Victory ships have suffered no major structural casualty during a period of service comparable to that in which there were eighty-eight major casualties in Liberty ships.⁽⁶⁹⁾

Since long before the ship problem arose, cleavage has been a source of trouble with steel, particularly at low-temperatures, when strain and strain-ageing have occurred and when notches are present. A really fine example unconnected with ships is reported by TOUR⁽⁷⁰⁾ in 30 in. diameter steel pipeline; a cleavage crack developed that was 3300 ft long. It was the enhanced liability to this type of fracture shown by Bessemer steels that rendered them unacceptable for many engineering applications and consequently was a factor in limiting the application of this process. The new Bessemer practices are based on a recognition that the high nitrogen and phosphorus contents are the cause, and a reduction to figures comparable to those obtained in the open-hearth is now possible (DICKIE,⁽⁷¹⁾ Bessemer Report⁽⁷²⁾).

This importance of cleavage in mild steel has resulted in very intensive study during the last few years, and the following discussion is practically entirely in terms of steel.

Testing

Grading into an order of liability to cleavage is normally done by notch impact (Izod or Charpy) or notch tensile tests. The comparison is

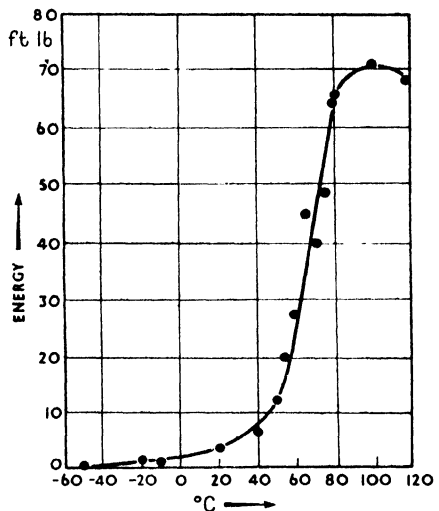


Fig. 14. The impact transition temperature for Zn⁽⁷³⁾

based on the temperature range over which cleavage, replaces plastic fracture, and this may be judged visually or from the impact figures, which show a considerable drop as the plastic fracture disappears. The transition temperature range for zinc⁽⁷³⁾ is shown in Fig. 14. In an impact test, a brittle specimen shows a dull zone of plastic fracture at the notch followed by a bright central zone of cleavage, with more plastic fracture around the edges where yielding is easier because of the proximity of the free surface. If very brittle, only cleavage appears.

Factors Controlling Cleavage Characteristics

Most of the information available is in terms of transition temperatures, and these depend upon both the cleavage strength and the yield stress, so there is an obvious need to separate the effects on these two properties if an understanding of the net result is to be achieved. At present, such separation is not generally possible.

If the blocked-dislocation theory of Griffith cracks is correct, it represents some progress towards understanding; on it, the cleavage strength is determined by the theoretical cleavage strength in the grain boundary region, the grain size and the internal stress.

Grain Size

The influence on cleavage strength has already been discussed. The increasing separation of σ_c and $\sigma_{l.y.p.}$ that occurs as the grain size of

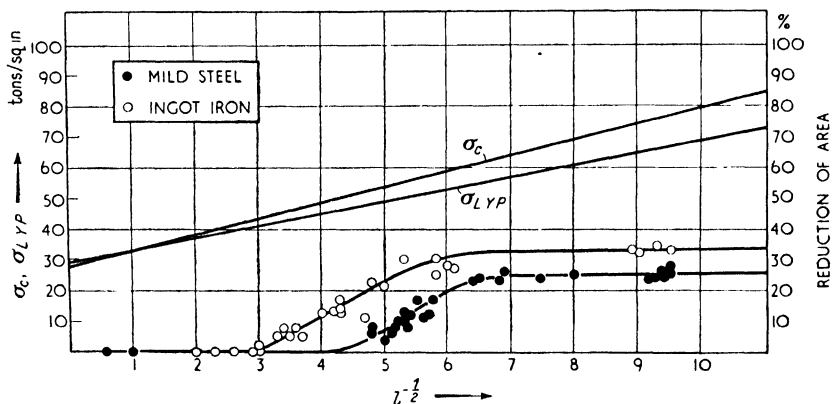


Fig. 15. The dependence of the cleavage strength, lower yield point and reduction in area of ferrite at -196°C on grain size⁽⁴²⁾

ferrite is reduced leads to increased ductility as shown in Fig. 15, but this increase is not continuous and eventually a steady value of the reduction in area is reached. To understand this, it must be remembered that the separation of $\sigma_{l.y.p.}$ and σ_c does not fully define the reduction in area, since these refer to zero deformation; the rates of increase of yield

stress and of σ_c with strain and the effect of grain size on these rates are also involved.

With a 0.02 per cent C iron, HODGE, MANNING and REICHHOLD⁽⁷⁴⁾ have found a linear relationship between the impact transition temperature and ASTM grain size number over the grain size range 1–6 (16 to 512 grains/mm²), an increase of one number decreasing the transition temperature by 30°F. A similar result has been obtained for steel plate by VANDERBECK,⁽⁷⁵⁾ and the effect of grain size has also been discussed by GORRISSEN.⁽⁷⁶⁾ Some measurements by BARR⁽⁷⁷⁾ are shown in Table 4.

With heat-treated steels, it is known that tempered martensite gives a lower transition temperature than bainite, which itself gives a lower one than pearlite, and it has been suggested that the mean free ferrite path is the controlling feature, but BAEYERTZ, CRAIG and BUMPS⁽⁵⁶⁾ have shown that the important point is in fact the ferrite grain size. This is reasonable, since the maximum, rather than the mean ferrite path will determine the length of the most dangerous dislocation arrays.

Composition

Fig. 8 shows that the variation in carbon content (0.04–0.15 per cent) between an iron and a mild steel has little, or no, effect on the cleavage

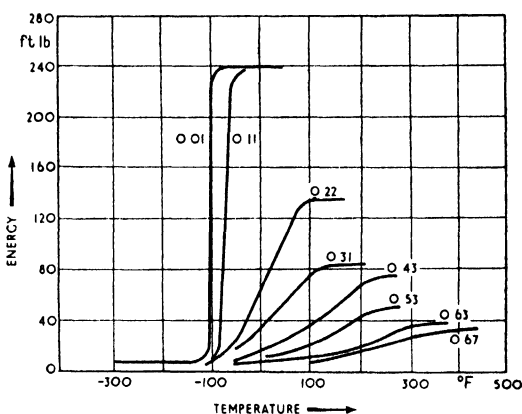


Fig. 16. The influence of carbon on the impact transition temperature of steel⁽⁷⁹⁾

strength (corrected to zero deformation) at constant grain size. This is understandable if the strength is determined by the cleavage of one ferrite grain under the influence of dislocations in another; the ferrite is in control and the presence of a limited amount of pearlite elsewhere in the structure should not be important. As would be expected, this also applies to the lower yield point (Fig. 9). However, the presence of carbon does increase the initial strain-hardening rate, so there is a

decrease in the plastic strain required to bridge the gap between $\sigma_{l.y.p.}$ and σ_e , thus producing a decrease in the reduction of area in tensile tests at -196°C (Fig. 15). SMITH, MOORE and BRICK⁽⁷⁸⁾ have examined a series of high purity iron-carbon alloys of 0.05–0.5 per cent C with ASTM No. 4–5 ferrite grain size and have observed some increase of fracture stress in liquid air with carbon content (7000 p.s.i. per 0.1 per cent C); the yield point showed a closely similar increase.

Fig. 16, due to RINEBOLT and HARRIS,⁽⁷⁹⁾ shows that an increase in carbon content raises and broadens the transition range, as might be expected from the increased strain-hardening rate. When this rate is low, a small temperature change, producing a small movement of the yield stress curve relative to the cleavage strength curve, leads to a

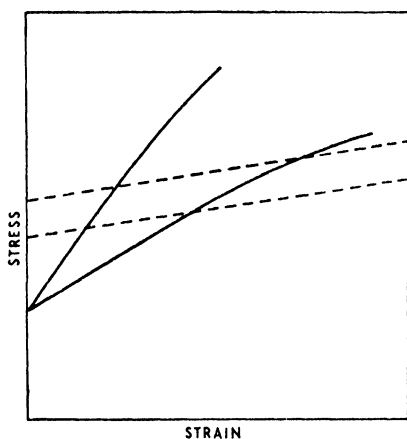


Fig. 17. Diagrammatic representation of the influence of strain-hardening rate on the sharpness of the plastic-brittle transition; yield stress —; cleavage strength - - - -

large change in the strain at which the curves intersect and, consequently, to a sharp transition range (Fig. 17). With a high strain-hardening rate, a small change in temperature will only produce a small change in the fracture strain and, consequently, there will be a broad transition temperature.

The importance of the Mn/C ratio in the cleavage of mild steel has been emphasized by BARR, HONEYMAN and TIPPER^{(80), (81)} and this is illustrated by Table 4 for a series of steels of constant ultimate strength (26–29 tons/in.²). The manganese refines the grain somewhat, but this appears

to account for only part of the improvement in impact properties. RINEBOLT and HARRIS⁽⁷⁹⁾ have also examined the effect of alloy additions, using a base composition of 0.30 per cent C, 1.00 per cent Mn, 0.30 per cent Si and attempting to keep the microstructure constant. Fig. 18 shows that the transition temperature was lowered by manganese and nickel, and raised by carbon, phosphorus, silicon, copper and molybdenum. Similar results have been obtained by WILLIAMS⁽⁸²⁾ in the examination of plates from fractured ships, with the principal exception that silicon was found to lower the transition temperature at the smaller concentrations found in plate and, up to 0.25 per cent, was three times as effective in this as manganese. WILLIAMS gives an empirical relationship for the transition temperature in terms of composition, which is applicable over a limited range, and he concludes that

THE FRACTURE OF METALS

TABLE 4
Effect of Mn/C Ratio on Transition Temperature⁽⁷⁷⁾

C%	Mn%	Mn/C	Heat Treatment °C	Grain Size Jernkontoret	Transition Temperature °C
0.19	0.27	1.4	N. 860	8.5	0
0.19	0.27	1.4	N. 900	10.0	20
0.19	0.27	1.4	A. 860	10.5	80
0.19	0.27	1.4	A. 900	11.0	90
0.17	0.68	4.0	N. 860	8.5	— 20
0.17	0.68	4.0	N. 900	9.0	— 20
0.17	0.68	4.0	A. 860	9.5	30
0.17	0.68	4.0	N. 900	10.5	50
0.115	0.89	7.8	N. 900	8.5	— 35
0.115	0.89	7.8	A. 900	10.0	40
0.10	1.19	11.9	N. 810	8.5	— 60
0.10	1.19	11.9	N. 900	9.0	— 50
0.10	1.19	11.9	N. 950	9.5	— 45
0.10	1.19	11.9	A. 880	10.0	10
0.10	1.19	11.9	A. 900	10.5	25
0.10	1.19	11.9	A. 950	11.0	60

N. = Normalize; A. = Anneal.

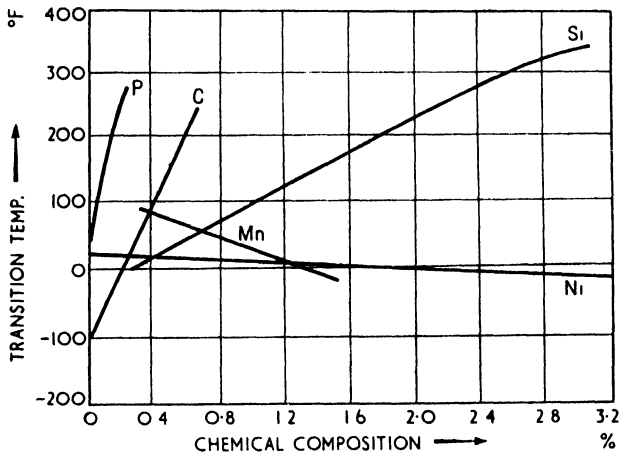


Fig. 18. The influence of alloy composition on the impact transition temperature of steel⁽⁷⁹⁾

the differences associated with plate thickness mainly arise from grain size. The influence of nitrogen and phosphorus is well-known; an ordinary Bessemer steel (0.0016 per cent N; 0.035–0.055 per cent P) commonly has a transition temperature about 20°C higher than a corresponding open hearth, or a modified Bessemer steel (0.006 per cent N₂, 0.025 per cent P) (DICKIE⁽⁸³⁾, ENZIAN,⁽⁸⁴⁾ GEIL *et al.*⁽⁸⁵⁾). A

slightly higher yield stress and an increased strain-hardening rate appear to be involved; also nitrogen increases the effect of strain-ageing.

At constant grain size, 3.6 per cent Ni lowers the transition temperature of a 0.02 per cent C, 0.5 per cent Mn iron by 60°F. It also leads to a fine grain size by lowering the transformation temperature (HODGE, MANNING and REICHOLD).⁽⁷⁴⁾ Deoxidation lowers the transition temperature, Si + Al being more effective than Al alone (SEENS, MILLER and JENSEN⁽⁸⁶⁾), but the relative importance of the fixation of oxygen and nitrogen and of grain refinement has not been established. The effect of composition has also been discussed by BANTA, FRAZIER and LORIG⁽⁸⁷⁾ and by AUSTIN.⁽⁸⁸⁾

High-purity irons, in which no element occurred in an amount exceeding the third decimal place, have been examined by the National Physical Laboratory (REES, HOPKINS and TIPLER⁽⁸⁹⁾). At an oxygen content > 0.002–0.003 per cent, these irons, which were very coarse-grained, failed by intercrystalline fracture in liquid nitrogen, and this was reflected in a much higher impact transition temperature. Increase in carbon beyond 0.01 per cent produced a sudden increase in transition temperature from 0°C for the low-oxygen irons up to 80°C at 0.03–0.05 per cent C. In the presence of this carbon, manganese had a marked effect, the addition of 2 per cent to the 0.05 per cent C alloy lowering the transition temperature to – 80°C, whereas, in the absence of carbon, manganese increased ductility at – 196°C, but had little effect on the transition temperature. Both the carbon and manganese produced considerable grain refinement.

Intercrystalline weakness in very pure irons due to oxygen has also been reported by FAST,⁽⁹⁰⁾ and the present writer has observed that fine-grained, high-oxygen, ingot iron (0.04 per cent O), which is normally ductile in liquid nitrogen, may become completely brittle with an intercrystalline fracture after sub-critical annealing.

Clearly, there is still a long way to go before the influence of composition upon cleavage is fully understood.

Metallography

Considerable discussion has centred around the role of twinning in the cleavage of ferrite. SHEVANDIN⁽⁹¹⁾ suggested that cracking along the twinning plane initiated cleavage. SULLIVAN and TIPPER,⁽⁵⁵⁾ in a paper on the spread of cleavage cracks from notches in silicon-iron at room temperature, concluded that Neumann bands are associated with the propagation of cleavage (shock loading) rather than with its initiation; on the other hand, in steel at – 196°C, GEIL and CORWILE⁽⁹²⁾ have shown that Neumann bands are in fact present before cleavage begins. BAEYERTZ, CRAIG and BUMPS⁽⁵⁶⁾ have observed twinning in impact tests at the bottom of the transition range, but cleavage still occurred

at higher temperatures in the range, although twinning was replaced by slip. BRUCKNER⁽⁹³⁾ found the twinning tendency was lower in killed, than in semi-killed steels and he thought that this might explain the transition temperature differences, but in later work he showed that these differences persisted when the steels were spheroidized, although no twins then formed. In an electron-microscope study of ferrite cleavage fractures, Klier⁽⁵⁴⁾ observed secondary cleavage along {112}, which is probably "parting" along a twin plane.

On the whole, the evidence suggests that there is no necessary association of cleavage in ferrite with twinning, but they are quite probable to occur together since the conditions of low temperature, high

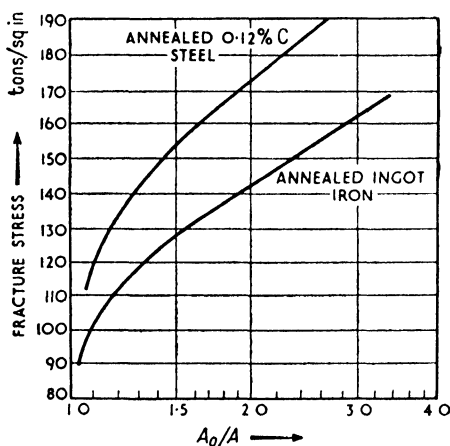


Fig. 19. The influence of room-temperature prestrain on the cleavage strength at -188°C of (a) 0.12 per cent C steel, (b) ingot iron⁽³⁷⁾

strain rate, etc., that favour cleavage also favour twinning. The whole question may well be of minor significance, since the stress concentration by a twin is probably very similar to that by a slip plane.

BRUCKNER⁽⁹³⁾ has published some interesting micrographs showing cracks across pearlite and grain-boundary cementite in tensile impact specimens, and he has suggested that these cracks may initiate cleavage, but Fig. 8 shows that they cannot be of primary significance in low carbon steels, since there is no certain difference between the cleavage strength of a mild steel and that of an iron in which no cementite is observed in an ordinary metallographic examination.

Strain and Ageing

Plastic extension raises the cleavage strength of ferrite as shown in Fig. 19, which was obtained by straining at room temperature and subsequent fracturing in liquid air (MCADAM, GEIL and MEBS⁽³⁷⁾). Similar curves have been published by HOLLOMON and ZENER⁽⁹⁴⁾ and

by SAKHAROV.⁽⁹⁵⁾ According to DAVIDENKOV and SHEVANDIN,⁽⁹⁶⁾ pre-compression lowers the strength for subsequent tension at a low temperature, but measurements by MCADAM⁽⁹⁷⁾ yielded the reverse result.

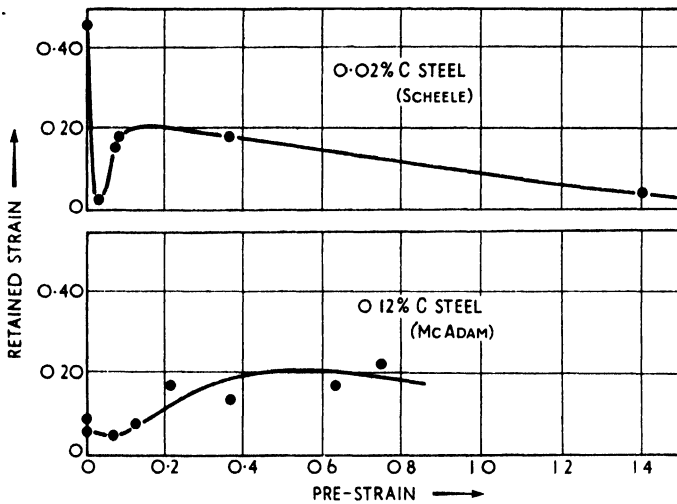


Fig. 20. The influence of room-temperature prestrain in tension upon the retained ductility in subsequent fracture under tension in liquid air^{(37), (98)}

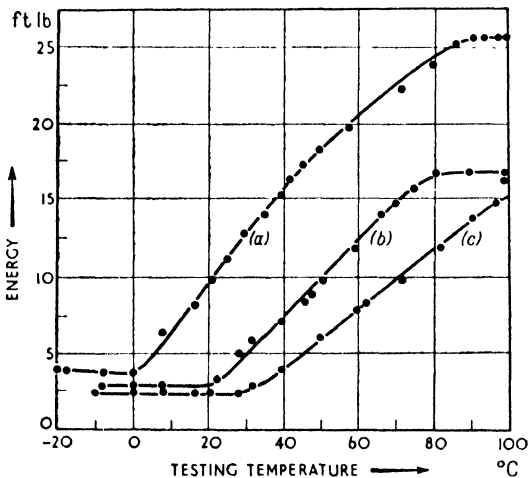


Fig. 21. The influence of strain and strain-ageing on the transition temperature of a 0.11 per cent C steel (a) annealed, (b) strained 10 per cent, (c) strained, then aged at 150°C (PATWARDHAN and PETCH⁽¹⁰²⁾)

With zinc single crystals, strain appears to have little effect on the cleavage strength (FAHRENHORST and SCHMID⁽²⁴⁾).

With many annealed steels, the ductility in liquid nitrogen is first

reduced by pre-straining at room temperature, then increased and finally decreased again (Fig. 20; McADAM,⁽³⁷⁾ SCHEELE⁽⁹⁸⁾). This effect has been extensively studied by RIPLING and BALDWIN,⁽⁹⁹⁾ who find it is very marked in heat treated steels tempered at 600°F, but disappears above 800°F. The impact transition temperature is raised by strain, and subsequent ageing produces a further increase (WRIGHT,⁽¹⁰⁰⁾ TIPPER,⁽¹⁰¹⁾ BARR,⁽⁷⁷⁾ Fig. 21). The influence of quench-ageing on the transition temperature is slight (Fig. 22).

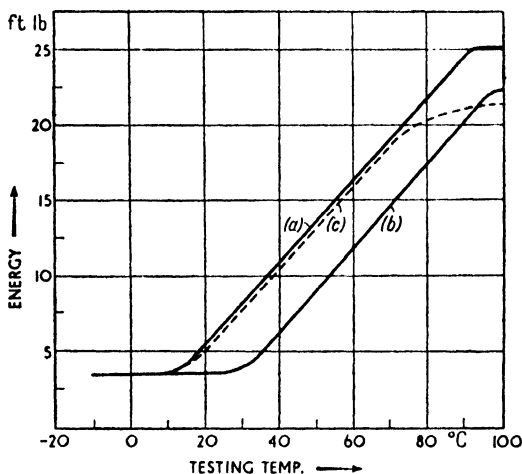


Fig. 22. The influence of quenching and quench-ageing on the transition temperature of a 0.11 per cent C steel (a) annealed, (b) quenched from 890°C, (c) quenched, then aged at 150°C (HESLOP and PETCH⁽¹⁰³⁾)

Intercrystalline Fractures

These may arise from actual precipitates at the grain boundaries and LORIG⁽¹⁰⁴⁾ has recently quoted examples in cast steel due to sulphides and aluminium nitride. "Overheating" in steel is due to the segregation of sulphides to the austenite grain boundaries (PREECE *et al.*,⁽¹⁰⁵⁾ ROLLASON and ROBERTS,⁽¹⁰⁶⁾ KO and HANSON⁽¹⁰⁷⁾). If the precipitate has a lower yield stress than the body of the crystals, the stress conditions become essentially the same as in a notch, and brittle fracture may take place through the nominally ductile constituent. Such brittleness is shown by hardened, cast steels if there is a ferrite network at the grain boundary (GROSSMAN⁽¹⁰⁸⁾).

McLEAN and NORTHOTT⁽¹⁰⁹⁾ have pointed out that sometimes there is no detectable precipitate and have emphasized that segregation to the grain boundary, while still remaining in solution, may be all that is necessary. K&E's⁽¹¹⁰⁾ anelastic measurements on Bi-embrittled copper are of interest in this connection, since he concluded that there was

precipitation only along certain grain boundaries and then not in a form that entirely took the habit of crystallized bismuth.

Temper-brittleness, a grain-boundary weakness first discovered in Ni-Cr steels after slow-cooling from the tempering temperature, has been the subject of continuous discussion since its discovery, and no general agreement has yet been reached. The various theories have recently been reviewed and extended by WOODFINE,⁽¹¹¹⁾ who supports the idea that solute atom segregation, rather than actual precipitation, is involved.

ADIABATIC FRACTURE

In an adiabatic deformation, the temperature rises with increasing strain and this produces a softening in opposition to the normal strain-hardening; consequently, the adiabatic shear-stress/strain curve shows a stress maximum. For strains beyond this maximum, homogeneous deformation becomes unstable, and it is replaced by localized deformation

in the zone of maximum shear stress. This zone becomes very hot; it loses most of its resistance to deformation and fracture may occur by a process of pure sliding apart.

This type of fracture has been discussed by ZENER.⁽³⁶⁾ It is of particular interest in the penetration of armour by projectiles, since the deformation rate is then high. Plate II illustrates such adiabatic localization of slip; it shows the difference between "static" punching, where plastic deformation is general, and dynamic punching, where

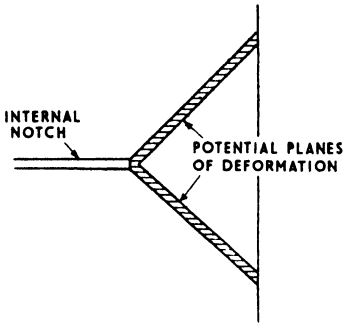


Fig. 23. Strain localization ahead of a notch⁽³⁶⁾

the deformation is essentially confined to the immediate vicinity of the fracture. The location of the maximum shear stress surface, and consequently of the adiabatic fracture, depends upon the stress system, and ZENER has given some interesting examples of how, in this way, transverse tensile and compressive stresses introduced by bending affect the shape of the plug forced out of armour plate. Martensite frequently forms in steel on the surface of these fractures, because of the high temperatures attained and the quenching action of the surrounding mass (ZENER,⁽³⁶⁾ ALLEN⁽¹¹²⁾).

Adiabatic shear localization may occur in simple compression. For example, the nose of projectiles may break up against armour by 45° adiabatic fractures. In tension, necking normally intervenes before the maximum in the adiabatic shear-stress : strain curve is reached, and this tends to confine the deformation to the narrowed cross-section of the neck and to inhibit 45° localization. However, the shear portion of

the normal cup and cone in a tensile fracture may be an example of adiabatic fracture. In plane strain, the shear strain ahead of an internal notch will be confined to the two hatched regions shown in Fig. 23 when strain-hardening is absent. In a cup and cone, the transverse fracture supplies an internal notch, the material in the neck has been deformed until the rate of strain-hardening is low and the strain becomes more and more two dimensional (plane strain) as the surface is approached. Further, when the isothermal strain-hardening rate is small but positive, it is easy for it to become negative under adiabatic conditions, and testing machines probably are normally sufficiently soft to develop such high deformation rates under the falling load of fracture that substantially adiabatic conditions are in fact established. Thus, the cone in the fracture may represent adiabatic confinement of the shear strain to 45° surfaces.

This idea supplies an explanation of an observation by BRIDGMAN⁽⁴¹⁾ on the effect of superimposed hydrostatic pressure on tensile fracture. As the pressure increases, the reduction in area prior to fracture also increases, but the proportion of the transverse fracture decreases. This can be accounted for as a consequence of the increased susceptibility to a negative strain-hardening rate in adiabatic deformation, arising from the increased strain prior to fracture.

Under the plane strain conditions that occur in sheet, or plate tensile specimens, the shear fracture is again accentuated.

PLASTIC FRACTURE

It is now possible to add a little to the previous remarks on plastic fracture.

Single crystals show cleavage and shear fractures, whereas polycrystals show cleavage, intercrystalline, plastic and shear fractures. It is now seen that what has been termed shear fracture in polycrystals probably arises from adiabatic strain localization, so, by elimination, it appears possible that plastic fracture in polycrystals may correspond with shear fracture in single crystals. It may be that a full understanding of the experimental evidence will support this view.

DORN⁽¹¹³⁾ has recently shown that the plastic fracture of polycrystalline aluminium and magnesium does obey approximately a maximum shear stress law under uni- and bi-axial stresses (Fig. 24). The evidence against the general applicability of this law is that the shear stress for fracture in a tensile test is raised by a superimposed hydrostatic, compressive stress and lowered by a superimposed hydrostatic tension, but DORN suggests that these effects may arise, not from the instantaneous action of the transverse stresses, but from the effect on the fracture shear-stress of prestrain under different stress conditions. In agreement with this, SACHS⁽¹¹⁴⁾ has found that the fracture shear-stress is greater

in an ordinary tensile test after a tensile prestrain with superimposed, hydrostatic, compressive stresses than after a similar prestrain with superimposed hydrostatic, tensile stresses.

This effect of prestrain may also explain the initiation of plastic fracture in the centre of the neck in a tensile test. The centre has a history of prestrain under higher hydrostatic tension, than the outside, so the critical shear stress should be lower. In addition, there may be higher strains at the centre (LUBAHN⁽¹¹⁵⁾).

Apparently, shear is an essential part of plastic fracture. The latter may be simply a process of slipping apart (OROWAN⁽⁴⁰⁾). However,

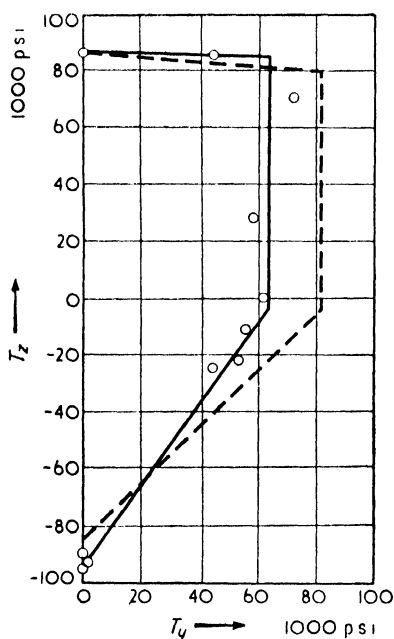


Fig. 24. The fracture of an aluminium alloy under biaxial stress; — experimental, max. shear stress law⁽¹¹³⁾

cleavage and plastic fracture are possibly not unrelated; perhaps both are initiated by the tensile stresses produced by a dislocation array compressed by shear stresses, but the crack in plastic fracture may be arrested after a short run because yielding becomes locally easier than fracture, and further deformation may then be necessary to initiate another crack. The final irregular fracture may represent the linking together of a number of separate sections. Thus, there is possibly no real difference in mechanism between plastic and cleavage fracture, but only a difference in the amount of deformation required during the spread of the crack.

Mention should also be made of a few other small points about plastic fracture. Measurements of the "technical cohesive strength" by notched specimens figured

largely in plastic fracture studies for some time.^{(116), (117)} It was thought that an infinite plastic constraint could be obtained with a sufficiently sharp notch, and that in this way, a tensile stress criterion for fracture unaffected by plastic deformation could be measured. But, as already indicated, the constraint factor cannot exceed ~ 3 , and the quantity measured was in fact the conventional maximum stress corresponding to a yield curve that had been raised by the constraint.

The directionality introduced by deformation in manufacture has little effect on the yield point or maximum stress, but the reduction in

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area at plastic fracture may show a large variation, e.g. from 60 per cent for longitudinal specimens down to 25–45 per cent for transverse specimens in steel.⁽¹¹⁸⁾

DELAYED FRACTURE—STATIC LOAD

Glass

The strength of glass tested in air decreases as the time for which the load is applied increases. Measurements by BAKER and PRESTON⁽¹¹⁹⁾ (1946) are shown in Table 5.

TABLE 5
Effect of Duration of Load (sec.) on the Strength (lb/in.²) of Glass Rods

<i>Time</i>	0.01	0.1	1.0	10	100	1000	86,400
Annealed soda lime glass .	19,900	15,900		10,500		7,950	6,450
Annealed lead glass .		19,000	14,900	11,200		9,400	7,950
Fused silica .		23,800		19,800	15,660	14,280	11,740

After baking in vacuum at 350°C, there is little or no time-effect on subsequent testing in vacuum, and the strength is similar to that obtained in the very short time tests in air.

A theory of this delayed fracture has been proposed by OROWAN⁽¹²⁰⁾ in terms of a lowering of surface energy by adsorption of atmospheric constituents.

The strength of a rapidly loaded specimen is given by the Griffith relationship

$$\sigma_c = \sqrt{\frac{2ES_c}{\pi_c}}$$

where S_c is the surface energy of a clean surface. S_c figures because the new surface produced by the fracture is clean. If, however, this surface can be covered by adsorbed atoms as soon as it forms, the strength will be the lower value σ_a given by replacing S_c by S_a , the energy of the surface covered by the adsorbed layer. In a specimen held at a stress above σ_a , but below σ_c , Griffith cracks will be unstable and an increment of unclean surface will form whenever the adsorbed atoms are available. This gradual extension will be replaced by sudden fracture when the crack has grown to such a size that a clean surface can be propagated by the applied stress. Thus, delayed fracture can occur; the strength will be time-dependent, but it cannot be lower than σ_a .

The absence of a time-effect with the baked-out, vacuum-tested

specimens is in agreement with this idea, since the external surfaces are then free from adsorbed atoms. The similarity between the strength *in vacuo* and under rapid testing in air is also in agreement. Further, although S_a and S_c for glass are unknown, the values of 327 and 4500 ergs/cm² obtained for mica (OBREIMOFF,⁽¹²¹⁾ OROWAN⁽¹²²⁾) are probably very similar, and these give $\sigma_c : \sigma_a$ as ~ 3.5 , which is borne out by the observed results.

A modification of OROWAN's theory has been proposed by GURNEY⁽¹²³⁾ in which surface adsorption is replaced by actual chemical attack at the root of the notch.

Other explanations of delayed fracture have also been suggested. The time-dependence might arise simply from thermal fluctuations in energy at the tip of the Griffith crack (SMEKAL⁽¹²⁴⁾), but it is apparent from the size of the cracks that cooperation between a large number of atoms (their coincident activation in fact) would be necessary for any marked fluctuation in crack length, and the probability of such cooperation is so small that only slight fluctuations can be expected. The fact that the cleavage strength of metals appears to be fairly independent of temperature indicates that fracture is independent of thermal activation.

In the theories of PONCELET⁽¹²⁵⁾ and SAIBEL,⁽¹²⁶⁾ it is assumed that the cracks can grow from below the critical Griffith size by a series of separate, activated jumps. But this postulates a process proceeding with an increase in free energy. Any enlargement of the crack below the critical size can only be maintained if there is an activation energy for the whole enlargement and, as already indicated, only small size fluctuations are probable.

MURGATROYD and SYKES⁽¹²⁷⁾ have suggested an explanation of delayed fracture in which the stress concentration takes place by gradual shear-stress relaxation in the viscous component of the elastic-viscous model that, from delayed elastic effects, appears to be reasonable for glass. However, in opposition to the view that this supplies the controlling stress concentration, GURNEY and PEARSON⁽¹²⁸⁾ have shown that the time-effect in fracture persists under tension-compression cyclic loading, although the viscous relaxation should be suppressed; in addition, the influence of the atmosphere does not fit very convincingly into this theory. This is also true of TAYLOR'S⁽¹²⁹⁾ explanation, which involves time-dependent atomic rearrangements.

At present, the suggestions of OROWAN and GURNEY appear to fit the facts most readily.

Metals

The hydrogen-embrittlement of steel may resemble the effect of air on glass. Hydrogen causes intercrystalline and cleavage fracture even under simple tension at room temperature,⁽¹³⁰⁾ and it has been widely

suggested that the stresses created around internal voids⁽¹³¹⁾ that became filled with hydrogen under high pressure are the cause; but, apart from doubts about the existence of the type of void postulated, it is not clear how this stress system produces cleavage. Another explanation could be simply that the hydrogen lowers the cleavage and inter-crystalline strengths; but the small quantity required (0.0001 per cent) suggests that some special mechanism operates. A new suggestion is that the embrittlement is produced by hydrogen adsorption in the Griffith cracks (PETCH and STABLES⁽¹³²⁾). On this view, the initial Griffith cracks (the blocked glide planes) gradually extend at stresses above σ_a of the glass theory by the formation of a surface with adsorbed hydrogen on it, and this gradual growth is replaced by sudden fracture when the crack has grown sufficiently.

The prediction on this theory of a time-delay in the development of embrittlement is borne out by the experimental evidence in Table 6 and by other measurements.^{(133), (134)} This delay accounts for the greater effect of hydrogen in a normal tensile test than in an Izod test.

TABLE 6

The Effect of Duration of Loading on the Hydrogen-embrittlement of Steel, as Measured by the Reduction in Area per cent⁽¹³²⁾

<i>Condition</i>	$\sim 10^{-3}$ sec.	1-2 min.
H ₂ -free .	60.5	61.0
H ₂ -charged .	60.5	27.8

A distinction from the glass theory is that the adsorbed atoms are supplied from solution, and this will be helped by a positive tendency for them to migrate into the stress concentration region, because of the possibility of elastic strain energy relief. For this reason, there should also be a migration of hydrogen atoms to the grain boundaries when a load is applied, and this will favour an intercrystalline path for the fracture as, in fact, is observed.

Shear-stress Relaxation

The elastic-viscous model that appears to represent the properties of some solids has already been mentioned. When a load is applied to such a model, there is an instantaneous elastic deformation in both components, but the shear-stress in the viscous one immediately begins to relax by replacement of the elastic, by viscous deformation and, for equilibrium, the shear stress in the adjacent volume of the elastic component must also relax (Fig. 25). Because of this local relaxation, the load is transferred to the neighbouring regions, and a stress concentration builds up at the end of the viscous component.

In the limit of complete relaxation, the stress concentration for an applied pure shear is the same as that produced by a cavity, and consequently a thin, viscous plate corresponds to a Griffith crack under those circumstances.

A grain boundary in a metal supplies a viscous component (ROSENHAIN,⁽¹³⁵⁾ ZENER,⁽⁸⁾ Kê,⁽¹³⁶⁾ KING, CAHN and CHALMERS⁽¹³⁷⁾).

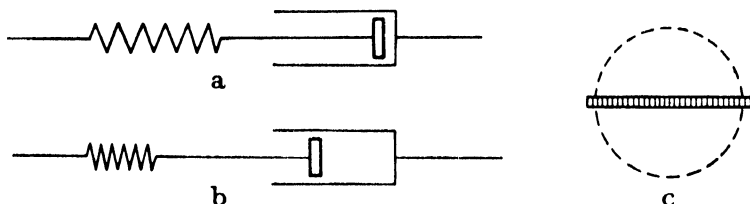


Fig. 25. The elastic-viscous model; (a) instantaneous elastic deformation (b) subsequent replacement of elastic, by viscous deformation (c) relaxation of shear stress in the volume adjacent to a viscous component

The shear stress τ in a viscous body is given by

$$\tau = \eta d\epsilon/dt$$

where ϵ is the shear strain and η the viscosity. The latter rapidly decreases with rise in temperature. Thus, at sufficiently high temperatures and low strain rates, the shear stress that can be sustained by a grain boundary becomes low, slip occurs along the boundary and the shear stress is relaxed in the surrounding volume. The result can be appreciated from Fig. 26, which shows the boundary between three grains. Slip will take place more readily along AO than along the less conveniently situated BO or CO , and the stress relaxation arising from this slip will build up a stress concentration at O , thus, eventually, initiating a fracture that spreads round the grain boundaries. Meanwhile, there may have been very little transcrystalline slip. In this way, the brittle, intercrystalline cracking that is characteristic of creep can be understood.

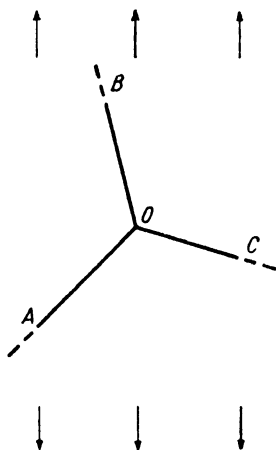


Fig. 26. Shear stress relaxation in grain boundaries

ROSENHAIN and ARCHBUTT⁽¹³⁸⁾ also ascribed season-cracking in brass to this grain boundary slip.

Various properties, for instance the anelasticity that they introduce, supports ROSENHAIN'S⁽¹³⁹⁾ suggestion that slip bands also can behave as viscous components, and this makes them a potential source of delayed fracture

by stress relaxation. The nose of a projectile may fly off some time after it has suffered plastic compression during the penetration of a plate and ZENER⁽⁸⁾ considers that the explanation lies in this shear-stress relaxation along slip planes. Also, the rather frequent case of delayed cracking in steels following quenching (e.g. BUCKNALL, NICHOLLS and TOFT⁽¹⁴⁰⁾) may arise in this way. The hair-line cracking of steel after cooling shows an induction period,⁽¹⁴¹⁾ and this possibly represents the build up of internal stresses by continuing, localized, phase transformation, but stress concentration arising from relaxation of a slip band formed during cooling may also take part.

This relaxation of elastic-viscous systems is of extreme importance in the theory of the mechanical properties of high polymers (ALFREY⁽¹⁴²⁾).

Stress Corrosion

Delayed fracture under tensile stresses may also be produced by corrosion.⁽¹⁴³⁾ Normally, this represents the accentuation of intergranular corrosion by the stress, and deep penetration into the specimen occurs. The problem is of considerable importance and has an extensive literature, but it mainly concerns corrosion and it will not be treated further here.

Intergranular penetration by molten metals is somewhat similar e.g. of solder into brass, copper or steel under tension. This appears to arise from the equilibrium of the interfacial energies (SMITH).⁽¹⁴⁴⁾

DELAYED FRACTURE—DYNAMIC LEADING

Fracture may occur under cyclic stressing even when the maximum stress is much less than either the normal ultimate stress or the yield stress. This effect is known as fatigue and it is one of the most common causes of the service failure of engineering parts.

The number of stress cycles required to produce fracture increases as the stress range decreases (Fig. 27) and, for steels, there is a fairly well-defined safe stress range (the endurance limit) within which failure does not occur. This range is commonly 80–90 per cent of the ultimate stress, and its magnitude is fairly independent of the mean stress, provided the yield stress is not exceeded in the cycle. With most non-ferrous alloys, no well-defined endurance limit is reached within the normal span of fatigue tests (10^6 – 10^{10} cycles) and it is only possible to quote a safe stress range for a given life. In these measurements, alterations in speed, e.g. from 900 to 12,000 cycles/min., have little effect.⁽¹⁴⁶⁾

A characteristic of fatigue is that the endurance limit is very sensitive to the presence of stress concentrations, so that the surface finish and the presence of notches or structural inhomogeneities, such as inclusions, are of great importance.

The early investigation of EWING and HUMFREY⁽¹⁴⁷⁾ showed that slip bands formed in Swedish iron under cyclic stressing, although the normal yield point was not exceeded and there was no major plastic deformation. As the number of cycles increased, these bands broadened until eventually cracks formed along them. Later work showed that

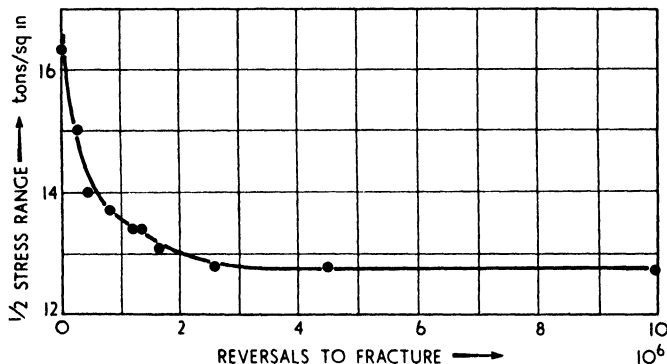


Fig. 27. The fatigue range for a mild steel⁽¹⁴⁵⁾

the cracks may form not only along slip planes, but also along twin planes, cleavage planes and grain boundaries (GOUGH⁽¹⁴⁸⁾). Total fracture does not immediately follow the formation of the crack; instead, the latter gradually grows as the cyclic stressing continues, and the markings produced by this gradual radial growth from an origin are a very typical feature of fatigue. Final rupture is usually completed by a sudden plastic or brittle fracture when the section is sufficiently reduced.

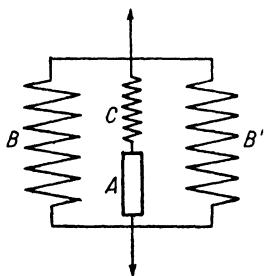


Fig. 28. Model of the behaviour of a plastic region in an elastic matrix⁽⁴⁰⁾

GOUGH and HANSON⁽¹⁴⁹⁾ associated fatigue with the formation of local plastic regions and with the increase in stress in and around these during cyclic loading. This idea has been developed by OROWAN⁽¹⁵⁰⁾ using the simplified model shown in Fig. 28. The purely plastic element *A* represents a region that, probably because of local stress concentration, becomes plastic while the main bulk of the metal, represented by the springs *B* and *B'*, is still elastic. *C* stands for the elasticity of the plastic region and its immediate surroundings, and the model is connected together by horizontal rigid bars.

The essential feature is that the total plastic strain experienced by the plastic region (α) increases with the number of cycles. Fracture may result after sufficient strain-hardening has taken place, but the increase

in plastic strain is limited, since the plastic strain amplitude simultaneously decreases; thus, the strain-hardening may stop before fracture can occur.

Suppose that a strain amplitude of $\pm \Delta$ is imposed upon $C + A$ by the surroundings. Then at each maximum of strain, the stress σ in α and the plastic deformation ε are related by

$$\Delta = k\sigma + \varepsilon$$

where $k\sigma$ is the elastic deformation. In Fig. 29, if $OB = \Delta$, the plastic deformation experienced by α if it were incapable of sustaining any

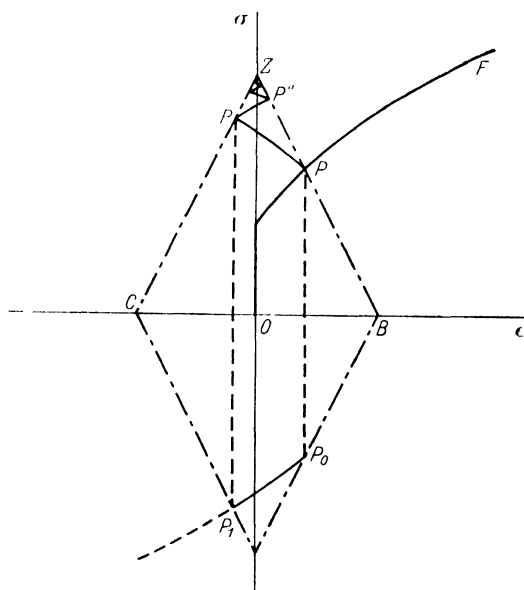


Fig. 29. The strain-hardening under cyclic stress of a plastic region in an elastic matrix⁽⁴⁰⁾

stress, and $OZ = \Delta/k$, the stress which would be reached if α behaved entirely elastically, then ZB defines the relation between σ and ε for any intermediate behaviour. If the curve OF represents the actual behaviour of α , then on the first imposition of a strain Δ , the material deforms to the point P where OF intersects ZB . On reversal of the stress, there will be elastic deformation to P_0 (neglecting any Bauschinger effect in α) and then plastic deformation to P_1 . Further reversal will produce elastic movement to P^1 and then plastic movement to P'' , and so on. Thus, an element of plastic deformation is performed at each stress reversal and strain-hardening proceeds. Meanwhile, the magnitude of the stress in α spirals up along $OPP^1 \dots$, but the strain amplitude concurrently decreases and converges upon Z , and, once there, α behaves elastically, so that the increase of stress is arrested.

This behaviour explains the general features of fatigue. If the critical conditions for fracture can only be achieved above Z , fracture cannot result however long the cyclic loading is continued, but if these conditions can be achieved below Z , fracture will eventually occur. The larger the applied stress amplitude, the larger OB and OZ , the greater the possibility of fracture and the fewer the cycles required to produce fracture. This number will also be reduced by an increase in the strain-hardening rate.

An alteration in the mean stress applied to the model alters the mean strain applied to $C + A$, but this merely corresponds to moving the triangle CZB along the ϵ axis in Fig. 29, and the critical stress amplitude for fracture should be unaffected. This agrees with the observed facts.

Once α has fractured, propagation of the crack will take place by a repetition of the cyclic strain-hardening in the region of stress concentration ahead of the fracture.

In this treatment of fatigue, compressive and tensile plastic strains are treated as additive with respect to fracture, but SACHS⁽¹¹⁴⁾ has shown in ordinary tensile tests that ductility lost by tensile prestrain may be partially regained by subsequent compressive strain. Thus, the effect of strain history on fracture is complicated, so it is not surprising that some complicated effects arise in fatigue. For instance, stressing just below the endurance limit for a large number of cycles ("under stressing") increases the endurance limit in subsequent tests, e.g. from 32,000 p.s.i. to 40,000 p.s.i. in a steel.⁽¹⁵¹⁾ A small number of cycles above the endurance limit ("overstressing") may also produce some improvement, although a larger number of cycles at the same stress, or a few at a higher stress, cause damage.⁽¹⁵²⁾ This damage can be removed by subsequent understressing.

Corrosion-fatigue

The endurance limit is lowered in corrosive media (HAIGH,⁽¹⁵³⁾ MCADAM,⁽¹⁵⁴⁾ EVANS⁽¹⁴³⁾). The cyclic stress accelerates localized corrosion, possibly because of potential differences produced by stress differences or because of the rupture of protective films. Thus, pits develop and, although the corrosion may be stifled when these get too deep, a notch for normal mechanical fatigue has been supplied by then.

SIZE AND STATISTICAL EFFECTS

When fracture is produced by Griffith cracks, the strength should decrease as the size of the sample increases, because there is then a greater probability of the occurrence of large cracks.

GRIFFITH⁽⁶⁾ found a very marked size effect in his glass fibres. The strength increased rapidly when the diameter fell below 0.001 in.

(Fig. 3), and the dependence of the strength σ on the diameter d could be expressed approximately by

$$\sigma = A + B/d$$

where A is the strength of large specimens and B is a constant. Extrapolation of this relationship to zero diameter gave $\sigma = 1.6 \times 10^6$ lb/in.², which agrees with the theoretical strength. ANDEREGG⁽¹²⁾ and REINKOBER⁽¹⁵⁵⁾ obtained similar results, and recently BIKERMANN and PASSMORE⁽¹⁵⁶⁾ have shown that the weakest of a batch of eight, 1.7 cm glass threads (each containing 102 fibres) had the same breaking strength as a single thread $8 \times 1.7 = 13.6$ cm long.

It is possible that these results are not solely due to statistical variations in the size of the cracks. GRIFFITH suggested that there might be some effect of preferred structural orientation developed by the drawing process. A similar idea was used in the calculations of FISHER and HOLLOMON,⁽¹⁶¹⁾ which indicated that the major part of the increase in strength could be accounted for by the re-orientation of defects, but it should be noted that, contrary to the assumption in these calculations, the cracks form after drawing.

The wide variation in strengths that can be obtained even in the absence of any reorientation effect was shown by POWELL and PRESTON,⁽¹⁵⁷⁾ who observed a range of $40\text{--}235 \times 10^3$ p.s.i. in the same piece of plate glass when the stressed volume was varied by loading with steel balls of different diameters.

When the fibre diameter becomes less than the normal crack size, a limitation is thereby imposed on the cracks that can occur in whole specimens and an increase in strength will result (OROWAN⁽⁴⁰⁾). Thus, the extrapolation to the theoretical strength at zero diameter agrees with the fact that such a specimen could not contain a Griffith crack.

Since PEIRCE,⁽¹⁵⁸⁾ the statistics of strength have received considerable attention (WEIBULL,⁽¹⁵⁹⁾ FRENKEL and KONTOROVA,⁽¹⁶⁰⁾ FISHER and HOLLOMON,⁽¹⁶¹⁾ GURNEY,⁽¹⁶²⁾ TIPPETT⁽¹⁶³⁾), the most general treatment being given by EPSTEIN.⁽¹⁶⁴⁾ If the strength is determined by the most effective Griffith crack, then the most probable strength and the scatter decrease as the number of cracks in the specimen increases. The actual figures will depend upon the distribution function of the crack lengths, and Fig. 30 shows some results of FISHER and HOLLOMON for which it was assumed that the frequency with which a crack of width c occurred was proportional to $e^{-c/h}$, where h is a constant. On the basis of the observed scatter for glass, they estimated that there were $\sim 10^3$ cracks/cm² of surface, and this high density is in line with the smallness of the stressed area at which low strengths were observed in the POWELL and PRESTON experiment.

Plastic, as opposed to brittle, fractures do not spread catastrophically from a crack; instead, necking first occurs, its location being determined by chance; fracture begins near the centre of the neck, and then each crystal in the path of the crack has to be deformed until it is prepared to fracture. Thus, instead of a single weak link, a number of links are involved in the fracture process and less scatter should occur than in Griffith-crack fractures. The experimental facts agree with this. Thus, the reproducibility of plastic fracture data on specimens of the same size can be within ± 1 per cent whereas a variation of ± 20 per cent

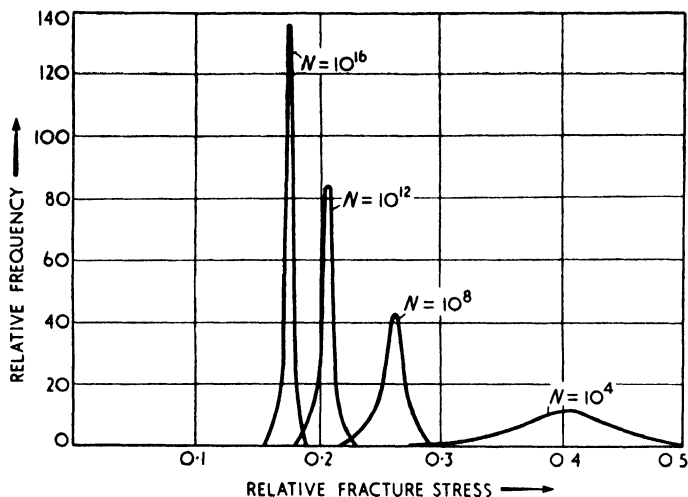


Fig. 30. The distribution of fracture stresses in specimens containing N cracks⁽¹⁶¹⁾

may occur in the brittle strength of glass. A number of investigations have shown that there is very little effect of size in plastic fracture, e.g. PARKER,⁽¹⁶⁵⁾ using specimens all cut from the same bar so as to keep the structure constant, has found little alteration in yield point, ultimate, elongation or reduction of area in mild steel specimens up to 7 in. diameter.

In a recent investigation of the statistical distribution of strengths in specimens taken from a phosphor-bronze wire (plastic fracture), PUTTICK and THRING⁽¹⁶⁶⁾ found that the random occurrence of regions of low strength at a mean distance apart of about 3 in. was indicated. This is probably a rather special case.

With notched specimens, even when geometrically similar, pronounced size effects occur (DOCHERTY,⁽¹⁶⁷⁾ PARKER,⁽¹⁶⁵⁾ SHEARIN, RUARK and TRIMBLE⁽¹⁶⁸⁾). The nominal stress at maximum load and the energy adsorbed in fracture decrease with increasing specimen size and there is

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greater liability to cleavage fracture (Table 7). Although the significance of the size effect in notched specimens has not been completely analysed, an important factor is that the geometrical similarity is destroyed as soon as a natural crack forms; such a crack is, in effect, a sharper notch in a large, than in a small specimen.

TABLE 7
Size Effect in Tensile Tests on Geometrically Similar Notched
Steel Specimens⁽¹⁶⁵⁾

<i>Size</i>	<i>Temperature of Test °F</i>	<i>Fracture</i>	<i>Nominal Stress at Max. Load (1000 p.s.i.)</i>
3 in. wide	0	Plastic	47.9
9 in. long	32	Plastic	45.2
$\frac{3}{16}$ in. thick	74	Plastic	47.7
6 in. wide	32	Cleavage	45.5
18 in. long	50	Pl. + Cl.	44.2
$\frac{3}{8}$ in. thick	70	Plastic	44.5
	90	Plastic	44.4
12 in. wide	32	Cleavage	40.9
36 in. long	70	Cleavage	39.9
$\frac{3}{4}$ in. thick	102	Cleavage	39.1

Various measurements indicate that, when the actual deformed volume is considered in a notched specimen, the energy adsorbed in fracture per unit of this volume is approximately constant, independent of specimen size.⁽¹⁶⁹⁾

FREUDENTHAL⁽¹⁷⁰⁾ has given a statistical treatment of fatigue in terms of hypothetical bonds that have a certain probability of breaking at each load application, but this has been rejected by EPSTEIN⁽¹⁶⁴⁾ on the basis that it is incorrect to treat time in the same way as length and volume.

THERMODYNAMIC THEORIES OF FRACTURE

FURTH⁽¹⁷¹⁾ and later SAIBEL⁽¹⁷²⁾ have proposed modifications to the theoretical strength calculations. Fracture occurs when the strain energy per unit volume equals the melting energy (FURTH) or that fraction of it associated with the volume change on melting (SAIBEL), so that the fracture criterion becomes

$$U = f(L)$$

where U is the strain energy and $f(L)$ is some thermodynamic function.

These theories have been criticized by ZENER⁽¹⁷³⁾ on the grounds that the value of U at fracture is structure sensitive (very markedly so in

GRIFFITH's fibres) and depends upon the stress system, whereas the thermodynamic properties are independent of these factors. Additionally, the mechanism by which the elastic energy is converted into heat is not clear, and it is not certain that local melting would in fact lead to fracture (SEITZ and READ⁽¹⁷⁴⁾).

FISHER⁽¹⁷⁵⁾ has examined the conditions under which bubbles form in a liquid under tension to give equilibrium with the vapour, and he has extended this to the fracture of glass on the supposition that cracks form in the same way. However, the calculated strengths are near the theoretical values for all-atom separation.

The possibility that fracture is initiated (particularly in creep) by the aggregation of the vacant lattice sites into cracks at the grain boundaries has recently been suggested by GREENWOOD.⁽¹⁷⁶⁾ However, thermodynamically, it is not clear why this condensation of the vacant sites should occur, although there is the interesting experimental evidence of ELLWOOD,⁽¹⁷⁷⁾ which indicates that grain boundary pores do form in certain metals on prolonged heating near the melting point.

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GEOMETRICAL ASPECTS OF THE PLASTIC DEFORMATION OF METAL SINGLE CRYSTALS

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THE early investigations up to 1935 on the plasticity of metal single crystals have been summarized in the well known volumes by SCHMID and BOAS⁽¹⁾ and ELAM.⁽²⁾ KOCHENDÖRFER⁽³⁾ extended the record of observations until 1941. Since 1941 there have been a number of extensive review chapters dealing with the phenomena of plastic deformation. Among these one should cite BARRETT,⁽⁴⁾ 1943, and the second edition,⁽⁵⁾ 1952.

In the past few years there have been a number of review articles which are concerned with specific aspects of crystal plasticity such as appearance of slip lines, by KUHLMANN,⁽⁶⁾ and by READ,⁽⁷⁾ and on the effect of surfaces on plastic deformation by BROWN.⁽⁸⁾ Other volumes on specific phases could also be mentioned.^{(9), (10), (11)} The role of twinning in plastic deformation has been considered by CLARK and CRAIG in Vol. 3 of this series.⁽¹²⁾

Many observations on specific phases of plastic deformation in metal crystals have been made in recent years. In the main, these observations can be generalized in the following way: the deformation band (kink band), the formation of slip lines, structural alterations accompanying plastic deformation, premature activity of collateral slip systems in face-centred cubic metals, renewed interest in the plastic behaviour of body-centred cubic metals, the role of the c/a ratio in close-packed hexagonal metals, and reports of the deformation of metals which do not fall into one of the three common crystal structures. References concerned with the theory of plastic deformation of crystalline solids are extensive and no attempt has been made to include them here.

A. GLIDE IN FACE-CENTRED CUBIC METALS

1. *Formation of Slip Lines—Dynamic vs. Static Observations*

Plastic deformation of face-centred cubic metals occurs predominantly by the process of glide of crystal lamellae over one other. The slip plane is usually a plane of the type $\{111\}$ (which is the most densely packed atomic plane), and the slip direction is always $\langle 110 \rangle$ (the direction of the

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most closely spaced row of atoms). Since slip is commonly recognized by the presence of slip lines which are formed by the intersections of slip planes with the surface of a crystal, a great amount of research on crystal plasticity has been devoted to the study of the appearance and formation of slip lines in the last fifty years.^{(1), (2), (5), (6), (7)}

In general, the study of slip lines is carried out on a polished surface of a single or polycrystalline solid which has undergone previous deformation, i.e. the load is generally released so that the observations can be made. This procedure was adopted by EWING and ROSENHAIN⁽¹³⁾ in 1900 in their first investigation of slip lines and has been followed generally ever since. It is certain that any picture of slip lines so obtained can represent the surface phenomena only in a static state of the strained material at a particular stage of strain. The conditions prior to their formation cannot be definitely and clearly assigned nor can the dynamic process of slip itself be rigorously considered. It is generally assumed that slip is an abrupt movement. Experimentally, there was the first observation by JOFFÉ⁽¹⁴⁾ who detected that slip was accompanied by an audible tick when the total deformation was small. In transparent crystals the intermittent nature of the process can be made evident by observations with polarized light.⁽¹⁵⁾ The usual appearance of suddenly and full developed slip lines has generally been considered as a consequence of uniform shear of the entire slip plane akin to a cataclysmic process.

There have been also many observations to indicate that slip lines may appear as the result of a growth process. The early work of YAMAGUCHI⁽¹⁶⁾ was performed in order to investigate the development of slip lines with increasing amount of strain. The number of slip lines was measured after each strain increment. He observed that the amount of shear in each visible slip line increased as well as the number of slip lines. Irregular and segmented slip lines were noted. Although cinematographic study was not carried out at that time to determine any growth process of slip, a segmented slip line would seem to suggest that further slip may continue at its terminals. Similar observations of segmented slip lines could be witnessed in many of the published static pictures.

However, there are several difficulties which may arise if one uses a static picture of a segmented slip line to argue that slip is a growth process. First of all, a segmented slip line is always associated with many others, fully developed. Without cinematographic evidence, the progressive nature of the formation of a segmented slip line cannot be deduced because the process is viewed only after its completion. Secondly, in many static pictures of slip lines, the crystallographic orientation of the observation surface is ill-defined. It is known that when the slip direction lies parallel to the crystal surface, there is no

upward displacement of one portion with respect to another, and thus slip lines are nearly invisible in this position. This fact has been used to determine the slip directions in cylindrical specimens.⁽¹⁷⁾ Therefore on deformed cylindrical crystals, the fact that slip segments whose ends seem to vanish in their path through the crystal may be mere geometrical consequences.

A direct approach for attempting to observe slip lines forming dynamically was conducted by CRUSSARD⁽¹⁸⁾ in 1945, who utilized a small, specially constructed machine by which he could pull, by hand, a specimen under the objective of a microscope. He watched the development of slip lines at $\times 100$ and $\times 600$ as the specimen was stretched. If the elongation was rapid, the lines appeared suddenly fully developed and remained unchanged as the load increased. If the stretching was slow and regular, then either a weak line appeared and became progressively stronger, or a segment of a fully formed line appeared and grew at both ends, frequently by jerks. Again, a line having developed to a certain extent ceased to grow as the stress was increased.

CRUSSARD, while giving definite qualitative evidence concerning the growth of slip lines at slow strain rates, did not submit the visual observation to rigorous analysis. For example, knowledge of the orientation of the specimen was lacking, the motion of each individual slip line was not recorded, and little clear-cut information was available with regard to the speed at which a slip band formed. As a study of the slip phenomena by an actual motion picture method, the recent investigation by CHEN and POND⁽¹⁹⁾ may be cited to illustrate these points. An experimental apparatus was designed by which the progressive formation of slip lines can be recorded while the specimen is undergoing deformation. The micro-tensile testing machine was so equipped that stress rate and strain rate could be controlled; both stress and strain could be automatically recorded, along with a time-correlation, through the movie of the photographically recorded slip lines. This is highly desirable in order to co-ordinate the photographic phenomena with stress, strain, and time.

In their experiments, they used single crystals of high purity aluminium of various orientations. It was found that when the observation plane is 90° away from the slip direction, every slip line appeared first as a segment and then propagated through the field of observation. An example showing this type of motion may be seen in Fig. 1. (The propagation of the line is clearly shown.) The movement was observed to proceed from either direction and was generally accompanied by an increase in intensity which undoubtedly indicates an increasing amount of shear in the "slip zone" concerned. The rates of propagation were measured at every $\frac{1}{32}$ sec. interval; the data from which the velocity of 30 slip lines was measured are presented in Fig. 2, together with

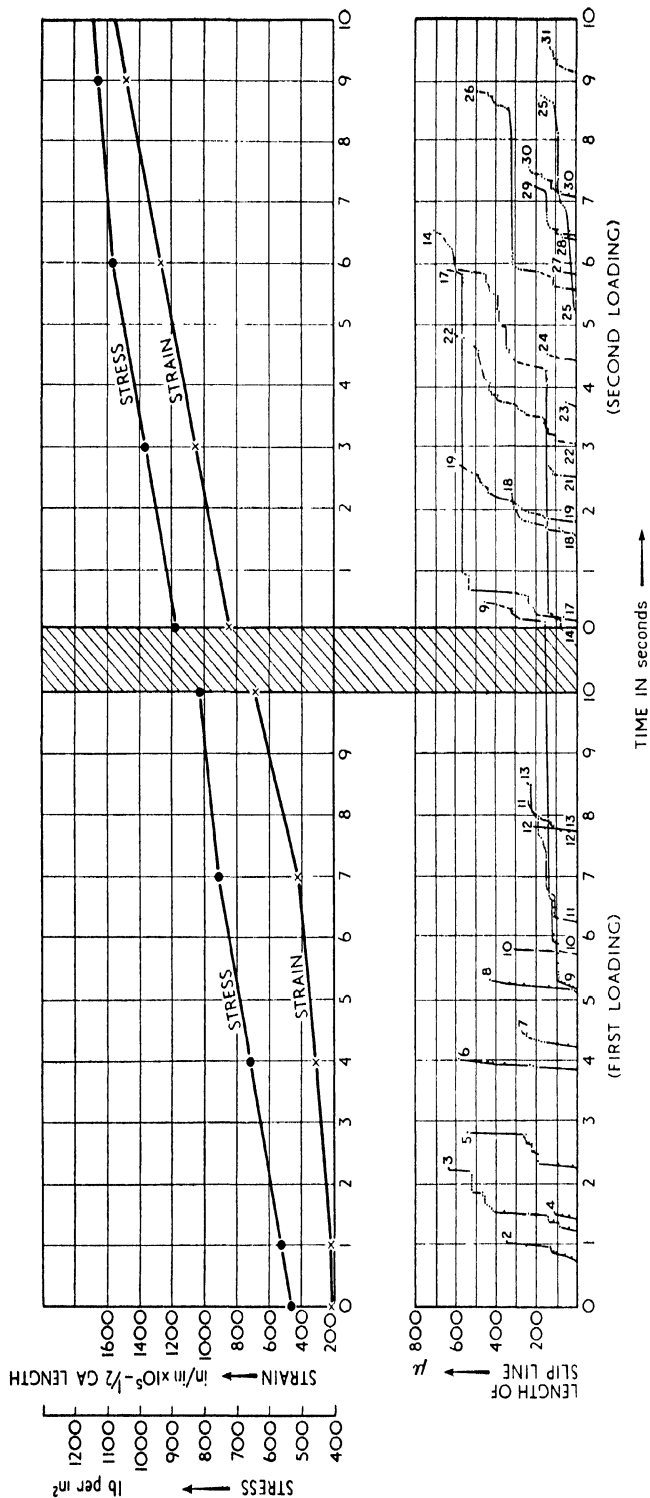


Fig. 2. Propagation of slip bands with time as correlated with stress and strain

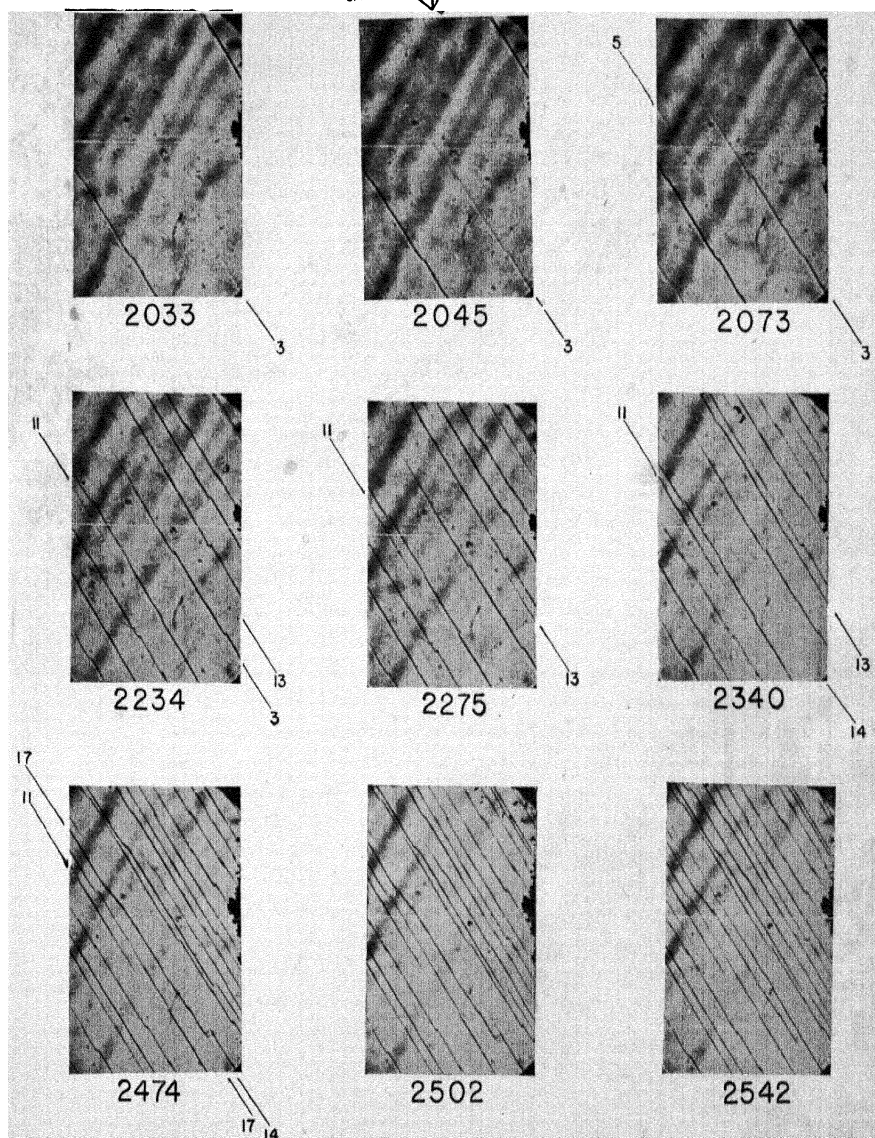
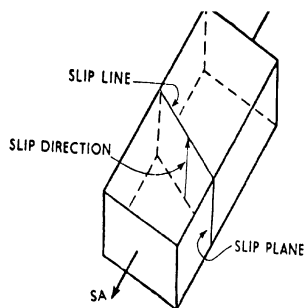


Fig. 1. Propagation of slip bands. Frame numbers are given. Speed of camera 32 ft/sec. Resolving power, 0.0022 mm.

stress rate and strain rate. It is seen from the slope of the curves that the rate of propagation varies from a maximum of about 7600 microns/sec. to a minimum of zero. From this curve, they have been led to conclude that strain hardening has the effect of retarding the propagation of slip lines. It should be emphasized that the above observations were at positions at the head of the slip direction, while a similar propagation of slip lines at positions parallel to the slip direction has not been observed to date. The implications may involve one or both of the

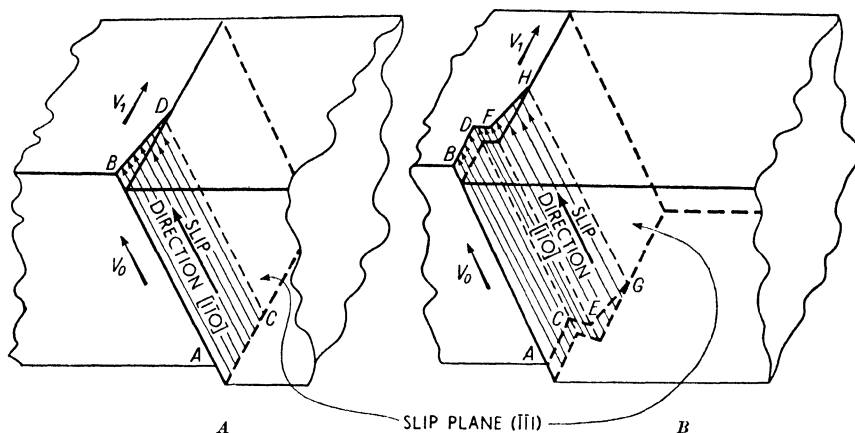


Fig. 3. Model for explaining the formation of a slip band. *A* = Growth of slip band. *B* = "Overlap" of slip bands

following two possibilities. First, the geometry of the slip process may make the observation of slip propagation at the latter position extremely difficult. For example, if the observation is made on the surface containing the line *AB* (Fig. 3), any appearance due to propagation may be hard to detect whatever the velocity, V_0 . Secondly, the velocity, V_0 , may be too large compared to V_1 to be measured by the present technique. CAHN⁽²⁰⁾ pointed out that judging from Fig. 1, the distance over which the slip line "fades out" (in frames 2234 and after) is about 70 microns. Most of the screw dislocations must be concentrated in this region, and when they have spilled over the edge of the crystal, the slip line will have appeared fully developed on the side face. Assuming a velocity of the screw dislocations of 7000 microns/sec., then the whole bunch will spill over the edge in 0.01 sec., which is less than the time between successive film frames. This would be one way to account for the sudden appearance of slip lines on the side face.

It is useful to cite a similar investigation by BECKER and HAASEN⁽²¹⁾ who measured the propagation of slip lines in aluminium photometrically. They were able to measure velocities of lengthening on the top surface up to 10 microns/sec. after loading the specimen by steps at a

relatively slower rate as compared with the strain rate, 0.00053/sec., used by CHEN and POND. In the latter case, a velocity of slip propagation up to 7600 microns/sec. was observed. It becomes apparent that an increased strain rate tends to increase the rate of slip propagation.

BECKER and HAASEN, by the photometric method, also measured the "deepening" of slip lines (propagation of slip in the direction of glide) and found that the intensity (the width) increased in a step-like fashion. One step seemingly corresponds to the formation of a new lamella in the slip band. In this connection the earlier work by TOLANSKY and HOLDEN⁽²²⁾ and HOLDEN⁽²³⁾ should be noted. They used a multiple-beam interferometric method to measure the slip steps on the surface. The accuracy in the measurement was about 100 Å. HOLDEN was able to watch the growth of the slip bands under very slow strain. His results indicated that the bands all appeared suddenly with a slip distance in the slip plane and direction of about 1000 Å. Then they grew steadily to about 2000 Å within 60 minutes and then stopped. This is in agreement with the fine structure observed under the electron microscope, i.e. one step would correspond with one HEIDENREICH and SHOCKLEY lamella.⁽²⁴⁾ Recently, however, KUHLMANN-WILSDORF and WILSDORF^(24a) using an improved electron microscope technique, and MADDIN *et al.*^(24b) using multiple beam interferometry, have shown that shear along glide planes in aluminium may vary from as little as 40 Å to values much in excess of 2000 Å. On these experimental bases, it may be concluded that the classical conception of glide should be at least modified as follows: the unit process of slip is now considered as a shear of a row, or rows, of atoms in the slip direction as represented in Fig. 3. Thus, shear of each successive row of atoms in the slip direction would lead to the observed phenomenon of propagation of a visible slip band in the position as shown in Fig. 1.

Two questions might be asked concerning the conclusions based upon the dynamic pictures of the slip bands. One is whether the micro-tensile apparatus used in the investigation by CHEN and POND was a hard machine and, as such, the rate of slip propagation could have been restricted by the rate of movement of the machine. This question was considered by testing similar specimens in a dead weight loading device at comparable load rates as used in the micro-tensile machine. Visual observations indicated that the slip propagation at positions nearly perpendicular to the slip direction was of a similar magnitude to that previously determined. This apparently eliminated the above uncertainty as far as the machine was concerned. However, it seems certain that strain rates would effect the rate of slip propagation.

The second question is concerned with the surface effect on the formation of slip lines. In this respect, both static and dynamic pictures of slip lines may be considered as a whole. The importance of an oxide

film has been studied by KEMSLEY,⁽²⁵⁾ HARPER and COTTRELL,⁽²⁶⁾ MENTER and HALL,⁽²⁷⁾ and ANDRADE, RANDALL and MAKIN,⁽²⁸⁾ since the discovery of the Reh binder effect.⁽²⁹⁾ It has been convincingly demonstrated that an oxide film on cadmium single crystals forms a tough skin which can hold up slip at the surface. If this is also true in aluminium, the velocities measured were affected by the thickness of the oxide coating. Moreover, the stress required to break the surface film might be greater at a position perpendicular to the slip direction as compared with that position parallel to the slip direction. This may perhaps account for the slow rate of slip at positions perpendicular to the slip direction as compared to the sudden appearance at positions parallel.⁽³⁰⁾

A survey of surface effects in plastic deformation⁽⁸⁾ has recently been conducted by BROWN who emphasized particularly that the micro-slip process at the first fractional per cent of strain may be nearly a homogeneous slip process. It has been demonstrated that mechanically polished surfaces show coarse slip lines while surfaces electropolished show fine lines, closely spaced.^{(31), (32)} Recent work by WILSDORF and KUHLMANN-WILSDORF⁽³³⁾ has also shown that, in stretched superpure aluminium polished electrolytically, an "elementary structure" of fine lamellae parallel to an octahedral plane always preceded normal glide band formation, which did not usually begin until 3-4 per cent glide had been exceeded. It should be pointed out, however, that while there exists a difference in the initial appearance of the slip lines on mechanically and electrolytically polished surface, a more detailed investigation of the nature of the surface *per se* after being prepared by different methods would be desirable in order to arrive at any rigorous conclusions concerning the surface effects on the appearance of slip lines or on the mechanism of slip itself. In the case of surfaces mechanically polished followed by an electropolish, slight variations of slip appearance between the two extremities mentioned above would be expected. In any event, since the usually observed slip bands always occur sooner or later on any surface prepared either way, it seems to indicate that surface condition alone could not account for the behaviour of inhomogeneous deformation.

2. *The Effect of Orientation on the Appearance and Formation of Slip Lines*

Since the effect of crystal orientation on the appearance of slip lines can best be understood from carefully documented analyses of systematic investigations, clear-cut information is quite rare. From a straightforward consideration of crystal mechanics, assuming a point in the standard unit stereographic triangle to represent the initial orientation of a crystal, it can be shown that differently orientated crystals will

require different stresses to initiate the glide, will rotate along different great circles (longitudinal axis rotation), and will glide a different amount before the participation of classical conjugate slip. ROSI and MATHEWSON⁽³⁴⁾ measured the number of slip lines for small extensions of aluminium single crystals with different orientations. At any constant value of shear strain, the density of slip bands varied markedly according to the initial orientation of the crystal. In some cases the difference in density of slip lines may be as great as 100 per cent for elongations below 2 per cent. No simple correlation was readily available with respect to the orientation effects. However, the general trend that crystals with their initial orientations near $[111]$ revealed a much smaller density than crystals of other orientations, was apparent.⁽³⁵⁾ This is in agreement with the findings of CHEN and MATHEWSON⁽³⁶⁾ that aluminium single crystals oriented near $\langle 111 \rangle$ developed a clustered appearance of slip bands similar to that of α -brass but no deformation bands. Cross-slip and premature conjugate slip were generally observed most readily between slip clusters. On the other hand, crystals of other orientations revealed more regularly dispersed slip lines together with the formation of deformation bands. A detailed discussion of deformation bands will be considered in a later section.

HONEYCOMBE⁽³⁷⁾ observed what he termed "bands of secondary slip" in extended aluminium single crystals. These bands are regions nearly devoid of primary slip traces in which slip on another system occurs preferentially. These bands are almost parallel to the primary slip lines in the early stages of deformation. According to HONEYCOMBE, they occur generally; and in crystals deforming by conjugate slip, they are often of macroscopic size. It seems quite certain, however, that crystals of certain orientations in which regularly dispersed slip lines have developed, do not show this kind of microscopic inhomogeneity. For example, CAHN⁽³⁸⁾ has studied slip lines and deformation bands in aluminium crystals with pre-determined orientations whose axes lie on the great circle joining the slip direction and the pole of the slip plane. While deformation bands are invariably observed, no indication of bands of secondary slip can be noted. Therefore the occurrence of "bands of secondary slip" may be also orientational dependent. In this connection, it may be noted that there is a great similarity in appearance of "bands of secondary slip" and the slip bands in distinct clusters for orientations near $\langle 111 \rangle$.⁽³⁶⁾

3. *The Effect of Temperature and Rate of Strain on the Appearance of Slip Lines*

It is generally observed that slip bands increase in number and at the same time the amount of shear on each band also increases during deformation. The relative rates of these two increases differ for different

metals and also with different temperatures and rates of deformation. They may presumably be related to strain hardening effects associated with the slipping process. Thus the stress-strain curve of aluminium shows marked strain hardening at room temperature and aluminium deforms by adding to the number of slip lines, while lead, cadmium and mercury when stretched at temperatures where little strain hardening results, deform on the previously formed slip planes.⁽³⁹⁾ The number of new lines that appear per increment of strain decreases as the temperature is raised and the displacement of each slip line increases.⁽⁴⁰⁾ Therefore with increasing deformation temperature, slip lines usually become fewer, broader and more contrasting. BROWN⁽⁴¹⁾ finds, with aid of the electron microscope, that shear on the individual lamellae which make up the slip bands does not alter appreciably with strain, with temperature or rate of deformation. The only major difference is their grouping into bands. After 15 per cent elongation, measurements from electron micrographs gave the following results:

<i>Deformation Temperature °C</i>	<i>Spacing between Bands Microns</i>	<i>Lines per Band</i>
- 180	$\frac{1}{2}$ -1	1-2
20	2	3-4
250	4	5-6
300	10	12

The plastic properties of aluminium single crystals were investigated at four temperatures in the range 77° to 350°K.⁽³⁴⁾ Both the critical resolved shear stress and the coefficient of shear-hardening were found to increase with a decrease in temperature, the former exponentially and the latter parabolically and were consistent with the Schmid formulation of constant critical resolved shear stress governing the initiation of the slip process. A similar investigation of silver single crystals is now in progress.⁽⁴²⁾ While the validity of the critical resolved shear stress law,^(42a) i.e. a critical value of the resolved shear stress is required for the initiation of glide on a substantial scale, seems to have been rather firmly established for hexagonal close packed metals,^{(56), (106)} LÜCKE and LANGE⁽⁴³⁾ find that the law does not appear to be even approximately obeyed in 99.5 and 99.99 per cent aluminium single crystals. Similar results for high purity copper single crystals have recently been reported by CUPP and CHALMERS.^(43a) However, FENN, HIBBARD and LEPPER'S^(43b) results on the axial extension of alpha brass (70/30) single crystals show good agreement with the critical resolved shear stress law. Nevertheless, it would appear that the law as applied to pure face-centred cubic crystals should again be tested.

Increased waviness of slip lines in aluminium (99.9 per cent pure) has been noted by LACOMBE and BEAUJARD⁽⁴⁴⁾ in crystals deformed at 450°C, probably as a result of $\{100\}$ planes becoming active along with $\{111\}$. The change of the slip system of aluminium from $\{111\} \langle 101 \rangle$ at room temperature to $\{100\} \langle 101 \rangle$ at high temperatures has been reported in the literature earlier.^(44a) However, in the case of aluminium deformed at high temperature, "cross-slip"⁽⁴⁵⁾ is very prominent. Although CAHN⁽⁴⁶⁾ has noticed cross-slip in aluminium on $\{100\}$ and $\{212\}$ as well as $\{111\}$ planes even at room temperature, recent observations by WILSDORF and KUHLMANN-WILSDORF⁽³³⁾ using an improved replica technique, concluded that only $\{111\}$ planes took part in cross-slip. Therefore slip systems of aluminium at high temperatures may be worth investigating again with particular emphasis on the study of the true crystallography of the slip process.

PARKER and SMITH⁽⁴⁷⁾ carried out some high speed tensile impact tests on single crystal and polycrystalline bars of copper at speeds of 25, 50, 75 and 100 ft/sec. Stress-strain curves show that in both types of specimens, tensile strength and elongation increase with impact velocity. Slip bands were examined both with the optical and electron microscope. It was found that a great number of slip bands function in the operating systems when crystals are fractured by rapidly applied loads. If the same amount of strain occurs in each slip band, the greater number of operating bands could account for the increased elongation. In crystals fractured at high speeds, the slip bands appeared to be much closer together, which they interpret as meaning that the material had undergone more strain per unit volume. It is therefore reasonable to expect a greater degree of strain hardening and hence a higher strength with higher strain rates.

The effect of strain rate on the plastic deformation of aluminium single crystals was studied by NISHIMURA and TAKAMURA.⁽⁴⁸⁾ Crystals subject to a slow rate of strain generally show wider slip bands and wider spacing between the slip bands, and a larger number of sets of active gliding planes than do crystals subjected to rapid strain, as determined from electron micrographs. In addition, slowly deformed crystals generally give rise to marked x-ray asterism and plastic flow. No mention was made concerning the presence of asterism in rapidly deformed crystals. Another electron-microscopic study of slip in aluminium during slow deformation at 200°C was conducted by TROTTER.⁽⁴⁹⁾ It was found that slip zones do not consist of bundles of long parallel slip lamellae but consist of segments of primary and "cross-slip." He observed that the direction of slip clusters was different from the directions of the primary slip traces, and, indeed, it may be far removed from it. Here is evidence that combinations of $\{111\}$ slip planes may lead to an apparently different trace on the crystal surface.

4. *Heterogeneity of Gliding*

It is necessary to discuss the lattice rotations accompanying the slip during plastic deformation. In a simple process such as axial extension of a single crystal, an oversimplified picture of the mechanism has been available^{(1), (2)} in that the slip direction always moves towards the stress axis in the early stages of the deformation until new geometric conditions occur to activate the conjugate slip system. This has been interpreted as a bulk rotation of the principal substance making up the shearing blocks. However, homogeneous rotation of the lattice during

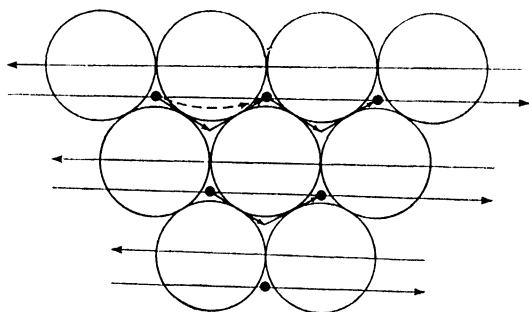


Fig. 4. Hypothetical mechanical twin formation by deviation of slip from "foothills" into "valleys" of close-packed face-centred cubic structure

extension is prohibited because of constraints imposed by the tensile grips and by the unslipped matrix material. Consequently, the crystal is forced to deform in some complex manner that will yield the observed rotation of the lattice. Two methods for adjusting the undeformed to the deformed regions have been suggested; namely, the participation of a second slip system ("premature conjugate slip system" and/or the "unpredicted cross-slip system"^{(45), (50)}) and the operation of a bending mechanism (bend planes,⁽⁵¹⁾ deformation bands^{(52), (53), (36), (37)} or kink bands^{(54), (55), (56)}). These two aspects will be considered in the following sections.

A detailed discussion of the strain redistribution has been given by MATHEWSON on the basis of a slip process in terms of incongruent shear.^{(57), (58)} The familiar $\{111\} \langle 110 \rangle$ slip in close-packed cubic structures and the corresponding slip in close-packed hexagonal structures is viewed as a two-stage movement, such as $(1\bar{1}1) [\bar{2}11]$, and $(1\bar{1}1) [\bar{1}12]$, in which the first stage places the plane of slip in a twin-relationship to the original structure ("faulted" position) and the second stage returns the structure to its original form, i.e. completes a slip in the direction of a close-packed line of atoms $\langle 110 \rangle$. This process is shown in Fig. 4.

Experimental evidence in favour of this can be summarized briefly as follows:

(1) The free development of faults by slip found by BARRETT⁽⁵⁹⁾ is analogous to the assumed development of twin faults at the shearing interfaces.

(2) Annealing twins, commonly observed in face-centred cubic metals could be considered as originating from twin-faulted regions resulting in the slip process.^{(45), (50)}

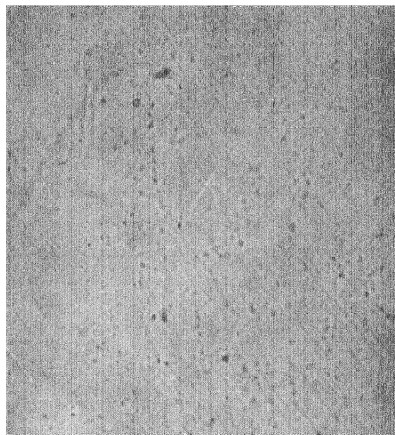
(3) The crystallographic mechanism of specific rotations involved in primary and secondary recrystallization^{(60), (50), (61)} could be related to the plastic deformation process.

(4) The rotation about the normal to the slip plane, a direct consequence of the incongruent shear process, has been confirmed by several investigators.^{(56), (57), (58), (24), (62), (63)}

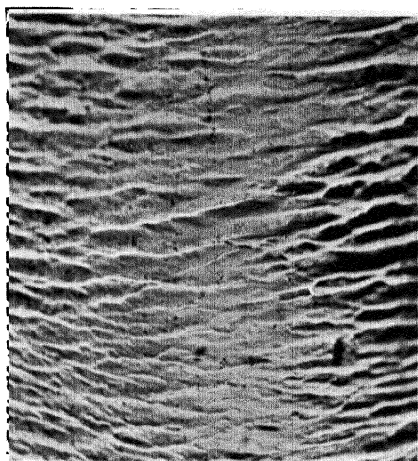
(5) The atomic movements in this process could be shown to represent easiest glide on the basis of a mechanical analogy⁽⁶⁴⁾ and from considerations of energy and the theory of elasticity.^{(57), (64), (65), (66)}

Returning to the discussion of the two particular modes of strain redistribution (and also the lattice reorientation), the operation of collateral slip, i.e. the cross-slip and/or the premature conjugate slip will now be considered. "Cross-slip" observed by MADDIN, MATHEWSON and HIBBARD in crystals of alpha brass,⁽⁴⁵⁾ when the specimen axis is wholly within a stereographic triangle, represents a slip system having a slip plane (111), 70° away from the primary slip plane ($1\bar{1}1$), and a slip direction $[\bar{1}01]$ as the common direction of glide. This system is well-defined in the case of alpha brass but less so in the case of aluminium. In the experiments of CAHN on cross-slip, planes other than the {111} were observed under the optical microscope.⁽⁴⁶⁾ ROSI and MATHEWSON⁽³⁴⁾ reported that in some cases complicated traces of cross-slip in aluminium could be resolved into composite {111} planes. In many cases, however, cross-slip in aluminium could not be viewed as lines; instead a rumpled surface is generally witnessed between the "overlapped" region of two primary slip segments. This difference in behaviour between alpha brass and aluminium has been pointed out recently.⁽⁶⁷⁾ Nevertheless this difference may be only a matter of degree as pointed out in the recent work by WILSDORF and KUHLMANN-WILSDORF,⁽³³⁾ who demonstrated from electron micrographs that only {111} planes were observed as the cross-slip planes in high purity aluminium.

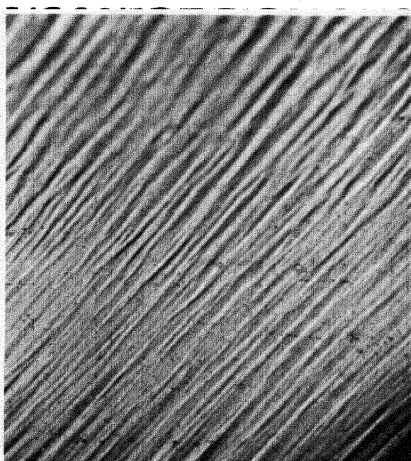
Other differences concerning slip lines in aluminium and alpha brass should be mentioned. For example, TREUTING and BRICK⁽⁶⁸⁾ observed slip lines in alpha brass to occur in clusters, at a magnification $\times 800$. The number of lines increased with elongation; new lines appearing preferentially in areas where earlier markings were present. In alu-



(a)

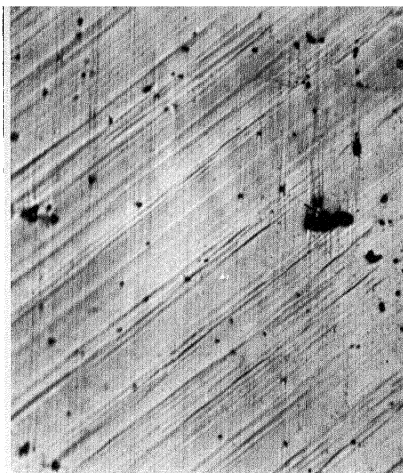


(b)

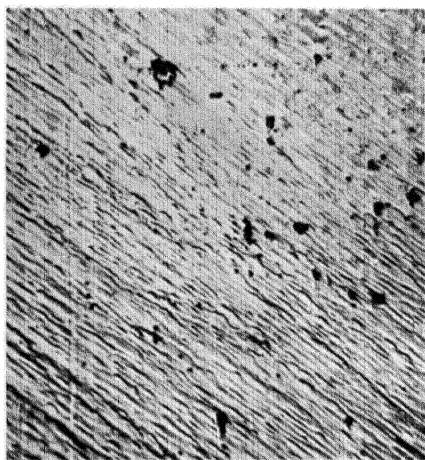


(c)

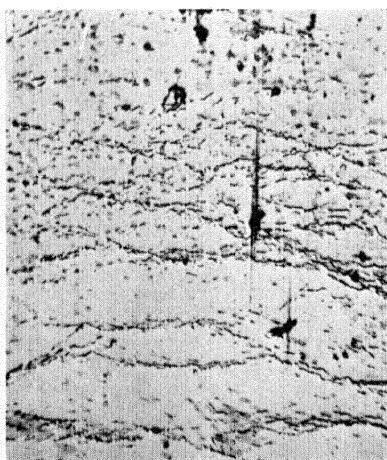
Fig. 5. Slip lines in molybdenum crystal. Stress axis vertical. ($\times 250$) (a) After the first extension; (b), (c) after the fourth extension at positions perpendicular and parallel to slip direction respectively



(a)



(b)



(c)

Fig. 6. Slip lines in alpha iron. (a) In plane almost parallel to slip direction; (b) in plane 45° from slip direction; (c) in plane perpendicular to plane of slip direction and specimen axis. ($\Delta 11 \times 150$) (VOGEL and BRICK)

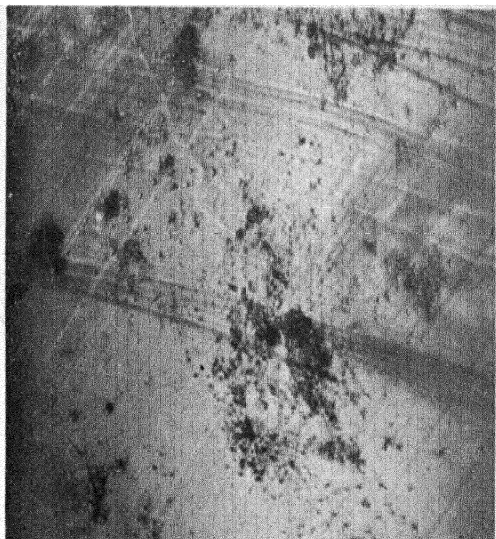


Fig. 7. Slip lines and deformation bands in compressed (5.97 per cent) niobium single crystals. ($\times 350$)

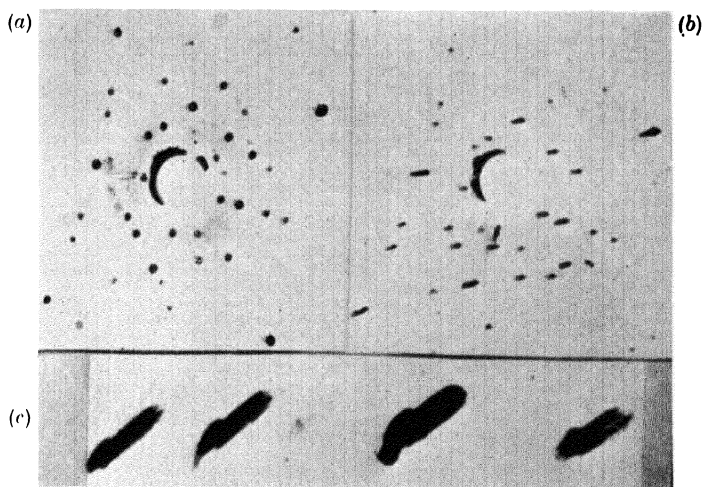
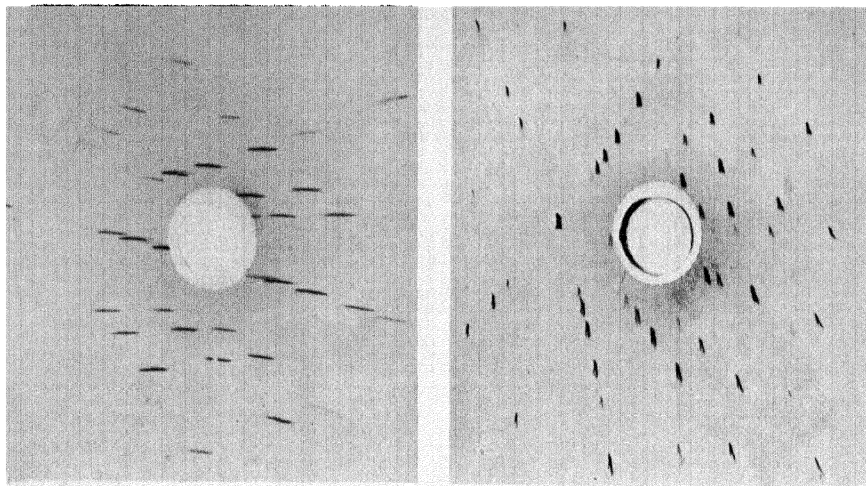


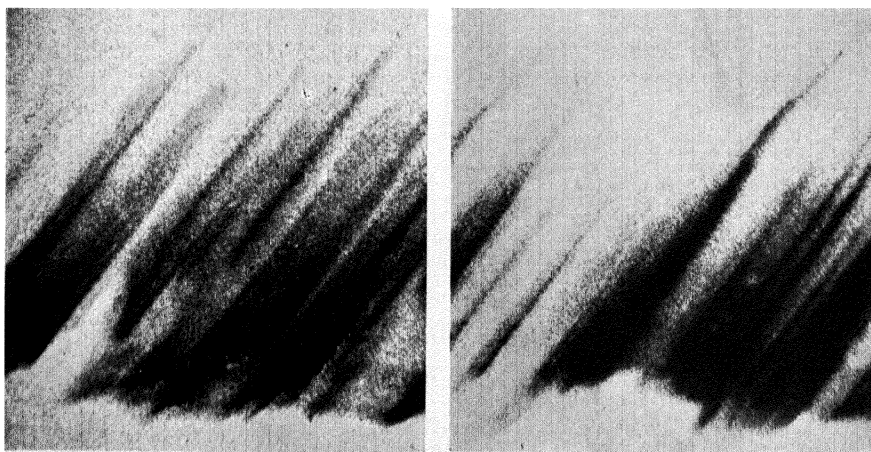
Fig. 8. Asterism in Laue reflections from extended molybdenum single crystal. (a) Before extension; (b) after first extension to 4.8 per cent; (c) enlargement of Laue spots in (b)



(a)

(b)

Fig. 9. Laue reflections from bent molybdenum single crystal. (a) Tension side; (b) compression side



(a)

(b)

Fig. 10. (a) X-ray micrograms of an extended molybdenum single crystal (4.1 per cent elongation) made using a bent quartz crystal monochromator. ($\times 50$); (b) same surface as (a) but another position. Showing "sharp bends." ($\times 50$)

minium, however, slip lines are generally dispersed, i.e. uniformly and regularly spaced presenting no cluster appearance (with the exception of crystals oriented near $\langle 111 \rangle$ ^{(36), (69)}). From the sequential addition of the new lines studied cinematographically in aluminium,⁽¹⁹⁾ the hardening effect associated with each slip line was found to influence the geometry of the addition of slip lines. Other factors are known to effect the appearance of the addition of slip lines. Thus BLEWITT⁽⁷⁰⁾ has shown that copper single crystals which would generally reveal dispersed slip lines developed clustered slip bands after being irradiated in a slow neutron beam of high flux density. The clustered appearance is quite similar to that generally observed in 70-30 alpha brass.

Another difference between the plastic behaviour of alpha brass and aluminium lies in their different capability of revealing "strain markings." BURKE and BARRETT⁽⁷¹⁾ found that strain markings in alpha brass which can be developed by polishing and etching are visible whenever slip has occurred. However, in aluminium, strain markings are seldom witnessed, probably due to their thermal instability at room temperature.⁽⁷²⁾

The formation of deformation bands represents another important mode of lattice reorientation. In the extension of aluminium single crystals, COLLINS and MATHEWSON⁽⁵²⁾ first noted a banded appearance and the intimate connection of this banded appearance with the recrystallization behaviour. The crystallography of the bands is now well established in that at the early stages of deformation, they form on planes normal to the active slip direction, which is $\langle 110 \rangle$ ^{(36), (37), (38), (69), (73)}. The mechanism for their formation could be explained on the basis of flexural gliding, i.e. an inhomogeneous rotation about an axis in the slip plane and roughly 90° to the slip direction (similar to the formation of bend planes⁽⁵¹⁾ or kink bands.^{(54), (55)}) The formation of deformation bands has been found to be orientation-dependent. In the case of aluminium during compression, most crystals near $\langle 110 \rangle$ do not develop deformation bands.⁽⁷⁴⁾ In tension, crystals oriented near $\langle 111 \rangle$ also do not lead to band formation.⁽³⁶⁾ In these orientations slip clusters were observed instead of the regularly dispersed slip lines of aluminium. It was pointed out⁽³⁶⁾ that this behaviour correlates properly with the plastic behaviour of alpha brass crystals which develop slip clusters in tension but no deformation bands, so far as is known at present. Other orientations which exhibit no band formation in the extension of aluminium have been found as follows: those mentioned by HONEYCOMBE⁽⁷⁵⁾ with crystal axes near $\langle 001 \rangle$ and those found by LÜCKE and LANGE⁽⁴³⁾ and IGARASHI, OKADA and HIROKATA⁽⁷⁶⁾ with crystal axes near the boundary between $\langle 111 \rangle$ and $\langle 001 \rangle$ in the unit stereographic triangle. In both cases, clustering of slip lines was also observed.

The spacing between deformation bands in aluminium at the early stages of extension (below 1 per cent elongation) may be of the order of 0.05 mm but may be as large as 1 mm.^{(36), (69)} In the latter case, x-ray asterism was accounted for merely on the presence of deformation bands, since an x-ray beam could be directed both on and between two deformation bands. This has been demonstrated clearly both by using a back-reflection⁽³⁶⁾ and also by transmission Laue techniques.⁽⁶⁹⁾ Analyses have indicated that the lattice within a band always lags behind the slipped matrix between two bands. Recently GAY and HONEYCOMBE⁽⁷⁷⁾ investigated the origin of x-ray asterisms by a micro-beam method in extended aluminium single crystals which had fine deformation bands. They pointed out that asterisms are attributable mainly to deformation bands. x-ray microscopy has also been successfully used to reveal the presence of deformation bands in extended aluminium.⁽⁷⁵⁾ The orientation of the bands so determined checked with the results obtained from optical determinations.

The effect of deformation bands on strain hardening is somewhat uncertain. HONEYCOMBE and others⁽⁷⁸⁾ believe that deformation bands exert considerable influence on the strain hardening characteristics; they explain on this basis the fact that face-centred cubic metals strain harden more rapidly than hexagonal metals. On the other hand, exceptions have been found in that rapid strain hardening is not to be associated with the occurrence of deformation bands in extended aluminium single crystals.⁽⁴³⁾ More documented investigations seem necessary to clarify the exact contribution of deformation bands to strain hardening.

The importance of deformation bands in the formation of preferred orientation has been extensively discussed by BARRETT⁽⁶⁾ and their effect in the process of polygonization, sub-grain formation and recrystallization has been reviewed recently in this series, Volume 2.

B. GLIDE IN BODY-CENTRED CUBIC METAL CRYSTALS

While the slip traces on cubic face-centred and hexagonal close-packed metals are straight, indicating glide across single planes of atoms, those on body-centred cubic metals are often branched and wavy; hence, the determination of the active plane becomes vague. As a consequence, the elementary mechanism of glide in body-centred cubic metals has been clouded in dispute for many years. From the fact that glide in both face-centred cubic and hexagonal close-packed metals occurs on planes of highest atomic density and the direction of closest packing, it would appear plausible to suggest that glide in the body-centred metals occurred on the {110} planes and in the $\langle 111 \rangle$ directions. However, it may be that there are more profound differences in the deformation

between these metals than their differences in crystal structure would suggest.

1. *The Appearance of Glide Traces*

The appearance of glide traces on these metals deserves some attention at this time. In Fig. 5 there is shown the appearance of slip lines on molybdenum single crystals after different amounts of extension.⁽⁷⁹⁾ It may be noted that after extension to just beyond the yield, the slip lines appear as fine striae with little contrast (Fig. 5a). After about 18 per cent elongation, however, the lines are distinct but wavy; the amount of waviness being dependent upon the position of observation. At the head of the ellipse the lines are branched whereas at a position which contains the predominant slip direction, they are fairly straight. This same effect may be seen in crystals of alpha iron pulled in tension⁽⁸⁰⁾ (Fig. 6). In niobium two types of markings could be noted: (1) lines which were straight and sharp wherever they could be viewed and may rightfully be called slip lines, and (2) bands with sensible widths which were branched and forked but appeared to be made up of small straight sharp lines. Quite often it was possible to see both types in the same area as shown in Fig. 7.⁽⁸¹⁾ The same effect may be noted in bent single crystals of molybdenum.

2. *Laue Asterisms*

The Laue reflections from undeformed crystals of molybdenum,⁽⁷⁹⁾ niobium,⁽⁸¹⁾ sodium and potassium,⁽⁸²⁾ are clear and free of any fine structure. After exceeding the yield, however, the Laue reflections become distorted (asterism) and are composed of fine structure Fig. 8a, b, c). With increasing deformation the asterism takes on a characteristic overall shape as well as a fine structure. Sodium and potassium, however, show distortion of Laue spots at room temperatures into continuous bands containing a series of more or less elongated discrete spots which become more widely separated as extension increases. The distortion corresponds with a rotation of crystallites about a single crystallographic axis in the glide plane and perpendicular to the glide direction.⁽⁸²⁾ Iron, on the other hand, does not exhibit large changes in the Laue reflections.⁽⁸⁰⁾ Alterations in Laue spots as a result of plastic bending in molybdenum can be seen in Fig. 9.⁽⁸³⁾ It may be pointed out that although the asterism characteristic of the tensile side of the bent molybdenum crystal is comparatively "simple," the asterism from the compression side is quite complex. The overall shape of the Laue reflections as well as their fine structure have been used to determine the glide elements and will be discussed shortly.

The technique introduced by BERG⁽⁸⁴⁾ and developed by BARRETT⁽⁸⁵⁾ which has come to be known as the Berg-Barrett method has found

application in the study of disorientation produced by deformation. By using an x-ray beam focused from a bent quartz crystal, good reflections have been obtained from molybdenum and niobium crystals deformed in tension and compression.⁽⁸¹⁾ In Fig. 10 there is shown enlarged x-ray reflections from an extended molybdenum crystal after the surface had been repolished electrolytically. The x-ray micrograms show the change of direction of the bands (the length of the band being straight).^(81a) Although no deformation bands could be observed optically after 4 per cent deformation in this molybdenum single crystal, the sharp bending of the bands (shown in Fig. 10b) may indicate the beginning of deformation bands. Contrasted with this, however, the surface of the crystal extended 21 per cent showed clearly defined deformation bands along $\{111\}$ planes as may be noted in Fig. 19. The corresponding x-ray micrograms, shown in Fig. 11, again exhibit band formation.

3. *Determination of Glide Elements*

The methods used in determining the elements of glide which were developed prior to 1935 are covered completely elsewhere⁽¹⁾ and consequently they need only be mentioned here. Where the normal to the glide plane is parallel to a symmetry axis of a crystal, a Laüé photogram is all that is necessary to identify the plane when it is possible to position an x-ray beam perpendicular to the plane. The direction of glide has been determined directly by means of rotation photograms⁽⁸⁶⁾ and more recently by Weissenberg techniques.⁽⁸⁷⁾

More indirect methods have been developed to determine both planes and directions; methods which are still used to-day. These involve the change in orientation caused by plastic deformation. For determining the slip direction, the initial and final orientations of the longitudinal axis of a tensile specimen are plotted stereographically from x-ray photograms. It can be shown that the direction in the plane of glide to which the longitudinal axis moves is the slip direction.⁽¹⁾ In the face-centred cubic and hexagonal close-packed metals, it has been possible to determine the glide plane from lattice rotation during compression since, here, the normal to the glide plane moves toward the axis of stress. The reorientation of body-centred cubic crystals during compression has been used to determine the active slip plane assuming that only one family of planes contributed to the reorientation.⁽⁸¹⁾ For the crystals so far investigated (niobium,⁽⁸¹⁾ molybdenum⁽⁸³⁾), good evidence has been obtained to show a migration of the compression axis towards the pole of a particular $\{110\}$ plane.

A more rigorous method for determining the slip planes depends upon the observation of the traces from more than one surface of a crystal. These traces are then referred to a stereographic plot of a Laüé photogram

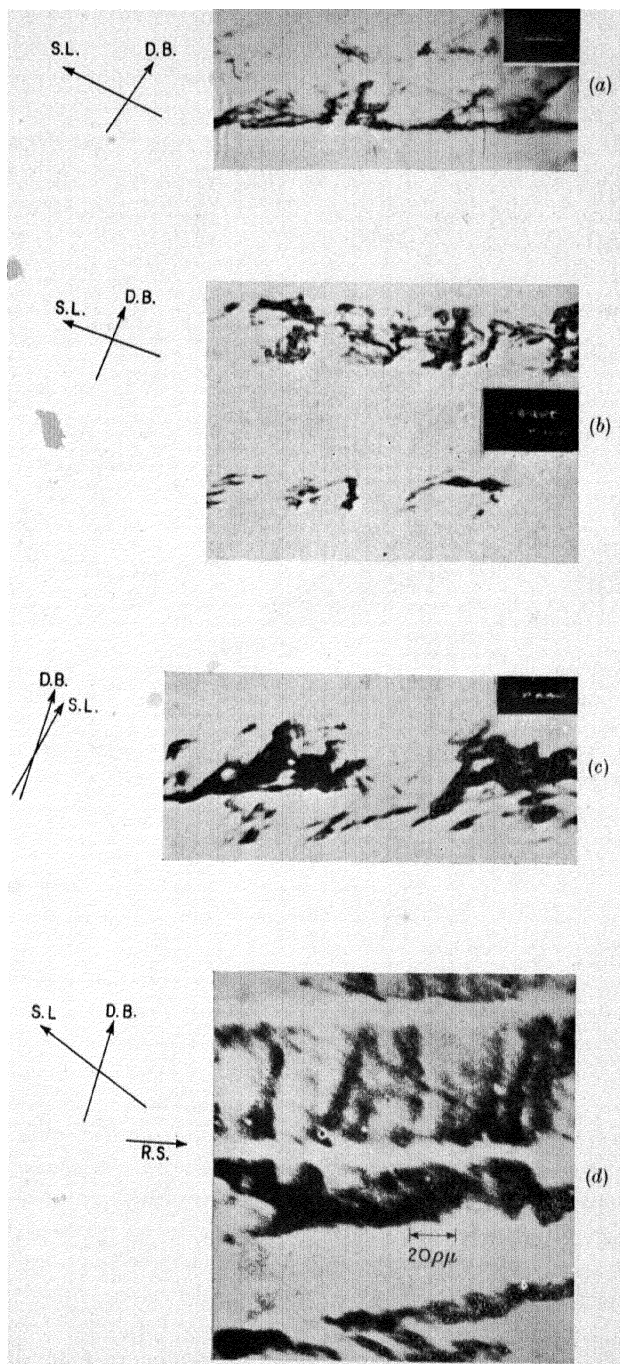


Fig. 11. X-ray micrograms of an extended molybdenum single crystal (20.6 per cent elongation) showing deformation bands (D.B.) and slip lines (S.L.). (a), (b), (c) Different surfaces of crystal. ($\times 30$)

along with the angle which the traces make in the plane of observation with a reference mark. Where the traces of glide planes are straight throughout their observable length at all positions of observation, and where there can be no doubt that the trace observed in one surface is caused by the same plane or belongs to the same (hkl) plane as the trace observed at different positions on the surface, this method would constitute proof. However, in the case of the body-centred cubic crystals, the traces are generally wavy. Consequently, it is sometimes extremely

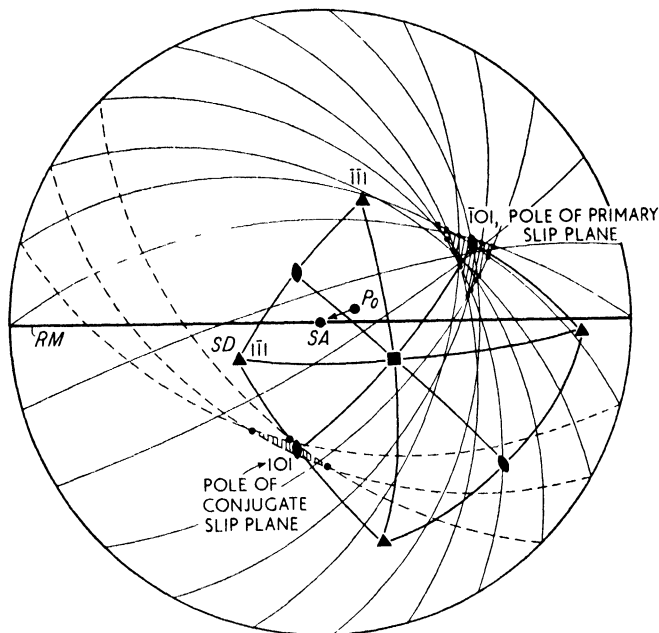


Fig. 12. Determination of the pole of the slip traces. Stress axis SA , at the centre of projection, and x-ray beam containing the reference mark RM is perpendicular to stress axis. P_0 is the initial orientation. Errors measured from (101) pole to each individual determination is 0° to 6°

difficult to assign a particular direction to a series of traces. In these cases, measurements can be made at many positions around the specimen axis. In Fig. 12, there is plotted a stereographic projection of an extended molybdenum single crystal.⁽⁷⁹⁾ An indicator was attached to the specimen along a reference mark that was also used for the reorientation determination by x-rays. The angle of rotation was measured on a protractor attached to the stage of a metallograph. Measurements, every 15°, of the angle between the specimen axis and the slip markings were made at a magnification of $\times 250$. These measurements were plotted stereographically and the pole representing the slip trace on

each surface of observation was located from the intersection of these plotted traces. The area, encompassing the $(\bar{1}01)$ pole can be considered to be caused by the inability to assign the correct direction to the traces in some positions. A modification of this method has been used recently by VOGEL and BRICK⁽⁸⁰⁾ in determining the glide planes of extended alpha iron single crystals. The angle representing the inclination of the trace with the specimen axis at each azimuthal position of observation was transferred to a stereographic projection and plotted as a point. The best great circle fitting these points was drawn and the pole

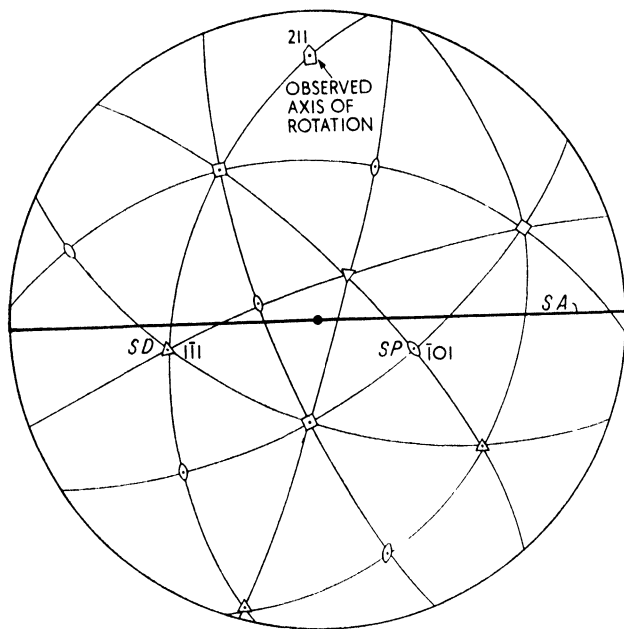


Fig. 13. Stereographic plot of asterism shown in Fig. 15

located in the usual manner. In this latter method, the error of assigning a particular direction to a set of wavy lines may be aggravated by assigning only one great circle through the set of points which results in one possible pole.

Still another method used in determining the active glide plane depends upon distortion of the lattice after extension. This method depends upon the asterism resulting from axial elongation of single crystals. If it is assumed that the asterism has its origin in the Taylor rotation, i.e. the axis of asterism is in the plane of glide at right angles to the direction of glide, then the axis of asterism coincides with a low indices zone axis in the cubic system. If the plane of slip is assumed to be a $\{110\}$, then this axis will be a $\langle 112 \rangle$. Consequently, if the axis of

well-defined asterism is determined, the plane of slip can be designated. This method may be illustrated in Figs. 13 and 15. For this case, the pole of the observed traces plotted stereographically shows $(\bar{1}01)$ to be the glide plane and the axis of the major asterism indicates $(\bar{1}01)$ to be the glide plane (Fig. 13). However, the stereographic plot of the traces of another molybdenum single crystal indicates a $\{112\}$ to be the slip plane (Fig. 14), yet analysis of the asterism (Fig. 8) indicates two co-operating $\{110\}$ planes to be the glide planes. If a $\{112\}$ was the plane of glide, a $\langle 110 \rangle$ axis, about which asterism should occur, is not observed.

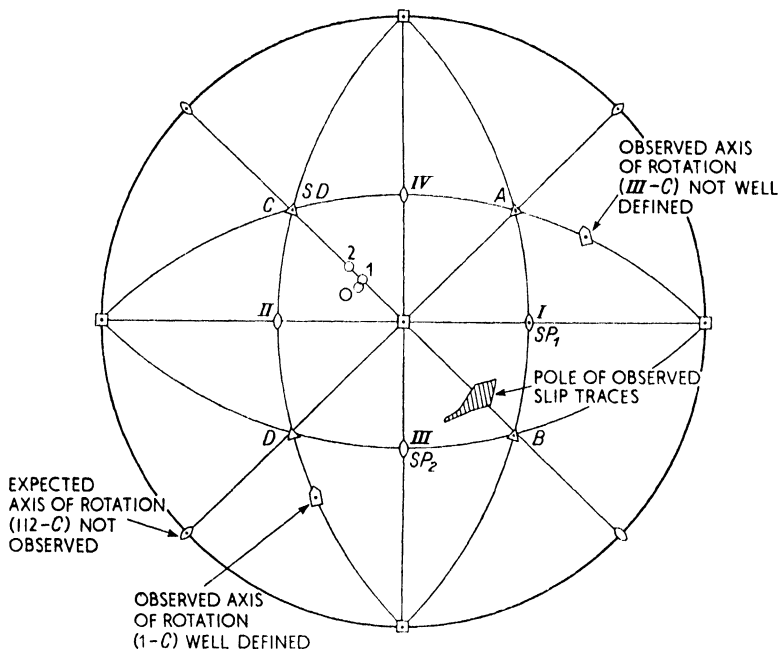


Fig. 14. Projection of M-12 showing the pole of observed slip traces, the axes of rotation determined from asterism, and the stress axis movement

The angular spread in asterism has also been used to determine the plane of glide in niobium.⁽⁸¹⁾ In Fig. 16 there is shown a photograph of a niobium crystal after about 6 per cent compression. Two distinct directions of the asterism can be noted. If the ends of these streaks are plotted in the same projection (Fig. 17), the reorientation of the compression axis can be noted. As stated earlier, if the reorientation of the compression axis specifies the pole of the slip plane, then it can be said that the $(\bar{1}01)$ and the (101) are the planes of glide. Another example of this method can be seen in Fig. 18 for the asterism on the tensile side of the bending of a molybdenum single crystal. Here the asterism spread

clearly demonstrates a rotation towards the $[1\bar{1}1]$ direction. It should be pointed out that these latter methods can only be applied where well-developed asterism can be noted. In the case of alpha iron, where asterism is difficult to detect, the technique has proved unsuccessful.

4. The Deformation Band

Little is known concerning the role of the deformation band in the deformation process of body-centred cubic crystals. BARRETT states

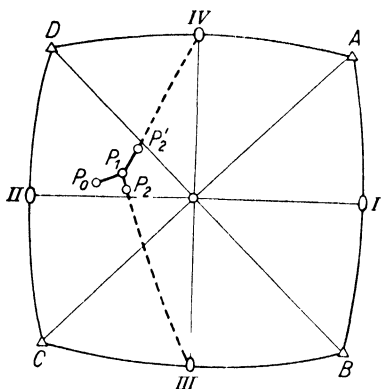


Fig. 17. Initial and final orientations of niobium single crystal compressed 11 per cent. P_2 and P_2' indicate end points of double asterism shown in

Fig. 16

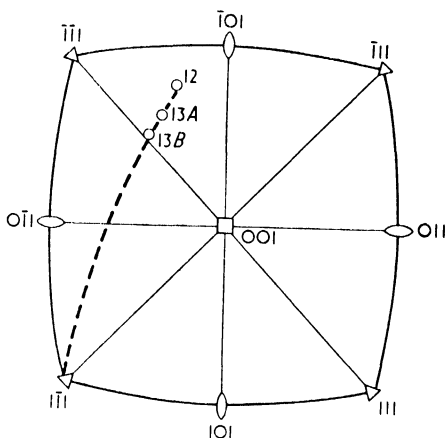


Fig. 18. Lattice rotations as determined from extent of asterism on tension side of bent molybdenum single crystal (Laue photograph shown in Fig. 9a)

that "body-centred cubic iron exhibits deformation bands after all types of deformation and with both homogeneous and heterogeneous strain, and it is not unlikely that bands are produced in all other body-centred cubic metals."⁽⁵⁾ In iron crystals, no bands are found⁽⁵⁾ for an orientation in which the $\langle 100 \rangle$ axis or the $\langle 111 \rangle$ axis is parallel to the axis of compression but they are formed in crystals of all other orientations. Although there has been no detailed investigation of the crystallography and progressive formation of bands, it is known that in iron after elongation, the boundaries of the deformation bands first form on $\{100\}$ and $\{111\}$ planes.⁽⁵⁾ Similar bands have been reported on beta brass by ELAM; these also form on $\{100\}$ and $\{111\}$ planes.⁽⁸⁸⁾ The appearance of the deformation band is illustrated in Fig. 19 which shows bands in an extended molybdenum single crystal.^(81a)

5. Delay Time Experiments

Among the more recent experiments pointing out differences between the behaviour of body-centred cubic and face-centred cubic crystals are

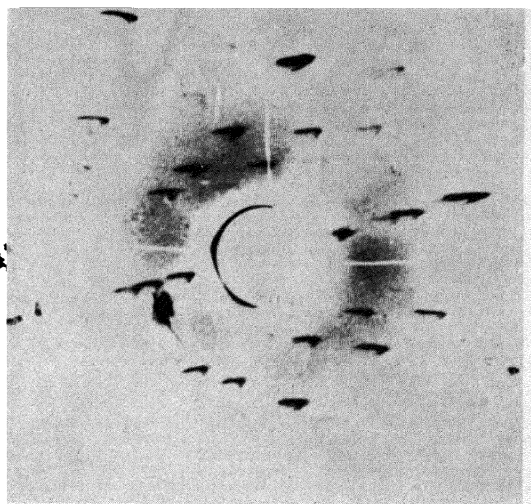


Fig. 15. Laue photograph of molybdenum single crystal after the fourth extension. X-ray beam perpendicular to plane containing specimen axis and minor elliptical axis

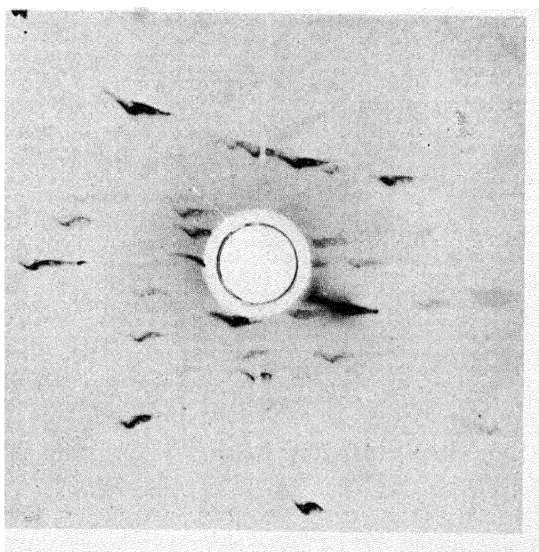


Fig. 16. X-ray photograph showing two asterisms. These are plotted in Fig. 17 as $P_2 - P_2^1$

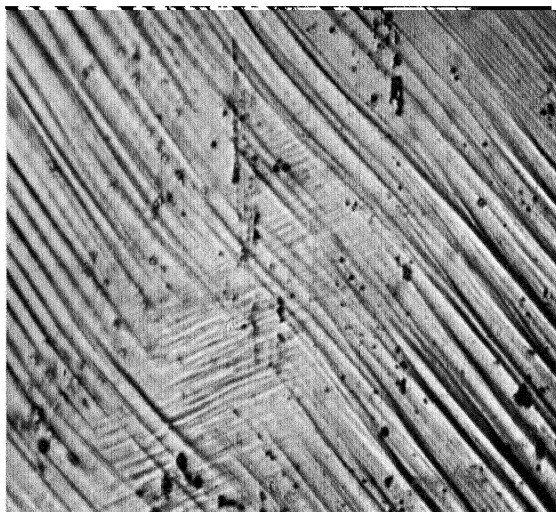


Fig. 19. Slip lines and deformation bands in an extended molybdenum single crystal (20·7 per cent elongation).
($\times 500$)

the investigations of KRAMER and MADDIN on delay times for the initiation of slip.⁽⁸⁹⁾ In these experiments, the investigators stressed single crystals of alpha brass, aluminium and beta brass at 28°C, - 52°C and - 190°C. The load was applied through pendula in such a way that the time duration of the stress could be varied from 1×10^{-6} to 1×10^{-2} sec. They found no delay in the glide initiation for alpha brass and aluminium down to - 190°C for 1×10^{-6} sec. duration of load. However, they found that beta brass could withstand stresses at - 190°C about ten

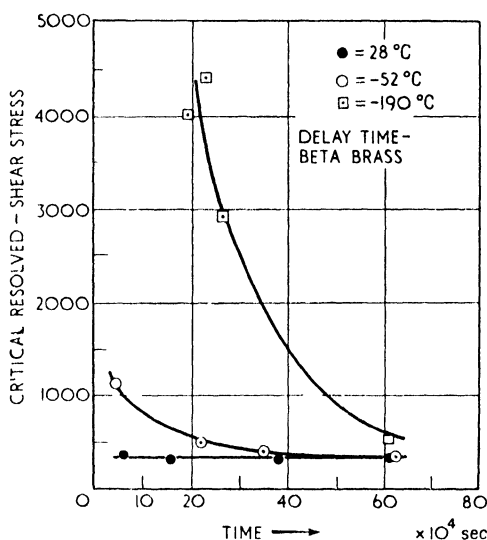


Fig. 20. Delay-time curves for β -brass at 28°C, - 52°C, and - 190°C

times the value at room temperature when the time application of load was 2×10^{-3} sec. or shorter. The results for beta brass are shown in Fig. 20. It is interesting to note that no measurable effects on critical resolved shear stress of the high "rate of strain" were observed in the aluminium and alpha brass crystals. While the moduli used in the calculation of stress were determined by static means and their application during dynamic loading might be open to question, the critical resolved shear stresses calculated using these moduli conformed closely to those for aluminium and alpha brass obtained by the usual stress-strain curves.

MATHEWSON⁽⁹⁰⁾ has considered one possibility to account for the high value of critical resolved shear stress for short times of loading observed in beta brass in these experiments. In Fig. 21 there are shown two atomic layers of the $\{110\}$ planes of slip in the body-centred cubic structure. Two possible paths of atoms during glide are indicated by the paths 1' 2 3' 4 and 1' 4. These may be compared with the movements in the

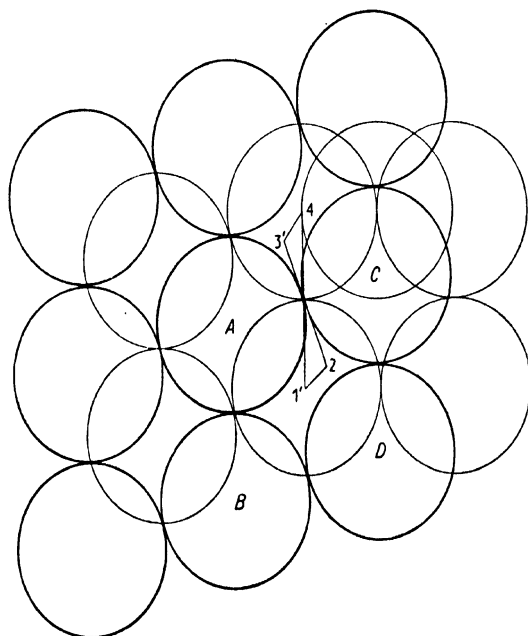


Fig. 21. Suggested paths of atoms as a result of short loading times

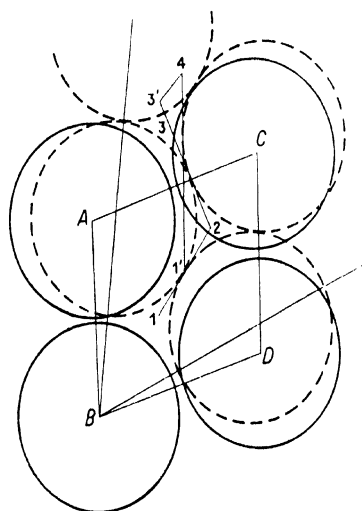


Fig. 22. Comparison of paths of atoms in face-centred cubic (dotted circles) and body-centred cubic lattices

face-centred cubic structure shown in Fig. 22 where the analogous paths would be 1, 2, 3, and 1, 3 (referring to the dotted circles). The path of easiest glide suggested by MATHEWSON⁽⁵⁷⁾ and shown to result in faulted positions by BARRETT⁽⁵⁹⁾ has been discussed earlier in this review. It might be argued that the slow movement from 1' to 2 (Fig. 22) in the body-centred cubic structure forms approximately a face-centred structure whose free energy may be assumed not to differ greatly from the free energy of the body-centred cubic structure, while the fast movement, without free redistribution of the plastic stress, from 1' to 4, requires the transient formation of a highly unsymmetrical lattice (or a much distorted simple lattice). With the face-centred structure, it may be imagined that the direct movement from 1 to 3 would produce a greater deviation from any simple lattice than can be tolerated, whatever the form of stress application. Consequently, along the enforced path 1' 4, in the case of body-centred cubic structure, a much higher critical stress would be required.

In a recent publication analyzing the delay time experiments, SEITZ⁽⁹¹⁾ suggests that the generators for plastic flow in beta brass are locked. Where stresses are applied for times greater than τ_c , the critical time of duration of stress below which an increase in stress is necessary to cause plastic flow, thermal fluctuations are adequate to free generating dislocations from the pinning points. When the time of application of load is less than τ_c , an increase in stress is needed to decrease the activation energy for freeing the generating dislocations from the pinning points. From the experiments of GALLAGHER⁽⁹²⁾ on silicon and germanium, SEITZ concludes that the incubation time satisfies an equation of the form $\tau = \tau_0 \exp(Q/RT)$. On the above assumption τ_c becomes essentially equal to τ if there is a measure of the time required to free dislocations without lowering the activation barrier. In a rough approximation with $\tau_c = 8.0 \times 10^{-3}$ sec. at -190°C and $\tau_c = 4.0 \times 10^{-3}$ sec. at -52°C (from Fig. 20) and using the equation $\tau_c = \tau_{0c} \exp(Q/RT)$, Q is of the order of 180 cal/mol and τ_{0c} is 3×10^{-3} sec. It is stated that the second relation is only roughly in agreement with the observations. The minimum possible values of τ_c would be about 3×10^{-3} sec. with values of the parameters as shown above. KRAMER and MADDIN did not observe a critical time at room temperature for times as short as 2.6×10^{-4} sec. However, Q is approximately 100 times smaller in the case of beta brass than in the cases of silicon and germanium (from GALLAGHER's work). SEITZ also points out that it is clear that an appropriate realm of τ_{0c} is much larger than 10^{-11} (the value of τ_0 determined from the first equation for a typical Frank-Read generator 10^4 atom distances long containing 100 locking points), and is actually comparable to the value of 10^{-5} (from the experiments of GALLAGHER for silicon and germanium).

6. *Crystallographic Mechanisms of Glide*

Among the earliest experiments concerned with the behaviour of body-centred cubic crystals are those of TAYLOR and ELAM.^{(88), (93), (94)} Small single crystals of ferrite were deformed in tension and compression. The operative slip systems were determined from measurements of the distortion of grids which were engraved on the specimen (the unstretched cone method). Their analyses indicated that glide occurred in the close-packed direction on planes close to those of maximum shear stress containing the close-packed direction. When deviations from the plane of maximum shear stress occurred, they were always towards the closest $\{112\}$ pole. Based upon these results, they proposed their theory of "pencil" glide (banal glide, non-crystallographic glide). The process was likened to the glide that would occur in a bundle of hexagonal rods where the lengths of the rods defined the slip direction and the surfaces of the rods defined the planes. With this analogy, it can quite easily be seen that if the traces of glide are observed at the rod ends, they would be wavy; if they were observed close to a plane containing the direction of glide, they would be straight. The photomicrographs in Fig. 6 illustrate that observations made at these positions bear out the predictions outlined by TAYLOR and ELAM. Investigations with beta brass crystals demonstrated a similarity to the behaviour of ferrite with the major difference being in the inclination of the deviation of the determined plane of glide. Whereas the deviation from the plane of maximum shear stress containing the slip direction was towards the closest $\{112\}$ in ferrite, it was towards the closest $\{110\}$ in beta brass. These observations led TAYLOR to suggest that the resistance to shearing on a given plane containing the slip direction was a function of the angle between the actual plane of glide and the closest $\{110\}$.

FAHRENHORST and SCHMID⁽⁹⁵⁾ measured the yield strength of a large number of ingot iron single crystals whose orientations were known. They calculated the critical resolved shear stress of the crystals by assuming that glide would occur on $\{110\}$, $\{112\}$, $\{123\}$ or on non-crystallographic planes of maximum resolved shear stress. They concluded that their measurements of yield strengths best fitted the assumption that slip had occurred on $\{123\}$. They compared the movement of the longitudinal axes before and after the deformation with predicted behaviour of axes assuming that the same four type planes would act. They concluded from these data that slip best obeyed the assumption of action on a $\{123\}$. In some of these experiments, there were fairly large deviations in the observed axis movement from what might be expected assuming slip on a $\{123\}$ plane.

The plot of shear stress versus shear strain assuming the four slip systems again showed that the slip system $\{123\} \langle 111 \rangle$ gave the least

variation of shear stresses at a given strain for all of the assumed slip systems.

It should be pointed out that the calculated value of the resolved shear stress based upon the four assumed slip systems is essentially constant within the limit of usual experimental error in measuring the load. It would seem that experiments of these sorts must await the development of more accurate methods for determining stress which would be well within the limits determined by the small differences in stress resolved on planes as close as the $\{123\}$, $\{112\}$, $\{110\}$ and appropriate non-crystallographic planes.

The deformation of iron and silicon ferrite single crystals was investigated in detail by BARRETT, ANSEL and MEHL.⁽⁹⁶⁾ No shear stresses were measured since the investigation was primarily concerned with the crystallography of the deformation process. Different types of deformation were employed and at temperatures from 500°C down to -195°C. The single surface method of stereographic analysis was used although a unique determination of the glide plane indices does not

TABLE 1
Arrangement of Acting Slip Planes in
Body-centred Cubic Metals

<i>Metals</i>	<i>T/T_m</i>	<i>Slip Plane</i>
W, Mo, Na	0.08-0.24	$\{112\}$
Mo, Na, Beta Brass	0.26-0.50	$\{110\}$
Na, K	0.80	$\{123\}$

result from this method. However, by making measurements on many specimens, the plane can generally be designated. From these measurements, they concluded that the slip planes are of the type $\{110\}$, $\{112\}$, and $\{123\}$. Nevertheless, about 85 per cent of their determinations showed $\{110\}$ to be predominant. The glide traces in silicon ferrite, for silicon contents above 4 per cent, however, were straight and proved to be $\{110\}$.

ANDRADE and TSIEN investigated the plastic behaviour of sodium and potassium single crystals determining the glide elements by means of x-rays.⁽⁸²⁾ These proved to be $\{123\} \langle 111 \rangle$. Based upon these results and other work on iron and molybdenum⁽⁹⁷⁾ from -190°C to 2000°C, ANDRADE and CHOW⁽⁹⁸⁾ correlated the operative slip planes with the testing temperature relative to the melting point. In this correlation, if T is the absolute temperature at which slip occurs and T_m the absolute melting point, then the acting slip planes in body-centred cubic metals may be arranged as shown in Table 1.

However, deviations from this correlation are known to exist in iron and iron-silicon, molybdenum, and niobium crystals.

ELAM⁽²⁾ suggested that slip lines may be formed by alternate slipping on non-parallel $\{110\}$ planes and not by slip on any plane of higher indices. Since $\{110\}$ planes are the planes of highest atomic density, this hypothesis would be in accordance with the plastic behaviour in other systems, i.e. face-centred cubic and hexagonal close-packed. A

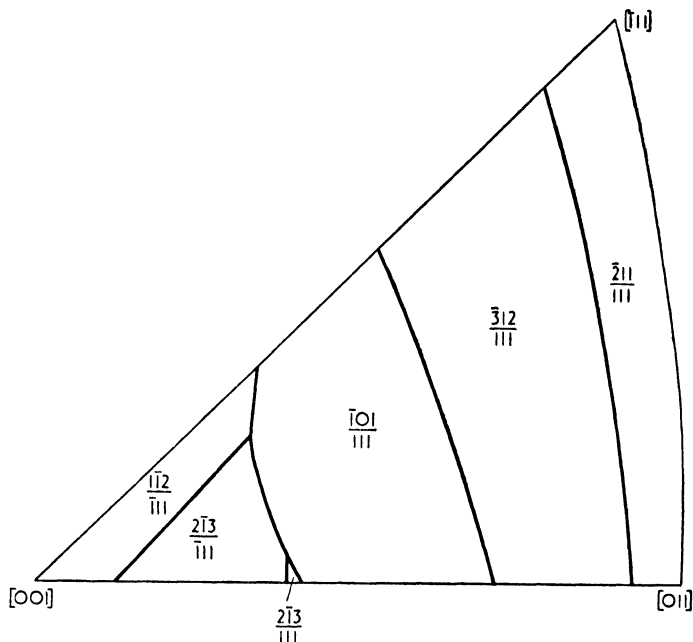


Fig. 23. Division of stereographic triangle into areas of highest resolved shear stress using planes of the type $\{110\}$, $\{112\}$ and $\{123\}$ (OPINSKY and SMOLUCHOWSKI)

similar suggestion was put forward by GRENINGER⁽⁹⁹⁾ in attempting to explain the observations of apparent slip on planes of relatively high indices. The work of BARRETT, ANSEL and MEHL has definitely demonstrated that the slip resistance on $\{110\}$ planes in iron is very much smaller than that on $\{112\}$ or $\{123\}$ planes.

On the basis of experiments on repeated torsion of iron single crystals, GOUGH⁽¹⁷⁾ assumed that the resolved shear stress is the deciding factor in determining the activity of the gliding plane. This view has recently received emphasis from the work of OPINSKY and SMOLUCHOWSKI on iron and iron-silicon alloy single crystals.^{(100), (101)} The basic stereographic triangle was divided into regions of highest resolved shear stress assuming slip to occur on planes of the type $\{110\}$, $\{112\}$, and $\{123\}$ assuming, also, that the slip resistance on these planes is the same.

PLASTIC DEFORMATION OF METAL SINGLE CRYSTALS

Realizing that it could hardly be expected that the slip resistance would be the same, they calculated the ratios of the resistances to shear on the planes at various temperatures from experimental data. For slip at -140°C , compression of silicon ferrite should show the glide elements to be $\{110\} \langle 111 \rangle$. The division of the triangle into areas of highest resolved shear stress is shown in Fig. 23 and the relative shearing strengths, S , of the various planes are shown in Table 2.

TABLE 2
Relative Shearing Strengths of Planes

Shearing Strength	Tension			Compression		
	Room Temp	190°C	-140°C	Room Temp.	190°C	-140°C
S(123)	1 07S(110)	—	—	1 11S(110)	1 06S(110)	1 13S(110)
S(123)	0 99S(112)	—	—	0 99S(112)	0 99S(112)	1 16S(112)

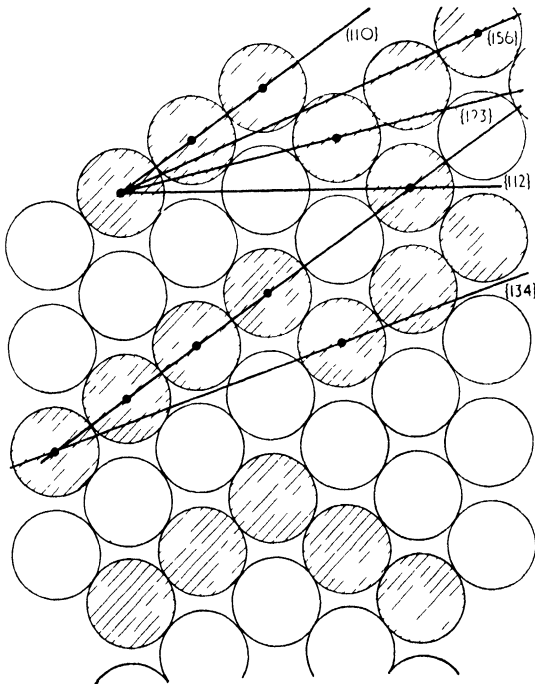


Fig. 24. Illustration showing the integrated trace produced by using different numbers of atoms in non-parallel $\{110\}$ planes

The behaviour of molybdenum single crystals has been investigated in tension⁽⁷⁹⁾ and in pure bending⁽⁸³⁾ and the behaviour of niobium single crystals in tension and compression.⁽⁸¹⁾ Although careful stereographic

analysis shows the glide planes to be $\{110\}$, $\{112\}$ and $\{123\}$, analysis of asterism suggests that glide occurs by a process of composite slip on non-parallel $\{110\}$ planes. Consider the schematic diagram shown in Fig. 24. The shaded circles represent atoms of $\{110\}$ planes assumed to be participating simultaneously or in intimate association with each other in the glide process. It may be seen that depending upon the numbers of atoms composing non-parallel $\{110\}$ planes, the integrated trace can represent any desired plane which will contain a close-packed $\langle 111 \rangle$ row. The waviness of unresolved slip traces can easily be explained by changing the number of atoms participating in the glide but keeping the ratio constant. For example, if the numbers of atoms taking

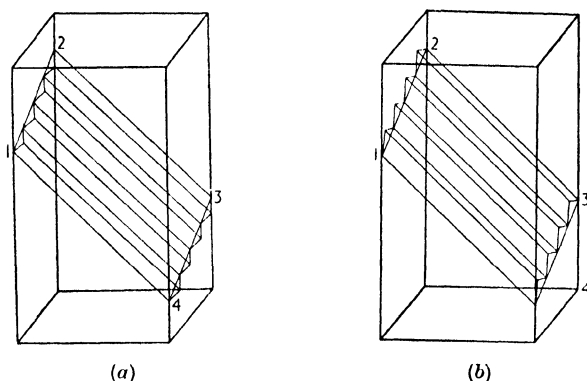
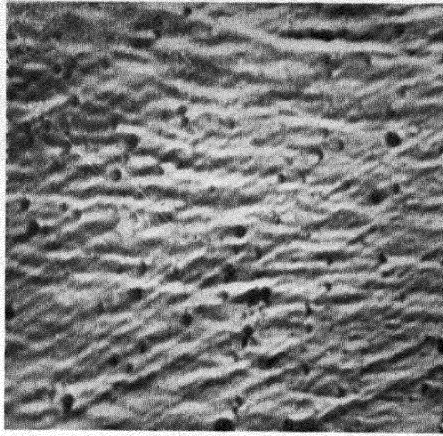


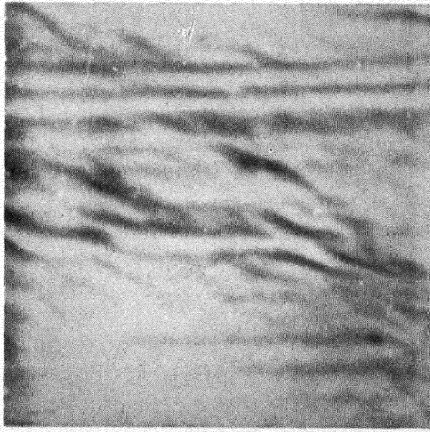
Fig. 25. (a) (112) plane as compared with "pseudo" (112) plane made by using equal numbers of atoms in two non-parallel $\{110\}$ planes. (b) (123) plane as compared with "pseudo" (123) plane made by using three atoms of one $\{110\}$ plane and one atom of a non-parallel $\{110\}$ plane

part in the gliding is, in one section of the slip, in the ratio of 3 and 2 atoms respectively and 6 and 4 in the adjacent section, the integrated trace could be a $\{123\}$ with a slight jog giving rise to a wavy slip line on the surface. Yet the same integrated trace viewed in a plane parallel to the slip direction would be straight.

In the cases where the apparent planes of glide are different from $\{110\}$ the following type of analysis was adopted. For example, a molybdenum single crystal designated as M-12 whose stereographic projection is shown in Fig. 14, has been analyzed. It was stated earlier that stereographic analysis of traces from many planes of observation indicated the plane of glide to be $\{112\}$. However, the expected axis about which a rotation to account for asterism should occur, $\langle 110 \rangle$, is not observed but two $\langle 112 \rangle$ axes are observed indicating that the planes of glide are III-C and I-C. The simultaneous action in a composite slip on these two planes would explain the observed longitudinal axis



(a)



(b)

Fig. 26. Wavy slip lines in an extended molybdenum single crystal as a result of two slip systems. (a) Optical ($\times 670$); (b) electron micrograph, using a 2 per cent parlodion replica shadow cast with chromium. ($\times 15,000$)

rotation towards the slip direction, C . Glide on the plane (112) in the direction C could also explain the observed longitudinal axis rotation. It could further be argued that the initial orientation of M-12 is on the border of an area where the (112) plane would contain the highest resolved shear stress.

In Fig. 25*a*, the corrugated surface made up of sections of two non-parallel $\{110\}$ planes containing the same number of atoms has the same mean orientation as the (112) plane. Its total area is only 1.15 times that of the (112) plane, so that the stress on the crystallographic plane resolved in the slip direction $\langle 111 \rangle$ is only 15 per cent greater than that similarly resolved on the corrugated surface. In Fig. 25*b* the corrugated surface constructed by using a ratio of three atoms of one $\{110\}$ plane to one atom of another non-parallel $\{110\}$ plane yields a pseudo (123) plane whose area is 1.134 that of the real (123) plane. In this case the resolved stress on the real plane is only 13.4 per cent greater than that on the corrugated surface. These differences are slight, so composite* slip would be expected to occur on the corrugated surface because of the greater ease with which slip occurs on close-packed $\{110\}$ planes.

In the case of M-25 (Fig. 27), the observed traces indicate the activity of a $\{123\}$ plane and asterism analysis indicates the activity of systems II- A and I- C . It would be difficult to account for the longitudinal axis movement observed on the basis of glide on the system (123) in direction C , but the conjugate or double action of I- C and II- A explains very nicely the observed movement from P_0 to P_1 .

It has been suggested by VOGEL and BRICK⁽⁸⁰⁾ in discussion of the mechanism of composite slip that the theory of CHEN and MADDIN fails to explain the observed behaviour when the great circle joining the slip direction and the specimen axis intersects the $\langle 111 \rangle$ zone at a $\{110\}$ pole. At this position the glide ellipse should be composed of only one $\{110\}$ plane, and therefore the slip lines should be straight regardless of where they are viewed with respect to the slip direction. Further, there should be a decrease in the degree of waviness of the lines observed at the head of the glide ellipse as the plane of shear varies from the (112) position to the (110) position. These predictions are not borne out by observations. The appearance of the slip lines in a body-centred cubic crystal, i.e. molybdenum, whose orientation coincides with the critical one suggested by VOGEL and BRICK above, can be likened to the appearance of slip traces on aluminium single crystals deformed at very low temperatures, e.g. — 190°C. At this temperature the glide plane traces are very close

* In the interest of clarity of definition, MATHEWSON has proposed that the term "composite slip" be used to signify the participation of two non-parallel planes with the same slip direction in a given slip process. Thus, the "cross-slip" originally observed by MADDIN, MATHEWSON and HIBBARD⁽⁴⁵⁾ in alpha brass would be a form of "composite slip."

together, so much so that an apparent waviness is noted at many positions of observation, especially where the observation is made on a plane which is perpendicular to the plane containing the specimen axis and the slip direction. The behaviour of aluminium single crystals at room temperature should be compared with the behaviour of molybdenum single crystals above 1000°C . The traces viewed anywhere on the periphery of a molybdenum single crystal extended at 2000°C are

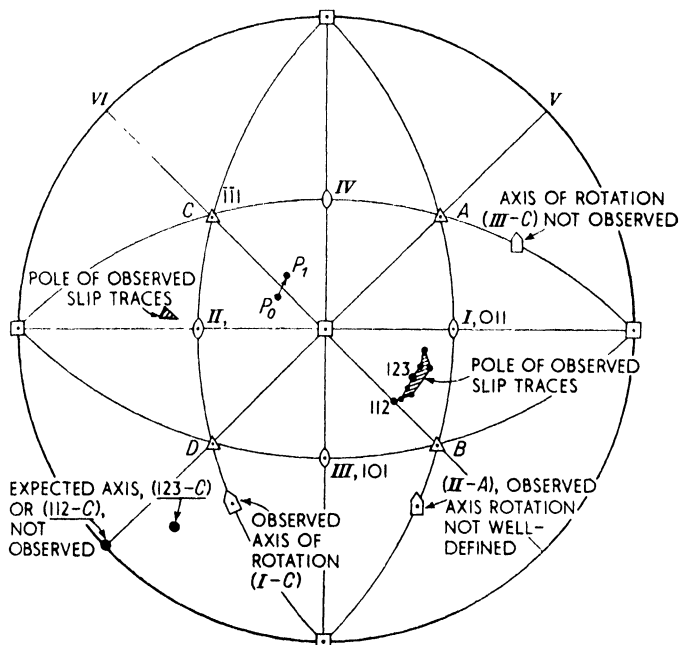


Fig. 27. Projection of M-25 showing the pole of the observed slip traces, the axis of rotation determined from asterism, and the stress axis movement

straight, much the same as the appearance of slip traces on aluminium single crystals extended at room temperature.

It is known, in the case of aluminium, that the activity of collateral slip, i.e. cross and premature conjugate slip, accompanies the activity of predominant primary slip. As a result, the appearance of slip traces is generally jagged at the head of the predominant glide ellipse. At lower temperatures where the slip lines are much closer together and the amount of collateral slip is greater, the jagged traces at the head of the ellipse take on a very wavy appearance. This is considered to be analogous to the behaviour of molybdenum at room temperature.

Some evidence in explaining waviness of slip traces in molybdenum on the basis of composite slip has been obtained using the electron microscope. In Fig. 26a, b there is shown an optical and electron micrograph

of slip traces in extended molybdenum single crystals. Close examination of these figures will show that the apparent waviness can be accounted for on the basis of interaction between the traces of two non-parallel planes; this can be seen more clearly in the electron micrograph.

The recent work of VOGEL and BRICK⁽⁸⁰⁾ in which the plastic deformation of ingot iron single crystals was studied, suggests that deformation occurs by glide on a non-crystallographic plane containing the $\langle 111 \rangle$. The pole of the glide plane is identified on the great circle (stereographic projection) joining the specimen axis and the slip direction $\langle 111 \rangle$. The authors state, however, that "means were not available in this investigation to examine details of the glide ellipses . . . no asterism was present in Laüé photograms of the deformed crystals which might offer evidence of the participation of crystal plane segments in forming the glide ellipse." Their investigation at room temperature included the extension of four single crystals and the compression of one. The pole of the slip plane determined stereographically in the four extended crystals showed a deviation from the pole of maximum shear stress plane (non-crystallographic) toward the (101) pole. This might be interpreted as the participation of more than one plane.

Their investigation demonstrates that the critical stress for plastic flow increases below room temperature and changes only slightly from room temperature up to 200°C. Flow lines appear on the single crystal concurrently with inhomogeneous yielding. VOGEL and BRICK state that below — 105°C. Neumann bands appear on planes of the type $\{112\}$ but that a critical resolved shear stress for twinning on the $\{112\}$ plane is not a criterion. However KING, GUMBRELL and MAKIN⁽¹⁰²⁾ concluded that there is a critical stress for twinning at least in cadmium.

The deformation of single crystals of specially prepared high purity ferrite containing less than 0.1 per cent titanium or less than 0.02 per cent carbon have been studied at room and sub-zero temperatures in slow tension and compression by BRICK and STEIJN.⁽¹⁰³⁾ The conclusions here are the same as related above for the work of VOGEL and BRICK. They state, however, that the normal stress exerts an influence on the selection of the plane of glide in compression as determined from comparison between compression and tension data. A model is suggested in which slip can occur by two different types of atom movements; (1) type *A* slip, (2) type *B* plus *C* slip. Varied proportions of these two can give slip on any plane in the zone of $\langle 111 \rangle$. The type *A* movements, suggested earlier as the direction of easiest glide with reference to a possible explanation for the delay time observed in body-centred cubic metals, may be illustrated with aid of Fig. 21. This is the path 1', 2, 3' 4; the movements 1', 2 and 3' 4 are in $[110]$ direction whereas the movement 2, 3' is in a $[112]$ direction. The resultant movement from 1 to 4 is effectively in a $[111]$ direction. The type (*B* plus *C*) movement

necessitates a cooperation between the atoms above and below the acting $\{112\}$ plane. This may be illustrated in Fig. 28. The hollow circles represent the atoms of a $\{112\}$ plane which move to the left. For this to be possible the shaded circles also forming $\{112\}$ planes above and below the centre line must move upward to permit the movement of the centre row.

STEIJN and BRICK suggest that glide on any plane in the $\langle 111 \rangle$ zone can be constructed from these two basic types of movements. For example, if $\{110\}$ slip consists solely of a type A movement and $\{112\}$ slip of type $(B \text{ plus } C)$ movements, then $\{123\}$ slip is described as being made up of one A and one $(B \text{ plus } C)$ movement.*

Although the observations of wavy traces may be explained by this cooperative movement, explanations of pole rotations such as are observed in many body-centred cubic crystals would be difficult.

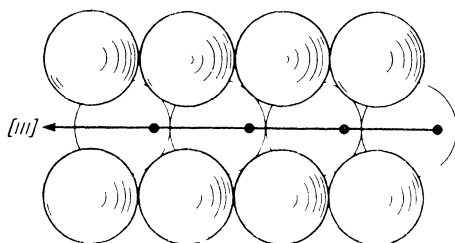


Fig. 28. Type $(B \text{ plus } C)$ movement (STEIJN and BRICK)

It is clear that the status of the crystallography of the deformation process in body-centred cubic crystals still remains in a somewhat obscure state. What seem to be needed most are carefully documented data of the deformation in different body-centred cubic crystals where newer techniques have been applied. The use of the Berg-Barrett x-ray microscopy and electron microscopy together with careful analysis of the structural irregularities arising from plastic deformation would seem to offer the prospect of shedding light on the behaviour of this important class of metals. The application of multiple beam interferometry in determining the extent of shear along gliding planes would also appear to be an extremely useful approach. Recent investigations on plastic deformation using this method have been made by HOLDEN⁽²³⁾ and GELINAS and MADDIN.⁽¹⁰⁴⁾

C. CLOSE-PACKED HEXAGONAL METALS

Research on close-packed hexagonal metal crystals during the past decade has brought into prominence certain phenomena which have

* In a recent publication CHEN and MADDIN^(103a) consider the slip process to occur on non-parallel $\{110\}$ planes on the basis of the energy of dislocations in the body-centred cubic structure.

emphasized the importance of the heterogeneity of the deformation process as related to the strength and strain hardening of metals. These observations, in the main, deal with the formation of kink bands (from bend planes), the role of the axial ratio in the crystallography of plastic deformation and with the role played by dissolved gases and surfaces upon the yield point and strain hardening. Among other experiments which should receive attention are the pure shear of zinc crystals and the deformation of odd shaped crystals. Since the effect of surfaces on plasticity is considered thoroughly in an article by BROWN⁽⁸⁾ and the role of dissolved gases is considered in the recent volume by BARRETT,⁽⁵⁾ no report on the status of plasticity concerned with these effects will be given here.

1. *Kink Bands*

OROWAN⁽⁵⁴⁾ demonstrated that if a long cadmium crystal with its basal plane parallel or nearly parallel to the longitudinal axis of the crystal is compressed, it may collapse forming a kink band. In a careful study of this phenomenon in zinc, HESS and BARRETT⁽⁵⁵⁾ were able to show that the kinks are a simple form of deformation band in which there is bending of the glide lamellae. The lattice accomplished this flow pattern by a bending of the glide lamellae about a Taylor-type axis, i.e. an axis in the plane of glide at right angles to the direction of glide. With larger deformation, they found that the lattice within the band re-orientes progressively and the lattice adjacent to the band is bent to smaller radii. The kinks or grooves formed by the deformation thus become sharper and do not move along the rod. Recently, however, WASHBURN and PARKER⁽¹⁰⁵⁾ have produced kinking in zinc single crystals deformed in tension. They could observe kinking in specimens varying widely in initial orientation, e.g. a scatter of angles about 45° between the slip plane and the specimen axis. An example of tensile kinking is shown in Fig. 29. Much earlier, MILLER⁽⁵¹⁾ demonstrated the existence of bend planes near the grip ends (where many grains existed) of zinc single crystals pulled in tension. WASHBURN and PARKER suggest that a non-uniform distribution of flow produced by or combined with constraints are the conditions leading to kinking. They suggest that non-uniform distribution of impurities, lineage structure, mishandling (slight bending), surface conditions and strain-ageing characteristics may be some of the factors which cause non-uniform flow. The observations of JILLSON⁽⁵⁶⁾ on unusual deformation of zinc crystals are explained on the basis of kink band formation.

2. *Zinc*

The behaviour of zinc under a variety of modes of deformation has been studied by JILLSON⁽⁵⁶⁾ on single crystals 99.999 per cent purity. JILLSON confirmed the conclusion of SCHMID's critical resolved shear stress

formulation⁽¹⁰⁶⁾ in the usual manner of observing the variation of yield stress with orientation. He also observed that a cylindrical single crystal whose basal planes were parallel to the cross-section could rotate about a normal to the planes so that a series of scratches on the surface parallel to the longitudinal axis formed a spiral along the rod. Such action was shown to exist for aluminium by HEIDENREICH and SHOCKLEY;⁽²⁴⁾ it had been proposed earlier by COLLINS and MATHEWSON,⁽⁵²⁾ by WILMAN⁽⁶²⁾ and by others.⁽⁴⁵⁾ More recently, GILMAN and READ,⁽¹⁰⁷⁾ investigating the extension of odd shaped zinc crystals, found that triangular and other specially shaped crystals twisted axially while elongating. Other unusual appearances of deformed zinc crystals were attributed to kinking of the lattice.

3. Cadmium

The deformation behaviour of cadmium single crystals has been studied by HONEYCOMBE⁽⁷⁵⁾ with regard to the occurrence of x-ray asterism. He found that cadmium could be extended by more than 100 per cent without the appearance of asterism whereas asterism occurred when crystals were bent macroscopically or kinked. It is interesting to note that single crystals of zinc deformed by "pure shear" exhibit no asterism and no strain hardening.^(107a) Other investigators considered that asterism is caused by macroscopically bent regions rather than local curvatures^{(16), (108), (109), (110)} Thus KOMAR and MOCHALOV,⁽¹¹¹⁾ OROWAN and PASCOE⁽¹¹²⁾ the former investigators with magnesium and the latter with cadmium crystals, were able to interpret their experiments as evidence in favour of the macroscopic bent-region theory.

Experimental observations in support of a third possibility, that of attributing x-ray asterism to fragmentation of the lattice, are rarely interpreted on this basis. Thus the work of OROWAN and PASCOE on cadmium, KOMAR and MOCHALOV on magnesium might also be interpreted on the basis of fragmentation. This appears to be the recent view of BECK,⁽¹¹³⁾ who suggests that the fragments resulting from deformation are misaligned slightly about an axis in the plane of glide and perpendicular to the direction of glide (polygonization occurs at the time of deformation).

4. Titanium

The mechanism of plastic flow in titanium has been considered by ROSI, DUBÉ and ALEXANDER.⁽¹¹⁴⁾ From tension, compression and bending of coarse grained titanium containing grains from two to six millimetres in length, at least two planes of glide were determined. These were identified by plotting stereographically traces from one surface and in some cases two surfaces as $(10\bar{1}0)$ which predominates and $(10\bar{1}1)$. Although the slip direction was not determined, since both

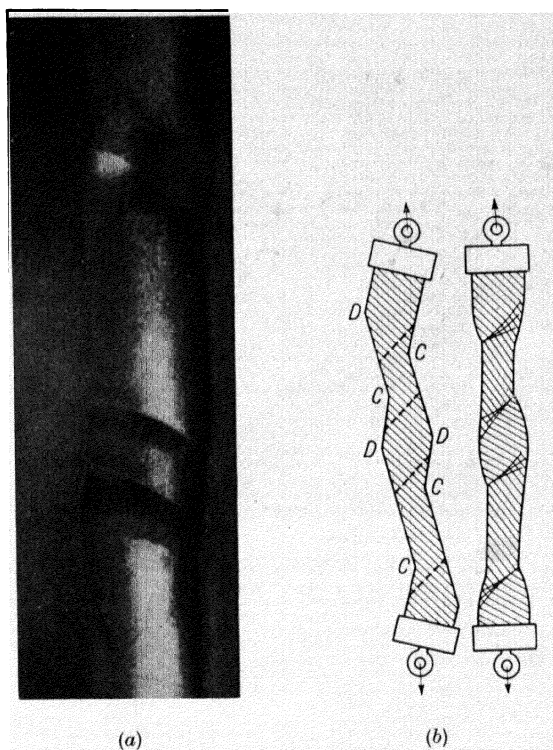


Fig. 29. (a) Zinc single crystal creep specimens showing kinks produced by tension loading. Original orientation: angle between tension axis and normal to slip plane, 62° ; angle between tension axis and active slip direction, 28° ; (b) formation of kinks due to non-uniform distribution of strain. Left—non-uniform slip without bending. Stress is concentrated at C and decreased at D. Right—observed structure of kinked specimen showing formation of bend planes. (WASHBURN and PARKER)

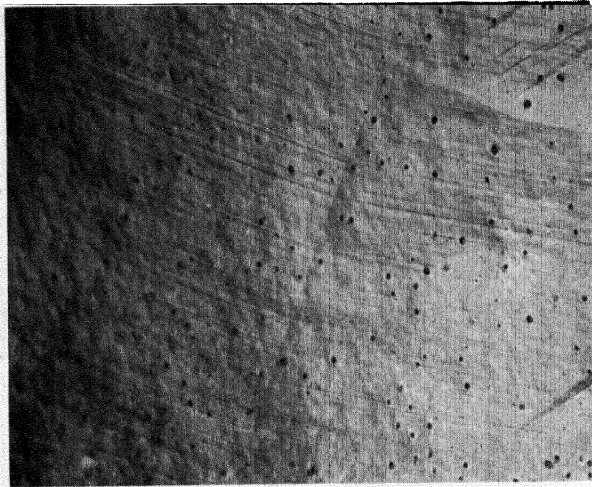


Fig. 30. Bend plane appearance in magnesium single crystal.
Axis vertical. ($\times 100$) (**BURKE and HIBBARD**)

the pyramidal plane ($10\bar{1}1$) and prismatic plane ($10\bar{1}0$) contain the direction of closest packing, it could be speculated that this direction [$11\bar{2}0$] is the slip direction. Although ROSI, DUBÉ and ALEXANDER state that there was no evidence of basal glide, research by ANDERSON and JILLSON⁽¹¹⁵⁾ demonstrates the existence of basal glide for certain orientations. ROSI and co-workers establish at least three twinning planes, i.e. ($10\bar{1}2$), ($11\bar{2}2$) and ($11\bar{2}1$). Since titanium belongs to the group of elements in which the c/a ratio (1.5907) is less than the theoretical for closest packing (1.633), basal plane glide activity would be reduced since the lattice along the c axis is compressed and hence the interplanar spacing and atomic density is reduced for this plane. Conversely the density of the prismatic plane is increased. However, in an extensive investigation of the plastic deformation of titanium single crystals, ANDERSON and JILLSON⁽¹¹⁵⁾ were able to show that for orientations in which the specimen axis was close to the $[0001]$ pole, the (0001) was the glide plane. Critical resolved shear stress for basal slip was, however, 11 kg/mm² as compared with only 5 kg/mm² for the much more predominant ($10\bar{1}0$) prismatic slip. Consequently it would be expected that basal slip would not be an important mode of deformation in alpha titanium. The twinning planes determined by ROSI and co-workers were confirmed in this investigation. ANDERSON and JILLSON establish a relationship for the deformation mode in terms of the initial orientation in the following manner: for orientations in which the angle between the basal plane and the tension axis is about 40° or less, prismatic slip occurs; for angles of about 40 to 60°, basal slip occurs but is replaced by ($11\bar{2}1$) twinning when restraints such as grips or grain boundaries are present; for compression ($11\bar{2}1$) twinning gives way to ($11\bar{2}2$); above 60°, ($11\bar{2}1$) and ($10\bar{1}2$) twinning occurs and at 75° twinning on ($10\bar{1}2$) is apparently the only mechanism.

5. *Beryllium*

Beryllium is another of the class of elements whose c/a ratio (1.5683) is less than the theoretical value for closest packing. Here, too, basal slip would not be expected to be the primary mode of deformation. LEE and BRICK⁽¹¹⁶⁾ have investigated slip and twinning in single crystals of beryllium and find prismatic slip along with ($10\bar{1}2$)* twinning. For compression perpendicular to the basal plane, they observe elastic deformation up to rupture at about 300,000 lb/in.²

6. *Magnesium*

Almost a borderline case could be found in magnesium whose axial ratio is 1.623. However, the participation of ($10\bar{1}1$) pyramidal slip is observed

* Reported much earlier by MATHEWSON and PHILLIPS in the *Proc. Inst. Metals Div.*, A.I.M.M.E. (1928), 445.

only for orientations in which the basal plane is within 6° of the specimen axis.^{(117), (118)} When constraints are imposed, such as action at the grip ends of tensile specimens, twinning on the $(10\bar{1}2)$ plane occurs followed by slip on the reoriented basal plane. BURKE and HIBBARD⁽¹¹⁸⁾ found that the critical resolved shear stress for slip on the basal plane (46g/mm^2) was only slightly less than for slip on the pyramidal plane (52g/mm^2). They observed the ratio of strain hardening for basal and pyramidal slip and find little or no difference between the two. For angles greater than 6° but less than 72° , basal slip was the sole mechanism. Between 72° and 84° , initial plastic flow occurred by basal slip, but rotation of the glide plane together with grip effects produced kinking or bend plane action which activated twinning. For these orientations the bend plane was found to be a $(11\bar{2}0)$ plane. An example of bend plane appearance in magnesium is shown in Fig. 30.

D. OTHER CRYSTAL FORMS

1. *Mercury*

Among the earliest investigations of plastic deformation on metal single crystals which crystallize in a system other than the face-centred cubic, body-centred cubic or close-packed hexagonal, those of GREENLAND⁽¹¹⁹⁾ on rhombohedral mercury deserve particular attention. GREENLAND grew single crystal wires of mercury at -60°C and studied the appearance of the glide ellipses produced by tension, bending and torsion. Those crystals which were extended axially developed wavy and branched glide bands whose general periphery was, however, elliptical. If the crystals were bent just slightly, the glide bands were faint but straight representing perfect ellipses. The crystals which were first bent slightly were then extended axially. Under these conditions slip occurred on the surfaces involved in bending and produced traces which were very straight. Initial torsional strains resulted in closely spaced elliptical bands but extension of these same crystals produced new sets of imperfect ellipses. GREENLAND proposed that gliding occurred on surfaces which were not smooth planes but whose segments all included a common slip direction. As a result of studies of the surface in the neighbourhood of the glide band, GREENLAND suggested that the surface of mercury at -60°C behaved as an elastic skin producing the effect of showing no sharp break at the intersection of the glide plane with the surface. No attempts at determining the acting glide planes were made.

The stress-strain curves for pure mercury crystals and for mercury crystals to which known amounts of silver were added exhibited three regions. The first portion of the curve was straight representing the elastic region; in the second portion there was an increase in extension for a given increase in stress slightly greater than in the elastic range

accompanied by a small permanent set. In the third region, there was a rapid increase in extension accompanied by the appearance of glide bands. Although the amount of strain hardening at -60°C is very small, the stress at which gliding occurs does not seem to be affected by the type of glide band produced, i.e. regular or wavy.

Further work on mercury by FISHER and ANDRADE⁽¹²⁰⁾ pointed out that the planes of closest packing in the rhombohedral mercury are the pyramidal (111) planes which were determined earlier by ANDRADE and HUTCHENS⁽¹²¹⁾ as the planes of glide but were erroneously stated to be (100) planes. However, ANDRADE in discussion observed that the glide planes are not necessarily the most closely packed planes and that x-ray evidence would be required before the glide plane can be assigned.

2. Uranium

More recently CAHN has investigated the crystallography of the plastic deformation of alpha uranium.⁽¹²²⁾ Alpha uranium is described by JACOBS and WARREN⁽¹²³⁾ and by LUKESH⁽¹²⁴⁾ as centrosymmetric orthorhombic ($a = 2.85$, $b = 5.865$, $c = 4.945$ Å). The structure of alpha uranium is shown in Fig. 31.

Using the method of pole locus, CAHN has identified two planes to be active in the glide, i.e. (010) and (110) with the former the more predominant. His method for determining the slip direction was dependent upon the assumption that glide on the cross-slip plane occurs in the same direction and is common to slip on the primary plane. By comparing the appearance of slip lines on a number of grains of known orientation with regard to the position of observation where the cross-slip traces could no longer be seen (where their traces are almost parallel to the main slip traces), he was able to assign indices to the direction of glide [100], which is the direction of closest packing. While the assumption made by CAHN is not always rigorous, the conclusion that the direction of glide is the most closely packed row, i.e. [100], seems justifiable since there are few cases, if any, where the direction of glide at least in the early stages of deformation is not the most closely packed row of atoms. His determinations of the indices of the cross-slip plane were dependent upon observations of minute traces. By restricting observations just to those traces where a definite direction could be assigned, he was able to determine at least two planes upon which cross-slip occurs. These were the (011) and (013) with two additional probable planes being (001) and (023). CAHN could not determine the direction of slip on the (110) planes since no cross-slip associated with these traces was observed. However, since the most closely packed row of atoms in this plane is $[1\bar{1}2]$ with $[1\bar{1}0]$ the next most closely packed row and since the $[1\bar{1}2]$ direction contains a jog, he reasons that in all probability the $[1\bar{1}0]$ direction is to be associated with slip on the (110) planes.

Kink bands were observed in deformed alpha uranium crystals. The determination of the bands by the pole locus method showed them to be approximately normal to $[100]$. The structure inside the bands is rotated a few degrees slightly from the adjacent material about an axis in the plane of slip at right angles to the slip direction. (This is in agreement with observations on aluminium, zinc and cadmium.) Since CAHN reports the existence of fourteen twinning planes and three slip

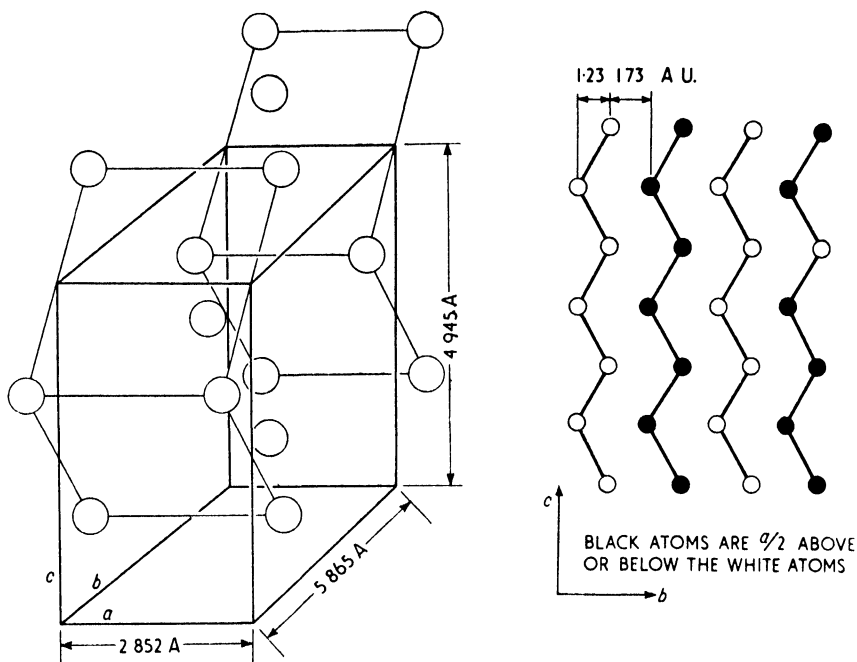


Fig. 31. The structure of alpha uranium. (a) Unit cell dimensions; (b) black atoms are $a/2$ above or below the white atoms

planes, it is difficult to see why alpha uranium kinks since kinks are generally formed when a material does not have the ability to twin or glide in order to relieve compression stresses. However, CAHN suggests that since twinning on all but four planes necessitates a contraction, the stresses required for kinking must be lower than those required for initiating twinning on the four planes.

Slip on the (010) planes becomes more widely spaced accompanied by an increase in the amount of shear on the planes with increasing temperature. Cross-slip becomes more abundant and the lines in general take on a more wavy appearance. It should be noted here that since twinning plays so important a role in the deformation, the crystallography of the deformation process in alpha uranium is more complex

than the mere detailing of the planes and directions upon which glide occurs would indicate.

3. *Silicon and Germanium*

The plastic flow of silicon and germanium (diamond cubic) has been investigated by GALLAGHER⁽⁹²⁾ and TREUTING.⁽¹²⁵⁾ In the temperature range between 500°C and 900°C, both silicon and germanium become ductile, slipping on planes of the type {111}; well developed slip lines appear. By observing the axis about which a Taylor-type rotation would occur, TREUTING⁽¹²⁵⁾ suggests that these experiments, incomplete at the present time, indicate that the glide direction is $\langle 112 \rangle$. An incubation time for the initiation of plastic flow of about 10^{-5} sec. was observed.⁽⁹²⁾ SEITZ⁽⁹¹⁾ has calculated an activation energy for plastic flow of 28,000 cal/mol.

SALKOWITZ and VON BATCHELDER⁽¹²⁶⁾ report that just as in the case of diamond and germanium, only (111) twinning occurs in silicon although the lateral boundaries of the twin may be along (112) planes.

4. *Tin*

Little research on the plasticity of tin single crystals has been performed during the last decade except for the effect of surface strength properties. The results of two investigations on tin should be recorded herein.

The investigation of CLARK, CRAIG and CHALMERS⁽¹²⁷⁾ establishes that the twinning plane of white tin is {301} referred to the axes $(a) = 5.82 \text{ \AA}$ and $(c) = 3.18 \text{ \AA}$. Where previously the twinning plane was believed to be {331}, these investigators succeeded in determining the twinning plane as {301} by taking Laue photograms of the twinned and untwinned sections of twinned crystals. The discrepancy between these results and the earlier data is explained as arising from a different choice of axes by previous investigators.*

HERRING and GALT⁽¹²⁸⁾ were able to bend whiskers of tin approximately 1.6 microns in diameter. Using the simple beam formula, they were able to show that the yield value approaches the theoretical strength. This very high strength value is interpreted as resulting from the very small (if any) number of dislocations present in tin crystals of such small size.

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* E. W. ROATH in an M.S. Report (Yale University, 1928) also found that tin twins about an axis normal to a given plane of form {301}, in agreement with the earlier findings (1899) of MÜGGE.

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THE STRUCTURE OF LIQUID METALS

B. R. T. Frost

1. INTRODUCTION

THE properties and behaviour of solid metals have been extensively investigated both from the point of view of the metallurgist and of the engineer. In recent years the substantial advances which have been made in the field of solid state physics have greatly improved the theoretical understanding of the subject. The study of metals in the solid state is relatively easy as the atoms are regularly arranged on a crystal lattice which can be examined in detail by means of x-rays and described in simple mathematical terms. A stage has now been reached at which many of the properties of solid metals can be quantitatively described in terms of the electron theory of metals or of dislocation theory.

In comparison with these studies of solids the investigation of the liquid state is still in its infancy. The experimental and mathematical problems are much greater because of the irregular atomic arrangement in the liquid state and the fact that in general the temperatures at which liquids exist are higher than those for solids. The study of gases is simpler than that of liquids since the interatomic forces in gases are much smaller and the ideal gas laws can be applied. From the practical point of view there is no lack of interest in liquid metals.⁽¹⁾ After the refining process, nearly all metals are melted and cast, either into a final shape or into a shape suitable for working in the solid state. Changes in the properties of the liquid metal may profoundly affect the soundness and quality of the casting. Increased interest is being shown in the use of liquid metals as heat exchange media in chemical and engineering plant and in nuclear reactors. The latter aspect has, in recent years, stimulated research on liquid metals and alloys in the United States and, to a lesser extent, the United Kingdom and Russia.

From the measurements of a number of physical properties of liquid metals and by comparison with the corresponding properties of solid metals, it is possible to derive a picture of the structure of liquids. On the basis of these observations a number of mathematical and empirical theories⁽²⁾ have been proposed to account for the phenomenon of melting and for the behaviour of liquids. Some thought has also been given to the problem of the stability of liquid metals. These studies, which may be classified as the indirect approach to the elucidation of the structural behaviour of liquids, will be dealt with in the first part of this survey.

Direct experimental investigation of the structure of liquids is possible by x-ray and neutron diffraction methods. Further evidence is provided, in the case of alloy systems, by thermo-chemical studies, which, although they do not directly examine the atomic scale processes, provide information from which details of such processes may be deduced. It is with these more direct methods of approach that the second part of this survey is mainly concerned.

PART I

1. *Indirect Experimental Evidence*

A simple distinction may be made between gases, liquids and solids on the basis of the properties of shape and volume.⁽³⁾ Gases have neither shape nor volume and completely fill any container in which they are placed. Liquids occupy a definite volume but have no shape, taking up the shape of the lowest part of the container in which they are placed. Solids have both shape and definite volume. The inference to be drawn from these properties is that the atoms in a liquid exert strong binding forces on one another, but are more mobile than those in the solid. The low values of the compressibility of liquids confirm that the atomic packing is fairly close but their fluidity shows that the regular atomic arrangement of the solid is lost. This property of fluidity is a fundamental characteristic of the liquid state and will be considered in more detail below.

Further evidence of the nature of the atomic arrangement in liquid metals is provided by the fact that the magnitude of the change of properties on melting is much less than the change on evaporation (compare the latent heats of fusion and of vaporization, Table 1). Close-packed metals show a volume expansion of the order of 2–6 per cent on melting and the latent heat of fusion is small, being one-thirtieth to one-fortieth the latent heat of vaporization.^{(4), (5)} Electrical and thermal conductivities are reduced on melting to between three-quarters and half their solid state values.^{(6)*} These observations show that the change of structure cannot be very drastic when melting occurs, since the properties mentioned, which vary with the atomic arrangement, do not show very marked changes at the melting point. The thermal motion of the atoms in the liquid cannot be greatly different from that of the solid, as is indicated by the small increase in specific heat at the melting point.⁽⁷⁾

Electrical resistivity and optical reflectivity measurements on close-packed metals have shown the effective numbers of free electrons in the

* Anomalous behaviour is observed when the metals Ge, Ga, Bi and Sb melt. A contraction in volume results, while the electrical and thermal conductivities increase. The reasons for this behaviour will be discussed when the direct experimental evidence of the structural changes is presented.

TABLE I
Changes in Properties on Melting and Thermal Data for Metals

Thermal Data				Changes at the Melting Point					
Element	M.P. °K*	Latent heat		Entropy ΔS_m	Volume $\Delta V\%$ †	Coordination $\Delta C^\ddagger$	Conductivity		Spec. heats $\frac{C_p(s)}{C_p(l)}$
		Fusion L_f K. cal/mol†	Vaporization L_v K. cal/mol†				Thermal K_s/K_L	Electrical $\sigma_s/\sigma_L^\ddagger$	
Li	452	0.69	32.3	1.53	1.65	+ 1.8	—	—	0.985
Na	370.5	0.63	23.4	1.70	2.5	0	1.31	1.46	1.01
K	336.6	0.57	19.0	1.70	2.55	0	—	—	1.0
Rb	311.5	0.525	18.1	1.68	2.5	—	—	—	—
Cs	299	0.50	15.9	1.65	2.6	—	—	—	—
Cu	1356	3.1	72.8	2.29	4.15	—	—	—	—
Ag	1233.5	2.69	60.7	2.22	3.8	—	—	—	—
Au	1336	3.05	82.0	2.29	5.1	- 1	—	—	—
Mg	923	2.0	32.0	2.25	4.1	—	—	—	—
Zn	692	1.74	27.5	2.48	4.2	- 1	1.53	2.11	0.97
Cd	594	1.53	23.9	2.57	4.7	- 4	2.4	1.89	1.04
Hg	234.2	0.55	14.1	2.57	3.7	0	3.43	3.36	1.0
Al	932	2.5	69.6	2.70	6.0	- 1.4	1.47	1.82	0.92
Ga	302.8	1.34	—	4.42	- 3.2	+ 4	—	—	—
In	429.4	0.78	55.5	1.82	(2.7)	0	—	—	1.08
Tl	430	1.03	39.7	1.79	3.2	0	2.04	2.0	—
Si	1694	11.1	72.6	6.5	—	—	—	—	—
Ge	1231	7.3	—	6.0	—	+ 4	—	—	—
Sn	505	1.69	79.0	3.35	2.8	0	1.8	2.11	—
Pb	600	1.19	42.5	1.98	3.5	0	1.53	1.98	1.0
Sb	903	4.75	46.7	5.25	- 0.95	—	1.1	0.71	—
Bi	544	2.60	41.1	4.78	- 3.35	+ 1.5	0.55	0.47	—

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liquid state to be similar to those in the solid. Some theories attribute the increase in resistivity on melting to the increased disorder of the atomic arrangement, although the earlier theories of MOTT⁽⁸⁾ implied that the structure of a liquid with the atoms at rest would be very little distorted from that of the solid. He assumed that the atoms in the liquid vibrate with a frequency γ_L about mean positions which are themselves altering at a relatively slow rate and the higher resistivity of the liquid was stated to be due to the increase in the amplitude of atomic vibration. The following expression was derived for the ratio of the resistivities:

$$\frac{\sigma_S}{\sigma_L} = \left(\frac{\gamma_S}{\gamma_L} \right)^2 = \frac{80L}{eT_M}$$

where L is latent heat of fusion and T_M the melting point ($^{\circ}\text{K}$). More recent theories indicate that the effect is probably due to a combination of irregularity of structure and increased amplitude of vibration.^{(9), (10)}

PERLITZ⁽¹¹⁾ considered that a relation existed between the change in specific resistance on melting and the crystal structure of the solid. The metals were divided into three groups in which σ_S/σ_L was respectively:

$\frac{1}{2}$: Bi, Sb and Ga, which have "open" crystal structures;

$\frac{3}{2}$: Na, Li, K, Rb, Cs and Al, all except Al being b.c.c.;

2: Ag, Cd, Pb, Tl, Cu, Zn, Te, Sn and Au, all of which are close-packed structures.

BERNAL⁽¹²⁾ has emphasized that the electron energies in a molten metal will have Brillouin Zone characteristics, although these will be to some extent masked by the irregular atomic arrangement. The nature of the atomic cohesion in the liquid metal is, therefore, similar to that in the solid. Attempts have been made to examine in more detail the cohesive forces in liquid metals. JANELLI and GIACOBBE⁽¹³⁾ have measured the influence of temperature on the Hall coefficient in molten antimony and bismuth. It does not seem possible at the moment to derive definite conclusions from these experiments, but a possible method of investigating the free electron energies is indicated.

The property of fluidity, which has already received mention, may be analysed by considering the resistance of materials to shearing forces.⁽¹⁴⁾ The greatly reduced resistance to shearing forces in the liquid is the fundamental property which distinguishes between the two condensed phases. The rate of flow of a liquid is proportional to the applied shear stress, the proportionality constant being called the coefficient of viscosity. At low temperatures solids have a high resistance to shear. Near the melting point, however, crystals can be made to flow in a similar manner to liquids under the application of very small shear stresses. Supercooled liquids, i.e. glasses, have a high resistance to shear at low temperatures, but this decreases rapidly as the softening temperature is approached. The behaviour of a material under shear stresses must

therefore be a function of temperature, as well as of the atomic arrangement. The phenomenon is related to that of self-diffusion. In a liquid the atoms on the average vibrate about their equilibrium positions for a time τ , after which each atom can jump to a new equilibrium position which is situated at a distance of about one atomic diameter from the first. The gross flow of a liquid is accomplished by this movement of atoms among their neighbours. At high temperatures the magnitude of τ is about 10^{-6} sec., and when stresses are applied to a liquid for longer than this viscous flow occurs. For times less than τ the liquid is rigid and resists shear, e.g. in glasses τ has a low value at low temperatures giving a high resistance to shear. Viscosity, a function of the ease with which liquids flow, has received more attention than any of the other dynamic properties of liquids.⁽¹⁵⁾ Experimental measurement of this property is relatively simple, but for the results to be of any value, certain precautions must be observed, e.g. the material must be very pure and the temperature of the experiment accurately known. The empirical statement that the viscosity varies exponentially, with the increase of the absolute temperature, was first made by REYNOLDS,⁽¹⁶⁾ the following formula being subsequently derived⁽¹⁷⁾:

$$\eta = Ae^{\frac{B}{RT}}$$

where η is the viscosity, A and B are constants, R the gas constant and T the absolute temperature. A more refined formula was proposed by ANDRADE,⁽¹⁸⁾ who treated liquids as being more akin to the solid than to the gaseous state. The early researches using x-ray methods were beginning to bear fruit when ANDRADE considered this problem and these results led him to propose a model of a solid-like liquid structure, in which the flow due to a shear stress was communicated from one layer of molecules to the next through the bulk of the liquid. The distance between the molecules increases as $v^{\frac{1}{3}}$ with temperature, where v is the specific volume, and the potential energy between molecules varies as $\frac{1}{v}$. Using these relationships, ANDRADE derived the formula:

$$\eta v^{\frac{1}{3}} = Ae^{\frac{c}{vT}}$$

where c is a constant, and T the absolute temperature. This formula gives good agreement with the experimental results for metals^{(19), (20)} (Fig. 1). ANDRADE⁽¹⁵⁾ attempted to show that A has a constant value for groups of liquid metals, this classification being similar to that made by PERLITZ⁽¹¹⁾ on the basis of the ratios of electrical conductivities. The deviations of A within each group are, however, much larger than can be explained by experimental errors. In the simpler (REYNOLDS) formula B will remain constant if the coordination of atoms remains

constant. WARD⁽²¹⁾ has summarized the evidence showing that B is related to the latent heat of fusion L_f . If, therefore, the coordination

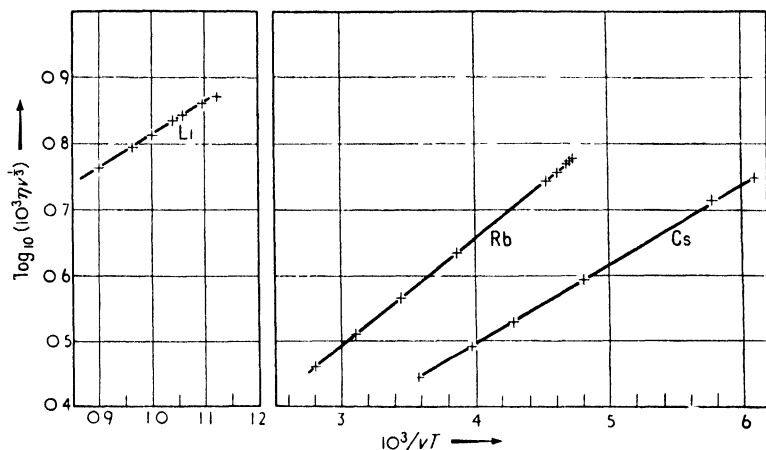


Fig. 1. Experimental value of $\log_{10} (\eta v^{1/3} \times 10^3)$ plotted against $10^3/vT$ (ANDRADE⁽¹⁹⁾)

changes B will change also and this will be reflected as a change of slope in a plot of $\log \eta$ versus $\frac{1}{T}$ (Fig. 2).

The evidence from viscosity experiments on the structural behaviour of liquids is conflicting. The experiments of ANDRADE's school using the

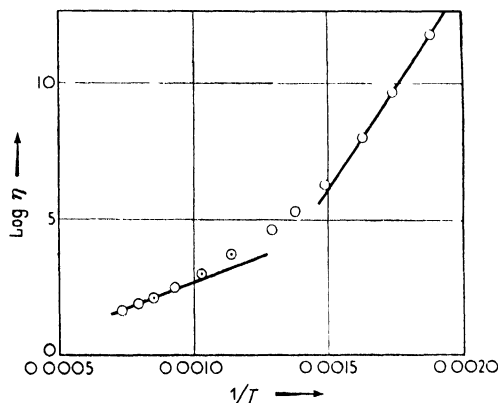


Fig. 2. Graph $\log \eta - 1/T$ boron trioxide (WARD⁽²¹⁾)

oscillating sphere method have shown a straight line plot of $\log \eta v^{1/3}$ versus $\frac{1}{vT}$ as far as the freezing point for all the metals examined.^{(15), (19)} Workers employing other methods⁽²²⁻²⁵⁾ such as the rotating crucible

or oscillating cylinder, have obtained curves of the form shown in Fig. 3, which gives results for tin. The curve is a plot of $\log \eta$ versus $\frac{1}{T}$ but plotting $\log \eta v^{\frac{1}{2}}$ versus $\frac{1}{vT}$ would show a similar change of slope, near the freezing point. This has been explained in two possible ways, the more immediately attractive being that structural changes occur as the freezing point is approached. In this theory the solid state structure is "foreshadowed" by the formation of fairly stable nuclei of the pure

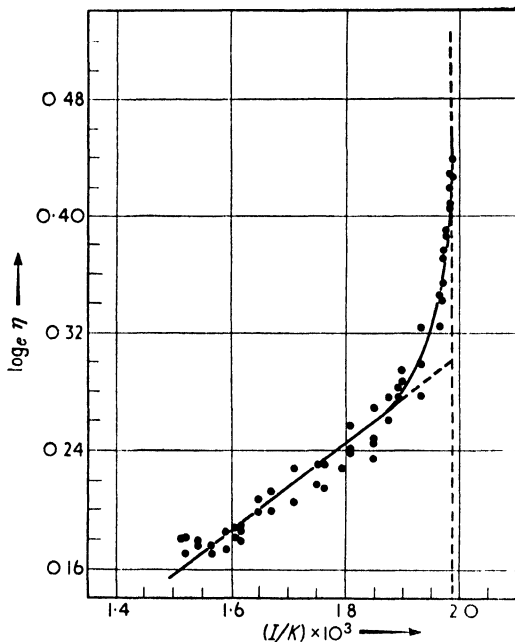


Fig. 3. Log viscosity of tin plotted against the inverse absolute temperature (YAO and KONDIC⁽²³⁾)

metal. This is explicable on the basis of the decreasing atomic mobility with fall in temperature. The theory implies that the liquid is "aware" of the approaching freezing point. The other and more likely, explanation is that it is an experimental effect. In the oscillating-crucible method used for these measurements it is possible that near the freezing point, temperature gradients will exist which cause solid metal to deposit on the surface of the crucible leading to a considerable increase in measured viscosity. Moreover, nuclei of high melting-point inter-metallic compounds may be formed due to the presence of impurities and so increase the viscosity.

While much interest attaches to the study of the surface-tension of liquid metals it provides little evidence of the structure in the bulk of

the metal. In practice, the investigation of interfacial energies between solid and liquid metals is an important branch of liquid metal studies. The interested reader is referred to a recent comprehensive review by BOND²⁶

From the industrial point of view the freezing of metals is of more interest than the melting process, since knowledge of the conditions obtaining when a metal is cast is more important than knowledge of what happens during the melting operation. An important observation, originally made many years ago, is that liquid metals may be cooled considerably below their true

freezing points before solidifying, whereas solid metals can never be heated above their true melting points. The explanation of supercooling lies in the mechanism of freezing by nucleation and growth. Modern ideas on the problem have been summarized recently by HOLLOMON and TURNBULL²⁷ (nucleation) and by MEHL²⁸ (crystal growth). The change in local free energy caused by the formation in the melt of a solid nucleus is made up of two parts; the change arising

from the difference in volume free energy between the liquid and the solid, and the free energy of forming the interface between the solid crystal and the liquid. The former has a negative value below the freezing point and increases in magnitude as the temperature falls, i.e. the solid is structurally more stable than the liquid form below the freezing point. The interfacial free energy always has a positive value and is approximately equal to half the heat of fusion. As the temperature of a liquid is lowered the critical size of a stable nucleus is reduced and consequently the local increase in energy which has to be provided by thermal fluctuations becomes smaller and hence more likely to occur. In practice the supercooling needed is considerably diminished by the presence of impurities, with higher freezing points than the matrix, which provide solid bases on which matrix atoms can deposit. Recent experiments²⁹⁻³² have attempted to isolate the impurities by dividing the bulk of the pure metal into droplets, some of which will, on a statistical distribution, be fairly free of impurities. The solidification of the droplets may be studied under a high temperature microscope or

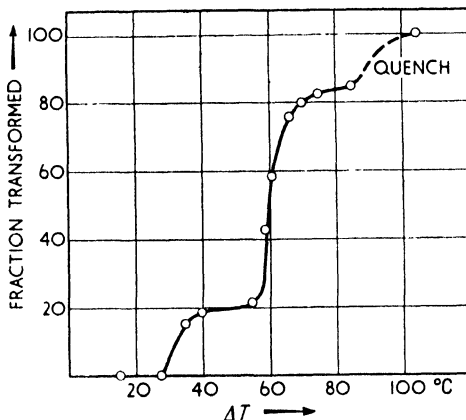


Fig. 4. Fraction of coated lead particles solidified as function of supercooling, ΔT (TURNBULL²⁹)

by dilatometric methods, when considerable undercooling is observed. Fig. 4, which shows TURNBULL's results on lead, is a plot of the fraction of the droplets which have solidified as a function of the degree of supercooling. In general, metals can be cooled by between 15 per cent and 25 per cent of their absolute melting points. The degree of undercooling depends very strongly on the nature of the medium employed to subdivide the metal. With some types of droplet coating the nucleation rate is proportional to the surface area of the droplets; with others it is proportional to their volume.

FRANK⁽³³⁾ explains the supercooling phenomenon as being due to the atoms in the liquid state assuming a structure which differs considerably from that of the solid state. The energy required to form the solid lattice from the liquid is therefore high. The proposed liquid structure consists of a group of 13 atoms, 1 of which is at the centre of a regular dodecahedron, the other 12 being situated in the centres of the faces of this figure. The body has five-fold symmetry and is incapable of extension into a long-range lattice structure. Such an arrangement gives closer packing and higher binding energy than the face-centred cubic or close-packed hexagonal arrangement, and is consistent with the x-ray observation that short range order exists in the liquid state but long range order does not. The mechanism succeeding nucleus formation, i.e. solidification, is fully discussed in a review by MARTIUS elsewhere in this volume.

In general, the properties of all liquid metals are more closely alike than are those of solids. As will be seen, when structural studies are discussed, there is a trend towards a common coordination of atoms in metals in the liquid state. The close-packed metals change to a lower coordination and the "open" structures of such metals as gallium and bismuth change to closer-packed, higher coordination structures. These changes are accompanied by corresponding changes in the values of electrical and thermal conductivities. The conductivities in the liquid state tend to approach a common value. BAUER, MAGAT and SURDIN⁽³⁴⁾ showed for a large number of liquids (mostly non-metallic) that a single function of the reduced temperature, θ , was capable of representing the properties of molecular volume, compressibility, surface tension and specific heat.

The reduced temperature

$$\theta = \frac{T - T_f}{T_c - T_f}$$

where T is the temperature of measurement of the properties, T_f is the melting temperature and T_c the critical temperature, all in degrees Kelvin. In the case of the compressibility β , the values for all the liquids examined fall on the curve described by the equation

$$\frac{\beta_T}{\beta_f} = \frac{1 - \theta^4}{(1 - \theta)^2}.$$

SIMON⁽³⁵⁾ has discussed the possibility of a critical point between solids and liquids. He has shown that, theoretically, liquids can always be compressed to the solid form provided the exerted pressure is sufficiently high. With increasing temperature and pressure the entropies of the liquid and solid states tend to approach a common value. In the solid the effect of temperature on the entropy prevails over the effect of pressure, with the result that the disorder of the phase increases. In the liquid state the reverse occurs, the pressure effect prevailing over that of temperature with the result that increasing pressure and temperature lead ultimately to a reduction in entropy. In Fig. 5 which shows the S - T curves for the gaseous, liquid and solid states the liquid and solid curves asymptotically approach a common value. In order to obtain these effects, however, the pressures exerted would be so high that structures of the electronic shells would probably be destroyed. It is likely, therefore, that the calculation represents a purely hypothetical state of affairs and a critical point is possible only in theory.

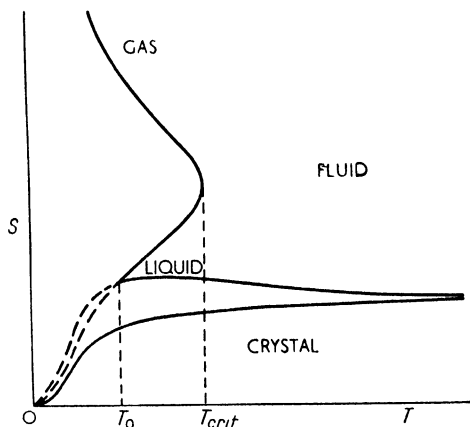


Fig. 5. Sketch of entropy along equilibrium curves for all states of aggregation (SIMON⁽³⁵⁾)

To summarize the indirect evidence, the process of melting leads to a breakdown of the regular lattice structure (with directed, homopolar forces in some cases) to a random arrangement of highly mobile atoms with randomly acting binding forces. The distinction between the different solid crystal structures tends to be lost and a trend towards common values of physical properties is observed.

To anticipate the section on the x-ray evidence for liquid metal structures, those properties which are dependent on long-range order change abruptly at the melting-point (e.g. deformation characteristics), while those dependent on short-range order show small changes on melting.

2. Theories of the Liquid State

The indirect evidence of physical properties outlined above has provided data enabling mathematical physicists to propose theories describing the phenomenon of melting and the properties of liquids, while the x-ray evidence has led to the development of more refined theories based on

solid-state behaviour. The theories described here are all of fairly recent origin and the influence of the x-ray results is present in every case. The most successful theories, however, are those of a fairly simple nature, and this is consistent with the latest interpretation of the x-ray data, which tends to show that the structures of liquid metals are quite simple. The object of the majority of the theories is to explain why, at a certain temperature, the regularly arranged solid crystal lattice becomes unstable relative to a disordered liquid arrangement of atoms (which have greater mobility than in the solid but similar binding forces) and why the transformation is of the first order. These treatments use idealized models of the melting process which also account for some of the changes in properties on melting. A number of critical reviews of theories of melting have been published⁽³⁶⁻⁴²⁾ so attention will only be directed towards the principles on which the theories are based. Most authors focus attention on two facts, one being that the liquid structure resembles the solid structure more strongly than the gaseous and the other being that an increase in volume occurs when most metals melt. A parameter is introduced which specifies the degree of order of the crystal lattice—as in superlattice theory—and the effect of temperature on this is examined. FRENKEL⁽²⁾ and BRESLER⁽⁴³⁾ in their theories, have based their calculations on the assumption that the degree of order is lowered by the formation of vacant sites in the lattice. Melting occurs when the number of vacant sites reaches a limiting value.⁽⁴⁴⁾ The calculations involved are similar to those of BRAGG and WILLIAMS on the loss of order in binary superlattices.

LENNARD-JONES and DEVONSHIRE⁽⁴⁵⁾ have proposed a mechanism which differs slightly from the vacant site theories. Disorder in the lattice is achieved by migration of atoms from their lattice sites to interstitial positions. A degree of order, P , may be defined as being equal to the ratio of number of atoms (N_A) in A (lattice) sites to the total number of atoms (N) in the crystal. The work required to move an atom from an A site into an interstitial (B) position is high at low temperatures due to repulsive forces. As the lattice expands with increase in temperature, it becomes easier for this migration to occur. The rate of decrease in order is slow at first, but P decreases more rapidly as the temperature increases until $P = \frac{1}{2}$, when it is impossible to distinguish between A and B sites. The sharpness of the melting point is due to the fact that when a number of atoms have succeeded in moving into B sites, the repulsive forces on another atom wishing to do so will be diminished. The more atoms there are in B sites the easier it will become for the change to occur and an "avalanche" or co-operative effect results in which the migration rate increases greatly until, at the melting point, all order is lost. On the basis of this theory, the melting points and

changes in volume and in entropy on fusion were calculated for argon and nitrogen. The quantitative agreement with experimental values was good although FRENKEL argues that such agreement can easily be obtained by a suitable choice of parameters.

The concept of the existence of holes in the liquid as distinct from vacant sites has been applied by some authors, notably FÜRTH.⁽⁴⁶⁾ The idea of holes existing as vacant lattice sites is devoid of meaning in the disordered liquid state. This is replaced by the notion of holes existing as gaps of indefinite size between the atoms in the liquid. These holes can freely change their shape and position. Evaporation is imagined as the merging together of the holes into macroscopic vapour bubbles, while melting consists of the transformation of unoccupied lattice sites into holes. The loss of long-range order is the effect of the disturbance of the lattice arrangement by these holes. If the liquid is compressed at a relatively low temperature these holes should be lost. The experiments of BRIDGMAN⁽⁴⁷⁾ show that this probably happens since the value of the bulk modulus for liquids is several times smaller than in the corresponding solid materials. This is due to the "porosity" which is removed under relatively low pressure. At higher pressure the compressibility falls to a value comparable with that of the solid state. The activation energy for the formation of a hole of radius r is $U = 4\pi r_0^2 \sigma$, where σ is the surface energy in the hole. FRENKEL derives ΔC_p , the change in specific heat on melting, in terms of U , of the change in free volume (i.e. the volume increment on melting) and of Δv the minimum possible volume of a hole.

$$\Delta C_p = \frac{V - V_0}{V_0 \Delta v} \cdot \frac{U^2}{kT^2}$$

where $V - V_0$ is the change of volume on melting, k is Boltzmann's constant and T the absolute temperature. Since the compressibility

$$K = \frac{V - V_0}{V_0} \frac{\Delta v}{kT}$$

$$\Delta C_p = \frac{K}{T} \left(\frac{U}{\Delta v} \right)^2$$

EYRING⁽⁴⁸⁾ and his collaborators have applied these concepts to flow phenomena in liquids.

KIRKWOOD⁽⁴⁹⁻⁵¹⁾ has based his theory on the dependence of the liquid structure on the free volume, which is the difference in volume between the "open" liquid structure and the close-packed arrangement of touching spheres. If the volume is V_1 under the latter conditions and V_2 at a higher temperature, $(V_2 - V_1)$ is small at low temperatures and the free volume is accommodated in the form of vacant lattice sites or

“holes.” When the number of holes reaches an appreciable value the lattice breaks down to the irregular liquid structure and the free volume is uniformly distributed among the atoms, giving rise to the high atomic mobility and the disordered structural arrangement. A distribution function $\rho(r)$ is defined by KIRKWOOD as being equal to the average number of atoms per unit volume at a distance r from a central atom in a liquid. By the use of statistical mechanics $\rho(r)$ is derived as a function of temperature and volume. As will be shown in the appropriate section, the results of x-ray diffraction experiments on liquids are given in terms of such a distribution function. The distributions derived by the free volume theory are in fair agreement with the x-ray experimental results. Once the radial distribution has been derived the equation of state and the internal energy can be calculated.

Few theories of the liquid state involve directly the cohesive forces between the atoms.⁽⁵²⁾ The action of heat motion in overcoming the cohesive forces, leading to a breakdown of the lattice to the liquid structure has been studied by LINDEMANN⁽⁵³⁾ and, more recently, by FRENKEL⁽²⁾ and by BORN.⁽⁵⁴⁾ LINDEMANN proposed the theory that fusion occurs when the amplitude of thermal vibrations of the atoms reaches a certain fraction γ , of the lattice constant, a . This hypothesis

may be expressed in the equation $(\gamma a)^2 = \frac{kT_f}{f}$, where k is Boltzmann's constant, T_f the melting temperature and f a constant which is related to the bulk modulus of the material. The formula yields a reasonable agreement with the experimental data if γ is given a value between $\frac{1}{4}$ and $\frac{1}{10}$. The later theories adopt a thermodynamical approach and derive the general principle that melting is an instability of the crystal lattice due to the volume expanding to a value which corresponds with the limit of tensile strength of the material. Agreement between theory and experiment is not good because, in practice, the solid lattice always contains imperfections.

MOTT⁽⁵⁵⁾ has recently compared the theories based on vacant site or hole formation with the theory of MACKENZIE and MOTT⁽⁵⁶⁾ in which melting is compared with a shearing process. The energy of grain boundaries is proportional to the product of the shear modulus G and the atomic volume, a^3 . MOTT calculates that the energy to form a vacant site in a solid rare gas equals the lattice energy, while the energy required in a metal equals half the lattice energy. The lattice energy is equal to the heat of sublimation L_s and if the latent heat of melting were associated with vacancy formation the values of $\frac{Ga^3}{L_s}$ for rare gases

and for metals should differ by a factor of two. The observed ratio is about five. In other words, the values of Ga^3 show a close correspondence with the latent heat of fusion, while the energy of vacancy formation

does not. This suggests that the lattice distortion on melting is of the same type as a shear.

Of the many mathematical treatments of the liquid state, none provides a completely satisfactory theory of the phenomenon of melting. Each has a limited success in describing certain aspects of the process. It is due to the indeterminate nature of the liquid state rather than to a lack of experimental data that the theories of the liquid state are far less precise than those of the solid state.

3. *The Stability of Liquids*

Attempts have been made in the previous sections to answer the questions: "Why do solids melt?" and "What happens to a solid when it melts?" A question which few have attempted to answer is: "Why do the elements have widely differing melting and boiling points?" The usual qualitative answer is that a high binding energy in the solid gives rise to a high melting point. The situation is, however, more complicated. The two metals sodium and gallium have melting points fairly close together (97.5°C and 29.9°C respectively) but their boiling points at 760 mm external pressure differ greatly (883°C and 1983°C respectively). A number of writers⁽⁵⁷⁻⁶⁰⁾ have examined the problem qualitatively and attempted to relate melting points and boiling points to the positions of the elements in the periodic table. BERTON⁽⁶¹⁾ observed that a constant relationship between the melting points and boiling points was apparent in certain groups of elements. Plotting melting points against boiling points yielded families of straight lines of similar slope.

Only one serious attempt has been made to examine the factors affecting the liquid ranges of the elements; liquid range being defined as the difference between the melting point and boiling point at a given pressure p . HUME-ROTHERY⁽⁶²⁾ showed that a semi-quantitative explanation of the variation of the liquid range throughout the periodic table was possible on the basis of the known behaviour of the free or binding electrons. For a really quantitative treatment of the subject, a knowledge of the complete equations of state of the different elements involved is essential. The relative proportions of the condensed range occupied by the solid and liquid states at 760 mm are listed in Table 2 for the non-transitional elements. The liquid ratio given in the table represents the difference between boiling and melting points divided by the boiling point in degrees Kelvin. Separating the melting and boiling phenomena, it is observed that the melting points of the *A sub-group elements* show their greatest increase between Groups I and II (see Fig. 6). After Group II the increase is much more gradual. In Group IA there is only one electron per atom, this being in one single s orbital. In the higher groups the s and p states overlap in the solid and four orbitals are

PROGRESS IN METAL PHYSICS

available for bond formation, giving rise to a much more strongly bound solid structure. The increase in stability beyond Group II is due to the continually increasing numbers of electrons in these four orbitals. The

TABLE 2
Liquid Ranges of Metals
(W. HUME-ROTHERY⁽⁶²⁾)

<i>Metal</i>	<i>°K at 760 mm Hg</i>		<i>Liquid Range</i>	<i>Liquid Ratio</i>
	<i>M. Pt.</i>	<i>B. Pt.</i>		
Li	452	1599	1147	0.717
Na	370.5	1156	785	0.679
K	336.6	1035	698	0.674
Rb	311.5	969	657	0.678
		986	674	0.684
Cs	299	943	644	0.683
		977	678	0.694
Be	1551	3243	1692	0.522
Mg	923	1380	457	0.331
Ca	1124	1712	588	0.343
Sr	1044	1639	595	0.363
Ba	977	1880	903	0.480
Al	932	2543	1611	0.634
Si	1694	2628	934	0.355
Cu	1356	2610	1254	0.480
Ag	1233.5	2424	1190	0.491
Au	1336	2983	1647	0.552
Zn	692	1180	488	0.414
Cd	594	1040	446	0.429
Hg	234.2	630	396	0.629
Ga	302.8	2300	1997	0.868
In	429.4	> 1720	> 1300	> 0.75
Tl	430	1730	1300	0.751
Ge	1231			
Sn	505	2635	2130	0.808
Pb	600	1965	1365	0.694
Sb	903	1910	1007	0.527
Bi	544	1833	1289	0.703

increase in boiling point on passing from Group IA to Group IIA is not so great because the free (vaporized) atoms in Group II form a stable sub-group of two *s* electrons, giving rise to a stable vapour phase. On passing from Group II to Group III a great increase in boiling point and heat of vaporization occurs. It is suggested that each atom in a liquid is bound to three neighbours by covalent bonds. This argument may appear to be inconsistent with the x-ray structural evidence. It is, however, with valency electrons and the way in which they act that the theory is concerned. On the basis of PAULING's theory⁽⁶³⁾ of metallic bonding, in Group III there are available for each atom three electrons

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which are able to form three covalent bonds, giving a very stable liquid structure. Since little is gained by the addition of a fourth electron there is little increase in boiling point on passing to Group IV. In Groups V, VI and VII very stable molecules are formed in the vapour

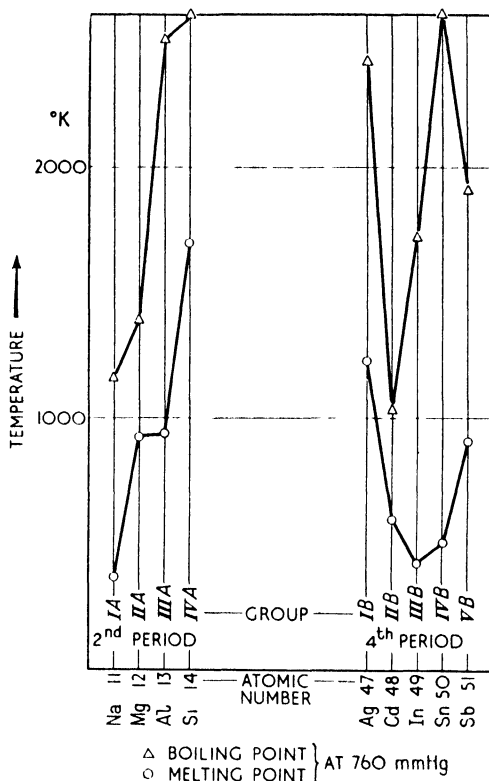


Fig. 6. The liquid ranges of the elements in the 2nd and 4th periods of the Periodic Table

phase and in some cases molecular crystals are formed in the solid state. Both factors limit the liquid range. Group IIIB and IVB elements have low melting points which are produced by incomplete ionization in the solid states. The high boiling points suggest, however, that ionization becomes complete in the liquid.

The high cohesion of the hybridized *s*, *p* and *d* orbitals in the transitional elements leads to high melting and boiling points.

In order to provide adequate proof of this theory, it is necessary to provide evidence that the type of bonding in liquid metals is such that the maximum liquid range is attained with an electron concentration of three per atom. The observation that greater liquid ranges occur at odd valencies than at even valencies is, however, very significant and has not

yet received the attention which it deserves from the mathematical physicist.

PART II

1. *Diffraction Studies of the Structures of Liquid Metals*

The results of x-ray diffraction experiments on liquids, in particular on liquid metals, led to a major change in outlook in the theories of the liquid state. For this reason, the theoretical and experimental aspects of x-ray diffraction by liquids is considered in some detail.

(a) *The Theory of Diffraction by Liquids*

A completely random assembly of atoms or molecules cannot, by definition, exist in reality. The fact that a molecule has finite size and occupies a certain volume prevents another molecule from occupying that particular volume. At any instant all positions in space are not equally likely to be occupied by a particular molecule in a gas. Even a gas, therefore, has a rudimentary ordering of the molecules which is, in principle, sufficient to produce some diffraction effects, although these effects are too small to be observed at normal pressures.^{(64), (65)} The effects which are observed in a gas at ordinary pressures are due largely to internal interference, that is, the regular repetition within each molecule of the atomic grouping, regardless of the external mutual arrangement of the molecules. Diffraction effects from gases were observed as early as 1911 and in 1913 FRIEDRICH⁽⁶⁶⁾ obtained diffraction patterns of Canada balsam, paraffin wax and amber, which were in the solid, non-crystalline state. DEBYE⁽⁶⁷⁾ began his important series of contributions to the study of diffraction by liquids in 1915, when he showed that the collection of electrons in groups around the nuclei of atoms must give rise to diffraction phenomena, even in gases. In the same year, EHRENFEST⁽⁶⁸⁾ gave a modified form of the Bragg equation in an attempt to interpret liquid diffraction phenomena. DEBYE and SCHERRER⁽⁶⁹⁾ in 1916 obtained diffraction rings from liquid benzene and a few years later KEESOM and DE SMEDT⁽⁷⁰⁾ produced diffraction patterns from liquid argon, oxygen and nitrogen. In the absence of a suitable mathematical method of analysis of the results, it was not possible to interpret these patterns in terms of atomic arrangements and until ZERNIKE and PRINS,⁽⁷²⁾ and DEBYE and MENKE⁽⁷³⁾ made important theoretical contributions to the subject, progress in the experimental field was slow.

In a liquid metal the density is so near to that of the solid that the atoms can only be a little farther apart than in the solid. X-rays scattered by one atom interfere with those scattered by its nearest neighbours and since these neighbours are constant neither in number nor distance, due to their high mobility, the observed diffraction effect results from the *average* distribution of atoms around one another. The

average distribution is, therefore, independent of the "reference" atom chosen. The purpose of x-ray analysis is to determine this average distribution in detail.

The early work of DEBYE⁽⁶⁷⁾ showed if one considered the n th pair of atoms of similar type separated by a distance r_n , the intensity I of the coherent scattered radiation is given by summing the intensities for all such pairs:

$$I = Nf^2 \sum_n \frac{\sin sr_n}{sr_n}$$

where N is the effective number of atoms in the sample, f is the structure factor, $s = 4\pi(\sin \theta)/\lambda$, θ is half the angle of scattering and λ the

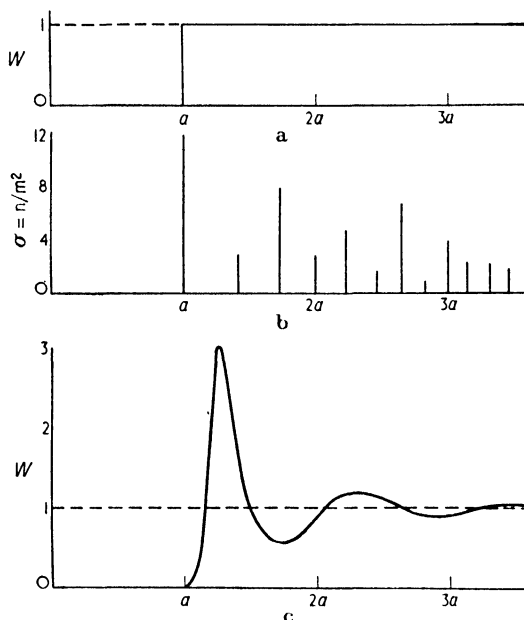


Fig. 7. Distribution functions: (a) gas consisting of monatomic molecules at low pressures; (b) close-packed spheres; (c) irregular close packing of spheres (JAMES⁽⁶⁴⁾)

wavelength of the incident radiation. In other words, one must consider two atoms whose scattered rays interfere with one another as a result of which an interference pattern is produced which is defined essentially by the relative separation of the two atoms.

In 1925 DEBYE⁽⁷¹⁾ introduced the idea of a probability function $W(r)$ expressing the probability of the occurrence of any given interatomic distance. This was in connection with the diffraction by gases. ZERNIKE and PRINS⁽⁷²⁾ in 1927 introduced a similar function, the radial distribution function, into their formula for diffraction by liquids. The radial distribution function $\rho(r)$ is so defined that $4\pi r^2 \rho(r) \cdot dr$ represents

the number of atoms lying at any instant at distances between r and $r + dr$ from the centre of a specified atom. In a solid crystal $\rho(r)$ is a discontinuous function of r . The two functions $W(r)$ and $\rho(r)$ have the same dependence on r and differ by a constant factor.

If the solid is visualized as a close-packed assembly of hard spheres of diameter a , only certain discrete interatomic distances can occur. The smallest distance is a , the next $\sqrt{2}a$, then $\sqrt{3}a$ i.e. in general $\sqrt{n} \cdot a$, where n can have any integral value from unity to infinity. For these

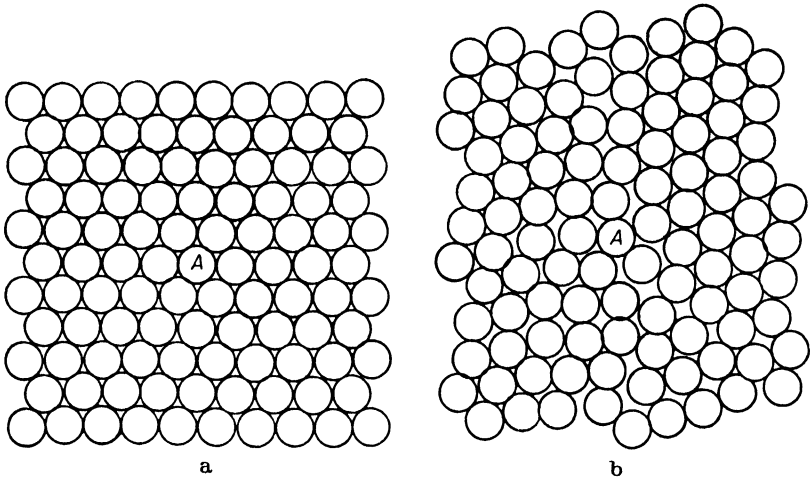


Fig. 8. (a) and (b) contain the same number of circles. In (a) every circle is surrounded by six others; in (b) the circle A is surrounded by five, but apart from this, the utmost effort has been made to achieve regularity, but without success

values $\rho(r)$ or $W(r)$ has a positive value, for all other values $\rho(r)$ or $W(r)$ is zero. If the close-packed array is rotated about a reference atom into all possible positions the centres of the other atoms lie on spheres of radii, a , $\sqrt{2}a$, $\sqrt{3}a$, etc. It is customary to represent such a distribution in the manner shown in Fig. 7b which is a plot of $W(r)$ versus a , the heights of the lines being proportional to the relative atomic density at that particular spacing.

If the effect of increasing temperature is represented when this close-packed array is loosened, i.e. expanded, and a degree of randomness introduced into the structure, the function $\rho(r)$ or $W(r)$ will become a continuous function of r . In a solid the atoms are vibrating about fixed lattice points, but in a liquid randomness is introduced by the slow migration of these lattice points. However, maxima will be present which are related to the positions of the spheres in the former case. Due to expansion these maxima will be situated at a slightly greater distance from the reference atom than in the solid, Fig. 7c. The first maxima are

well marked with the second and third fairly strong, but with increasing r , $W(r)$ approximates more nearly to the uniform average density of distribution. In such a structure a fair degree of local order persists around a given atom but on the large scale the arrangement is completely random; there is no long range order. Such an arrangement is illustrated by Fig. 8*b*, in which the drastic effect of a small local change in coordination on the degree of order is clearly shown.

An indication that the picture just presented is identical with the picture of the liquid state as shown by x-ray diffraction was first given by ZERNIKE and PRINS.⁽⁷²⁾ Starting from the one-dimensional case of an assembly of rods, it was shown that certain distances of separation are significant in giving rise to interference, i.e. diffraction, effects.

For the three dimensional case they were able to show that the distribution function, which was derived purely from geometrical considerations, was in accord with the general characteristics of diffraction by liquids.

ZERNIKE and PRINS⁽⁷²⁾ and WARREN⁽⁷⁴⁾ have shown that the intensity of the radiation I_{eu} (expressed in electron units) scattered coherently by an array of atoms can be expressed in the form:

$$I_{eu} = Nf^2 \left[1 + \int_0^R 4\pi r^2 \{ \rho(r) - \rho_0 \} \left\{ \frac{(\sin sr)}{sr} \right\} dr + \int_0^R 4\pi r^2 \rho_0 \left\{ \frac{(\sin sr)}{sr} \right\} dr \right]$$

where N is the number of atoms in the array, f is the atomic scattering factor, R is the radius of the liquid sample, $\rho(r)$ is the radial distribution function, ρ_0 is the constant average density of atoms and $s = \frac{4\pi \sin \theta}{\lambda}$.

By writing $i(s) = \{I_{eu}/Nf^2\} - 1$ the equation becomes:

$$si(s) = \int_0^\infty 4\pi r \{ \rho(r) - \rho_0 \} \sin sr \cdot dr$$

By performing a Fourier inversion, the radial distribution function may be expressed in terms of the intensity of x-radiation:

$$r\{\rho(r) - \rho_0\} = \left(\frac{1}{2\pi^2} \right) \int_0^\infty si(s) \sin rs \, ds$$

or

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty si(s) \sin rs \, ds$$

The two essential steps in determining the radial distribution function are to evaluate $i(s)$ from experimental measurements and then to evaluate the integral in the above equation for each of a series of values of r .

(b) *Experimental Procedure*

The first application of this formula to a practical measurement was made by DEBYE and MENKE,⁽⁷³⁾ who measured the intensity distribution of CuK_α and MoK_α radiation from liquid mercury. Subsequently a large number of workers have successfully used the method to derive radial distribution curves for a number of elements. To use the method successfully a number of conditions must be satisfied.⁽⁶⁵⁾ These may be summarized as:

- (i) Use of monochromatic x-rays.
- (ii) Well-defined directions of incidence.
- (iii) An absolute measure must be made of the coherently scattered intensity from the liquid as a function of s over a wide range of s .
- (iv) Corrections must be made for distortion in the relative intensity measurements, due to polarization or to absorption effects.
- (v) The same units must be employed for I_{eu} and Nf^2 in the equation.

In order that the value of $s = 4\pi \sin \theta/\lambda$ be known accurately, λ must be an accurately determined single value. This is best achieved by the use of a monochromator. It is also important that a wide range of values of s be covered to include all interference effects in the analysis, and to determine accurately the values of the incoherent scattering. Values of I_{eu} and Nf^2 may then be reduced to the same units. This object is attained by measurements at high scattering angles where the scattering of an atom is virtually independent of that of its neighbours. A wide range of s can be obtained only by changing λ , i.e. changing the characteristic radiation since θ is limited by the geometry of the diffraction arrangement, and even so the variation in λ which is practically obtainable is relatively small.

A typical film obtained by diffraction from a liquid is shown in Fig. 9. Such a film is examined with a microphotometer and the relative intensities obtained. The intensities are then corrected for polarization of the beam by the monochromator and by the sample and for absorption in the sample.

The resulting value represents the sum of the coherent and the incoherent scattering, but not in absolute units. To express the intensity in absolute units and to correct for the incoherent scattering use is made of the fact that at large scattering angles, where interference effects are not visible in the pattern, the observed coherently scattered x-rays have the same intensity as that produced by an entirely random assemblage of atoms (f^2). The observed intensity curve is, therefore, drawn on such a scale that at large values of s it coincides with the sum of the f^2 and incoherent intensity curves, both of which can be drawn from published tables. The curve for coherent scattering per atom can then be drawn by subtracting the incoherent scattering from the total scattering at a series of values of s .

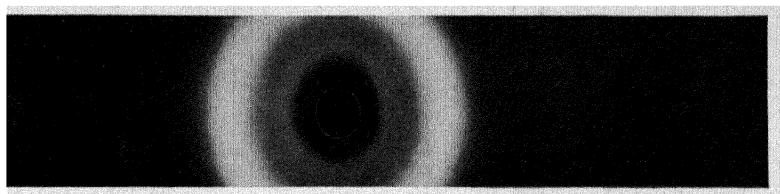


Fig. 9. Negative taken from a typical liquid x-ray diffraction photograph

Having derived the intensity function $i(s)$, the integral in the above equation has to be evaluated for a series of values of r . This is performed by one of the standard methods of analysis, viz. (a) use of a harmonic analyser, (b) graphical integration, or (c) trigonometric interpolation.

The whole problem of the analysis of the results of x-ray diffraction experiments on liquids has been recently discussed by FINBAK.⁽⁷⁵⁾ He emphasizes that any errors which are introduced into the intensity function due to the application of faulty corrections for absorption and for film exposure undergo a Fourier transformation and may have the effect of introducing spurious ripples on the radial distribution curve. Another source of error is introduced by the fact that, practically, it is not possible to perform the integration within the limits of $0 \rightarrow \infty$; in fact, the limits rarely exceed $1 \text{ \AA}^{-1}$ to $12 \text{ \AA}^{-1}$. The effect of this also is to produce false ripples on the radial distribution curve. FINBAK has re-examined the results of several workers in the light of these considerations and has found that the patterns for metals indicate simple monatomic liquid structures. EISENSTEIN and GINGRICH⁽⁷⁶⁾ have shown that the use of Geiger counter detectors in place of films may eliminate many sources of error.

(c) *Experimental Results*

Fig. 10a shows the experimental intensity in electron units per atom for liquid sodium⁽⁷⁷⁾ at 100° and 400°C plotted against $\frac{\sin \theta}{\lambda}$. The curves for incoherent scattering (b) and the total independent scattering per atom (c) are plotted on the same scale. Similar curves for lithium⁽⁷⁸⁾ at 200°C are shown in Fig. 11. The high incoherent scattering will be noticed. Lithium, being the metal with the lowest atomic number, displays the greatest amount of incoherent scattering. For elements of high atomic number, e.g. tin, the incoherent scattering is negligible.

The atomic radial distribution curves, obtained by analysis using the Zernike and Prins formula, for sodium and lithium, are shown in Figs. 12 and 13 respectively. The significance of these curves was discussed above. The average density curves (b) and the distribution of atoms in the crystalline state (c) are given for comparison. These liquid distribution curves are typical of those obtained for all metals. They are explained simply on the basis of the occupation of space by a collection of randomly arranged yet fairly closely packed atoms. Similar distribution curves have been obtained by geometrical experiments. DEBYE⁽⁷³⁾ analysed the two-dimensional case by means of a set of steel balls of similar size which were loosely packed in a flat box with a glass lid. Two of the balls were marked and after shaking the box, the distance between the balls was measured. The box was left in a convenient place in the

laboratory where anyone could shake it and record the result. The distribution curve, when plotted, was of the same general form as the

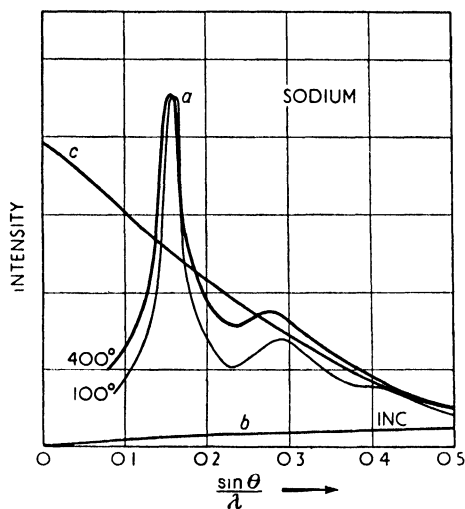


Fig. 10. Intensity versus $\sin \theta/\lambda$ for liquid sodium. (a) Corrected experimental intensity curves for liquid sodium at 100°C and 400°C; (b) incoherent scattering curve; (c) total independent scattering per atom (GINGRICH⁽⁶⁵⁾)

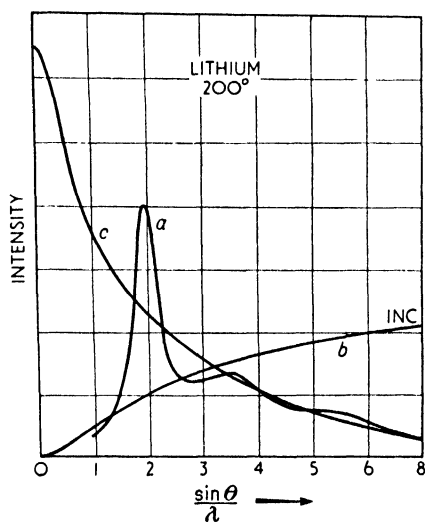


Fig. 11. Intensity versus $\sin \theta/\lambda$ for liquid lithium. (a) Corrected experimental intensity curve for liquid lithium at 200°C; (b) Incoherent scattering curve; (c) total independent scattering per atom (GINGRICH⁽⁶⁵⁾)

curve obtained by these workers for liquid mercury. The three-dimensional case was examined by MORRELL and HILDEBRAND,⁽⁷⁹⁾ who suspended coloured gelatin balls in an array of transparent gelatin balls of similar size in a gelatin solution of the same density and refractive index. They photographed the arrangement simultaneously in pairs at right angles and from thousands of observations again derived a similar

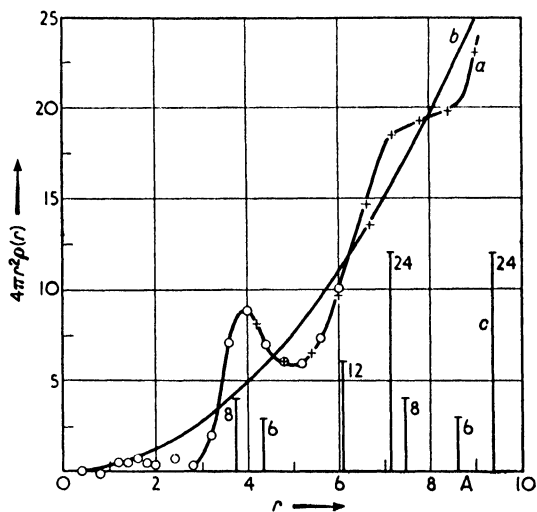


Fig. 12. (a) Radial distribution curve for liquid sodium; (b) average density; (c) distribution of neighbours in crystalline sodium (JAMES⁽⁶⁴⁾)

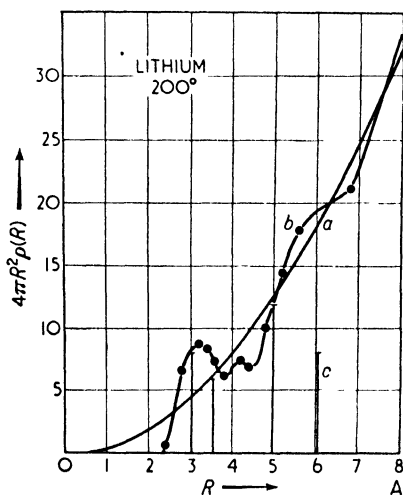


Fig. 13. (a) Radial distribution curve for liquid lithium; (b) average density curve; (c) distribution of neighbours in crystalline lithium (GINGRICH⁽⁶⁵⁾)

distribution to that obtained from mercury, which is believed to behave as an ideal monatomic liquid.⁽⁸⁰⁾

PRINS,⁽⁸¹⁾ starting from a solid state model, was able to calculate liquid models by introducing an error function, thereby "blurring" the lattice structure. The physical picture of a liquid described in this way is identical with a model consisting of atoms vibrating independently about sites, which are themselves slowly varying in position. A theory of BERNAL⁽⁸⁴⁾ starts from the fact that the probability of finding a molecule at a given distance from another molecule is independent of the position of either of them in a liquid. The radial distribution function can be determined by three variables only, the mean distance of closest approach of the molecules (r), the number of close neighbours of any molecule (N), and the irregularity of the distribution λ which determines the breadths of the peaks on the distribution curves. The effect of changes of temperature and pressure is shown to consist of changes in the equilibrium values of r , N and λ , i.e. the configuration of a liquid is a function of temperature and pressure. This explains the extra specific heats and compressibilities of liquids as being due to configurational specific heats and compressibilities respectively. Furthermore, the higher irregularity factor of liquids causes the free energy of liquids to decrease more rapidly with temperature than that of the corresponding solid, and thus a temperature is reached at which equilibrium between the two distinct phases is possible, since the free energy curves will intersect and the sharpness of the melting point is explained.

The statistical nature of the radial distribution curves has been emphasized since some writers have tended to exaggerate the structural order in a liquid. Some confusion was introduced by Stewart⁽⁸²⁾ who proposed the term "cybotaxis" for liquid structure. This was more specifically intended to describe molecular assemblies, e.g. water and hydrocarbons. It implied that the tendency existed for the solid state structure to persist into the liquid phase. FRENKEL⁽²⁾ added to the confusion by interpreting Stewart's results as meaning that a liquid consisted of a very large number of randomly oriented crystals of sub-microscopic size. In a more recent paper, however, STEWART⁽⁸³⁾ defines his conception more carefully, stressing the essentially transient nature of the local order. From the theoretical point of view the closer the analogy between liquid and solid structures the easier are the calculations, but this temptation to idealize the conditions and to use the experimental evidence as proof leads to false conclusions. The conclusions of FINBAK⁽⁷⁵⁾ emphasize this only too clearly.

GINGRICH⁽⁶⁵⁾ has given in some detail the results of x-ray investigations on liquid metals up to 1943 and, more recently, SAUERWALD⁽⁸⁵⁾ has summarized the results on all the metals examined up to 1950. Table 3 reproduces the latter results, d , the closest distances of approach

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TABLE 3
X-ray Data on Liquid Metals
(after SAUERWALD⁽⁸⁵⁾)

Metal	Solid		Liquid		
	Coordination No.	Distance Å	Coordination No.	Distance Å	Temp. °C
Hg	6 + 6	3.0 + 3.47	12	3.30	20
Cd	6 + 6	2.97 + 3.29	8 + 4	3.06 + 4.0	350
Zn	6 + 6	2.66 + 2.90	11	2.94	460
Au	12	2.88	11	2.86	~ 1100
Pb	12	3.49	8 + 4	3.40 + 4.37	375
Al	12	2.86	10.6	2.96	700
Tl	6 + 6	3.40 + 3.45	8 + 4	3.30 + 4.22	375
In	4 + 8	3.24 + 3.37	8 + 4	3.17 + 3.88	165
			8 + 4	3.30 + 4.0	160
			8	3.36	390
Na	8	3.72	8	4.385	100
			8	3.90	400
			9.28	3.79	100
			8.95	3.79	400
K	8	4.62 *	8	4.64; 9.0	70
Rb	8	4.87 *		4.85; 9.2	395
Li	8	3.31 *	Analogous with f.c.c.		
			Analogous with f.c.c.		
			Analogous with f.c.c.		
			9.8	3.24	
		3.02 *			
Sn	4 + 2 + 4	3.15 + 3.76	10	3.20	280
			10	3.38	480
Ga	1 + 6	2.71 + 2.79	11	2.77	20
Bi	3 + 3	3.09 + 3.46	7 -> 8	3.32	340
Ge	4	2.43	8	2.70	1000

* Values from W. HUME-ROTHERY, Institute of Metals Monograph, No. 1, London, 1947

(i.e. the values of r for the first radial distribution maxima) and coordinations in the solid and liquid phase being given. d values are given to facilitate comparison between the solid and liquid structures. The metals having face centred cubic solid structures show a slight decrease in coordination⁽⁸⁶⁾, e.g. Al 12 $\rightarrow$ 10.6 and Au 12 $\rightarrow$ 11. Metals which crystallize in the hexagonal structure in which each atom has six near neighbours and six at a little greater distance, i.e. Cd and Zn, gain more nearest neighbours and lose some of the next nearest. The body centred cubic metals with coordination number eight in the solid, show virtually no reduction in the liquid, merely an increase in spacing. Sodium, which has been very widely studied, shows an *increase* in coordination on melting. WALL⁽⁸⁷⁾ found from the experimental data of TRIMBLE and GINGRICH⁽⁷⁷⁾ that at 100°C 9.28 atoms surround each sodium atom at a

distance of 3.79 Å corresponding to a free space of radius 0.6 Å. At 400°C, the coordination is 8.95 atoms lying at the same distance; the radius of free space is then 0.77 Å. From these data WALL has calculated the latent heats of fusion and of vapourization of the metal with fair success. A similar calculation was carried out for potassium by GINGRICH and WALL.⁽⁸⁸⁾

The metals which have complex, open-packed crystal structures show distinct changes in coordination on melting. Mercury, which has a rhombohedral crystal structure with six nearest neighbours, assumes an ideal monatomic structure on melting with a twelve-fold coordination. Tin also shows a tendency towards simpler, closer packing in the liquid. It is in the four metals germanium, gallium, bismuth and antimony that a marked change is observed on melting. In these elements the percentage of the total volume of the crystal occupied by the ions is less than 50 per cent. The bonding is of a homopolar nature and the coordination is very low. On melting the open structures are no longer stable and a much higher coordination is attained. This is due to the increased kinetic energy and mobility of the atoms, and to the disappearance of the homopolar bonding which is reflected in the other properties such as thermal and electrical conductivity which increase on melting.

The general problem of the change of binding state, entropy and volume on melting, including the evidence of the x-ray measurements of coordination numbers, has been discussed by KUBASCHEWSKI.⁽⁴⁾ Elements are classified as true metals, meta-metals, semi-metals and non-metals. In true metals pure metallic bondings are responsible for the stability of the lattice. Meta-metals and semi-metals display increasing amounts of homopolar bonding. The classification may also be made on the basis of the values of $\frac{C_p}{T_m} \cdot \alpha = \delta_K$, where C_p is the molar heat capacity at the melting point, T_m and α is the cubic coefficient of expansion. The ratio is nearly constant for true and meta-metals, is much greater and varies within wider limits for semi-metals and is smaller for non-metals. The changes in coordination numbers and in δ_K show that the semi-metals tend to lose their homopolar bonding on melting. This is confirmed by the changes of entropy and of conductivity. Table 4 summarizes KUBASCHEWSKI's classification in terms of physical constants. MOTT⁽⁸⁾ has considered the case of bismuth and shown that on melting the Brillouin zone which contains five electrons per atom disappears and he has calculated that the liquid metal should have a resistance comparable with that of lead. It is of interest that RANDALL and ROOKSBY⁽⁸⁹⁾ showed the diffraction patterns of liquid lead and bismuth to be similar, although they did not use the complete Fourier analysis to derive this result and more recent work by HENDUS⁽⁹⁰⁾ has shown there to be a slight difference between the two.

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TABLE 4

(KUBASCHEWSKI)⁽⁴⁾

<i>Property</i>	<i>True Metals</i>	<i>Meta-Metals</i>	<i>Semi-Metals</i>	<i>Non-Metals</i>
Coordination number	12 or 8	6 + 6, 4 + 8	< 6	Low
κ Electrical conductivity	$3 \times 10^4 \rightarrow 7 \times 10^5$	$10^4 \rightarrow 10^5$	$10^{-5} \rightarrow 10^4$	$< 10^{-8}$
χ Magnetic susceptibility	Para, ferro-	Weakly dia-	Weak $\rightarrow$ strong dia-	dia-
$\delta_{\text{Solid}} = \frac{\Delta s}{\Delta V}$	85	90-120	150-400	< 70
$\kappa_{\text{Liquid}} - \kappa_{\text{Solid}}$	$\leftarrow$ — Weakly — ve — $\rightarrow$		$\leftarrow$ — + ve — $\rightarrow$	$\rightarrow$
δ_m	65	65	— ve	< 40
Liquid coordination number	8-11	8-11	7.5-11	Variable
δ_{Liquid}	75	75	80-180	< 50
Elements	Li, Na, K, Rb, Cs, Cu, Ag, Au, Mg, Ca, Al, Co, Ni, Ti, Pb	Zn, Cd, Hg, In	C, Sn, Si, Ge, Sb, Bi, Te, Ga, Se, P	P, S, Se, F, Cl, Br, I

(d) Investigation of the Structure of Liquids by Diffraction of neutrons

With the construction of atomic piles it has become possible to investigate the structure of liquids by the diffraction of neutrons.⁽⁹¹⁾ The principles involved are, broadly speaking, the same as those used in x-ray diffraction. In the study of liquid structures neutrons have the advantage that some of the heavy elements have small neutron capture cross-sections while their x-ray absorption coefficients are high. Also the incoherent scattering for neutrons is small and nearly spherically symmetric. The basic experimental procedure is to collimate a beam of slow neutrons from a pile, and monochromatize it by means of a crystal, usually calcium fluoride. The beam is then directed on to the sample and the scattering of the neutrons by the sample at varying angles of incidence is measured by means of a neutron counter (Fig. 14). A difficulty in neutron diffraction studies of solids has been the small effective flux of the slow neutrons available. This is much smaller in magnitude than the effective flux density of x-rays from existing x-ray tubes. Also the slow neutrons, unlike the x-rays from a tube, have a broad energy spectrum. Both these factors give rise to long exposure

times. CHAMBERLAIN⁽⁹²⁾ has, however, devised an experimental arrangement whereby a more intense beam can be used. The value of $\frac{\sin \theta}{\lambda}$ is kept constant instead of λ . The factor by which the cross-section of a

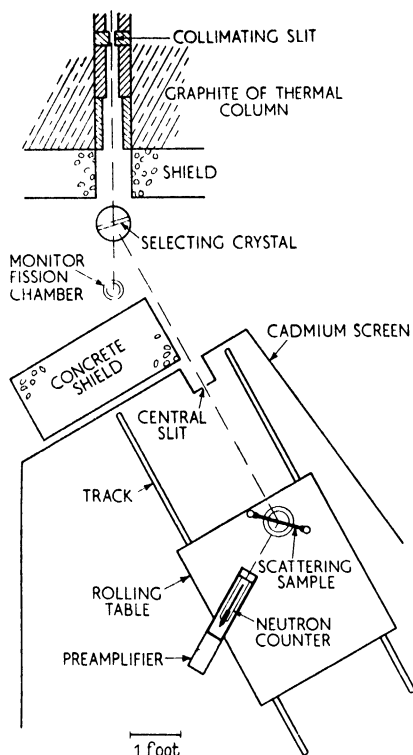


Fig. 14. Neutron diffraction spectrometer arrangement for the examination of liquids (CHAMBERLAIN⁽⁹²⁾)

single atom must be multiplied to give the cross-section of the bulk liquid is a function of $\frac{\sin \theta}{\lambda}$. These results can be interpreted in terms of a formula similar to that derived by ZERNIKE and PRINS⁽⁷²⁾ for x-rays by the analogous process of introducing a radial distribution function. The radial distribution curves are derived by evaluation of the integral in the equation given below by means of a Fourier analysis, using the method of trigonometric interpolation.

$$\chi \left(\frac{4\pi}{\sigma_s} \cdot \frac{d\sigma}{dw} - 1 \right) = \int_0^\infty dR \cdot R(\rho - \rho_0) \sin(4\pi\chi R)$$

where $\chi = \frac{\sin \theta}{\lambda}$, ρ_0 is the over-all average density of atoms in the liquid,

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ρ is the average density of atoms at a distance R from a given atom, σ , is the scattering cross-section of an atom and $\frac{d\sigma}{dw}$ is the differential scattering cross-section.

Sulphur at 141°C, lead at 390°C and bismuth at 310°C have been examined by this method. The radial distribution curves for lead and bismuth are given in Figs. 15 and 16 respectively. It is of interest to

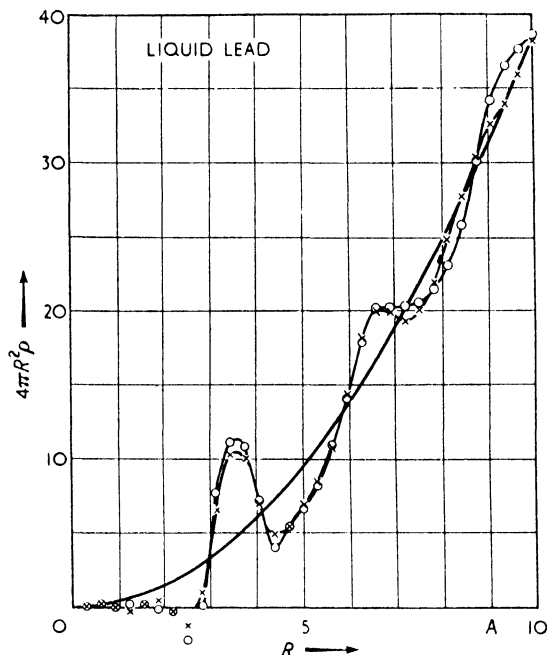


Fig. 15. The number of atoms per unit distance from one atom as a function of the distance. Results from two runs are shown (CHAMBERLAIN⁽⁹²⁾)

note that the first maxima on the radial distribution curves for bismuth and lead occur at similar values of R but that the coordinations at these maxima differ. A small hump appears on the bismuth curve at 5 Å which is absent from the lead curve. It is interesting to speculate whether this hump is due to an integration error of the type discussed by FINBAK⁽⁷⁵⁾ for X-rays.

2. The Structure and Behaviour of Liquid Alloys

(a) Introduction⁽⁹³⁻⁹⁷⁾

Studies of liquid alloys have been mainly concerned with their chemical rather than their physical properties. While alloying produces changes in physical properties, these are usually not very great; the resultant

properties are often the mean of those of the constituents. From the practical point of view the interaction between the different species of atom is the more interesting field of study. It is important to know whether the atoms attract one another strongly to form intermetallic compounds or repel one another to produce immiscibility. These equilibrium relations and the way in which they vary with temperature and composition are best examined by thermodynamical methods.

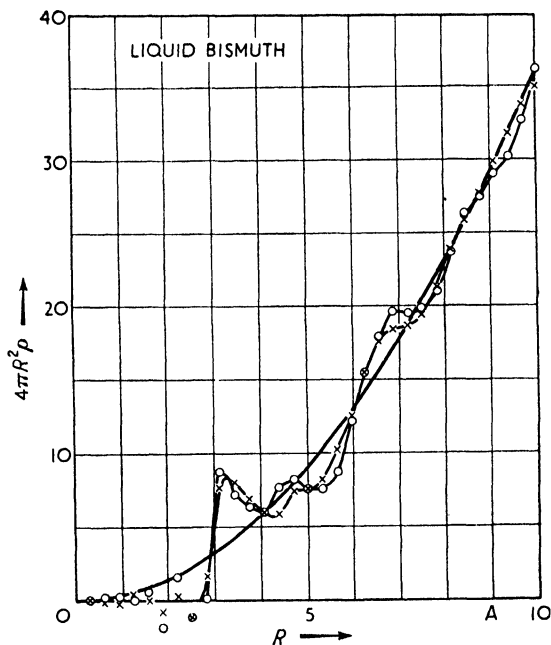


Fig. 16. The number of atoms per unit distance from one atom as a function of the distance. Results from two runs are shown (CHAMBERLAIN⁽⁹²⁾)

The thermodynamics of simple systems was well established by the beginning of the present century. Subsequent developments have attempted to take into account in more detail the nature of the interatomic forces operating, the methods of statistical mechanics being introduced as the Quantum theory became established. A large amount of data on binary and ternary liquid systems exists to-day, and the general principles governing their equilibrium behaviour are beginning to be fairly well understood. As far as liquid alloys are concerned, current work is mainly concerned with determining the extent to which the interatomic forces may be satisfied in the irregular, highly mobile liquid structure. Consider a solution consisting of A and B atoms. If interatomic forces were not acting the entire solution would evaporate. The forces acting may be symbolized as $A-A$, $B-B$ and $A-B$. Then the

relative strengths of these interactions will determine the behaviour of the solution. If,

(i) $A-A = B-B = A-B$. This represents an ideal solution in which the effective concentration of A and B for thermodynamical purposes is equal to their actual concentration. This case is rarely found in practice.

(ii) $A-A < A-B > B-B$. The atoms tend to combine to form a compound, thereby reducing the effective concentration of A atoms and B atoms for such purposes as evaporation or reaction with a third component.

(iii) $A-A > A-B < B-B$. The atoms of the two species are repelled by one another and, unless the entropy of mixing can overcome this, immiscibility is observed in the system. The effective concentration of A and B atoms is thereby increased.

In order to account for the deviation from ideal behaviour observed in cases (ii) and (iii), LEWIS⁽⁹⁴⁾ introduced the functions "fugacity" and "activity." Fugacity expresses the effective pressure of a component in a system. In metallic systems in which the vapours are generally monatomic and the pressures involved are relatively low, fugacity can be regarded as equal to the observed vapour pressure. The activity or "degree of ideality" of the component A in a system is proportional to the fugacity, i.e. to the partial vapour pressure p_A . If the vapour pressure of pure A is p_A^0 , the activity a_A is defined: $a_A = \frac{p_A}{p_A^0}$.

An alternative definition may be given in terms of chemical potential. If μ_A is the chemical potential of A in solution and μ_A^0 the chemical potential of pure A .

$$\mu_A - \mu_A^0 = RT \log \frac{p_A}{p_A^0} = RT \log a_A = \Delta \bar{G}_A$$

where $\Delta \bar{G}_A$ is the partial molal free energy of the vapour.

An ideal solution obeys RAOULT'S Law which states that the activity of the solvent in a dilute solution is proportional to its atomic fraction. A plot of activity *vs.* the mole fraction of solute for an ideal solution is a straight line (Fig. 17*a*). Metallic solutions generally show deviations from the straight line as demonstrated by the plots for bismuth-mercury and thallium-mercury in Fig. 17*b* and *c*. The attractive forces between unlike atoms, which give rise to the formation of intermetallic compounds [case (ii)] lead to negative deviations (thallium). Where these interatomic forces are smaller than those between like atoms [case (iii)] positive deviations occur (bismuth). To indicate these deviations from the ideal state the activity coefficient, γ , is introduced. It is defined as the ratio of the activity to the mole fraction, i.e. to the atomic fraction in alloys.

HILDEBRAND⁽⁹⁵⁾ has defined a "regular" solution as one in which the

distribution of molecules is completely random. The heat of mixing may be positive or negative, and this determines the deviation from **RAOULT'S** Law. It can be shown that:

$$RT \log \gamma_A = L_A$$

where L_A is the partial molar heat content of the component A . This

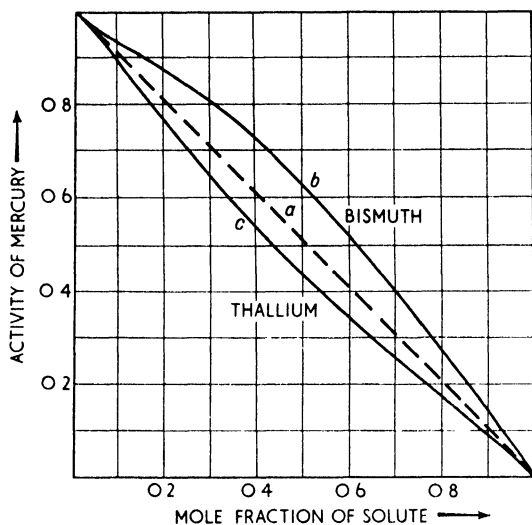


Fig. 17. Activities of thallium and bismuth in amalgams at 325°C, showing typical deviation from **RAOULT'S** law (**CHIPMAN**⁽⁹³⁾)

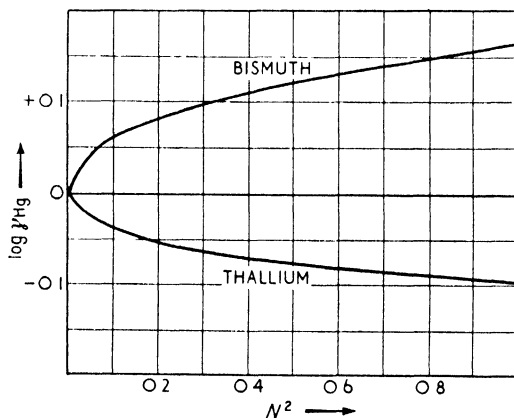


Fig. 18. Logarithm of the activity coefficient of mercury as a function of the square of the mole fraction of bismuth and thallium (**CHIPMAN**⁽⁹³⁾)

may be expressed in another form to describe systems which do not display regular behaviour:

$$RT \log \gamma_A = bN_B^2$$

where N_B is the mole fraction of the solute B , and b a constant. As is shown in Fig. 18 in which $\log \gamma_{\text{Hg}}$ is plotted against the squares of the mole fractions of bismuth and thallium, this formula gives a sensitive picture of the departure from an ideal solution. When the activity of one component (A) in the system A - B , is known over a range of compositions the variation in activity of the second may be derived from the Gibbs-Duhem equation:

$$N_A d \log a_A + N_B d \log a_B = 0$$

(b) *Experimental Determination of activity*

Using these concepts the activities of the components in a large number of binary systems have been investigated. Several experimental methods can be employed, the principal ones being:

1. Vapour pressure. In a system containing a fairly volatile component, e.g. Zn in Cu-Zn or Hg in Sn-Hg, the vapour pressure of this component can be measured over a range of temperature and composition. If the variation of vapour pressure with temperature has been determined for the pure metal the activity of the metal in the alloy is easily derived.

2. Electromotive force measurements. If one constructs a cell with two electrodes of the same alloying constituents, but of differing composition, and the electrolyte contains the ion of the more electropositive metal, the reaction will involve the transfer of the latter from one electrode to the other.

The activity a_A of the more positive metal is derived from the equation:

$$RT \log a_A = \Delta \bar{G}_A = -zFE$$

Where $\Delta \bar{G}_A$ is the partial molar free energy, z is the charge on the ion of the metal, F is the Faraday and E the e.m.f. of the cell, which is the property measured.

3. Distribution equilibrium. The distribution of a solute element C between two solvent metals A and B , which are immiscible, can be measured at a series of temperatures. At a constant temperature the ratio of the activity of C in A to C in B is constant with increasing concentration of C . If one of these activities is previously known, the other can be derived. The activity coefficient is known from the distribution ratio.⁽⁹⁸⁾

Using the above methods the activities of a large number of liquid systems have been derived. Generally the motives for selecting the systems have been dictated either by ease of experimentation or by industrial interests. Only recently have attempts been made to systematize the results. CHIPMAN^{(30), (93)} has discussed the subject in several publications while LUMSDEN⁽⁹⁾ in his recent book provides several examples of the calculations involved in binary alloy systems.

KLEPPA,⁽⁹⁹⁾ in a series of publications generally entitled: *A Thermodynamic Study of Liquid Metallic Solutions*, has described the use of the e.m.f. method to derive the thermodynamic properties of the alloys of gold with lead, tin, bismuth and thallium. The emphasis is placed on the entropy of mixing in the systems and in order to describe the deviations of this quantity from that of ideal regular solutions an "entropy mole fraction" is defined. $\Delta\bar{s}_i$, the partial molar entropy of mixing is derived from e.m.f. measurements by the formula

$$\Delta\bar{s}_i = 2F \cdot z \cdot \frac{dE}{dT}$$

where the symbols are the same as in the previous equation. The entropy mol fraction N_i is the *calculated* mol fraction corresponding to

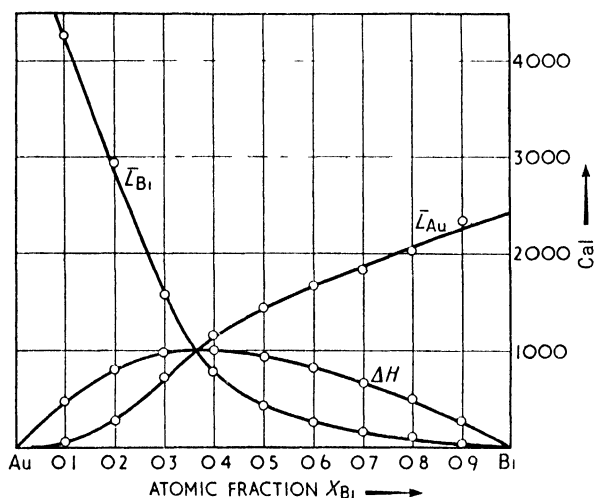


Fig. 19. Relative partial molar heat contents, and integral heats of mixing in the system Bi(1)-Au(1) (KLEPPA⁽⁹⁹⁾)

the *actual* partial molar entropy. The systems investigated all showed deviations in *entropies of mixing* from the ideal. Such deviations may be due to the following causes:

Factor	Effect on S
Short range order	-ve
Net volume change on mixing	$\Delta v > 0$: +ve, $\Delta v < 0$: -ve
Difference in space required of each component	+ve
Change in specific heats on mixing	+ve or -ve
Change in coordination number on mixing	+ve or -ve

In each of these gold systems the difference in atomic diameters is large. The vibrational entropy terms will be large due to the packing problem, giving rise to large positive entropy deviations. In addition, the size difference has an effect on the partial molar heat contents. The variation with composition of these heat contents ($\bar{L}_{\text{Bi}}$ and $\bar{L}_{\text{Au}}$) and the integral heat of mixing (ΔH) are plotted in Fig. 19 for the system Au-Bi. The maximum in the ΔH curve is displaced to the gold-rich side of the system. When two metals show a marked positive ΔH , the maximum is usually displaced towards the side of the smaller atom. The effect may arise from the coordination of atoms in the mixture. Large Bi atoms in a matrix consisting mainly of smaller gold atoms will have a larger number of nearest neighbours than the small gold atom surrounded mainly by larger Bi atoms. Qualitative support for this explanation is given by the fact that atoms of widely differing sizes often show limited miscibility in the liquid state and the size-factor effect in the limitation of solid solutions may be analogous.

(c) Immiscibility

Mention has already been made of the problem of liquid immiscibility. Although extensive data are available on the temperature and composition limits of the fields of immiscibility in many metallic systems, no quantitative theory has yet been proposed for the phenomenon. Qualitatively it is generally agreed that it is due to a considerable difference in size or binding energy between the pair of elements concerned. From the statistical-mechanical point of view, if the interaction potentials are such that $V_{AB} < \frac{V_{AA} + V_{BB}}{2}$ and entropy effects are overcome, complete immiscibility should occur. If $V_{AA} > V_{AB} > V_{BB}$ limited miscibility may occur. In either case the activities will show positive deviations from RAOULT'S Law. HILDEBRAND⁽⁹⁵⁾ has attempted to draw more quantitative conclusions by the concept of the "solubility parameter." This is a measure of the binding energy of an element and is defined as the energy of vaporization per cubic centimetre. Two metals *A* and *B* with atomic volumes v_A and v_B and solubility parameters δ_A and δ_B will, in general, be completely miscible if

$$\frac{v_A + v_B}{2} (\delta_A - \delta_B)^2 < 2RT$$

Beyond these limits immiscibility is observed at certain unspecified temperatures and compositions. For many metals, the atomic volumes of which are about 10 c.c., for two liquids to be miscible ($\delta_A - \delta_B$) must not exceed (approximately) 20 at 1000°K and 28 at 2000°K. In 47 systems listed by HILDEBRAND, in which liquid separation is observed (Table 5), agreement with the formula is good. Only five systems

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TABLE 5

Two-phase Liquid Systems (HILDEBRAND)⁽⁹⁵⁾

<i>System</i>	<i>Temperature</i> °C	$\pm (\delta_1 - \delta_2)$	<i>System</i>	<i>Temperature</i> °C	$\pm (\delta_1 - \delta_2)$
Ag-Co	1900	44	Cd-K	800	23
Ag-Cr	1800	26	Co-Pb	1700	75
Ag-Fe	1900	35	Cr-Pb	1800	57
Ag-Mn	1500	13	Cr-Sn	1700	43
Ag-Ni	1800	42	Cu-Pb	1300	56
			Cu-Tl	1300	58
Ag-V	2100	37	Fe-Pb	1800	66
Al-Bi	1000	35†	Ga-Hg	400	43
Al-Cd	1000	41†	Ga-Pb	600	23
Al-K	1000	62†	K-Li	500	30*
Al-Na	1000	52†	K-Mg	1000	24†
Al-Pb	1000	32†	K-Zn	900	33†
Al-Tl	1000	34†	Li-Na	500	19*
As-Tl	500	18*	Mg-Na	900	14†
Bi-Co	1600	78	Mn-Pb	1500	44
Bi-Cr	1900	60	Mn-Tl	1500	46
Bi-Fe	1800	69	Na-Zn	900	23†
Bi-Ga	500	26	Ni-Pb	1600	73
Bi-Mn	1500	47	Ni-Tl	1700	75
Bi-Si	1700	40	Pb-Si	1700	37
Bi-Zn	700	6†	Pb-Zn	700	3†
Ca-Cd	1000	5	Si-Tl	1700	39
Ca-Na	1000	10†	Tl-Zn	700	5†
Cd-Fe	1800	72			
Cd-Ga	600	29			

* at 500°K † at 1000°K

disagree markedly with the theory, while two others are borderline cases within the limits of experimental error. The converse of this postulate is not true, however. Many metals with large differences in solubility parameters form homogeneous phases. Most of these display compound formation, e.g. Cu and Zn over a wide temperature range show a constant value of $\delta_{\text{Cu}} - \delta_{\text{Zn}}$ of about 50, form a series of electron compounds in the phase diagram and show complete liquid miscibility.

LUMSDEN⁽⁹⁾ has attempted in the case of the system lead-zinc to apply statistical mechanics to the problem of immiscibility, which is displayed over a wide temperature range by this system. The effect of the interaction between non-adjacent atoms is accounted for in the free energy equation:

$$\Delta G = RT(N_A \log N_A + N_B \log N_B) + N_A N_B (\epsilon - \sigma T + \eta) - \frac{N_A^2 N_B^2 (\epsilon - \sigma T)^2}{10RT}$$

The first term deals with the ideal free energy of mixing, the second with the difference from ideality, assuming random distribution of atoms

and the third term corrects for deviations from randomness. ϵ is a parameter specifying the change of potential energy between nearest neighbours, η specifies the change of energy between non-nearest neighbours and σ is defined by the rate at which the potential energy varies with distance between neighbouring atoms. The theory uses x-ray data for typical elemental metals and introduces so many similar simplifying assumptions that its value is doubtful as a quantitative treatment. It does, however, make an attempt to use statistical mechanics to solve a problem made difficult by such a large number of variables.

If we believe the "hole" or vacancy theory of the liquid state, it is difficult to apply nearest neighbour interaction concepts in theories with any accuracy. SAUERWALD⁽¹⁰⁰⁻¹⁰³⁾ who has studied liquid alloys from the structural and statistical viewpoint has derived many interesting facts, one being that if a metal, on melting, shows an expansion of 6 per cent in volume and this is assumed to be accomplished by the formation of vacant lattice sites, then, in a cube of 1000 atoms *at least* 60 holes will be present. With a coordination of 12 in the liquid the total number of atoms lying next to holes, assuming a random distribution, is $60 \times 12 = 720$. That is, three-quarters of all the atoms will lie next to a hole and form an irregular bond.

If, in a two component (AB) system, considerable heat is developed during the process of mixing, AA and BB bonds will be broken and AB bonds formed.⁽¹⁰⁴⁾ The heat evolved is the excess of the heat of formation of AB over the heat of dissociation of AA and BB bonds. The probability of the formation of an AB bond in a 50 per cent mixture is $2N_A N_B$ (where N_A and N_B are the mole fractions of A and B respectively) when the heat of formation U is zero. When $U \neq 0$ a correction factor is applied:

$$(1 + N_A N_B)^{\frac{2U}{nRT}}$$

where n is the coordination number. In this case, at 100°C with $n = 12$ and $U = 3000$ cal, the probability of AB formation is increased by 6 per cent.

When studying the purely statistical approach the transient nature of the liquid structure must be considered. If a strong AB attraction exists, atoms of one species will attempt to satisfy electronic or electrochemical factors by combining with atoms of the other species. It is extremely unlikely, however, due to the thermal vibration effects, that atoms succeed in keeping next to one another for long periods, except, possibly, close to the freezing point.

(d) X-ray Examination of Alloys

The number of x-ray diffraction studies of liquid alloys is small in comparison with that of pure metals. In the main, such investigations have

aimed at determining whether the interatomic forces which cause compound formation in the solid state persist into the liquid state. Grave difficulties arise in the interpretation of liquid alloy structures since one cannot easily assess the relative contributions of the two species of atom present. The best one can do is to select elements with similar scattering factors and measure the variation of interatomic distances with composition.

Of particular interest is the system gold-tin which was studied by x-rays by HENDUS⁽⁹⁰⁾ and thermodynamically by KLEPPA.⁽⁹⁹⁾ A compound, AuSn, which has the nickel arsenide structure in the solid state, melts at 418°C, giving rise to a liquidus maximum in the phase diagram. HENDUS obtained diffraction patterns of liquid alloys containing 50 atomic per cent, 29.4 atomic per cent and 16.3 atomic per cent of tin at temperatures close to the liquidus. At the composition of AuSn, two distinct maxima are apparent in the diffraction pattern. One, with a d value* of 2.62 Å, corresponds with the mean of the spacings of the two components and indicates a statistical distribution. The other maximum corresponds with the strong (012) reflection of AuSn in the solid state. It is concluded that sufficient tendency towards compound formation exists to give rise to a pattern. At the lower tin contents the compound pattern is no longer evident; in fact, at 16.3 per cent Sn the d spacings correspond closely with those of pure gold.

KLEPPA derived the entropy fraction for gold-tin alloys over the whole composition range. The curves of the entropy fraction and activity versus composition are shown in Fig. 20. The strange shape of the curves is partly due to the short range ordering effect of compound formation and partly to the large difference in size between the gold atom and the tin atom. The former leads to strong negative deviations from *RAOULT'S* Law and to negative entropy deviations, the latter to large positive entropy deviations. The mean vibrational frequency of the atoms is reduced by the packing problems of mixing two types of atom of different sizes. This causes a positive contribution to the entropy by the vibrational entropy terms. The slopes of the entropy fraction curves are discussed in terms of the "quasi-chemical" theories of GUGGENHEIM⁽⁹⁶⁾ and of RUSHBROOKE⁽¹⁰⁴⁾ which are based on nearest neighbour interactions. From these theories the contribution of the short range ordering at equi-atomic composition to the entropy of mixing can be calculated. It is concluded that strong short-range ordering exists in the alloy.

These two investigations represent the first serious attempts by the two different methods to determine the effect of strong interatomic attraction in a liquid alloy and it is gratifying to see that the results are

* It will be noted that the maxima in the radial distribution curves are given in terms of d values; this makes comparison with the solid metal parameters easier.

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consistent with one another. The way is thereby pointed to further investigation of this problem. The majority of alloy systems investi-

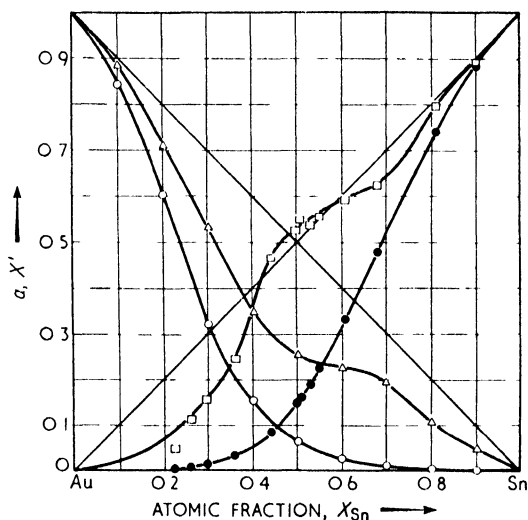


Fig. 20. Activities, a and "entropy fractions," X' , in system tin-gold:
 ●, a_{Sn} , 600°; □, X'_{Sn} , 500–600° (experimental); ○, a_{Au} , 600°; △, X'_{Au} ,
 500–600° (computed) (KLEPPA⁽⁹⁹¹¹⁾)

gated by x-ray diffraction have given reflections whose spacings are the mean of those of the constituents, as shown in Table 6, which SAUERWALD⁽¹⁰⁰⁾ has compiled.

TABLE 6
 X-ray Data for Molten Alloys
 (after SAUERWALD)⁽¹⁰⁰⁾

System	First Peak	a_1 on Average Law
	a_1 Å	
Bi-Pb eutectic . . .	2.98	2.96
Bi-Sn eutectic . . .	2.90	2.90
50 atomic per cent Hg-Pb	2.77	2.78
Pb-Sn eutectic . . .	2.85	2.84
Sn-Zn (8 per cent Zn)	Sn spacing	
Hg-Tl, Hg ₅ Tl ₃ . . .	2.67	Approx. additive
Au-Sn {	Compound AuSn . . .	2.61
	Sn 29.4 atomic per cent . . .	2.51
	Sn 16.3 atomic per cent . . .	2.45
	Rose's metal . . .	2.92
	Lipowitz metal . . .	2.85
	Wood's alloy . . .	3.14

(e) *Density Studies*

To examine interatomic forces in alloys the systems must be carefully chosen. A difficulty is encountered in systems with strong binding forces, e.g. Mg_2Sn , Mg_2Pb whose melting points have proved in the past too high for reliable x-ray experiments. However, some information on the behaviour of this type of compound has been obtained by density measurements. SAUERWALD⁽¹⁰³⁾ determined the densities of Mg_2Pb , Mg_2Sn and Mg_3Ce in the liquid state and KUBASCHEWSKI and HORNLE⁽¹⁰⁵⁾ subsequently made further measurements on Mg_2Pb and examined Mg_3Bi_2 .

The formation of these compounds in the solid state is accompanied by a volume expansion. In the case of Mg_2Pb and Mg_2Sn the expansions are 3.4 per cent and 6.7 per cent respectively. Formation in the liquid state is characterized by a volume contraction of 1.6 per cent and 4.1 per cent respectively. These two compounds are anti-isomorphous with CaF_2 and have a fairly low packing density in the solid state. This cannot be maintained in the liquid state since the interatomic forces are strong, but the atoms are more mobile and have greater kinetic energy than in the solid. It is probable that different coordinations from the solid exist in the liquid state, allowing the strong interatomic forces to exert their maximum effect; this can only be proved by x-ray methods. It would also be instructive to determine the density of CaF_2 in the liquid state. If no contraction occurred it could be assumed that the heteropolar forces would be operating to maintain the pattern of the solid lattice. It would then follow that a considerable part of the bonding in the liquid metallic compounds would probably be non-polar in character, which would be consistent with the observation that the heats of mixing are less in the liquid state than in the solid.

(f) *Viscosity and Surface-tension*

As is the case for pure metals, the evidence that structural groupings in liquid alloys are indicated by the small number of measurements which have been made of their viscosities and surface tensions is rather ambiguous. Recent work by YAO and KONDIC⁽²³⁾ on the viscosity of molten tin, lead, zinc, aluminium and some of their alloys favours the structural picture. At high temperatures a plot of $\log \eta$ versus $\frac{1}{T^\circ\text{K}}$ gave a straight line in all cases, in agreement with the exponential formula.⁽¹⁶⁾ According to this theory the straight line relationship should be valid down to the freezing point of the metal or alloy. This investigation, and others on aluminium-silicon,⁽²⁴⁾ sodium-potassium alloys,⁽¹⁰⁶⁾ and several other systems⁽¹⁰⁷⁻¹¹⁰⁾ have shown that curves of the type shown in Fig. 21 for the viscosity of pure aluminium and aluminium containing 0.05 per cent titanium are obtained. A deviation from the straight line begins several

degrees above the freezing point. The marked increase in viscosity by the addition of so small a quantity of titanium could indicate that the deviation from viscosity laws close to the freezing point is a structural phenomenon. It may be due to formation of solid nuclei or even particles of a higher melting point phase by impurities. Alternatively it may be due to a "foreshadowing" of the solid state, as was suggested in the case of pure metals, by the grouping of atoms into nuclei with a coordination and structure close to that of the solid state, their decreasing kinetic energy permitting the groups to remain stable for long periods of time.⁽¹¹¹⁾ Again, as for pure metals, experimental errors may have led to these results.

PELZEL⁽¹¹²⁾ has measured the variation of surface tension with composition for four binary alloy systems (Sn/Zn, Al/Zn, Al/Mg and Mg/Zn). This has allowed comparison between systems with and without compound formation in the solid state. The systems Al-Mg and Mg-Zn show marked deviations in the surface-tension/composition curves at compositions corresponding to the solid compounds. Moreover the other two systems also display marked deviations even though compounds are absent in the solid state. This cannot be taken as proof of molecular association in the liquid as the fact has been overlooked that in binary systems the species with the lowest surface energy is selectively adsorbed at a free surface.

(g) Diffusion

The study of diffusion in molten metals has received little attention in spite of obvious practical applications to such problems as the freezing of alloys. The principles governing diffusion in liquid metals have been studied by SAMARIN⁽¹¹³⁾ who drew attention to two relationships. Firstly, the Stokes-Einstein equation is applicable to metals both at low and high temperatures. The diffusion constant

$$D = \frac{RT}{N} \cdot \frac{1}{\pi \eta r}$$

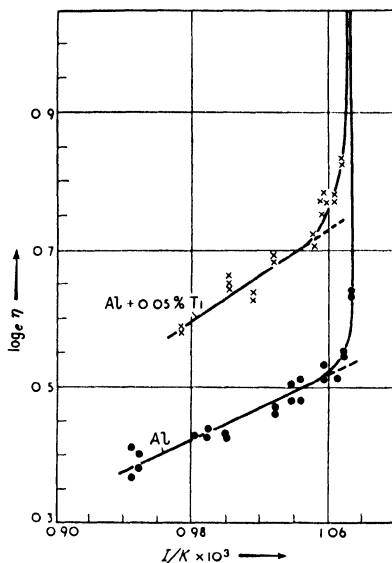


Fig. 21. Log viscosity of aluminium and of aluminium with 0.05 per cent titanium plotted against the inverse absolute temperature (YAO and KONDIC⁽²³⁾)

where R is the gas-constant, T the absolute temperature, N Avogadro's number, η the viscosity of the medium and r the radius of the diffusing atom. Calculation of D for a number of metals from known data showed that the metals could be classified in groups. In particular the variation of D among the alkali- and alkaline-earth metals in mercury was less than 10 per cent.

For diffusion in one solvent at the same temperature the product of D and r is stated to be a constant. While this is true of the alkali- and alkaline-earth metals it is not true of the heavier metals, e.g. cadmium, zinc and lead. The conclusion to be drawn from these relationships is that for any group of metals, e.g. the alkali metals, processes which rely on diffusion in the liquid state will proceed at approximately the same rates.

(h) *Freezing and nucleation*

The process of freezing of alloys is more complex than that of pure metals. The same mechanisms of nucleation and growth occur, but the form of equilibrium diagrams complicate the issue since a small change of composition may change the order in which phases solidify. This order is dictated by the relative free energies of the phases present.

Two characteristic features of alloy freezing which have received some attention are peritectic reactions and eutectic solidification.⁽¹¹⁴⁾ These studies have been concerned either with the kinetics of the processes or with the large-scale effects. Little attention has been paid to atomic scale effects which, in the case of peritectic reactions, might prove to be of importance. ELLWOOD and BAGLEY⁽¹¹⁵⁾ examined the solid structure of several eutectics by means of x-rays and showed that the particles of the two phases precipitated so that they were favourably oriented with respect to one another. The interfaces between the particles of different phases met in such a manner as to give the easiest alignment of planes of one phase with those of the other. This means that the process of solidification of a eutectic which, by definition, occurs at a fixed temperature, as in the case of a pure metal, must be of greater complexity than in the latter. This subject is discussed at greater length in the review of "Solidification of Metals," by MARTIUS. Eutectic alloys of Bi-Sn, Sn-Pb, Pb-Bi and Sn-Zn have been examined by means of x-rays in the liquid state.⁽¹¹⁶⁾ The d values in each case were the mean of those of the constituents. DANILOV and RADTCHENKO interpreted this as meaning that the melts consisted of small separate regions of the pure metals—a conclusion which is hardly justified. SAUERWALD⁽¹⁰⁰⁾ interprets similar results, more rationally, on the basis of a random atomic distribution.

(i) *Liquidus and Solidus Curves*

Attempts have been made to relate the forms of liquidus and solidus curves to atomic properties in a quantitative manner. In particular

STOCKDALE⁽¹¹⁷⁾ put forward the theory that the appearance of a new phase is dictated by a simple numerical relationship between solute and solvent atoms. From this postulate rules governing the formation of eutectics were derived. These ideas are linked with those of HUME-ROTHERY and his co-workers who proposed in 1934,⁽¹¹⁸⁾ after a survey of a number of binary alloy systems, that the atomic depression of the freezing point is approximately proportional to the valency of the solute. STOCKDALE examined a number of additional systems experimentally and came to the following conclusions with regard to liquid-solid equilibria:

(1) In a saturated solution at the temperature of the eutectic or peritectic horizontal there is a simple integral relationship between the numbers of solvent and solute atoms.

(2) In a eutectic mixture the elements are present in a simple integral atomic ratio.

(3) In a eutectic mixture the ratio of numbers of atoms, irrespective of kind, in the two component phases is simple.

This approach is somewhat empirical, but does attempt to extend the theory of binary systems beyond HUME-ROTHERY's rules. In contrast with this approach is the thermodynamic theory outlined by JONES⁽¹¹⁹⁾ which was also inspired by the publications of HUME-ROTHERY and his co-workers.

The liquidus and solidus temperatures can be expressed in terms of the latent heat of fusion of the particular alloy, this value changing with composition. The latent heat of fusion can be regarded as arising from (1) the change in energy of the lowest free electron state, which depends on the distortion, and volume change of the lattice on melting, and (2) from the change in Fermi energy which also depends on changes of volume and structure. The first factor is largely independent of composition, so the variation in latent heat of fusion with change of composition arises mainly from the variation of the change of Fermi energy on melting, in which case the latent heat, and hence the liquidus and solidus temperatures are determined by the electron to atom ratio. Fermi energies have not been accurately calculated in the liquid state, so that quantitative results are not available.

CONCLUSION

The study of liquid alloys in its many diverse aspects has not yet reached the state when any quantitative theories can be readily applied. Data of the more informative kind are only just beginning to accumulate. Even the study of pure metals is still at an early stage. It is difficult to estimate whether or not the study of alloys will accelerate the general progress towards a complete understanding of the liquid state.

While the presence of a second type of atom may tend to complicate the structural picture, it does provide a known means of varying the properties to determine the effect of changing valency, electrochemical factor and other "static" properties on the kinetic and thermodynamic properties.

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REPORT ON PRECIPITATION

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I. INTRODUCTION

THE study of precipitation phenomena has provided a major field of metallurgical investigation during the period of more than forty years since WILM found that certain aluminium alloys changed in hardness on storage at room temperature.⁽¹⁾ During the succeeding decade it was widely realized that the precipitation process could materially enhance the properties of technological importance and this philosophy has continued to stimulate the search for new age-hardenable alloys. The expansion of experimental work after the First World War rapidly confirmed that age-hardening originated in the atomic rearrangements accompanying the breakdown of supersaturated solid solutions. Investigations carried out between the two wars showed that these changes were frequently sub-microscopic and often highly complex. The challenge presented by our ignorance of such fine scale reactions has stimulated much fundamental work and notable contributions have been made to theoretical and experimental knowledge during the past twenty years.

A voluminous literature is growing at an accelerating pace and, even ignoring the patent field, nearly a thousand papers have been published which deal directly, significantly or otherwise, with various aspects of precipitation. There is probably an equal number of papers of varying importance which more remotely affect the thought and studies of the subject—for example profitable hints may be obtained from the theory of diffuse scattering of x-rays and from the thermodynamic characteristics of polymer solutions.

The present paper has naturally been preceded by a number of reviews varying from the discursive to the critical. The following papers cover the more thorough and more significant accounts which have appeared during or subsequent to the Second World War. MEHL and JETTER⁽²⁾ and HARDY⁽³⁾ have given full reviews of the structural and physical property changes. The slightly more recent works of HARDY⁽⁴⁾ and JAGODZINSKI and LAVES⁽⁵⁾ relate to the various stages in the precipitation process. GEISLER⁽⁶⁾ has also given a general account with particular emphasis on the grain boundary reactions whilst an earlier paper in this series, by SMITH,⁽⁷⁾ has presented a chronological review of age-hardening.

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The report which follows is intended to provide a critical study of the relationship between the fundamental theories of precipitation and the experimental observations. Considerable emphasis is therefore placed on the thermodynamics and kinetics of precipitation. The structural changes accompanying the decomposition of the supersaturated solution are also dealt with in detail and an assessment is made of the validity of the interpretation of the latest x-ray work. A full account of the changes in the mechanical and physical properties has not been attempted as these may be obtained from several of the reviews noted immediately above. However, illustrations are drawn from the large body of experimental evidence to support or oppose the theoretical opinions. The final discussion allows an opportunity to assess the minimum number of experimental techniques which are essential for the full study of precipitation in a complex system.

II. THERMODYNAMIC THEORIES OF PRECIPITATION

The free energy change provides the driving force for precipitation and the process is controlled by the thermodynamic factors underlying the solid solution state, diffusion, nucleation and the free energy relationships between the phases. It is almost a cliché in recent textbooks on thermodynamics that, although much has been written on the general theory of precipitation, little material progress has been made since the work of GIBBS and his contemporaries. This pessimistic assessment arises because the free energy changes associated with precipitation are small in relation to those associated with chemical reactions and therefore do not lend themselves to easy proof of the theoretical deductions except in general terms. The free energy change on precipitation of alloy systems may easily be less than a hundred calories per gramme atom. The additional complexities of precipitation in the solid state fully merit a description of the current views. Essentially similar accounts of the thermodynamics of precipitation in alloys have been given by HARDY,⁽⁸⁾ LAURENT⁽⁹⁾ and SMOLUCHOWSKI⁽¹⁰⁾ and will here be brought up to date. The more general approach may be found in the standard texts and is excellently covered by BRADLEY.⁽¹¹⁾

A knowledge of the free energy change on precipitation may be obtained from the free energy/compositional relationships of an alloy system and is required for the analysis of the nucleation process. Free energy as the driving force for diffusion is an integral part of the fluctuation theories of precipitation. An attempt to combine the fluctuation and nucleation theories and a discussion of metastable states serves to introduce an account of the sequence of precipitates in a hypothetical system in which the principle is adopted that the reaction follows the path of minimum activation energy.

The Solid Solution and Free Energy Changes on Precipitation

The stable alloy structure is that in which the thermodynamic potential F (the Helmholtz free energy in condensed systems) is a minimum where:

$$F = H - TS \quad (1)$$

H being the internal energy (or enthalpy), T the absolute temperature and S the entropy. The free energy will vary with composition and, since the stable structure is that of lowest free energy, the equilibrium diagrams may be accounted for in terms of the free energy/compositional curves of the different phases.^{(12), (13), (14)}

Consider the hypothetical equilibrium diagram of Fig. 1a in which two solid solutions of identical lattice structure are formed on cooling. The free energy/compositional curve at T_1 has the form shown in Fig. 1b. An alloy quenched from the single phase region into the two phase region may be regarded as having the free energy which would be possessed by the single phase alloy, could it exist at the lower temperature. Thus the portion $F_{x_1} - R - F_{x_2}$ of the free energy/compositional curve of Fig. 1b lying above the lowest common tangent gives the free energy of the alloys, quenched to the temperature T_1 , which still retain the single-phase structure. The portion $y - R - y$ is concave downwards so that over this region the second differential $\partial^2 F / \partial x^2$ is negative. Dashed curves have been inserted in Fig. 1a giving the locus of the points of inflection of the free energy/compositional curves as the temperature is changed. These "spinodal" curves⁽¹⁵⁾ correspond to $\partial^2 F / \partial x^2$ equal to zero.

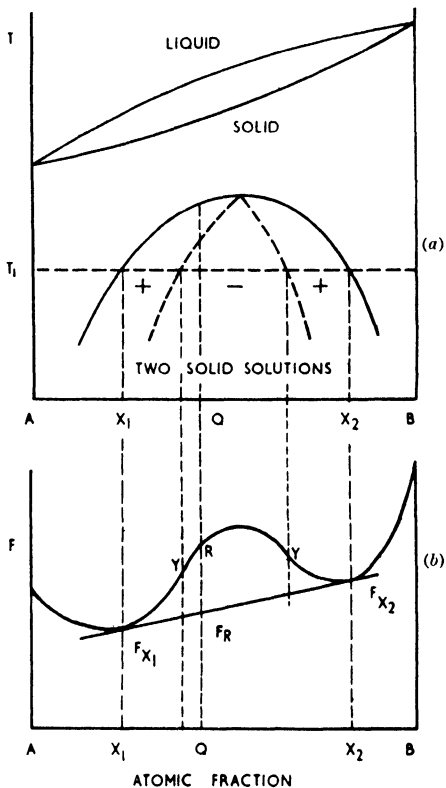


Fig. 1. (a) Equilibrium diagram of system solidifying to a continuous series of solid solutions which break up into two solid solutions as a lower temperature; (b) the free energy/composition curve at T_1 for the hypothetical diagram of (a)⁽¹⁸⁾

The free energy change associated with precipitation can readily be obtained from the free energy/compositional curve. Fig. 2 shows an alloy of composition x and free energy f precipitating a β phase of composition x_2 and free energy f_2 and forming a matrix α of composition x_1 and free energy f_1 . The supersaturated alloy falls on the free energy curve at B whilst AC is the lowest common tangent. Complete precipitation of x leads to $\frac{x_2 - x}{x_2 - x_1}$ parts of α and $\frac{x - x_1}{x_2 - x_1}$ parts of β .

The free energy change on complete precipitation is:

$$\Delta f = \frac{x_2 - x}{x_2 - x_1} f_1 + \frac{x - x_1}{x_2 - x_1} f_2 - f \quad . \quad . \quad . \quad (2)$$

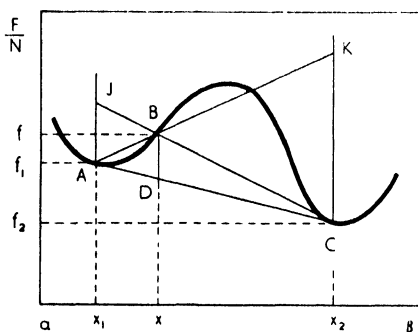


Fig. 2. Free-energy changes for complete precipitation⁽⁸⁾

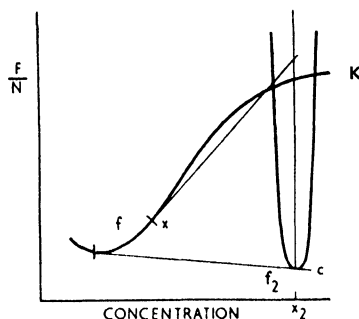


Fig. 3. The free-energy change at the beginning of precipitation equals (KC) per atom of precipitate

and can readily be reduced by straightforward geometry to

$$\Delta f \text{ per atom of alloy} = f_1 + \frac{\partial f_1}{\partial x_1} (x - x_1) - f \quad . \quad . \quad (3)$$

which is represented by the line BD in Fig. 2.

Dividing the free energy change per atom of alloy by the volume fraction of β gives the free energy change per atom of β . This reduces geometrically to

$$\Delta f \text{ per atom of } \beta = [KC] \text{ (see Fig. 2)} \quad . \quad . \quad . \quad (4)$$

Fig. 3 shows the position at the beginning of precipitation of an intermetallic compound where xK is the tangent to the curve at x and it is assumed that the first particle of precipitate does not alter the matrix composition appreciably. The free energy change per gramme atom of the initial precipitate is

$$\Delta f / \text{atom of ppt} = \left[f_2 - f - \frac{\partial f}{\partial x} (x_2 - x) \right] = [KC] \quad . \quad . \quad (5)$$

and is represented by the line KC in Fig. 3. The rate of change of KC with variation in the initial composition, x , is given by

$$\frac{\partial \Delta f}{\partial x} = -(x_2 - x) \frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (6)$$

An inflected free energy/compositional curve for the solid solution (as in Fig. 3) gives a maximum KC at the inflection point ($\partial^2 f / \partial x^2 = 0$). If the free energy/compositional curve is always concave upwards KC will be a maximum when x coincides with K , i.e., $x_2 = x$.

The second differential is given by:

$$\frac{\partial^2 \Delta f}{\partial x^2} = -(x_2 - x) \frac{\partial^3 f}{\partial x^3} + \frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (7)$$

and can be estimated for particular systems.

Diffusion and Fluctuations

The basic expressions for diffusion problems are given by Fick's first and second equations for one-dimensional flow along the y axis which are⁽¹⁶⁾

$$P = -D \frac{\partial x}{\partial y} \quad \text{and} \quad \frac{\partial x}{\partial t} = \frac{\partial}{\partial y} \left(D \frac{\partial x}{\partial y} \right) \quad . \quad . \quad . \quad (8)$$

where the flow P is placed proportional to the volume concentration gradient, $\partial x / \partial y$, and D is the diffusion coefficient. $\partial x / \partial t$ is the quantity transferred in unit time.

Taking the driving force for diffusion as the free energy gradient^{(17), (18)} the diffusion equations become

$$P = -D^0 D^T \frac{\partial x}{\partial y} \quad \text{and} \quad \frac{\partial x}{\partial t} = \frac{\partial}{\partial y} \left(D^0 D^T \frac{\partial x}{\partial y} \right) \quad . \quad . \quad . \quad (9)$$

where D^0 involves the statistical probability of a place change and D^T is a thermodynamic factor based on the free energy/composition gradient.

For a regular binary solution

$$D_{ab}^T = \frac{x_a x_b}{RT} \frac{\partial^2 F}{\partial x_a^2} \quad . \quad . \quad . \quad (10)$$

where x_a and x_b are the atomic fractions of the components. D_{ab}^T is equal to unity for an ideal solution. It was first pointed out by DEHLINGER⁽¹⁷⁾ that the sign of $\partial^2 F / \partial x^2$ determines the sign of the diffusion equation through its effect on the sign of D_{ab}^T . Concentration differences will be accentuated when $\partial^2 F / \partial x^2$ is negative.

Although nominally statistically disordered, all solid solutions will show, within small regions, fluctuations from the mean value of the composition. The statistical probability of a given composition fluctuation may easily be calculated⁽¹⁹⁾ but fluctuations requiring a

change in energy involve also the Boltzmann factor. The probability of an atom having an energy ΔF higher than the average is proportional to

$$e^{-\Delta F/kT} \quad . \quad . \quad . \quad . \quad (11)$$

where k is Boltzmann's constant. The thermodynamic probability of a fluctuation (defined as the square of the difference from the mean) is proportional^{(20), (21)} to

$$e^{-(x-x_0)^2(\partial^2 F/\partial x^2)/RT} \quad . \quad . \quad . \quad . \quad (12)$$

An attempt has been made to apply fluctuation theory to precipitation by LAURENT⁽²²⁾ but the complexity of the integrals precludes an exact evaluation.

The sign of $\partial^2 F/\partial x^2$ frequently occurs in different facets of precipitation theory and will be discussed more thoroughly later.

Nucleation Theories of Precipitation

A new phase is formed by the creation of a nucleus capable of growth and possessing an interface with the parent matrix. A nucleus smaller than the minimum critical size for stability and growth is normally termed an "embryo." Phase transformations will only occur with a reduction in free energy. Some of this may be absorbed by the interfacial energy of the nucleus (including coherency strains holding the lattice of the precipitate in register with the lattice of the matrix) and the strain energy due to volume changes. The conditions are:

Cubical Nucleus	Spherical Nucleus
$\Sigma F_p = a^3 \frac{\Delta F}{N} + 6a^2\sigma + a^3\varepsilon$	$\Sigma F_p = \frac{4}{3}\pi a^3 \frac{\Delta F}{N} + 4\pi a^2\sigma + \frac{4}{3}\pi a^3\varepsilon$
. . . . (13)	

where ΣF_p is the free-energy change on the formation of a nucleus (or an embryo) of the precipitate, ΔF is the free energy change per gramme atom of the new phase,* N is Avogadro's number, σ is the interfacial energy per atom, a is a measure of the size of nucleus and ε is the strain energy per atom of the precipitate and is independent of the size of the particles.^{(23), (24)}

The variation of ΣF_p with the size of the nucleus is shown in Fig. 4. Nuclei larger than the critical size a_0 are capable of growth with a fall in free energy. The critical size is given by

Cubical Nucleus	Spherical Nucleus
$a_0 = \frac{4N\sigma}{-\Delta F - N\varepsilon}$	$a_0 = \frac{2N\sigma}{-\Delta F - N\varepsilon} \quad . \quad . \quad (14)$

* In accordance with thermodynamic practice a negative value of ΔF is associated with a heat evolution (heat lost by the system) on the precipitation of a phase more stable than the supersaturated solution.

where the strain energy term reduces the change in free energy but does not affect the form of the equations.

The activation energy or the work of formation of the surface, A_0 , which has to be supplied in forming a nucleus of the critical size is given by

Cubical Nucleus	Spherical Nucleus
$A_0 = 2a_0^2\sigma$	$A_0 = \frac{4}{3}\pi a_0^2\sigma$ (15)

$A_0 = \frac{32\sigma^3 N^2}{(\Delta F + N\varepsilon)^2}$	$A_0 = \frac{16}{3}\pi \frac{\sigma^3 N^2}{(\Delta F + N\varepsilon)^2}$. . (16)
--	---

The work of formation is equal to one third the surface energy term associated with the critical nucleus size⁽²⁵⁾ and is also inversely proportional to the square of the free energy change per atom of precipitate. Neglecting the strain energy term this means that the work of formation is inversely proportional to $(KC)^2$ in Fig. 3. The critical nucleus size is inversely proportional to the free energy change per atom of precipitate, i.e. to $1/KC$ in Fig. 3.

The Thomson-Freundlich formula for the variation of solubility with particle size is closely related to equation (14). Replacing Avogadro's number by the gramme molecular volume (molecular weight divided by the density), and expressing the free energy change as that for an ideal dilute solution gives

$$\ln \frac{c_a}{c_\infty} = \frac{2\sigma M}{RT\rho a} \quad . \quad . \quad . \quad (17)$$

where c_a is the solubility of particles of radius a and c_∞ is the solubility limit of particles of infinite radius.

Rapid precipitation is frequently preceded by an incubation period during which the rate of decomposition is small. An incubation period may arise from two sources. A delay period is to be expected when a distribution of nuclei has been inherited from a previous treatment. For example, in recrystallization the relatively few points of highest free energy have the greatest probability of transformation but the maximum rate is determined by the very much larger number of points of slightly lower energy. In this case, the incubation period is a function of the particular distribution. An incubation period will also occur when no nuclei have been inherited and the transformation must be initiated by atomic rearrangements and energy fluctuations.

Of several investigations, FRENKEL's account of pre-transition effects associated with an allotropic change^{(26), (27), (28)} was particularly thorough. An essentially similar treatment has been extended to precipitation phenomena by FISHER, HOLLOMON and TURNBULL,⁽²⁹⁾ and TURNBULL.⁽³⁰⁾ Embryos with the structure of the new phase are formed

by unit processes involving the addition or removal of one atom at a time. Their free energy is higher than that of the matrix, as given by the curves in Fig. 4, consequently they have a greater tendency to re-dissolve than to grow. However, there will be a steady size distribution, considered statistically, of embryos which individually are in the process of growth and re-resolution. This is termed a "transient-steady" size distribution.⁽²⁹⁾ The probability of an embryo containing a^3 atoms being formed is proportional to

$$e^{-\Sigma F_p/kT} \quad . \quad . \quad . \quad (18a)$$

where ΣF_p is the additional energy for its formation. The number of such embryos containing a^3 atoms out of all the embryos is

$$\frac{n_a}{n} = e^{-\Sigma F_p/kT} \quad . \quad . \quad . \quad (18b)$$

The steady size distribution may be derived from the curves of Fig. 4 and is given in Fig. 5. The incubation period now represents the time

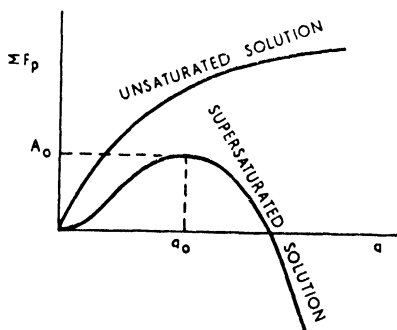


Fig. 4. Variation of ΣF_p with size of embryo for unsaturated and supersaturated solutions⁽⁸⁾

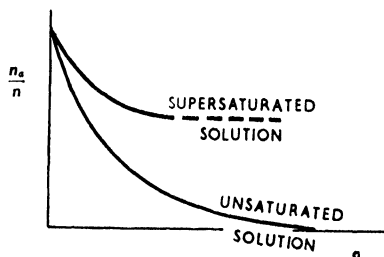


Fig. 5. Steady size distribution for embryos in supersaturated and unsaturated solutions n_a/n is the number of embryos containing a atoms out of all the embryos⁽⁸⁾

for the steady size distribution of embryos to change from that characteristic of the high temperature unsaturated solution to that characteristic of the supersaturated quenched material. Embryos arise initially by an energy fluctuation involving a small number of atoms having the precipitate composition; such groups of atoms are inherent in the statistical distribution within a solid solution. When the embryos have grown to a size equal to a_0 , see Fig. 4, they will rapidly be removed from the "transient-steady" size distribution because further growth is accompanied by a fall in free energy. Any embryo in the unsaturated solution larger than the critical size a_0 will immediately transform on quenching without any incubation period.

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The VOLMER-WEBER⁽³¹⁾-BECKER-DÖRING⁽³²⁾ theory of phase changes sets the initial rate of reaction as

$$I = K^0 e^{-A_0/RT} \quad . \quad . \quad . \quad (19)$$

in which A_0 is given by equations (15) and (16) and K^0 expresses the maximum possible frequency of the process. The calculated value of A_0 depends on the value assigned to the surface energy. TOLMAN⁽³³⁾ has shown that the surface tension is dependent on the particle size when the particles are very small. This is for ranges of particle sizes so small that the macroscopic thermodynamic concepts are becoming ambiguous due to the small number of atoms involved.⁽³⁴⁾ An attempt by REISS⁽³⁵⁾ to overcome this difficulty by formulating a statistical theory of condensation without an explicit consideration of the phase equilibrium between the embryos and the parent phase led to

$$I = K' e^{-A(a^*)/kT} \quad . \quad . \quad . \quad (20)$$

in which $A(a^*)$ is the reversible work on forming a nucleus of critical size. The identity of form of equations (19) and (20) obtained from different physical models provides confidence that they can be used for a phenomenological approach even though the theory is not sufficiently refined to allow an accurate quantitative calculation.

BECKER⁽³⁶⁾, ⁽³⁷⁾ has extended the theory of phase transition to precipitation by writing equation (19) for the initial rate of nucleation as

$$I = K'' e^{-(A_0 + Q)/RT} \quad . \quad . \quad . \quad (21)$$

in which Q is the activation energy for diffusion. He applied this equation to regular solutions whose excess free energy of solution is given by⁽³⁸⁾⁻⁽⁴¹⁾

$$\Delta F_{\text{soln}} = \Delta E x(1 - x) + RT(x \ln x + (1 - x) \ln (1 - x)) \quad . \quad (22)$$

$$\text{where} \quad \Delta E = \frac{1}{2} Z N (2 V_{XY} - (V_{XX} + V_{YY})) = \frac{1}{2} Z N V \quad . \quad . \quad (23)$$

in which Z is the coordination number, V_{XY} etc., are the interaction energies between neighbouring pairs of atoms and V is termed the exchange interaction energy. The free energy change for the formation of the initial precipitate for the reaction in Fig. 6 is obtained from equation 5, i.e.

$$\Delta F_{\text{init. ppt.}} = \Delta F_{\text{soln}}(x_2) - \Delta F_{\text{soln}}(x) - \frac{\partial \Delta F_{\text{soln}}(x)}{\partial x} (x_2 - x) \quad . \quad (24)$$

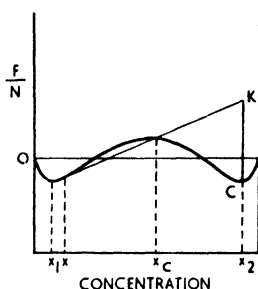


Fig. 6. Precipitation in a regular solution

By counting the number of atomic bonds BECKER was able to set the surface energy of a cubical nucleus as

$$\sigma = \frac{V}{2} (x_2 - x)^2 \quad . \quad . \quad . \quad (25)$$

The critical nucleus size (from equation (14)) is

$$a_0 = \frac{2V(x_2 - x)^2 N}{-\Delta F_{\text{init. ppt.}}} \quad . \quad . \quad . \quad (26)$$

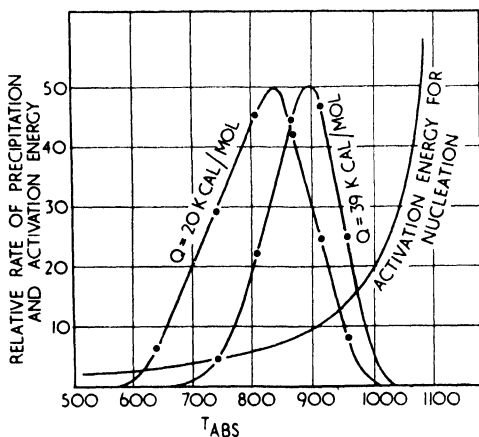


Fig. 7. Relative probability of nucleation at different temperatures below T_c (of Au-Pt alloys) for two values of Q ⁽³⁷⁾

and the activation energy becomes (equations (15) and (16))

$$A_0 = a_0^2 V (x_2 - x)^2 \quad . \quad . \quad . \quad (27)$$

$$= \frac{4V^3 (x_2 - x)^6 N^2}{[\Delta F_{\text{init. ppt.}}]^2} \quad . \quad . \quad . \quad (28)$$

V is related to the critical temperature for phase separation (i.e. the highest temperature to which the miscibility gap exists) by the relation

$$\frac{ZN V}{2} = 2RT_c \quad . \quad . \quad . \quad (29)$$

so that the exponential term in the equation for the initial rate of precipitation (equation (21)) can be calculated for regular solutions when Q is known. Fig. 7 shows the relative variation with temperature of the initial rate of precipitation calculated by BECKER⁽³⁷⁾ for the case of gold-platinum alloys assuming two different values for Q . Both A_0 and a_0 become equal to infinity at the solubility curve (i.e. when x becomes equal to x_1) where the rate of precipitation is zero.

BECKER adopted the view that the initial precipitate possessed the composition of the second equilibrium solid solution (x_2 in Fig. 6). However, it will be seen that a fall in free energy will accompany precipitates of all concentrations higher than x_c (Fig. 6) which is found by placing equation (24) equal to zero. For a regular solution this reduces to

$$\Delta F_{\text{init. ppt.}} = -\frac{1}{2}ZN V(x_i - x)^2 + RT(x_i \ln \frac{x_i}{x} + (1 - x_i) \ln \frac{(1 - x_i)}{(1 - x)}) = 0 \quad (30)$$

and can be solved either for x or x_i (the composition of the initial precipitate here equal to x_c).

The most probable precipitate is that given by the combination of composition and size requiring the lowest activation energy.

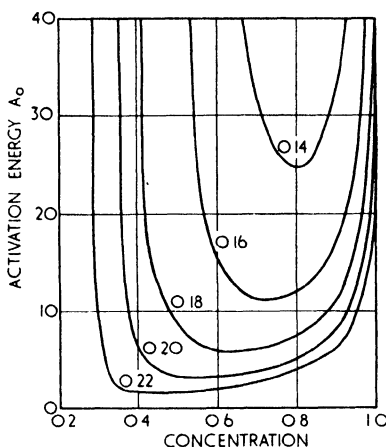


Fig. 8. The relationship between the activation energy for nucleation and the composition of the nucleus. The figures on the curves are the supersaturated concentrations and the temperature has been chosen so that the equilibrium concentrations are 0.1 and 0.9⁽⁴³⁾

HOBSTETTER⁽⁴²⁾ and SCHEIL⁽⁴³⁾ have attempted to solve this problem and found that the composition of the initial precipitate fell as the supersaturation was increased. SCHEIL's curves are given in Fig. 8 for the case when the solubility gap extends from $x_1 = 0.1$ to $x_2 = 0.9$. As the quenched concentration is raised from 0.14 to 0.22 the composition of the initial precipitate changed from 0.8 to 0.4. The actual value of x_i represents a balance between the term $(x_i - x)^6$ in equation (28) which strongly favours a low concentration in the precipitate and the term $1/(\Delta F)^2$ which favours a high concentration in the precipitate. x_c becomes identical with x when the initial supersaturation is high enough to exceed the inflection point ($\partial^2 F / \partial x^2 = 0$) of the free energy/compositional curve.

The results of the straight-forward nucleation theory of precipitation can be summarized in the following rules:

(1) There will be an incubation period during which stable nuclei are being formed.

(2) The activation energy decreases from infinity as the supersaturation is increased from zero.

(3) The minimum critical nucleus size decreases from infinity as the supersaturation is increased from zero.

(4) The initial precipitate will be less rich in solute than the equilibrium precipitate provided that the free energy/compositional curve is not very sharply curved close to the precipitate composition. A rapid rate of nucleation could even force a reduction in the volume fraction of the precipitate as it became richer in solute at a later stage in the ageing process.

(5) The temperature dependence of the rate of initial precipitation can be described by a simple equation and will be discussed later (p. 175).

(6) Reversion, that is the re-resolution of small particles, will occur if the precipitation temperature is raised and will be described fully later (p. 168).

(7) The possibility that one or more metastable precipitates may be formed is not excluded. In this case conclusion (4) will apply separately to each of them.

Fluctuation Theories of Precipitation

It is quite clear that the nucleation theories of precipitation described in the preceding section must involve fluctuations of composition and energy. The energy required to form the new interface is taken to have a predominant effect on the precipitation process. It is convenient to describe separately the theories of precipitation which do not accept this hypothesis and which examine more closely the factors controlling the fluctuations of composition.

As mentioned above, DEHLINGER⁽¹⁷⁾ pointed out that an alloy quenched to the part of the free energy/compositional curve which is concave downwards ($y-R-y$ in Fig. 1) will be unstable and will undergo decomposition by segregation without the need for nucleation processes. When the degree of supersaturation is lower, $\partial^2 F/\partial x^2$ is positive and from equation (12) the thermodynamic probability of a small fluctuation of n atoms in one gramme atom of solution is proportional to

$$e^{-n(x-x_0)^2(\partial^2 F/\partial x^2)/RT} \quad . \quad . \quad . \quad (31)$$

as described by BORELIUS who has extended the theory to the case of large fluctuations within solid solutions.^{(44), (45)} BORELIUS showed that, when the supersaturation is such that $\partial^2 F/\partial x^2$ is positive, the activation

energy for large segregations is given by W/N in Fig. 9. Segregates of concentration lower than x_s will have a greater tendency to re-dissolve than to grow but once the composition x_s has been reached they will be capable of increase in concentration with reduction in free energy. An incubation period will be required to set up the "transient-steady" size distribution of segregates. W/N represents the energy barrier for segregation in the same way that A_0 represents the energy barrier for the formation of a nucleus possessing an interface. W/N is given by an equation analogous to equation (5) and for a segregate of n atoms

$$\frac{nW}{N} = n \left[f_s - f - (x_s - x) \frac{\partial f}{\partial x} \right] \quad (32)$$

BORELIUS^{(45), (46), (47)} and his collaborators^{(48), (49)} deduced that the initial rate of precipitation should fall as the supersaturation is decreased past the spinodal point because the additional activation energy for segregation, W , then has to be supplied before the reaction can proceed. The abruptness of the change in the rate of precipitation will depend on the rate of change of W with respect to x which is given by

$$\frac{\partial(W/N)}{\partial x} = -(x_s - x) \frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (33)$$

in which f and x_s have been held independent of small variations of x . The second differential is given by

$$\frac{\partial^2(W/N)}{\partial x^2} = -(x_s - x) \frac{\partial^3 f}{\partial x^3} + \frac{\partial^2 f}{\partial x^2} \quad . \quad . \quad . \quad (34)$$

The initial comparisons between theory and experiment were made by correlating the shape of the temperature/rate of precipitation curve for different alloys across a phase diagram with the spinodal curve computed from the solubility curves. For a system similar to Fig. 1, in which two components can form an uninterrupted series of solid solutions at a high temperature (which may exist only hypothetically above the melting point), BORELIUS fitted a free energy/compositional relation of the form

$$\Delta F_{\text{soln}} = ax^4(1 - x) + bx^3(1 - x)^2 + cx^2(1 - x)^3 + dx(1 - x)^4 + RT[x \ln x + (1 - x) \ln (1 - x)] \quad . \quad . \quad . \quad (35)$$

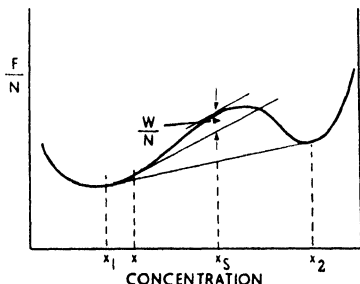


Fig. 9. The activation energy for segregation is W/N . The free energy/compositional curve has the same slope at x and x_s .

to the solubility data. A self-consistent set of constants a , b , c and d was then used to calculate the spinodal curve when the second differential of equation (35) has been made equal to zero.

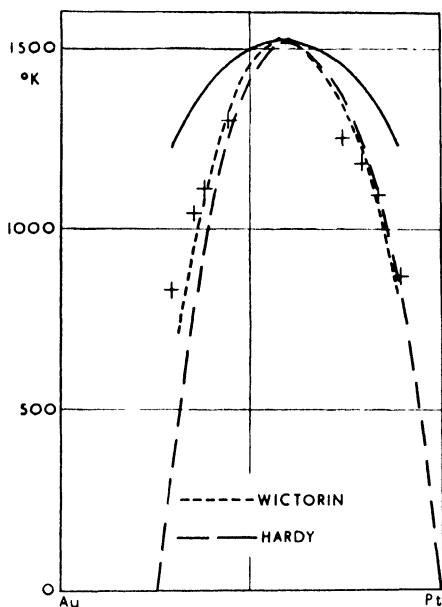


Fig. 10. The solid solubility curve and the calculated spinodal curves for gold-platinum alloys. The crosses for the limit of retardation in precipitation experiments are from WICTORIN⁽⁵²⁾

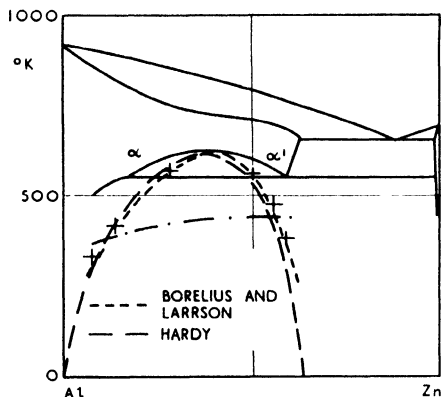


Fig. 11. The spinodal curves for aluminum-zinc alloys calculated from the α/α' phase boundary. The crosses for the limit of retardation in precipitation experiments are from BORELIUS and LARRSON.⁽⁵³⁾ The chain line is the supposed upper limit of clusters⁽⁴⁷⁾

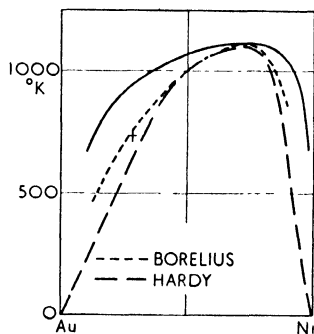


Fig. 12. The solid solubility curves and the calculated spinodal curves for gold-nickel alloys. The cross for the limit of retardation in precipitation experiments is from BORELIUS⁽⁴⁷⁾

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HARDY has also calculated the spinodal curve starting from a sub-regular solution model⁽⁵⁰⁾ in which

$$\Delta F_{\text{soln}} = A_1 x^2(1-x) + A_2 x(1-x)^2 + RT[x \ln x + (1-x) \ln (1-x)] \quad . \quad . \quad . \quad (36)$$

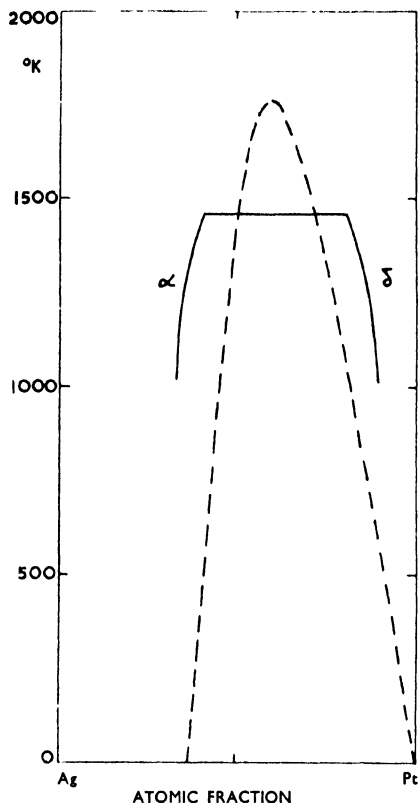


Fig. 13. The solid solubility curve and the calculated spinodal curve for silver-platinum alloys

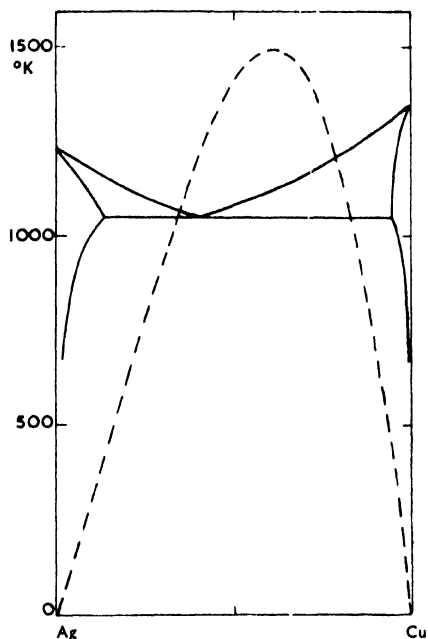


Fig. 14. The spinodal curve for silver-copper alloys

where the arbitrary constants A_1 and A_2 can be temperature dependent. The results⁽⁵¹⁾ are given in Figs. 10–14 and show a satisfactory agreement with those of BORELIUS and his co-workers. Comparison with the precipitation experiments can therefore be made with the knowledge that the calculated spinodal curves are not very sensitive to the equation assumed for the free energy/compositional relationship.

When the solid solution is in equilibrium with a phase of different crystal structure BORELIUS^{(46), (49)} obtained the free energy/compositional relationship by series of successive approximations. In the equation for the free energy

$$F = H + RT[x \ln x + (1-x) \ln (1-x)] \quad . \quad . \quad (37)$$

H is taken as independent of temperature and dependent only on composition. Differentiation of equation (37) and integration for values of x along the solubility curve gives

$$\frac{H}{R} = \int_0^x \left[-T \ln \frac{x}{1-x} \right]_b dx + \int_0^x \left[\frac{\partial(F/R)}{\partial x} \right]_b dx \quad . \quad (38)$$

where b signifies a boundary value of x and T . H is taken as zero for the pure metal. H/R is obtained by graphical integration of the first

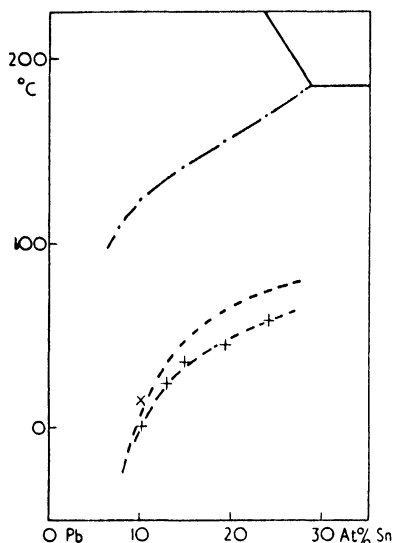


Fig. 15. The solid solubility curve and calculated spinodal curve for lead-tin alloys. The crosses give the limit of retardation in precipitation experiments⁽⁴⁷⁾

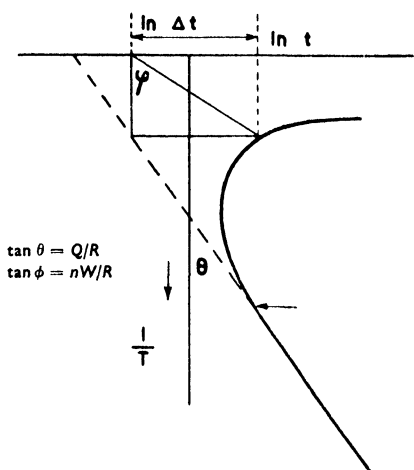


Fig. 16. The relation between temperature and the time for the beginning of decomposition when nW is an activation energy for segregation and Q the activation energy for diffusion. The arrow gives the lower limit of retardation

term on the right hand side. The values are put into equation (37) and differentiated to give the second term on the right hand side of equation (38). Integration gives the second approximation to H/R and the accuracy can be improved by repeating the process. BORELIUS, LARRIS and OHLSSON⁽⁴⁹⁾ showed how an additional correction may be applied when the solute rich phase has a slight solubility for the solvent (e.g. lead dissolved in tin). The results can be used to calculate W from equation (32) although it is useful to use

$$\left[N \frac{\partial f}{\partial x} \right]_{T=T} = \left[\frac{\partial F}{\partial x} \right]_{T=T} = \left[\frac{\partial F}{\partial x} \right]_b + R(T_b - T) \ln \frac{1-x}{x} \quad . \quad (39)$$

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which allows $\partial f/\partial x$ for a given composition to be obtained at different temperatures provided $(\partial F/\partial x)_0$ has been estimated.⁽⁴⁶⁾ The spinodal curve for lead-tin alloys obtained by a further development of this method is given in Fig. 15.

The initial rate of precipitation may be set as

$$I = K'''e^{-(nW+Q)/RT} \quad . \quad . \quad . \quad (40)$$

so that the time for the formation of a segregate is given by

$$t = \kappa_2 e^{(nW+Q)/RT} \quad . \quad . \quad . \quad (41)$$

A plot of the time to reach a given stage of the precipitation process against $1/T$ has the form shown in Fig. 16. nW is negligibly small at low temperatures and the graph is a straight line of slope Q/R . The additional time required for precipitation at higher temperatures, when nW becomes appreciable, causes the curves to turn to longer times. The arrow indicates the "limit of retardation" and according to the theory this should be close to the temperature of the spinodal curve at the composition of the alloy under test. The retardation is indicated by $\ln \Delta t$ and

$$\tan \phi = \frac{nW}{R} = \frac{\ln \Delta t}{(1/T)} \quad . \quad . \quad . \quad (42)$$

consequently

$$n = \frac{RT}{W} \ln \Delta t \quad . \quad . \quad . \quad (43)$$

in which W can be calculated from equation (32) provided that the free energy/compositional relationships have been computed from the phase diagram. Table 1 gives the results of BORELIUS⁽⁴⁶⁾ for W and n in the

TABLE 1
The number of atoms forming a segregate in lead-tin alloys
(BORELIUS⁽⁴⁶⁾)

	360°K			380°K			400°K		
At. per cent Sn	10.0	11.7	14.8	11.7	14.8	19.2	14.8	19.2	23.5
W/R	11.0	6.4	3.4	14.2	8.9	3.6	17.5	8.5	3.8
n	(150)	120	90	150	90	100	140	120	(120)

case of lead-tin alloys. ALLEN and EARLEY⁽⁵⁴⁾ have included a term for W in their expression for the rate of precipitation of γ -Fe-Ni solid solution from the α phase and have obtained the figure of 300 atoms in the nucleus.

The fluctuation theory of precipitation developed by BORELIUS involves fewer assumptions than the nucleation theory of BECKER and

it will be shown later that there is good correlation between the spinodal curves and the supersaturation at which the time for precipitation starts to lengthen ($\Delta t > 1$). The major weakness in the theory is its inability to assess the value of n without appeal to the experimental results so that n becomes an adjustable parameter.

The fluctuation theory of precipitation leads to the following rules:

(1) There will be an incubation period during which stable segregates are being formed.

(2) The temperature and concentration dependence of the rate of initial precipitation can be written from the free energy/compositional relationships but the number of atoms in a fluctuation cannot be assessed theoretically.

(3) The segregates will become richer in solute during the course of the precipitation process.

(4) An abrupt increase in the ageing temperature will alter the "transient-steady" size distribution of segregates but reversion can only be predicted by a knowledge of the experimental value of n .

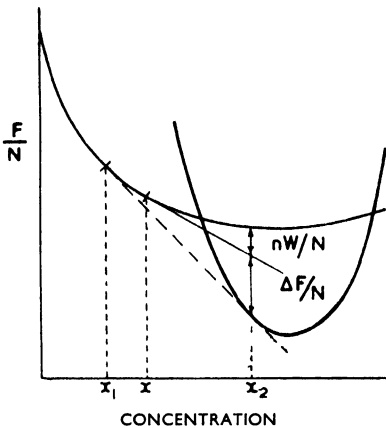


Fig. 17. The free energy changes for segregation to the precipitate composition, nW/N , and for precipitation, $\Delta F/N$

Combined Fluctuation and Nucleation Theory

Surprisingly little attention has been given to combining the philosophies underlying the methods of BECKER and of BORELIUS. HOBSTET-

TER⁽⁴²⁾ claimed to have examined this problem but, as described above, he actually obtained the most likely composition for a Becker nucleus. Consider the free energy/compositional system in Fig. 17 in which x_2 is the composition of the most probable nucleus. Equation (13) has to be extended to include the energy for segregation to this composition and, for a cubical nucleus, becomes

$$\sum Fp = \frac{a^3 W}{N} + \frac{(\Delta F + W)}{N} a^3 + 6a^2\sigma + a^3\epsilon \quad (44)$$

in which the first term is positive and the second negative so that the $\frac{W}{N}$ does not affect the activation energy for the formation of an interface (equations (15) and (16)). However, the preferred path of the reaction will be influenced by the relation between $a^3 W/N$ and the activation

energy, A_0 , and two cases are shown in Fig. 18. In the first case less additional energy is required to form segregates of the same composition as the precipitate and consequently a distribution of segregates will be preferred to a distribution of embryos with the lattice structure of the new phase. The conditions in Fig. 18a suggest that segregates will grow to a size greater than a_0 before they transform. Fig. 18b illustrates the reverse condition in which there is a greater probability of embryos of the new phase than of untransformed segregates with the lattice of the matrix. Naturally, the incubation period will allow both a distribution of segregates and of embryos to be set up and it will be realized that curves similar to Fig. 18 will apply to precipitates of other compositions. Segregates of lower concentration will be more likely but such concentrations would require a higher activation energy for the nucleus formation. The probability of precipitation should therefore be written

$$e^{-(A+Q)/RT} \quad . \quad . \quad . \quad . \quad (45)$$

where A implies the most probable path involving both segregates and embryos, and can be calculated if the free energy relationships and surface tension terms are known or determinable.

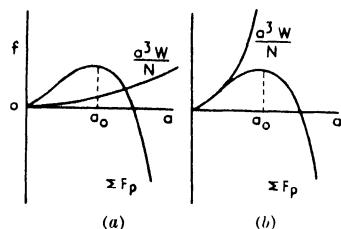


Fig. 18. Different relations between the a^3W/N curve for segregation to the precipitate composition and the ΣFp curves for the formation of the new phase with an interface

Existence of Metastable Solid Solutions

Experimental experience with aluminium alloys has shown that a decomposition process possessing several anomalous features may occur rapidly at low temperatures. For example, the process occurs at room temperature in aluminium-copper alloys with less than 2 atomic per cent copper. The decomposition product consists of extremely small solute rich regions which are difficult to account for by a simple extension of the theories described above. DEHLINGER has favoured the view that the process (described as "single phase decomposition" in German writing) is to be associated with segregation in a region where $\partial^2 F/\partial x^2$ is negative. However, his calculation⁽⁵⁵⁾ that the spinodal point for the aluminium—2 atomic per cent copper alloy is at 330°C overlooked the fact that the solid solution is in equilibrium with a compound and not with another face centred cubic solid solution. Two terminal solid solutions of similar lattice structure in stable equilibrium require that the heat of solution shall be positive and consequently $\partial^2 F/\partial x^2$ will be negative over part of the super-saturated range (Figs. 1 and 19 curve a). A negative heat of solution which is convex downwards over the whole composition range (Fig. 19 curve b) will, in the absence of compound

formation or ordering, produce an uninterrupted series of solid solutions so that $\partial^2 F/\partial x^2$ will be positive over the whole range. A positive heat of solution cannot immediately be assumed when the terminal solid solution is in equilibrium with an intermetallic compound or even a solid solution with a different lattice structure. Intermetallic compounds, provided they are clearly not packing compounds of high coordination number due to a large disparity in the sizes of the atoms, are generally interpreted as evidence that the heat of solution is negative. Because this condition does not favour a supersaturated range of negative

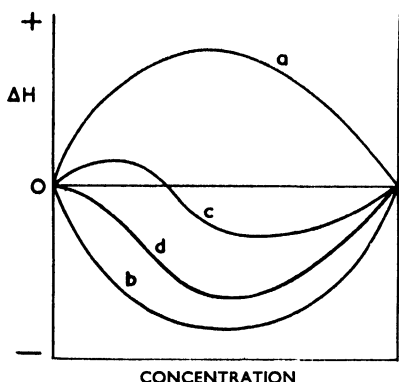


Fig. 19. Different types of integral molar heats of solution

$\partial^2 F/\partial x^2$, SCHEEL⁽⁵⁶⁾ suggested that the initial decomposition product in aluminium-copper alloys involved an ordering reaction. A necessary corollary of his treatment is that the ordering reaction should be of the lambda or second order type^{(57), (58)} which does not involve a nucleation process for the transformation disorder $\rightarrow$ order. More refined statistical analysis^{(59)–(63)} implies that second order reactions do not occur in face-centred cubic lattices although this does not rule out the possibility

that an ordered compound is precipitated by the normal process of nucleation and growth. However, MEIJERING⁽⁶⁴⁾ has concluded that the heat of solution of aluminium-copper alloys possesses an inflected form so that the first decomposition product may be taken to be a disordered copper rich solution. The same assumption implicitly underlies the theoretical treatment of aluminium-silver alloys by DEHLINGER and KNAPP.⁽⁶⁵⁾

MEIJERING'S analysis⁽⁶⁴⁾ started with the experimentally determined solubility equations of copper in aluminium for which he gives

$$\log_{10} x = 1.00 - 2150/T \text{ (from FINK and FRECHE⁽⁶⁶⁾)} \quad (46)$$

$$\log_{10} x = 1.61 - 2650/T \text{ (from BORELIUS *et al.*⁽⁶⁷⁾)} \quad (47)$$

The slope is

$$2.3R \frac{\partial \log_{10} x}{\partial (1/T)} = -\Delta H \quad (48)$$

where ΔH is the energy required to transfer one mole of copper from $\text{CuAl}_2(\theta)$ to an infinite quantity of aluminium. Equations (46) and (47) produce values of 9.8 kcal and 12.1 kcal respectively. The calorimetric measurements of OELSEN and MIDDEL⁽⁶⁸⁾ gave the energy evolved

on the formation of CuAl_2 from copper and aluminium as 3.2 kcal/mole of alloy or 9.5 kcal/mole of CuAl_2 . Subtractions gives the energy of solution of copper in aluminium as 0.3 or 2.6 kcal depending whether equation (46) or (47) is accepted and corresponds to the initial slope of the curve for the integral molar heat of solution as a function of composition. A small positive region is therefore to be expected at the aluminium rich end and the curve will be similar to *c* in Fig. 19. A positive initial slope is a sufficient condition for a metastable immiscibility gap

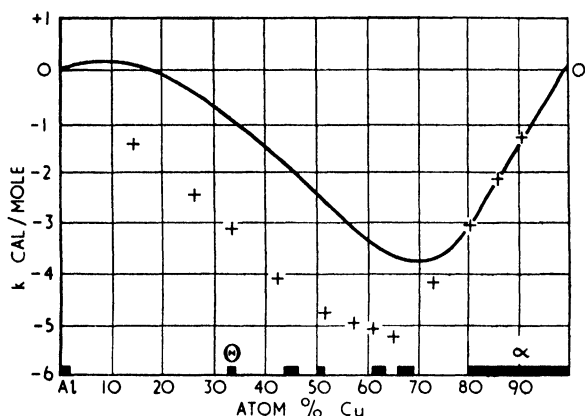


Fig. 20. The integral molar heat of solution of aluminium-copper alloys.⁽⁶⁴⁾ The crosses refer to the measurements of OELSEN and MIDDEL.⁽⁶⁸⁾

at a sufficiently low temperature but this may also be anticipated when the heat of solution is wholly negative provided it is sufficiently inflected—e.g. curve *d* in Fig. 19.

Starting from the solubility equation (47), and using the measurements of OELSEN and MIDDEL, MEIJERING was able to obtain the integral molar heat of solution as

$$\Delta H = 2.6x - 10x^2 - 30.9x^3 + 41.4x^4 \quad . \quad . \quad (49)$$

where x is the atomic fraction of copper and the curve is given in Fig. 20. The entropy was given as

$$\Delta S = -R[x \ln x + (1-x) \ln (1-x) - 3.7(x - 2x^2 + x^3)] \quad . \quad (50)$$

The corresponding metastable solubility curve is indicated by the dashed line in Fig. 21 whilst the full line is the stable solubility curve of BORELIUS (equation (47)). The solubility temperature for 2 atomic per cent copper is 435° (or 390°C) using equation (46) whilst the phase in equilibrium contains 55 atomic per cent copper. It may be noted that equations (49) and (50) give a positive value of $\partial^2 F / \partial x^2$ for a 5.7 weight per cent copper alloy at 0°C.

The calculations are necessarily very approximate but indicate the possibility that a metastable disordered copper rich solution may form the initial decomposition product in aluminium-copper alloys. MEIJERING remarks that similar effects may be encountered in other alloy systems when the effective valency of one of the components changes

across the phase diagram thus leading to an inflected curve for the heat of solution.

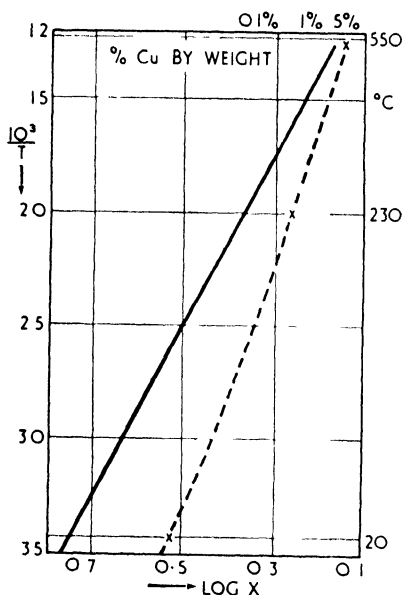


Fig. 21. Solubilities of copper in aluminium. The full line applies to the stable solution given by equation (46), the dashed line is for the calculated solubility of face-centred cubic copper

The assumption of a metastable inflected free energy/compositional curve forms an essential part of the treatment used by DEHLINGER and KNAPP⁽⁶⁵⁾ to study the size and distribution of the silver rich clusters which form the first decomposition product of aluminium-silver alloys. The equality of the atomic size of aluminium and silver atoms allows the strain energy factor to be neglected as a first approximation. DEHLINGER and KNAPP's method is equivalent to maximizing the fall in free energy during the decomposition process.

The free energy of the final state is balanced between several opposing factors: the loss in internal energy due to an increase in the number and size of the clusters has to be offset by the gain in entropy

of the saturated solution together with the entropy due to the distribution of the clusters.

Let N_A = number of aluminium atoms

N_B = number of silver atoms

$M_B(i)$ = number of clusters of pure silver

i = number of silver atoms in a cluster

$N_B(l)$ = number of silver atoms on the lattice outside the clusters

the total number of lattice sites

$$N = N_A + N_B = N_A + N_B(l) + iM_B(i).$$

The entropy of solution of the quenched alloy is

$$\Delta S_{\text{init.}} = -k \left[N_A \ln \frac{N_A}{N} + N_B \ln \frac{N_B}{N} \right] \quad . \quad . \quad . \quad (51)$$

$$= -R[(1-x) \ln(1-x) + x \ln x]$$

where x is the atomic fraction of silver. DEHLINGER and KNAPP's terms for the entropy of the alloy after decomposition are exactly equivalent to

$$\Delta S_{\text{final}} = \Delta S_{\text{lattice}} + \Delta S_{\text{clusters}} \quad . \quad . \quad . \quad (52)$$

and

$$\Delta S_{\text{lattice}} = -k \left[N_A \ln \frac{N_A}{N - iM_{B(i)}} + N_{B(l)} \ln \frac{N_{B(l)}}{N - iM_{B(i)}} \right] \quad (53)$$

$$= -R[(1-x) \ln(1-x)' + x(l) \ln x(l)'] \quad . \quad . \quad . \quad (54)$$

where the primes indicate the atomic fractions over the lattice sites outside the complexes

$$\Delta S_{\text{clusters}} = -k \left[M_{B(i)} \ln \frac{iM_{B(i)}}{N} + \left(\frac{N}{i} - M_{B(i)} \right) \ln \frac{\left(\frac{N}{i} - M_{B(i)} \right)}{\frac{N}{i}} \right] \quad . \quad . \quad . \quad (55)$$

$$= -k [(\text{number of clusters}) \ln (\text{vol. fraction of clusters}) + (\text{number of unfilled clusters}) \ln (\text{vol. fraction unfilled})] \quad . \quad . \quad . \quad (56)$$

$$= -R \left[c_i \ln c_i + \left(\frac{1}{i} - c_i \right) \ln (1 - ic_i) \right] \quad . \quad . \quad . \quad (57)$$

where c_i is "atomic" fraction of the clusters.

Equation (56) is identical with FLORY's equation for linear flexible chain polymers⁽⁶⁹⁾

$$\Delta S = -k \Sigma n_j \ln \phi_j \quad . \quad . \quad . \quad (58)$$

when n_j is the number of molecules and ϕ_j is the volume fraction of kind j . HUGGINS⁽⁷⁰⁾ and TOMPA⁽⁷¹⁾ have shown that FLORY's expression is much too large when the polymers are compact and have given alternative equations for spherical particles. The reason is that a single-atomed chain only forbids the lattice sites it actually occupies whereas two spheres cannot approach within twice their diameters (eight times their volume). However, the objection to equation (56) for the entropy of spherical clusters is not serious as long as the concentration ic_i remains very small—preferably much less than 0.1.

DEHLINGER and KNAPP set the energy change on full decomposition, for small values of x , as

$$\Delta u_{\text{complete}} = \Delta u_{\text{final}} - \Delta u_{\text{init.}} = R[\alpha x + \beta x^2 + \gamma x^3] \quad (59)$$

where α , β and γ were obtained (by a method undisclosed) from the temperature limit observed by KÖSTER and BRAUMANN⁽⁷²⁾ for the first stage of ageing. On partial decomposition

$$\begin{aligned} \overline{\Delta u}_{\text{partial}} &= (\Delta u_{\text{final}} - \Delta u_{\text{init.}}) - (\Delta u_{\text{final}} - \Delta u_{\text{partial}}) \\ &= R[\alpha x + \beta x^2 + \gamma x^3 - (1 - ic_i)\{\alpha x(l)' + \beta(x(l)')^2 + \gamma(x(l)')^3\}] \quad (60) \end{aligned}$$

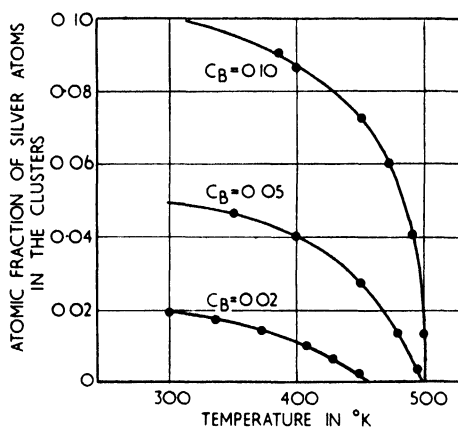


Fig. 22. Calculated fractions of silver atoms in the clusters for different temperatures and supersaturated compositions (C_B)⁽⁶⁵⁾

in which $x(l)'$ can, with little loss in accuracy, be equated to $x - ic_i$ and the internal energy of the silver clusters has been taken as zero.

The loss in free energy is given by

$$\Delta f = \Delta f_{\text{partial}} - \Delta f_{\text{init.}} = \overline{\Delta u}_{\text{partial}} - T(\Delta S_{\text{partial}} - \Delta S_{\text{init.}}) \quad (61)$$

and can be obtained from equations (60), (54), (57) and (51). Equation (61) is maximized by setting the differentials with respect to i and c_i equal to zero and solved for ic_i by numerical approximation. DEHLINGER and KNAPP'S results are given in Figs. 22 and 23. The metastable solubility curve is obtained from the temperatures at which ic_i is equal to zero and is very strongly asymmetrical (Fig. 23) as at low silver concentrations it must lie very close to the equilibrium solubility curves.

The approximations which have been made, namely FLORY'S entropy expression and the view that the clusters are pure silver could be overcome by more generalized (and more laborious) treatments but the inaccuracies are masked by the use of direct experimental values in the

expression for the energy change. As in the case of MEIJERING's calculation a high degree of accuracy is not to be expected. However, the two papers under discussion represent marked advances in the theoretical argument.

Particle Shape, Coherence, Allotropy and Maximum Size

The surface energy term in equation (13) will favour a spherical particle shape. However, NABARRO^{(23), (24), (73)} has shown that the elastic energy

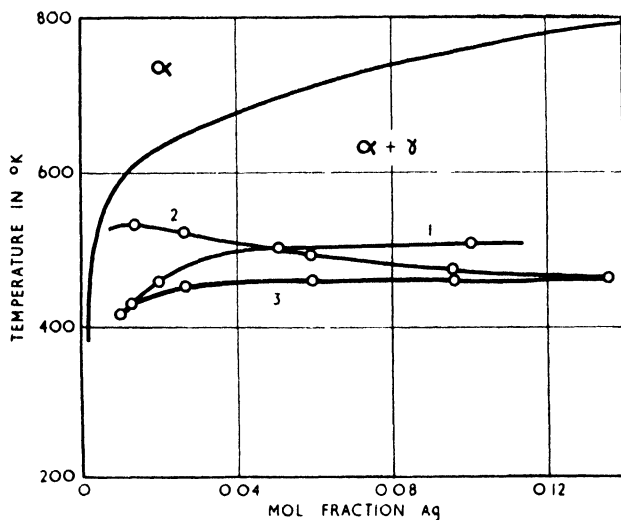


Fig. 23. Boundary curves in the ageing of Al-Ag alloys.⁽⁶⁵⁾ Curve 1 is the calculated solubility curve of the clusters. Curve 2 is the temperature limit of the first stage on the hardness-ageing curves (KOSTER and BRAUMANN⁽⁷²⁾). Curve 3 is the limit obtained by thermal measurements (KOSTER and SCHELL⁽²⁵⁷⁾)

due to a difference in volume between the precipitate and the matrix can be reduced by a change of shape from spheres to plates (and to a lesser extent to needles). The surface energy terms will be greatly reduced on crystallographic planes across which there is perfect matching between the atomic array of the matrix and the precipitate⁽²⁾—such particles are said to be coherent with the matrix. A preferred plane of precipitation leads to the WIDMANSTÄTTEN figures.⁽⁷⁴⁾ Minor disregistry between the lattices will cause coherency stresses which will grow as the particle size increases. At a critical size, the particles will break away and form an interface so that the strain energy in the bulk of the precipitate will be exchanged for the energy of a dislocation array forming the surfaces. According to BROOKS,⁽⁷⁵⁾ the exchange will begin when the smallest dimension of the precipitate becomes comparable with the spacing of the dislocations necessary to join the unstrained

lattices. The process will be facilitated when it is accompanied by a change to a more stable structure and the transition may be termed allotropic when it involves no change in composition. The general energy equations governing the change may easily be set up⁽²³⁾ but the calculation of the critical size, *ab initio*, demands assumptions of the elastic constants over small numbers of atoms thus introducing notable uncertainties.^{(73), (76)}

The upper critical size of the intermediate precipitates is clearly dependent on both interfacial and coherency strain energy factors. KONOBEVSKI^{(77), (78)} has suggested that the Thomson-Freundlich formula (equation (17)) should, in addition to indicating the minimum particle size, also be used to give the upper limiting size to which the particles grow. This will apply to the non-coherent equilibrium precipitate where only the interfacial energy terms need be considered. The final size will be dependent on temperature but not on the initial concentration.⁽⁷⁸⁾ More rigorous treatments will allow for the entropy of the particles (p. 165).

Reversion

Experimental work on aluminium alloys revealed that an alloy aged at a low temperature was softened by rapid heating to a higher temperature. Further ageing at either the higher or lower temperatures led to renewed hardening. The effect is known as reversion and has been widely studied.

The Volmer-Weber-Becker-Döring theory of nucleation provides a ready explanation since the critical particle size for a stable nucleus increases with increasing temperature (decreasing supersaturation). Particles formed by precipitation at a low temperature will be forced to re-dissolve when the temperature is raised should their size be less than the critical size for growth at the new temperature. However, the numerical treatments of the problem have been very unsatisfactory chiefly because of the difficulty of fixing theoretically the number and size of the particles produced during precipitation at the lower temperature. HASIGUTI⁽⁷⁹⁾ has calculated the critical particle size for aluminium-copper alloys at different temperatures determining the exchange interaction energy (equation (23)) from the metastable solubility curve deduced by identification of the precipitates in aged alloys. The results have little numerical significance but merely confirm the general deduction of increasing size with increasing temperature.

KONOBEVSKI'S views^{(77), (78)} on the existence of an upper limit for the particle size on precipitation have been mentioned above. An attempt is made in his second paper⁽⁷⁸⁾ to relate the number and size of the particles to the reversion behaviour of aluminium-copper alloys. However, it has been shown that the particle size is so small that it is

no longer commensurate with the physical constants used in the calculation.⁽⁸⁰⁾ The method of SUZUKI⁽⁸¹⁾ contained the assumption that the particle size on precipitation at low temperatures never reaches the critical nucleus size for growth with a reduction in free energy. This seems contradictory to the experimental observation that a heat evolution accompanies the ageing of aluminium-copper alloys at room temperature.⁽⁶⁷⁾ The number of particles at different temperatures is dependent on equations similar to equation (18b). SUZUKI's paper showed how the anomalous specific heat of aged aluminium-copper alloys undergoing heating may be calculated within the frame of these assumptions.

Reversion is also to be expected when the higher temperature is in excess of a metastable solubility curve so that an early decomposition product will be re-dissolved when the temperature is raised. It will be shown in the next section that re-solution is also caused by the formation of a more stable decomposition product.

The Pattern of Precipitates

An account will now be given of a supersaturated alloy undergoing precipitation in terms of the hypothetical free energy/compositional relationships shown in Fig. 24. The system can be simplified or complicated at will but a fairly complex case has been taken in order to illustrate the rich variety of structures likely to be found during precipitation.

The free energy/compositional curve of the solid solution is negative but inflected ($\partial^2 F/\partial x^2$ is negative between x_5 and x_6). Four stages have been assumed for the decomposition process from the highest supersaturations. The decomposition products are (a) the disordered solid solution, x_7 , of about 40 atomic per cent solute in metastable equilibrium with x_4 , (b) an ordered solid solution, x_8 , of about 50 atomic per cent solute in metastable equilibrium with x_3 , (c) an intermediate precipitate, x_9 , of about 30 atomic per cent solute in metastable equilibrium with x_2 and (d) the final precipitate, x_{10} , in equilibrium with the solid solution of composition x_1 . It is assumed that the only true allotropic change is from the intermediate to the final precipitate. For simplicity, it is assumed that the intermediate and

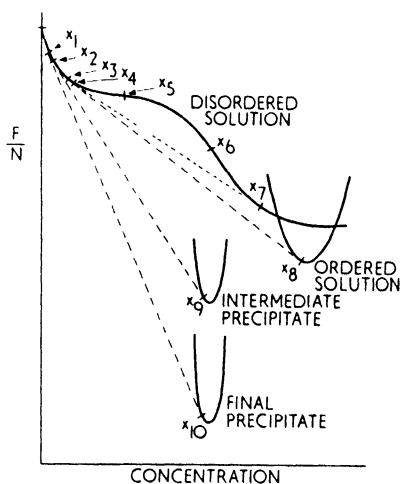


Fig. 24. Hypothetical free energy/compositional relationships for alloys undergoing precipitation

final precipitates are not formed by transformation within the ordered, x_8 , regions. The generality may be increased by allowing a different matching plane between the matrix and the ordered solution and between the matrix and the intermediate or final precipitates. Throughout the following description the general principle is adopted that the precipitation process will follow the path of minimum activation energy.

At initial concentrations higher than x_5 (Fig. 24) all segregations of "like" atoms to form clusters are accompanied by a decrease in overall free energy and will occur provided that energy fluctuations are available for the diffusion mechanism. The probability of segregation is proportional to

$$e^{-Q/RT} \quad . \quad . \quad . \quad . \quad (62)$$

At concentrations between x_5 and x_4 an activation energy will be required to form the clusters of disordered solid solution by segregation. The value is given by W in Fig. 9 and the probability is proportional to

$$e^{-(Q+nW)/RT} \quad . \quad . \quad . \quad . \quad (63)$$

The interfacial energy is assumed negligibly small so that no interface is formed. The shape, size and distribution of the clusters will maximize the fall in free energy resulting from their formation. The solid solution will tend to the composition limit x_4 .

Clusters of the disordered solid solution cannot achieve even metastability when the initial concentration is less than x_4 but a statistical distribution may be formed by fluctuations. It will be assumed that a small surface energy term is associated with the ordered solid solution so that an activation energy is required for the formation of the "interface." As described in a preceding section (p. 160) the path followed in forming the ordered phase will involve both fluctuations of composition and embryos with the new lattice structure. The exact details will depend on the free energy relationships but the ordered structure will probably be formed by fluctuations within the clusters. Even when the clusters possess metastability, time will still be required for the incubation period of the ordered phase irrespective of its exact mode of formation and the majority of clusters will be unaffected by the process. The probability of the formation of the ordered structure is proportional to

$$e^{-(Q+A_1)/RT} \quad . \quad . \quad . \quad . \quad (64)$$

The ordered solid solution does not constitute a metastable decomposition product when the initial concentration is less than x_3 although there may be a statistical distribution of such particles. At concentrations greater than x_2 the intermediate precipitate will be formed from the matrix by nucleation (and fluctuation of composition). The probability of its formation is proportional to

$$e^{-(Q+A_2)/RT} \quad . \quad . \quad . \quad . \quad (65)$$

REPORT ON PRECIPITATION

Fig. 25a shows the conditions at a composition above x_3 when the ordered compound will be formed more rapidly than the intermediate precipitate which has the higher activation energy. In Fig. 25b only the intermediate (and final) precipitates can form a stable nucleus as the composition is below x_3 . Fig. 25c refers to an initial supersaturation

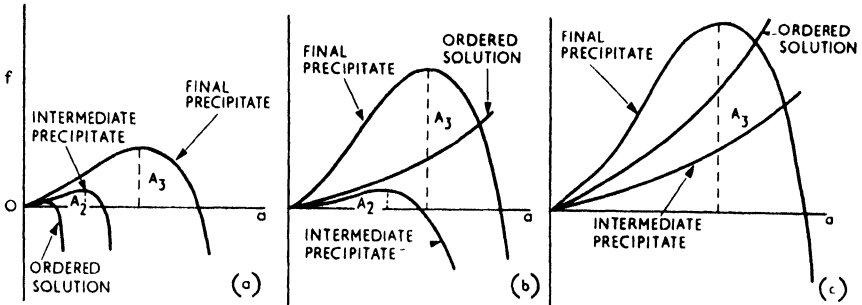


Fig. 25. Relation between the ΣFp curves for the ordered solution, intermediate and final precipitates from supersaturations between
 (a) x_4 and x_3 ; (b) x_3 and x_2 ; (c) x_2 and x_1

between x_1 and x_2 when only the stable precipitate can be formed. The probability may be set proportional to

$$e^{-(Q+A_3)/RT} \quad . \quad . \quad . \quad (66)$$

A_1 , A_2 and A_3 contain energy fluctuations for segregation but the straightforward Becker treatment makes Fig. 25 more simple to follow.

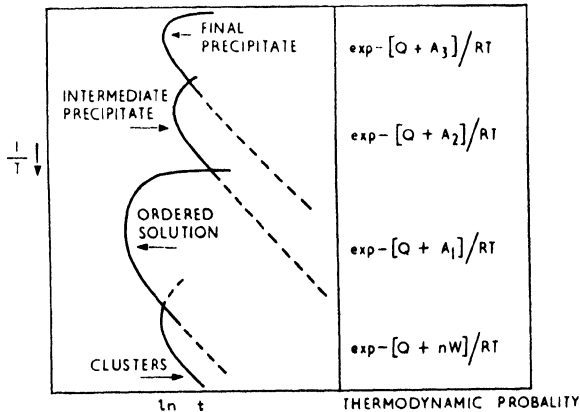


Fig. 26. Reciprocal rate curves for the precipitation processes of
 Fig. 24

The intermediate precipitate will transform to the final structure when the particle size exceeds the critical value and the ΣFp (final) and ΣFp (intermediate) curves in Fig. 25b have crossed.

The A and nW terms in equations (63–66) are temperature dependent and increase as the temperature is raised. The reciprocal rate curves for the time to the different stages of precipitation form a series of C curves when plotted against temperature—Fig. 26. The crossing points of equal probability of different reactions serve to emphasize that all processes are occurring simultaneously and dominance depends entirely on the height of the various energy barriers.

Allow a nucleus of the intermediate precipitate to form in a metastable mixture of ordered regions and solid solution of composition x_3 . The composition adjacent to the nucleus of the intermediate precipitate will tend towards x_2 and solute will be transferred by diffusion to the growing nucleus. The particle of intermediate precipitate will be surrounded by a region in which the composition is less than x_3 . Any particles of the ordered compound which lie within the volume affected will be forced to re-dissolve in an attempt to maintain the solid solution at their interface at the composition x_3 . The general rule applies⁽⁸⁾ that the appearance of a more stable decomposition product causes the resolution of its immediate forerunner.

Precipitation from Ternary Solutions

Precipitation theory for binary systems is at present descriptive and qualitative rather than rigorous and quantitative. An extension to three component systems is therefore regarded as being beyond the scope of immediate interest. All the effects postulated for binary systems are also possible in ternary alloys and, in some cases, appeal to experimental observations on three component alloys has been used below to illustrate details of the precipitation process.

III. KINETICS OF PRECIPITATION

Time Dependence at Constant Temperature

Several analyses have been made of the rate of transformation for reactions such as recrystallization, phase changes and growth of precipitates. AUSTIN and RICKETT⁽⁸²⁾ have chosen to set the fraction transformed

$$\alpha = K_1(1 - \alpha)t'^p \quad . \quad . \quad . \quad (67)$$

where K_1 and p are constant and t' is the growth time. MISHIMA⁽⁸³⁾ has given a more complete derivation of equation (67).

For precipitation the fraction transformed can conveniently be put

$$\alpha = \frac{c_0 - c}{c_0 - c_f} \quad . \quad . \quad . \quad (68)$$

with c_0 and c_f as the initial and final concentrations and c the concentration of the solute dissolved in the matrix after the growth time t' . Equation (67) can then be re-written

$$\ln \frac{c_0 - c}{c - c_f} = p \ln t' + \ln K_1 \quad . \quad . \quad . \quad (69)$$

The rate of reaction was given by MISHIMA, HASIGUTI and KIMURA⁽⁸⁴⁾ as

$$\frac{d\alpha}{dt'} = K_2 \alpha^{(p-1)/p} (1 - \alpha)^{(p+1)/p} \quad . \quad . \quad . \quad (70)$$

$$(K_2 = p K_1^{1/p})$$

in which $K_2 = B e^{-E/RT}$ where E is the activation energy.

An approach more generally used is to place the right-hand side of equation (67) as the rate of transformation and

$$\frac{d\alpha}{dt'} = K_3 (1 - \alpha) t'^{m-1} \quad . \quad . \quad . \quad (71)$$

where $(1 - \alpha)$ allows for the interference of the growing particles and of the depleted areas. Integration gives

$$\alpha = 1 - \exp[-K_4 t'^m] = 1 - \exp\left[-\left(\frac{t'}{\tau}\right)^m\right] \quad (72)$$

$$K_4 = K_3/m = \tau^{-m}$$

with τ as a time constant. Suitable choices of τ and m convert equation (72) to the equations of JOHNSON and MEHL,⁽⁸⁵⁾ EVANS,⁽⁸⁶⁾ AVRAMI,^{(87), (88), (89)} COOK and RICHARDS,⁽⁹⁰⁾ WERT^{(91), (92)} and EROFEEV⁽⁹³⁾ and the resulting expressions cover the time dependence for the appearance of the nuclei. When t' is the growth time of nuclei which appear simultaneously the size of a growing particle in an infinite matrix may be taken as⁽⁹⁴⁾

$$s \propto \delta(Dt')^{\frac{1}{2}} \quad . \quad . \quad . \quad (73)$$

with D as the diffusion coefficient. The volume of a particle or of precipitate becomes^{(91), (92), (94)}

$$\left. \begin{array}{ll} \text{spheres radius } \propto t'^{\frac{1}{2}} & V_{\text{sphere}} \propto t'^{\frac{3}{2}} \\ \text{discs radius } \propto t', \text{ thickness } \propto t'^{\frac{1}{2}} & V_{\text{disc}} \propto t'^{\frac{3}{2}} \\ \text{cylinder length } \propto t', \text{ radius } \propto t'^{\frac{1}{2}} & V_{\text{cyl.}} \propto t'^{\frac{3}{2}} \end{array} \right\} \quad . \quad . \quad (74)$$

and $m = \frac{3}{2}, \frac{5}{2}$ or $\frac{4}{3}$ can be used in equation (72) since ZENER⁽⁹⁴⁾ assumed that the growth law for the whole process mirrors the growth law for the individual particles.

Equation (72) can be re-written

$$\ln \ln \frac{1}{1-\alpha} = \ln \ln \frac{c_0 - c_f}{c - c_f} = m \ln t' - m \ln \tau \quad . \quad . \quad (75)$$

from which τ is seen to be the growth time when

$$\alpha = \frac{e-1}{e} \simeq 0.63 \quad . \quad . \quad . \quad (76)$$

On the other hand K_4 is related to the fraction transformed when $t' = 1$. Plotting the left hand side of equation (75) against $\ln t$ allows

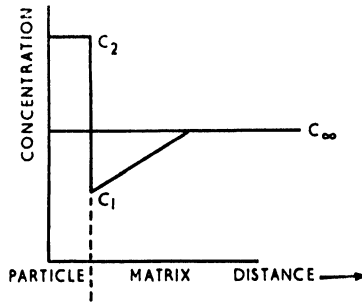


Fig. 27. Idealized concentration distribution around a growing particle⁽⁹⁴⁾

m to be determined experimentally for comparison with the deductions of ZENER and WERT.

Using the idealized concentration around a growing particle given in Fig. 27, ZENER⁽⁹⁴⁾ obtained δ of equation (73)

$$\text{(half thickness of disc)} \quad \delta_1 = \frac{c_\infty - c_2}{(c_2 - c_1)^{\frac{1}{2}}(c_2 - c_\infty)^{\frac{1}{2}}} \quad . \quad . \quad . \quad (77)$$

$$\text{(radius of sphere)} \quad \delta_3 = \sqrt{2} \frac{(c_\infty - c_1)^{\frac{1}{2}}}{(c_2 - c_1)^{\frac{1}{2}}} \quad . \quad . \quad . \quad (78)$$

Equations (77) and (78) only apply as long as the concentration gradient changes slowly so that the proportionality constant in equation (73) does not vary far from unity.* The number of particles, N_p , can be determined^{(91), (92)} since, for spheres, the volume of precipitate

$$V = 4 \frac{\pi}{3} \delta_3^3 (Dt')^{\frac{3}{2}} N_p \quad . \quad . \quad . \quad (79)$$

* Both the Thomson-Freundlich formula (equation (17)) and recent work of MACH-LIN⁽⁹⁵⁾ suggest that c_1 will not correspond exactly to the (meta-)stable equilibrium concentration.

provided V can be estimated from the fall in concentration and density of the precipitate. A further refinement has been given by WERT and ZENER⁽⁹⁶⁾ who obtained

$$N_p = (\frac{3}{4}\pi)2^{-\frac{1}{2}}[(c_2 - c_1)/(c_\infty(o) - c_1)]^{\frac{1}{2}}(D\tau)^{-\frac{1}{2}} \quad . \quad . \quad . \quad (80)$$

where $c_\infty(o)$ is the matrix composition at zero time and

$$\tau = 3/(8\pi N_p R_f D) \quad . \quad . \quad . \quad (81)$$

in which R_f is the final radius of the particle. An empirical value of τ has to be used in equation (80).

These authors⁽⁹⁶⁾ also improved the allowance for interference and obtained the governing equation for spherical particles as

$$\tau \frac{d\alpha}{dt'} = \frac{3}{2} (1 - \alpha)\alpha^{\frac{1}{2}} \quad . \quad . \quad . \quad (82)$$

which they determined by numerical integration although an analytical solution was given later.⁽⁹⁷⁾

ROBERTS, AVERBACH and COHEN⁽⁹⁸⁾ have used a similar concentration distribution to Fig. 27 in order to analyze the rate of reaction for the first stage of tempering quenched carbon steel. In this case n_0 is the average (carbon) concentration of the planar region containing the nuclei of ϵ -carbide. The transformation is assumed to consist of a thickening of these regions so that

$$\frac{d\alpha}{dt'} = K_5 N_p D^{\frac{1}{2}} \frac{(c_\infty - c_1)}{(c_2 - c_1)} (1 - \alpha)t'^{-\frac{1}{2}} \quad . \quad . \quad . \quad (83)$$

which is of similar form to equation (71) with $m = \frac{1}{2}$ for the thickening of discs (cf. equation (74)) and can be integrated to an equation similar to (72) since all the terms on the right hand side are treated as constant except α and t' . However, equation (83) adds the additional information that K_3 (and K_4 cf. equation (93)) should be a linear function of the initial carbon content (c_∞) and should go to zero at the metastable solubility limit. The same result can be inferred when ZENER's equation (77) is used to calculate the volume of plates of constant radius and α is taken as the ratio of volume of precipitate to final volume of precipitate. For spheres, ZENER's equations (78) and (79) suggest that K_3 should be proportional to the supersaturation raised to the power of 1.5 provided the number of particles does not change.

Temperature Dependence

BECKER put the rate of initial precipitation as

$$I = K e^{-(Q+A)/RT} \quad . \quad . \quad . \quad (84)$$

which is of closely similar form to the equation of TURNBULL and FISHER⁽⁹⁹⁾

$$I \simeq \frac{NkT}{h} e^{-(\Delta f^* + \Delta F^*)/kT} \quad . \quad . \quad . \quad (85)$$

obtained from chemical reaction rate theory with Δf^* as the free energy of activation for diffusion over an interface between two lattices and ΔF^* a free energy of activation for nucleation.

Equation (84) can be written in terms of time (reciprocal rate)

$$\ln t = \kappa_1 + \frac{Q}{RT} + \frac{A}{RT} \quad . \quad . \quad . \quad (86)$$

when A , which is temperature dependent, can be obtained from the plot of $\ln t$ against $1/T$ by the geometrical relation shown in Fig. 16 with A replacing nW . The slope

$$\frac{\partial \ln t}{\partial (1/T)} = \frac{Q}{R} + \frac{A}{R} + \frac{1}{RT} \frac{\partial A}{\partial (1/T)} \quad . \quad . \quad . \quad (87)$$

will be Q/R when A is very small compared with Q . The slope at low temperatures is usually less than the value of Q determined by high temperature diffusion tests and JETTER and MEHL⁽¹⁰⁰⁾ pointed out that this will follow when A is not negligible provided that

$$\frac{A}{R} < \frac{1}{RT} \frac{\partial A}{\partial (1/T)} \quad . \quad . \quad . \quad (88)$$

since the last term in equation (87) is negative. HARDY⁽¹⁰¹⁾ has analyzed the temperature dependence of A necessary to give a straight line plot of slope Q' less than Q and finds the condition to be

$$A = (Q - Q')(T - T_0)/T_0 \quad . \quad . \quad . \quad (89)$$

where T_0 is a fixed temperature for any particular reaction. Consequently A must be a linear function of T which is unlikely in the original BECKER theory.

The rate of precipitation is most rapid at the temperature corresponding to the nose of reciprocal rate curve when equation (87) is equal to zero. This temperature could be found across a phase system by solving equation (30) for x , then for A and $\partial A/\partial (1/T)$ but the laborious nature of the calculations and the doubtful reliability of the results are strong deterrents.

WERT⁽⁹¹⁾ suggested that the temperature dependence of the rate of precipitation can be obtained by analyzing the temperature dependence of τ in equation (72). He put

$$\tau = L^2/D = (L^2/D_0)e^{Q/RT} \quad . \quad . \quad . \quad (90)$$

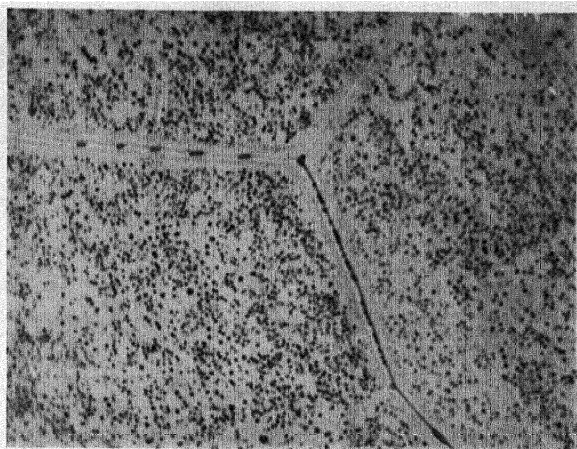


Fig. 28. Grain boundary precipitation and depleted regions in a copper-5-per-cent-nickel-1.3-per-cent-iron alloy slowly cooled from 900° to 600°C .⁽¹⁰²⁾ ($\times 2000$)

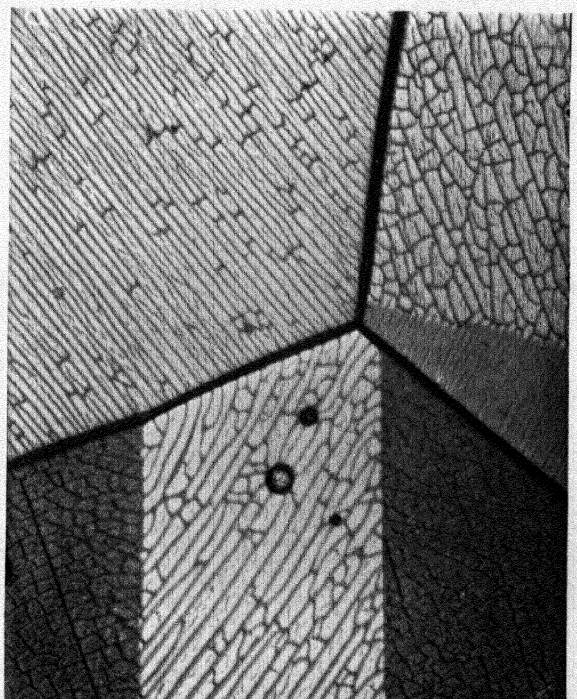


Fig. 29. Veining along sub-boundaries in an over-aged copper-1.05-per-cent-beryllium alloy.⁽¹⁰³⁾ ($\times 500$)

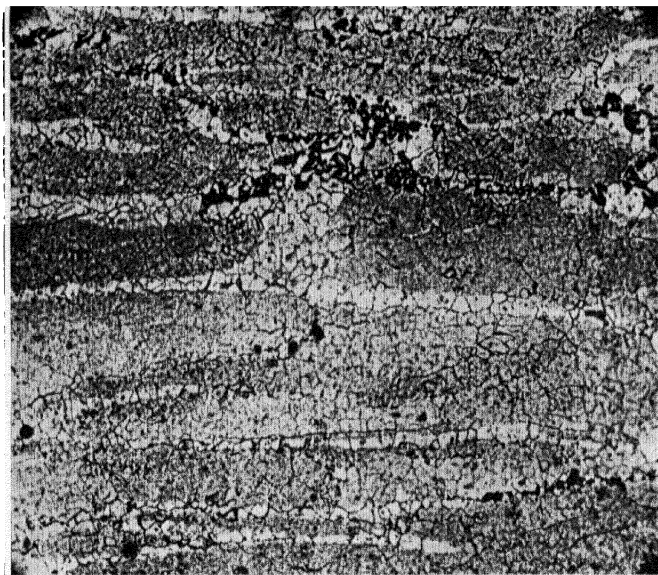


Fig. 30. Veining in a duralumin-type alloy polygonized during extrusion and heat treatment.⁽¹⁰⁴⁾ ($\times 300$)

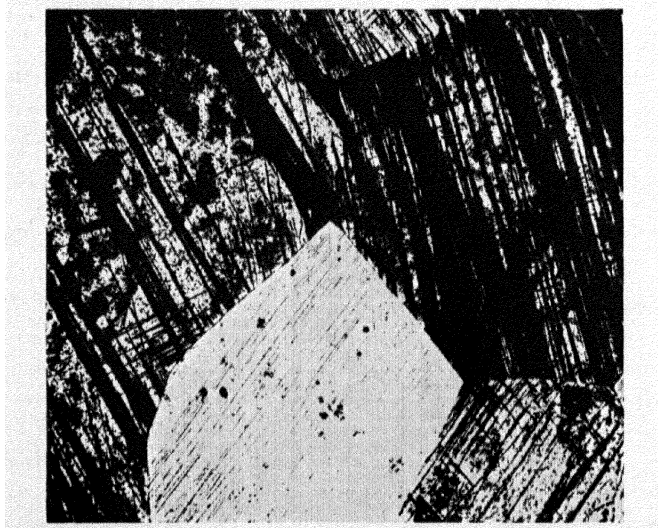


Fig. 31. Preferential precipitation in slip bands formed at the surface on quenching an aluminium-4-per-cent-copper alloy, aged 100 hr at room temperature.⁽¹⁰⁵⁾ ($\times 100$)



Fig. 32. Precipitation along a slip band in an aluminium-4-per-cent-copper alloy aged 3 hr at 190°C .^{(106), (107)} ($\times 25,000$)

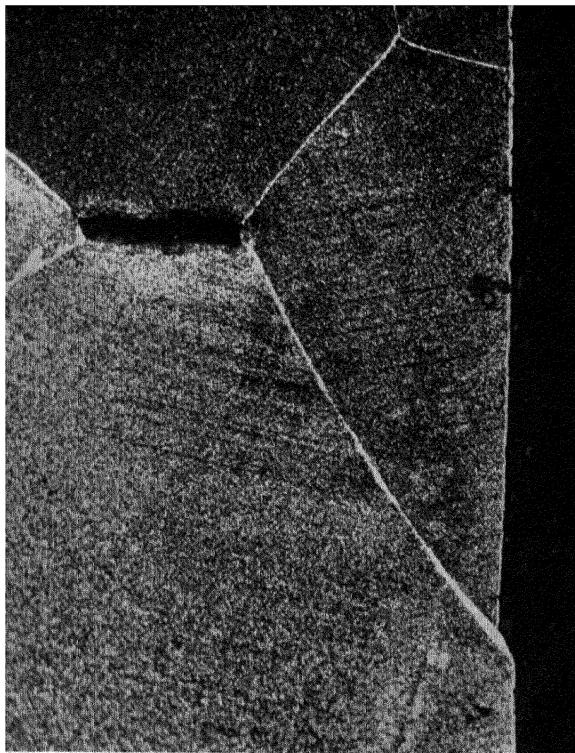


Fig. 33. Creep at grain boundaries as a consequence and cause of excessive depleted regions in an aluminium-4-per-cent-copper alloy aged at 190°C and tested at $4\frac{1}{2}$ tons/in.² at 190°C failed after 231 hr.⁽¹⁰⁸⁾ ($\times 200$)



Fig. 34. Typical discontinuous precipitation starting from grain boundaries in a copper-1.97-per-cent-beryllium-0.03-per-cent-iron alloy aged 2 hr at 325°C.⁽²⁾ ($\times 75$)

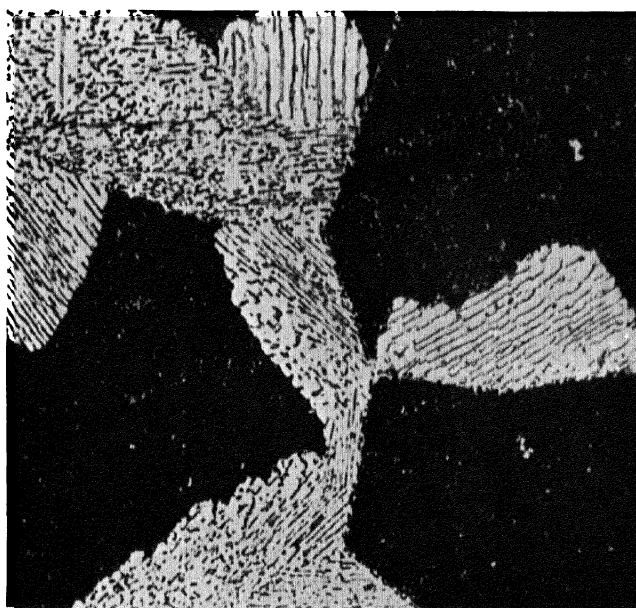


Fig. 35. Microstructure of an aluminium-20-per-cent-silver alloy aged 6 hr at 303°C, showing the formation of nodules with a new orientation containing plates of the equilibrium precipitate γ . This involves a discontinuous change from the matrix, etched black, which contains the intermediate precipitate γ' .⁽¹⁶⁹⁾ ($\times 1000$)

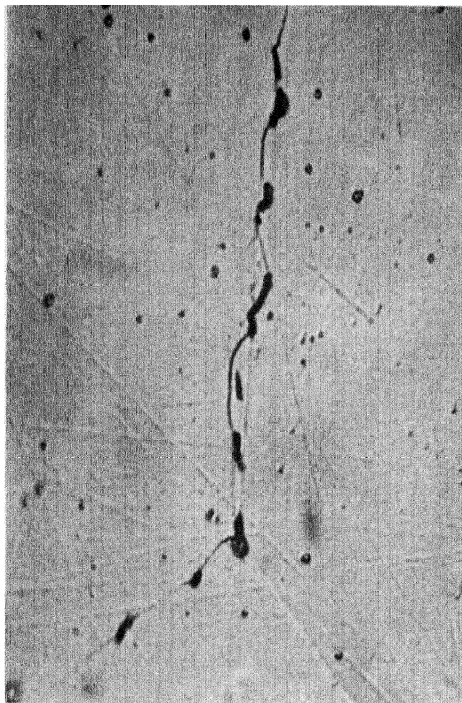


Fig. 36. GAYLER's light phenomenon at the grain boundaries of an aluminium-4-per-cent-copper alloy quenched in boiling water and aged 327 days at room temperature.⁽¹¹⁰⁾ ($\times 2000$)

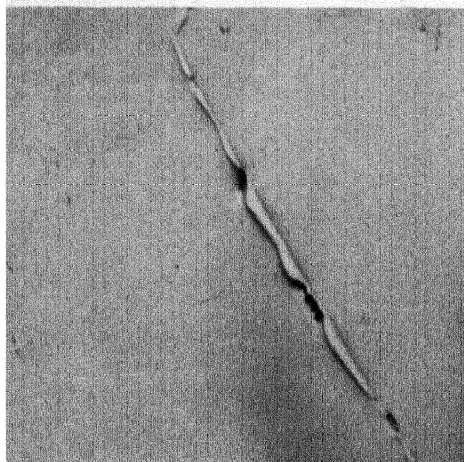


Fig. 37. The light phenomenon and grain boundary movement in an aluminium-10-per-cent-zinc alloy aged 12 days at 50°C.⁽¹¹¹⁾ ($\times 1500$)

where L is related to the mean distance between particles. Equation (72) is then

$$\alpha = 1 - \exp \left[- (D_0 t' e^{-Q/RT} / L^2)^m \right] \quad . \quad . \quad . \quad (91)$$

and α can be held temperature independent by observing the time to the same degree of precipitation and different temperatures so that

$$\frac{Q}{R} = \left[d \ln t' / d \left(\frac{1}{T} \right) \right]_{\alpha} \quad . \quad . \quad . \quad (92)$$

as long as L is reasonably constant over the range investigated. It is necessary to impose experimental conditions such that variations of L do not interfere since under normal conditions L is a function of the temperature dependent rate of nucleation.

ROBERTS, AVERBACH and COHEN⁽⁹⁸⁾ claimed that the temperature dependence of K_3 in equation (71) involves $Q^\ddagger$ through the presence of $D^\ddagger$ in their equation (83). The following relations hold

$$\begin{aligned} K_4 = \frac{K_3}{m} &= \frac{K_5}{m} N_p D^\ddagger \frac{(c_\infty - c_1)}{(c_2 - c_1)} = K_6 (D_0 e^{-Q/RT})^m \\ &= \tau^{-m} = (D_0 e^{-Q/RT} / L^2)^m \quad . \quad . \quad . \quad (93) \end{aligned}$$

in which the power to $\frac{1}{2}$ has been generalized by m in the last three equalities. Differentiation of equation (93) gives

$$\left[\frac{d \ln K_4}{d(1/T)} \right]_{\nu} = \frac{-mQ}{R} \quad . \quad . \quad . \quad (94)$$

whereas

$$\left[\frac{d \ln \tau}{d(1/T)} \right]_{\alpha} = \frac{Q}{R} \quad . \quad . \quad . \quad (95)$$

and is identical with equation 92, but in both cases N_p or L has to be held constant.

IV. PRECIPITATION AS A STRUCTURE SENSITIVE PROCESS

Because the rate of precipitation is very strongly dependent on the rate of nucleation it is not surprising to find the precipitation process occurs more rapidly in regions favouring easy nucleation. Figs. 28–33 show how lattice disturbances due to grain boundaries, macro-mosaic boundaries and slip bands promote precipitation whilst Figs. 34–37 show how a grain boundary reaction has led to “discontinuous” precipitation.

It has often been demonstrated that the rate of ageing is affected by cold work either after solution treatment or as a result of quenching stresses. Full references will be found in the earlier reviews whilst Figs. 38 and 39 show the type of effects.^(112–120) Although cold work and lattice distortion usually accelerate the precipitation⁽¹¹¹⁾ the effects

are not always straightforward. For example, GRUHL and WASSERMANN⁽¹²¹⁾ found that cold work before ageing a copper-beryllium alloy

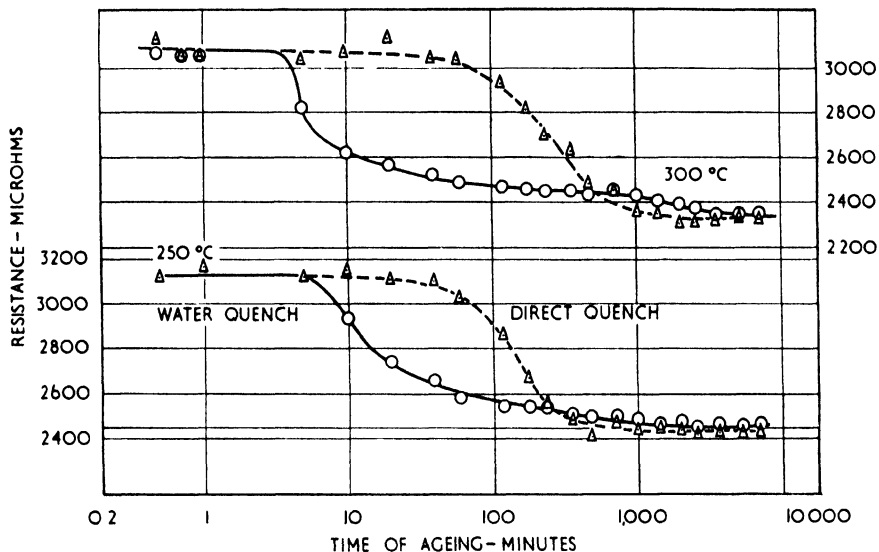


Fig. 38. Electrical resistance as a function of ageing time at constant ageing temperatures in water quenched and directly quenched specimens of an aluminium-copper alloy⁽¹¹³⁾

below 325°C brought the precipitation nearer to completion because it introduced the stable γ precipitate which was not observed in the

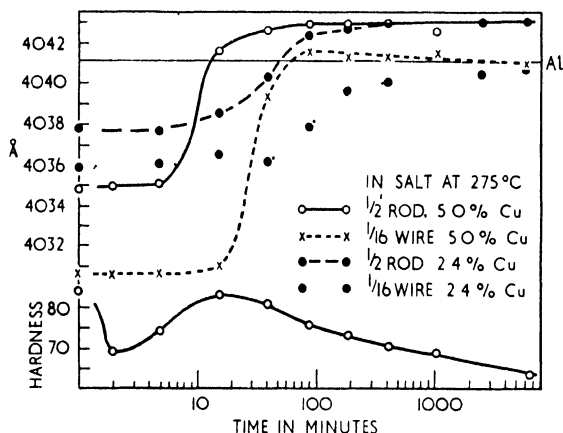


Fig. 39. Effect of quenching stresses on the rate of ageing of aluminium-copper alloys⁽¹¹⁴⁾

unworked material. On the other hand the tendency to form the intermediate γ' precipitate as the first decomposition product was reduced

by cold working even though the γ precipitate did not occur until ageing times greater than those to produce γ' in the absence of cold work.

The lattice distortions due to quenching strains frequently form a source of embarrassment particularly if the structure or properties are being determined close to the quenched surface. When quenching strains cannot be avoided it is essential that the experimental technique should be adjusted so that they occur equally in all specimens. Stress relief has occasionally been adopted before ageing.⁽¹²²⁾

MEHL and JETTER⁽²⁾ have enumerated the following idealized types of precipitation:

(a) *Ideal Precipitation* in which the distribution of precipitate is uniform and the concentration of the solute in the matrix decreases continuously and uniformly.

(b) *Continuous General Precipitation* in which the distribution of precipitate is uniform and the concentration of the solute in the matrix decreases continuously but not uniformly.

(c) *Continuous Localized Precipitation* in which the distribution of precipitate is non-uniform with a preference for grain boundaries and slip planes. The concentration of the solute in the matrix decreases continuously in restricted regions, but with differences between these regions.

(d) *Discontinuous Precipitation* in which the distribution of the precipitate is non-uniform, spreading into the grains from the grain boundaries, and the concentration of the solute in the matrix decreases discontinuously (cf. Figs. 34-37).

Real, as opposed to ideal, continuous precipitation may be taken as a mixture of types (b) and (c). The further proviso should be added to discontinuous precipitation that it involves fragmentation and recrystallization of the matrix and may occur in single crystals. Precipitation starts first at the grain boundaries in both real continuous and in discontinuous precipitation. In the real continuous type this initial precipitation at the grain boundaries has no further influence on the course of precipitation as a whole, which becomes continuous throughout the crystals. On the other hand, in the discontinuous type the initial grain boundary precipitation affects the whole course of the breakdown of the solid solution. The unchanged matrix immediately adjacent to this first-formed precipitate decomposes next and, since this occurs continually, the region containing precipitate spreads into the crystals (Figs. 34 and 35). The propagation of a decomposed region into an unchanged region is an essential part of this definition of discontinuous precipitation.

The evidence on discontinuous precipitation has been reviewed by HARDY⁽⁴⁾ and GEISLER⁽⁶⁾ both of whom concluded that discontinuous

precipitation would occur at any stage in the precipitation process at which the lattice distortions due to quenching strains and precipitation strains were sufficiently great to provide the necessary energy for recrystallization. If the initial nucleation in the grain boundaries leads rapidly to fragmentation (and recrystallization) the typical form of discontinuous precipitation spreading into the grain boundaries will occur before continuous precipitation has started. On the contrary, if the build-up of lattice strain at the grain boundaries proceeds more slowly, continuous precipitation will have commenced before the discontinuous type has started and the latter may have little influence on the process as a whole. The extreme case is when the "recrystallization"

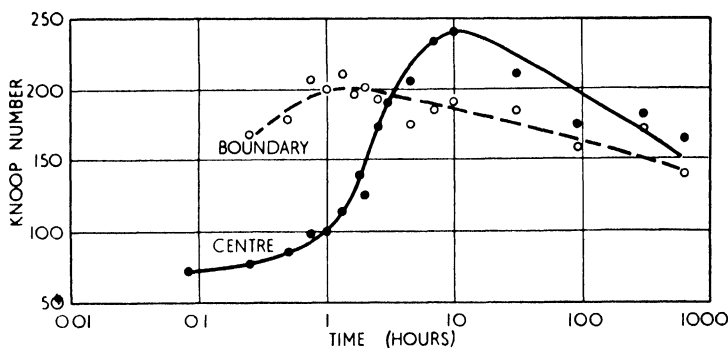


Fig. 40. Microhardness changes in a single crystal and grain boundary regions of a copper-1.6-per-cent-beryllium alloy aged at 400°C⁽¹²⁸⁾

involves only grain boundary movements⁽¹²³⁾ (Figs. 36 and 37). Discontinuous precipitation in single crystals is not ruled out although it must originate in lattice defects other than grain boundaries. The grain boundary precipitate and surrounding depleted regions illustrated in Fig. 28 is an example of localized precipitation which may or may not involve minor grain boundary adjustments.

The property changes during precipitation integrate the effect of the different extent to which the process has occurred throughout the specimen. GEISLER^{(6), (124), (125)} has elaborated this view and believes that the detailed shape of the ageing curve, notably the "multiple ageing peaks"⁽¹²⁶⁾ and "flats or plateaus"⁽¹²⁷⁾ are due to over-ageing and softening in the grain boundaries and slip bands before continuous precipitation in the remainder of the specimen leads to the second hardness rise. Over-ageing undoubtedly occurs more rapidly in grain boundary regions particularly when discontinuous precipitation has occurred,⁽¹²⁸⁾ see Fig. 40; but to conclude that this is usually responsible for anomalies on the ageing curves is to argue from the particular to the general. It also necessitates the view that the x-ray diffraction effects in the early stages of ageing result from the small particle size of the

precipitate rather than its detailed structure. There are occasions when the grain boundary reactions involving depletion of the solute and recrystallization exert a dominant influence. In particular, the decrease in the ductility because of the low strength and small volume of the material adjacent to the grain boundaries⁽¹²⁹⁻¹³¹⁾ may have an important effect on the corrosion properties.^{(111), (132)}

V. STRUCTURAL STATES IN PRECIPITATION

As explained in the Introduction a fairly detailed account is given of the structural changes accompanying precipitation in the relatively few systems which have been investigated with any degree of thoroughness.

X-ray Analysis

The study of the intensity distribution of x-radiation diffracted by the atomic arrangements in alloys undergoing precipitation has provided the bulk of the experimental evidence of the actual structural changes. The most significant results have been obtained from the anomalous non-Bragg diffractions arising out of departures from strict periodicity in the distribution of electron density in these alloys. The evidence consists of diffuse diffraction patterns which have to be interpreted in terms of atomic groupings and the validity of the individual interpretations has been, and still is, a matter of dispute. In this section of the report the evidence will be presented with any necessary discussion of the validity of alternative interpretations.

Interpretation of Diffraction Effects

The use of the reciprocal lattice concept is essential to interpret anomalous diffraction effects. Books by BUEGER⁽¹³³⁾ WILSON⁽¹³⁴⁾ or BUNN⁽¹³⁵⁾ should be consulted for a full treatment of the use of the reciprocal lattice. The following non-mathematical account is adequate for the purposes of describing the reciprocal lattice representation of a random solid solution and of the modifications to be expected during the course of precipitation.

Each set of parallel diffracting planes in the lattice of the crystal examined is represented by a point in the reciprocal lattice. This point lies on a line drawn through the origin of the reciprocal lattice parallel to the normal to the real lattice planes. The distance from that origin is proportional to the reciprocal of the inter-planar spacing of the real lattice planes. By thus representing all such sets of parallel diffracting planes an assembly of points is built up which can be shown to form a new lattice, the reciprocal lattice. The sets of parallel diffracting planes in the real crystal lattice produce diffraction spots on the x-ray photographs which can more readily be related to the reciprocal lattice points

solid solution cannot have strictly periodic electron density distribution unless the solute atoms are ordered. Thus prior to the first diffuse diffraction effects due to the initiation of the precipitation process the reciprocal lattice has already been modified by thermal scattering and solid solution effects. The former are of significant intensity and can readily be seen in single crystal photographs. Thus in Figs. 42-47, the diffuse bands running at 45° to the edges of the photograph are streaks due to thermal scattering. Diffraction theory due to LAÛE⁽¹³⁷⁾ predicts that the scattering due to random distribution of solute atoms in the solvent will form a very feeble continuous background which decreases in intensity with increasing distance from the origin of the reciprocal lattice. The x-ray work considered in this section of the report relates to alloys containing small concentrations of solute and it is unlikely that the predicted diffractions for random solutions would be of sufficient intensity to be detected. Thus prior to the initiation of precipitation we have an ideal reciprocal lattice modified only by some diffuse diffraction due to thermal vibration of the atoms.

Three Laïe conditions determine the direction of diffraction of the x-ray beam from a given set of planes in a crystal in which the electron density distribution is strictly periodic. Destruction of the strictly periodic distribution in one, two, or all three of the principal directions of the crystal, leads to relaxation of one, two, or all three of the Laïe conditions with consequent increasing indeterminacy of the direction of diffraction of the incident beam. The reciprocal lattice representation is appropriately modified as illustrated in Fig. 48. If the electron density distribution ceases to be strictly periodic in one direction only, i.e. one Laïe condition relaxed, the reciprocal lattice point is replaced by a line or rod. If a second Laïe condition is relaxed the rod becomes a plane. Thus atomic arrangements in which periodicity exists in two directions are represented by rods in reciprocal space. While arrangements in which periodicity exists in one direction only are represented by planar areas of diffraction in reciprocal space. For a mathematical treatment of these modifications, papers by EWALD⁽¹³⁸⁾ and PATERSON⁽¹³⁹⁾ should be consulted.

The terms reciprocal lattice points, reciprocal lattice rods and planar areas of diffraction in reciprocal space, are somewhat cumbersome. RAMACHANDRAN and WOOSTER⁽¹⁴⁰⁾ have already introduced the term "relp" for any reciprocal lattice point. In order to simplify and abbreviate the present discussion we shall give all reciprocal lattice terms the prefix rel, e.g. relrod for reciprocal lattice rod, relplane for a planar area of diffraction in reciprocal space, and relvolume for a diffuse volume of diffraction in reciprocal space. We prefer to use relpoint instead of relp for reciprocal lattice point as it is more in keeping with the other terms. Some of these terms are illustrated in Fig. 48.

The electron density distribution in a given direction ceases to be strictly periodic for one or more of the following reasons:

- (i) The distance between successive atoms ceases to be periodic;
- (ii) The x-ray scattering factors, i.e. electron densities of the successive atoms cease to be arranged in a periodic manner;
- (iii) The number of repeat units of the atomic arrangement becomes

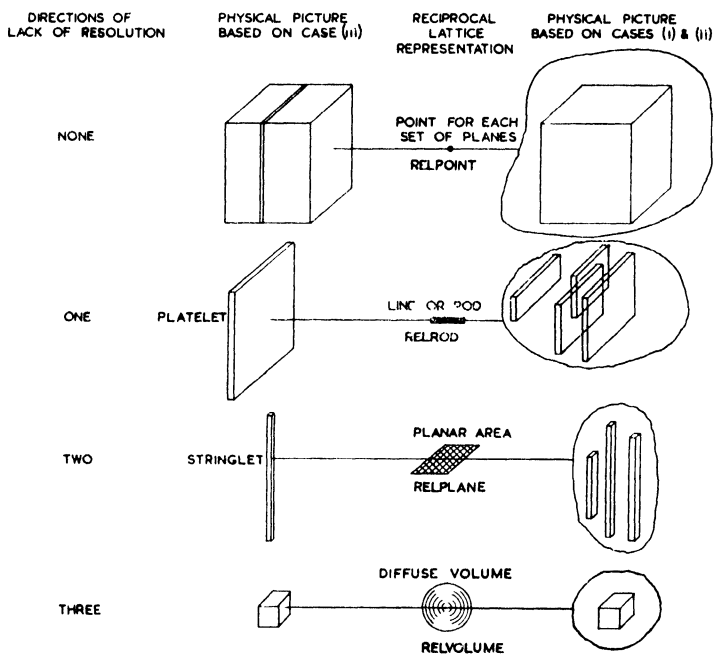


Fig. 48. Alternative interpretations of diffuse volumes (relvolumes), planar areas (relplanes) and rods (relrods) in reciprocal space

too small. This is analogous to the case of an optical diffraction grating with too few lines.

The cases (i) and (ii) in practice represent disordered arrangements of atoms. (i) represents irregularity in spacing, (ii) irregularity in the arrangement of different types of atoms which are regularly spaced. Conditions (i) and (ii) apply to a random distribution of solute atoms in solid solutions if the difference between the sizes and the scattering factors of the solute and solvent atoms are large enough but, as has been stated above, modifications of the reciprocal lattice due to this cause are unlikely to be detected. Case (iii) represents periodic or ordered arrangements of atoms insufficiently repeated, examples are very small particles and short range order.

GEISLER and HILL⁽¹⁴¹⁾ have chosen the small particle interpretation,

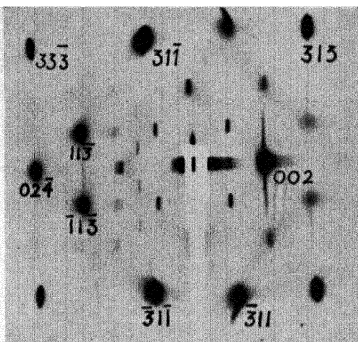


Fig. 42. Aged 8 hr at 130°C. Aluminium matrix diffraction spots have been indexed. Uniform streaks run to higher angles along $\langle 100 \rangle$ directions from $(002)_{Al}$ spot. $\lambda/2$ $(002)_{Al}$ spot can be seen in the streak from (000) towards $(002)_{Al}$. G.P. [1] structure

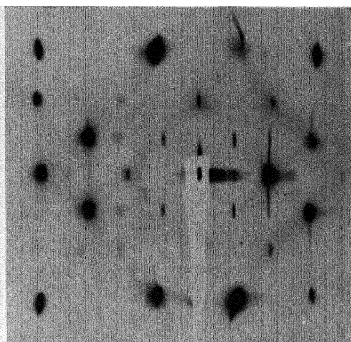


Fig. 43. Aged 3 days at 130°C. Intensity maxima are appearing in the streaks

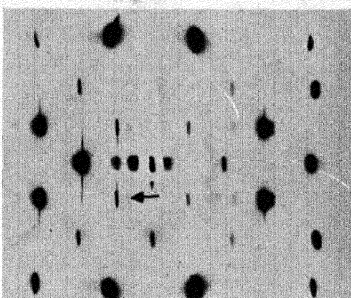


Fig. 44. Aged 11 days at 130°C. G.P. [2] spots have appeared in the G.P. [1] streaks and some faint θ' precipitate spots are present. The $(111) \theta'$ spot C orientation is marked

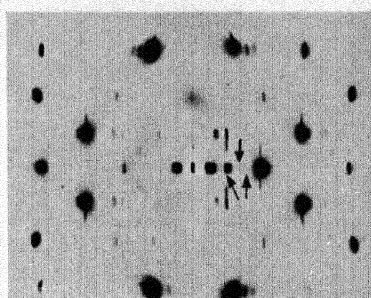


Fig. 45. Aged 8 hr at 190°C. θ' spots obvious. G.P. [2] is still present. The G.P. [2] spots near $(001)_{Al}$ and $(003)_{Al}$ and the θ' $(002) C$ orientation have been marked

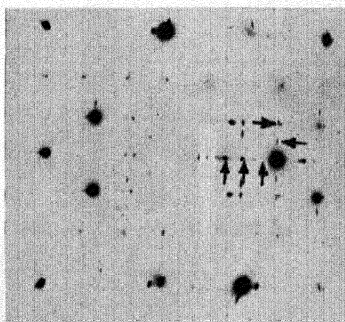


Fig. 46. Aged 1 day at 190°C. G.P. [2] and θ' structures present. The G.P. [2] spots at positions close to $(00\frac{1}{2})_{Al}$, $(001)_{Al}$, $(00\frac{3}{2})_{Al}$, $(0\frac{1}{2}2)_{Al}$ and $(012)_{Al}$ have been marked

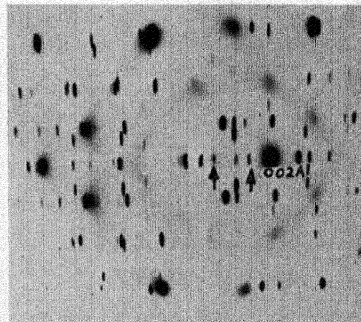


Fig. 47. Aged 100 days at 190°C. θ' structure. The two marked spots are the $(002) \theta' C$ orientation and that from θ' planes of 10.5 Å spacing

Single crystal films of aluminium-4-per-cent-copper alloys taken with monochromatic radiation (MoK_{α}) [100] vertical, crystal oscillated 15° from [010] parallel to the incident x-ray beam. Thermal scattering streaks run at 45° to the edges of the photographs⁽¹⁴⁵⁾

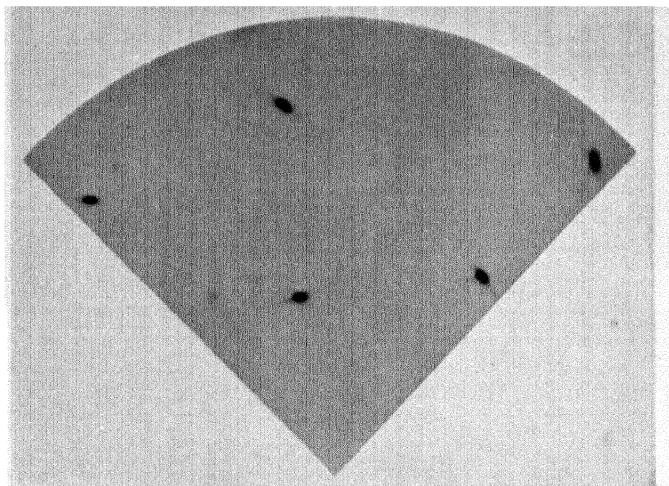


Fig. 49. 10 hr ageing. Monochromatic radiation

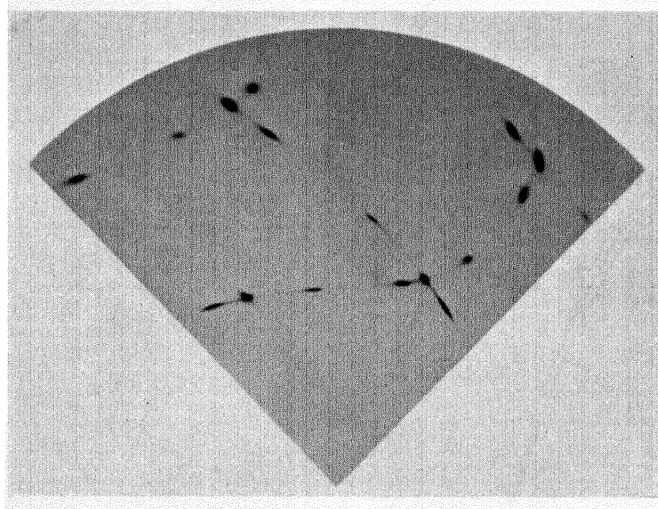


Fig. 50. 6 days ageing. Monochromatic radiation

Schiebold-Sauter photographs of an aluminium-38-per-cent-silver alloy, aged at 150°C⁽¹⁴²⁾

i.e. case (iii), as the correct explanation of diffuse diffractions in precipitation hardening alloys and have termed such particles stringlets and platelets as shown in Fig. 48. An attempt has also been made in Fig. 48 to illustrate the alternative interpretations based on cases (i) and (ii). Disturbance of periodicity will only be detectable in regions where a sufficiently high concentration of solute atoms has assembled. The boundaries of these regions have been defined in Fig. 48 and inside them the limited regions in which a periodicity in general different from that of the matrix lattice has been established. The external shape of the solute rich regions need bear no relation to the direction(s) in which periodicity exists.

Attempts have been made to use the position of the relrods to support one or other of these alternative interpretations. Thus, if the relrods pass through and are symmetrical about matrix relpoints then it is argued that the rods are merely an extension of those points due to disturbed periodicity in the matrix lattice in that direction: the disturbance being caused by segregation of solute atoms to form solute rich regions. Whereas if the rods pass through and are symmetrical about the points in reciprocal space where later precipitate relpoints appear it is argued that the initial diffraction effects are due to small particles of precipitate and result only from the particle size. The usefulness of this approach depends largely on the ease with which the alternatives can be distinguished and in the more difficult cases is very much dependent on the accuracy of the relplot.

Types of X-ray Photograph

A variety of x-ray techniques have been used by the numerous authors investigating precipitation processes. The diffracted intensity has usually been recorded on photographic film but in recent years use has been made of Geiger counters. These latter, and proportional counters which may soon be used, have advantages where quantitative measurements are involved.

The salient features of the x-ray techniques will be briefly outlined as a necessary preliminary to a discussion of the validity of evidence obtained by widely differing experimental methods. In the view of the present authors, techniques using single crystals and monochromatic radiation have advantages of ease and certainty of interpretation in terms of a relplot that more than justify the added experimental difficulties.

Single Crystal Methods employing Monochromatic Radiation

The moving film methods such as the Schiebold-Sauter used by GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ to investigate aluminium-silver agehardening alloys provide direct but somewhat distorted

pictures of the variation of diffracted intensity over an area of a plane in reciprocal space. Figs. 49, 50, 51 and 52 are photographs taken from their paper⁽¹⁴²⁾ and Fig. 53 identifies the diffraction spots in Fig. 50.

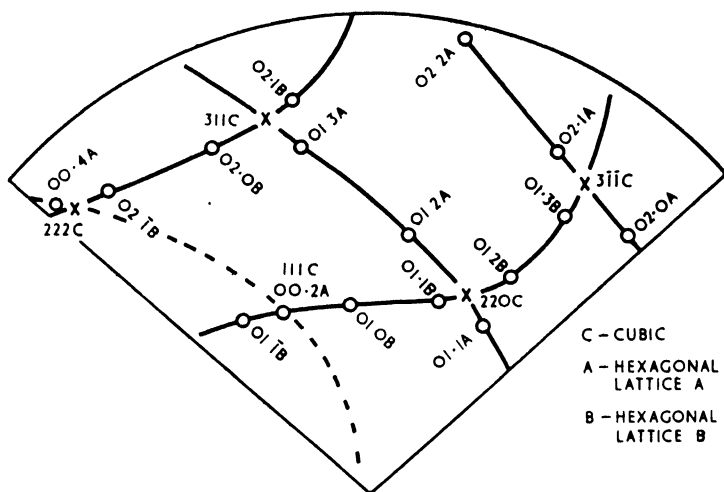


Fig. 53. Indices of diffraction spots in Fig. 50⁽¹⁴²⁾

The comparative simplicity of the monochromatic radiation photographs, Figs. 49 and 50, as compared with those employing both the

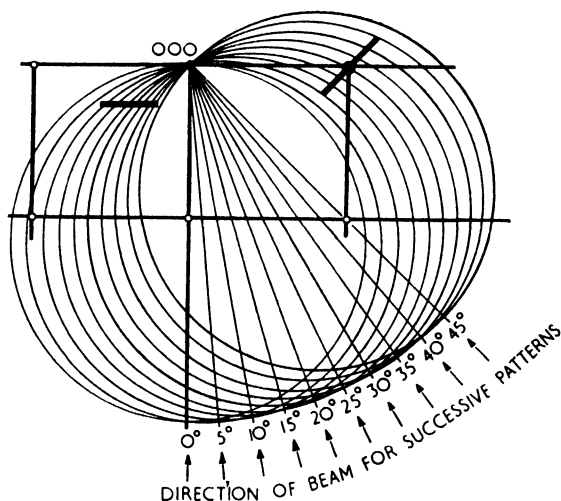


Fig. 54. Method of locating reciprocal lattice rods (relrods)⁽¹⁴¹⁾

characteristic and white radiations, Figs. 51 and 52, is apparent. Stationary film methods employing oscillating and stationary crystals as used by GUINIER⁽¹⁴³⁾, ⁽¹⁴⁴⁾ and by SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾

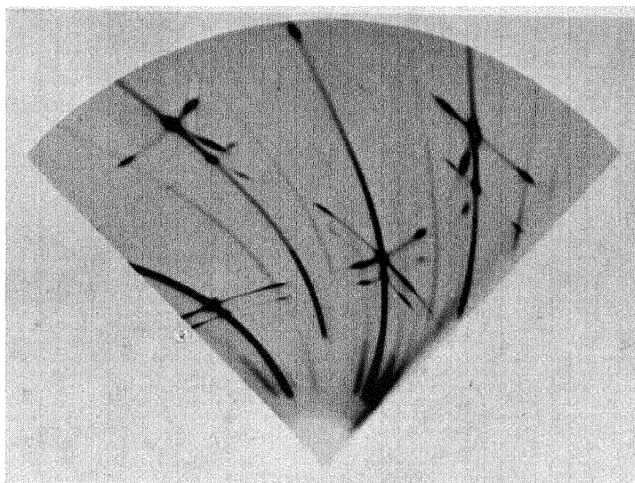


Fig. 51. 2 days ageing. White and characteristic radiation

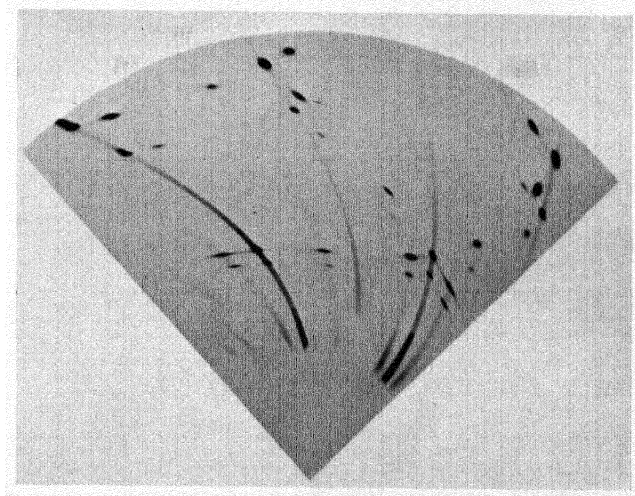


Fig. 52. 36 days ageing. White and characteristic radiation

Schiebold-Sauter photographs of an aluminium-38-per-cent-silver alloy, aged at $150^{\circ}\text{C}^{(142)}$

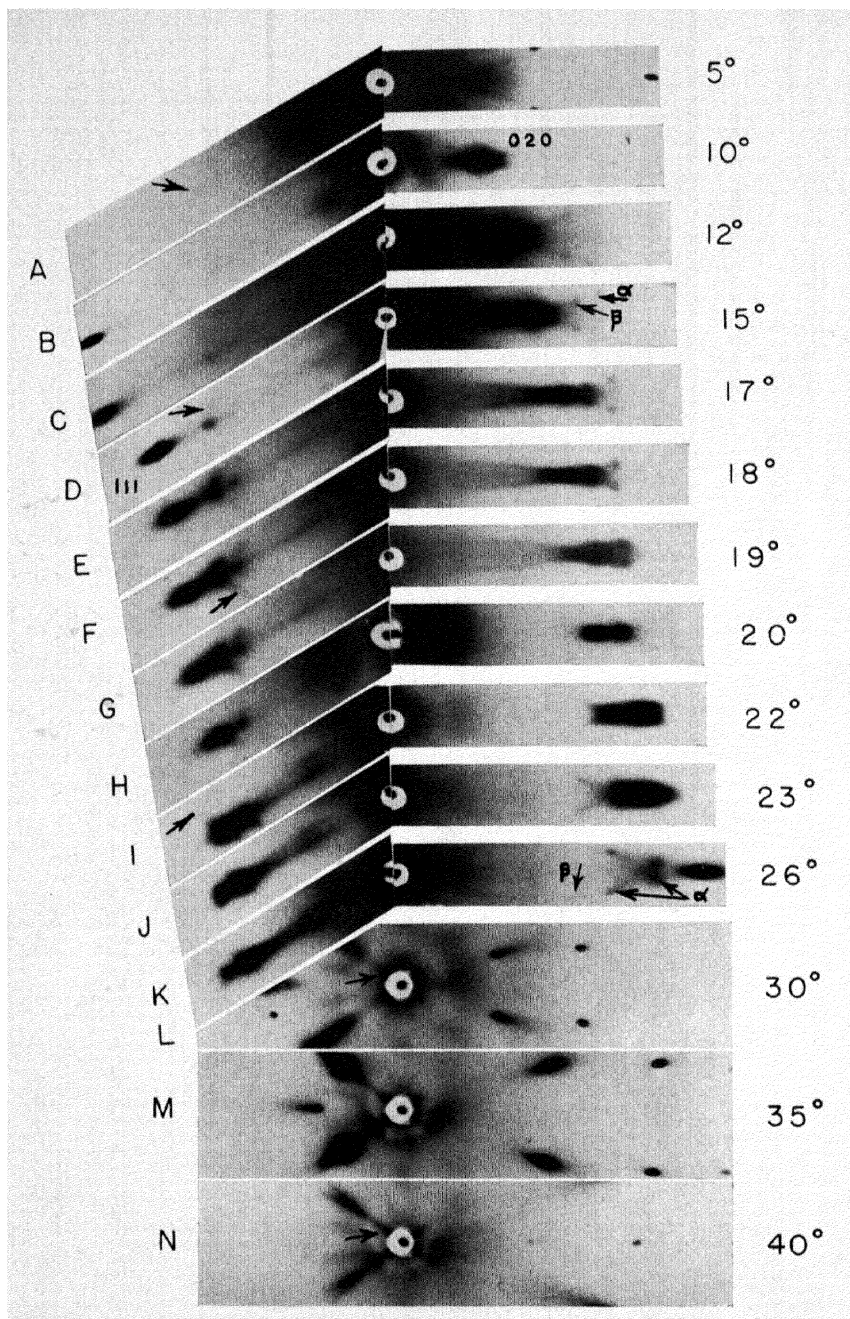


Fig. 56. Series of Laue patterns taken by GEISLER and HILL⁽¹⁴¹⁾ for an aged aluminium-20-per-cent-silver alloy. The angles given are those between [100] and the direct beam. White and characteristic radiation (Cu— K_{α} and K_{β}) used. These authors interpret the characteristic radiation effects as due to precipitate particles ranging from stringlets to platelets

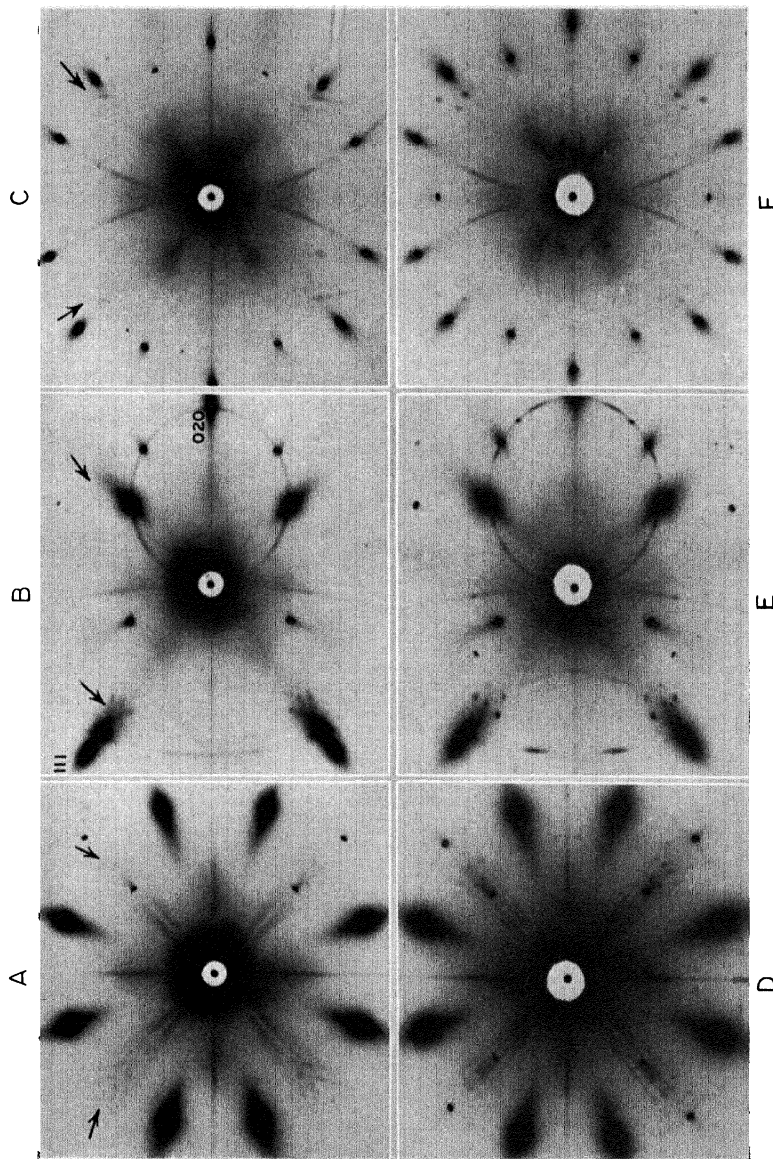


Fig. 57. Laue patterns of aged aluminium-1.4-per-cent-Mg₂Si alloys in stages which are predominantly stringlet (A, B and C) and platelet (D, E and F) Cu radiation. A, B and C aged 4 hr at 220°C; D, E and F aged $\frac{5}{8}$ hr at 300°C. A and D [100] parallel to beam and [001] vertical; B and E rotated 20° about [001]; C and F [110] parallel to beam⁽¹⁴¹⁾

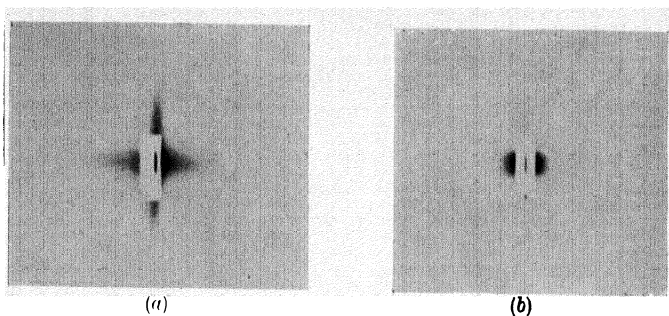


Fig. 58. (a) Small angle scatter film of aluminium-4-per-cent-copper alloy, aged 6 months at 30°C. Interpreted as G.P. [1] platelets 46 Å diameter; (b) small angle scatter film, aluminium-4½-per-cent-copper alloy aged 15 days at 130°C. Interpreted as G.P. [2] platelets 400 Å diameter⁽¹⁴⁵⁾

yield diffraction patterns which have to be converted by graphical methods, such as that illustrated in Fig. 54, to actual plots of the variation of diffracted intensity in planes in reciprocal space. The example chosen in Fig. 54 illustrates the location of relrods from a series of ten stationary photographs at 5° intervals, the changes in position of the appropriate diffraction spots on the series of films define the intersections of the rods with the reflection sphere. Six oscillating crystal photographs due to SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾ are reproduced in Figs. 42–47. The oscillation chosen was 15° about $[001]$ from $[100]$ parallel to the x-ray beam. Three such photographs would cover the

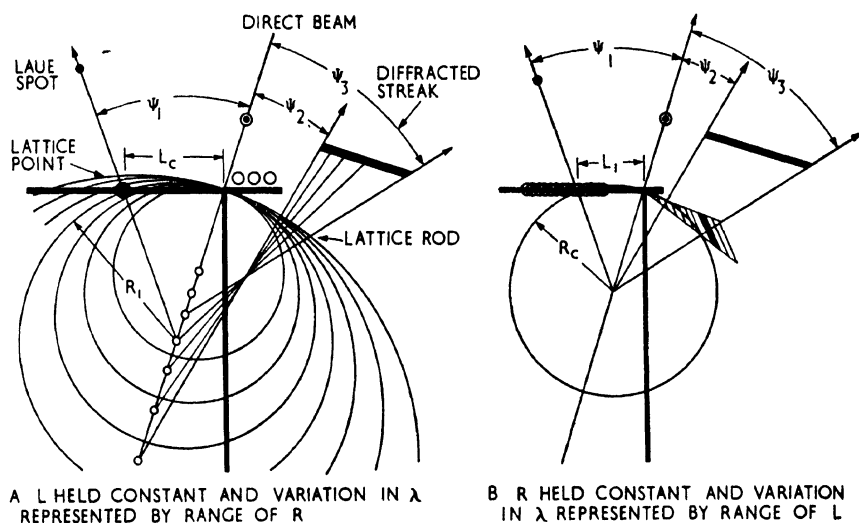


Fig. 55. Reciprocal lattice construction for white radiation⁽¹⁴¹⁾

45° range explored in Fig. 54 and would cover it more completely as the intensity changes of the relrods, which now appear as streaks on the films, would be continuously and not intermittently portrayed. Oscillating crystal methods are clearly to be preferred for the location of relrods. If weak diffraction effects such as those due to relplanes are believed to exist the stationary crystal method is more likely to detect them. It is not possible to distinguish between relplanes and relrods on oscillating crystal films if the planes or rods are parallel or perpendicular to the oscillation axis.

The Laue Method

This employs a stationary film, a stationary single crystal and white radiation, i.e. a polychromatic x-ray beam. The method has been used extensively by PRESTON,^{(146), (147)} and by BARRETT and GEISLER and

their co-workers.^{(148), (109), (128), (149)} It has the advantage of great experimental simplicity but the interpretation of the films is complicated by the many possible values of the x-ray wavelength as illustrated by Fig. 55 from GEISLER and HILL.⁽¹⁴¹⁾ The distance from the origin (000) to the (hkl) point, L , in relspace can be written as

$$L = R\lambda/d_{hkl} \quad . \quad . \quad . \quad (96)$$

where R is the radius of the sphere of reflection. The range of wavelengths in white radiation employed can be represented either by a range of R as in Fig. 55a or a range of L as in Fig. 55b.

Laüé films are of value when sufficient work is done by more precise methods to ensure that misleading assumptions are not being made. For instance SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾ have used the Laüé method extensively on aluminium-copper single crystals situated in actual hardness test pieces because of the experimental difficulties of applying monochromatic techniques to these particular crystals. The details of the structural changes had already been obtained by other methods on other single crystals and the Laüé work was merely used to establish the time relationship between the structural changes and the hardness changes. GEISLER and HILL⁽¹⁴¹⁾ have criticized the Laüé method and have shown that white radiation streaks through matrix spots in Laüé photographs do not necessarily correspond, as has been generally assumed, to relrods through matrix relpoints.

GEISLER and HILL have evolved a method in which the diffraction effects due to the characteristic K_α and K_β radiation are used to interpret Laüé photographs. Some of their photographs are reproduced in Fig. 56 and 57. The weak characteristic K_α and K_β diffraction effects which they employ are marked with arrows on some of the films, others may be seen without this assistance. The intense diffractions are those due to white radiation which are not used. The method would appear to be time consuming, since a large number of stationary films has to be taken whilst the interpretation of the films is difficult and not as certain as in the case of methods employing monochromatic radiation.

Methods of Examining Polycrystalline Aggregates

These include the normal powder methods, DEBYE, SCHERRER and SEEMAN-BOHLIN, which for many years were used in fruitless attempts to shed light on the early structural changes in agehardening alloys. The accuracy and sensitivity of the Debye-Scherrer method have recently been enhanced enormously by the use of the K_α component of monochromatic radiation in lieu of the characteristic components of white radiation. HARGREAVES⁽¹⁵⁰⁾ and JACK⁽¹⁵¹⁾ have detected early structural changes in precipitation processes in copper-nickel-iron alloys, iron-carbon, and iron-nitrogen alloys. JACK in particular has

claimed that he obtains diffraction patterns in which one and sometimes two Laue conditions are relaxed. The validity of this claim is discussed later.

The Russian worker ELISTRATOV⁽¹⁵²⁾ has developed an ingenious method based on the use of characteristic radiation effects in the presence of white radiation Laue spots. His method differs from that of GEISLER and HILL only in that glancing incidence, and not transmission films are taken, whilst the specimen is a coarse grained polycrystalline mass not a single crystal. The method (described fully in reference⁽¹⁵²⁾) must be time-consuming and tedious to a degree. A measure of doubt must always be attached to the details of the interpretation.

The Small Angle Scatter Method

The techniques employing monochromatic radiation described above are those normally employed in x-ray structural analysis. They determine the broad pattern of the distribution of diffracted intensity in reciprocal space. More refined experimental techniques are required to examine the intensity distribution at very small angles close to the origin of reciprocal space. GUINIER⁽¹⁵³⁾ has developed and applied these "small angle scatter" methods to agehardening alloys and has obtained much valuable information. The diffraction patterns can indicate the shape and approximate size of any group of atoms of x-ray scattering power sufficiently different from that of the matrix. In the general case when the solute rich regions or precipitate particles are of a range of shapes, sizes and orientations, the intensity of diffraction near (000) varies in a complex manner with the angle of diffraction and the results are difficult to interpret. GUINIER⁽¹⁵³⁾ and GUINIER and FOURNET⁽¹⁵⁴⁾ have shown that two special cases exist where an interpretation can readily be made. They are: (i) particles of fixed shape and orientation; and (ii) particles of uniform size. Widmanstätten patterns obtained in the later stages of the precipitation process in agehardening alloys suggested that first formed precipitate or solute rich regions would be of fixed orientation with respect to the matrix. GUINIER obtained small angle scatter patterns of aluminium-copper⁽¹⁵³⁾ and copper-beryllium⁽¹⁵⁵⁾ alloys which indicated regions of the expected platelike shape parallel to the {100} planes of the matrix. The two patterns reproduced in Figs. 58*a* and 58*b*, due to SILCOCK *et al.*,⁽¹⁴⁵⁾ are of aluminium-copper alloys and are interpreted as due to copper rich platelets 46 and 400 Å diameter respectively. GUINIER also examined aluminium-silver^{(143), (156)} and aluminium-zinc⁽¹⁵⁷⁾ alloys in the early stages of agehardening and obtained surprisingly different patterns of the type reproduced in Fig. 59 (facing p. 200) (GUINIER⁽¹⁵⁶⁾) which were interpreted as due to roughly spherical solute rich regions.

The diffraction patterns obtained at very small angles to (000) must in theory occur about other relpoints and GUINIER⁽¹⁵⁶⁾ and SILCOCK *et al.*⁽¹⁴⁵⁾ amongst others have presented evidence of their detection. They are, however, most intense and most readily detected about (000) where no Bragg diffraction occurs, elsewhere they are sometimes masked by the halation due to the necessarily over-exposed Bragg spots. The patterns do not provide any information about the structure of the groups unless they can be detected about relpoints other than (000); it can then be said that the structure of the group of atoms must be related to the structure represented by the relpoint in question. If the patterns are symmetrical about matrix relpoints as GUINIER⁽¹⁵⁶⁾ has shown to be the case for aluminium-silver alloys in the early stages of ageing at 150°C the groups of atoms can be said to occupy matrix lattice sites. GUINIER,⁽¹⁵³⁾ PRESTON^{(146), (147)} and SILCOCK *et al.*⁽¹⁴⁵⁾ have shown that for aluminium-copper alloys the patterns detected in the region of (000) are also obtained in the region of matrix relpoints but in this case they are asymmetrical with respect to those points indicating a relationship with a modified matrix structure.

Referring back to Fig. 48 and the relevant discussion it will be recalled that the shape of the first formed solute rich regions could not be readily determined from the reciprocal lattice plots because of the alternative interpretations; the evidence supplied by the small angle scatter results is therefore of primary importance. Thus if the small angle scatter patterns show that spherical solute rich regions are being formed and concurrently relrods are found in other parts of reciprocal space then the rods in question cannot be due principally to particle size effects and a disordered arrangement of atoms in the direction of the rods must be the principal cause of their existence.

The small angle scatter method has two limitations, the difference in scattering power $|f_P - f_M|$ must be significant otherwise patterns cannot be obtained, secondly the size range of the method is very restricted. The first limitation prevents the method from being of any value for aluminium-magnesium or aluminium-magnesium-silicon age-hardening alloys. The smallest spheres detected in the aluminium-silver case were 16 Å diameter, the largest 60 Å.⁽¹⁵⁶⁾ These results were obtained using a double monochromator, a refinement of experimental technique⁽¹⁵⁸⁾ by which the upper limit of the range is increased somewhat. The pattern reproduced in Fig. 58a represents the lower limit of size in the aluminium-copper agehardening alloys. The upper limit is of the order of 600 Å.

Experimental Evidence

Individual papers will now be grouped under the alloy systems to which they relate and an attempt will be made to assess the validity of the

evidence they present in order to arrive at the most probable precipitation mechanism in each system. Precipitation alloys which have not been studied in sufficient detail or with suitably sensitive experimental methods will not be discussed.

Aluminium-copper Agehardening Alloys

In 1938 GUINIER^{(159), (160)} and PRESTON⁽¹⁶¹⁾ independently announced new experimental results from x-ray studies of aluminium-copper alloys and gave interpretations which were in remarkably good agreement. Previous x-ray work had been carried out on polycrystalline aggregates: both GUINIER and PRESTON confined their attention to single crystals and were able to detect anomalous diffraction effects at early stages in the ageing process which they interpreted as being due to groups of copper atoms segregating on to {100} planes in the aluminium lattice. The copper-rich zones produced streaks on PRESTON's Laüé photographs which he interpreted as relrods associated with and passing through the aluminium matrix relpoints but not symmetrical about them. In three further papers PRESTON^{(146), (147), (162)} amplified his results and developed a theory of diffraction by a lattice modulated in both inter-atomic spacing and scattering power. He showed that such a modulated lattice could be responsible for the asymmetry of the position of the relrods with respect to the aluminium matrix relpoints and hence suggested that the net effect of the re-grouping of the copper atoms was to modify the x-ray scattering power of, and spacing between, very small groups of (100) planes distributed through the crystal. Aluminium atoms were replaced by the smaller copper atoms with approximately twice the x-ray scattering power and localized modulations of the aluminium lattice took place but no new structure developed.

Later in the ageing process the streaks on the Laüé photographs broke up into discrete spots represented by relpoints when, in PRESTON's view, the zones rich in copper had grown to an extent which permitted the development of a new structure, θ' ,⁽¹⁴⁵⁾ coherent with the aluminium matrix across the {100} planes. Over-ageing produced the conversion from θ' to the equilibrium precipitate $\theta(\text{CuAl}_2)$.

* GUINIER's views were in complete accordance with those of PRESTON at this stage. Details of his work were given in two papers published in 1939.^{(153), (163)} The zones rich in solute atoms, formed on certain planes in the solvent matrix and retaining what is essentially the structure of the matrix, are now generally referred to as Guinier-Preston zones. Subsequently GUINIER published two important papers^{(143), (164)} in which he claimed to have convincing evidence of the formation of an ordered structure subsequent to the initial Guinier-Preston zones and prior to the formation of the intermediate coherent

precipitate θ' , with which it was shown to co-exist. GUINIER has termed this structure θ'' and HARDY⁽⁴⁾ has used G.P. zone [2], reserving the term G.P. zone [1] for the first formed solute rich regions. The sequence of photographs⁽¹⁴⁵⁾ of oscillating crystal films of a 4 per cent Cu alloy aged at 130°C and at 190°C shown in Figs. 42–47, will be used to illustrate the validity of GUINIER's claim. If the variation in the distribution of diffracted intensity along the line (000) to the (002) Bragg spot from the aluminium matrix is studied, it will be seen that in Fig. 42 the intensity of the streak falls uniformly from a maximum at the edge of the beam trap to vanish close to (002)_{Al}. The only irregularity is that caused by the Bragg diffraction of the $\lambda/2$ harmonic from the (002)_{Al} planes. This $\lambda/2$ (002)_{Al} Bragg diffraction can be seen to cause a maximum halfway between (000) and (002)_{Al}. Turning to Fig. 43, after three days' ageing two intensity maxima can be seen appearing; after eleven days three maxima occur, Fig. 44. These maxima are the G.P. [2] spots appearing in what was (Fig. 42) a G.P. [1] streak. In Fig. 45, θ' spots can be clearly seen concurrently with those due to G.P. [2]. The θ' spots are also visible in Fig. 44 where the (111) spot of θ' in the *C* orientation is marked with a small arrow. Figs. 44 and 45 show the separation of the (002)_{Al} $\lambda/2$ spot and the second G.P. [2] maximum. Figs. 46 and 47 will help to identify the θ' and G.P. [2] spots. Fig. 46 shows both structures with some of the G.P. [2] spots marked with arrows. In Fig. 47 only θ' appears and the (002) spot of θ' in the *C* orientation and the spot near (000) due to θ' planes of 10.5 Å spacing have been marked. Neither of these spots should appear if either of the θ' structures given by PRESTON⁽¹⁴⁷⁾ and WASSERMANN and WEERTS⁽¹⁶⁵⁾ were correct. The three G.P. [2] spots could be given approximate indices (00 $\frac{1}{2}$) (001) and (00 $\frac{3}{2}$) with respect to the aluminium lattice. They are, in fact, a little displaced towards the higher angles, the (001) G.P. [2] lies outside the (002)_{Al} $\lambda/2$ spot as has been pointed out with reference to Fig. 44 and to Fig. 45 where the doublet is marked with an arrow. The (00 $\frac{3}{2}$) G.P. [2] and the (002) *C* orientation θ' have also been marked in Fig. 45. GUINIER⁽¹⁶⁴⁾ found that several weeks' ageing of a 4 per cent copper alloy at 150°C gave his sharpest G.P. [2] spots but some months at 140°C failed to achieve similar sharpness and at 180°C θ' succeeds G.P. [2] without sharp G.P. [2] spots ever forming. It is clear from GUINIER's work and that of SILCOCK *et al.*⁽¹⁴⁵⁾ that the conditions for formation of large fully ordered G.P. [2] platelets capable of yielding really sharp diffraction spots are critical.

JAGODZINSKI and LAVES⁽⁵⁾ in a paper published in 1949 have criticized GUINIER's interpretation of his results. Their criticism is based on the fact that the diffusion coefficients for copper in aluminium, obtained by extrapolation from experimental values at higher temperatures, are not consistent with the concentration of copper which GUINIER estimates

the G.P. [1] platelets contain. They argue that the maximum copper content of these platelets is 10 per cent and hence infer that the number of platelets is much greater than that visualized by GUINIER. The diffraction effects due to the platelets they therefore associate more with lattice distortion than with increased scattering power. They further argue that this distortion due to a large number of platelets will tend to cause the platelets to take up a preferred spacing. The diffracted intensity along (000) to (004)_{Al} from a model such as that they postulate has recently been calculated by BAGARYATSKII⁽¹⁶⁶⁾ by a method due to

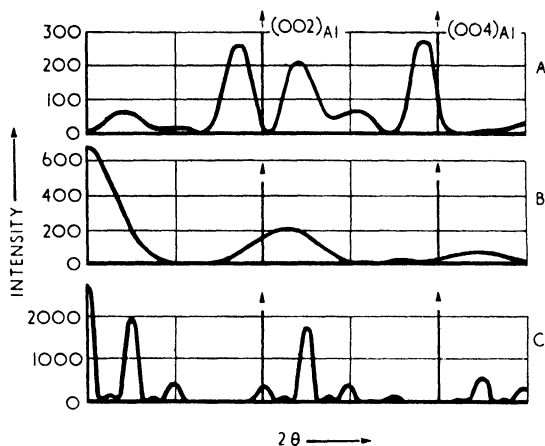


Fig. 60. Calculated diffracted intensity distribution along (000) $\rightarrow$ (004)_{Al} for aluminium-copper alloys⁽¹⁶⁶⁾

(A) For the model suggested by JAGODZINSKI and LAVES.

(B) For the G.P. [1] structure due to PRESTON and GUINIER.

(C) For the G.P. [2] structure due to GUINIER with the simplifying assumption that $c = 2a$.

MERING.⁽¹⁶⁷⁾ Fig. 60 is reproduced from BAGARYATSKII's paper: curve (A) is the calculated intensity distribution for JAGODZINSKI and LAVES⁽⁵⁾ model; (B) that for the model visualized by GUINIER and PRESTON in the early stages of agehardening; (C) corresponds to the structure put forward by GUINIER for G.P. [2]. Clearly there is no agreement between (A) and experiment whereas (B) and (C) are in good agreement with the intensity distribution along (000) $\rightarrow$ (002)_{Al} at the appropriate stages in the precipitation process, as may be seen by comparing these curves with Figs. 42 and 43 or 44 respectively. It would appear that the conclusions drawn by JAGODZINSKI and LAVES from the extrapolation of the diffusion coefficients in this case were not justified.

GUINIER⁽¹⁶⁸⁾ has recently attempted to estimate the fraction of the total quantity of the G.P. [2] and θ' precipitated as a function of ageing time. He has shown that, in the case of θ' for a 4 per cent copper alloy

aged at 200°C, his results are in good agreement with those obtained by LANKES and WASSERMANN⁽¹²²⁾ by dilatometric measurements. Fig. 61 illustrates the agreement. Fig. 62 also from GUINIER's paper⁽¹⁶⁸⁾ compares the fractions of G.P. [2] and θ' precipitated at 150°C, 180°C and

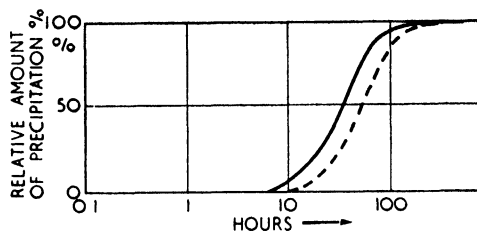


Fig. 61. Variation of the fraction of θ' precipitated in aluminium-4-per-cent-copper alloys as a function of ageing time at 200°C⁽¹⁶⁸⁾
 — From the dilatometric measurements of LANKES and WASSERMANN,⁽¹²²⁾
 --- From GUINIER's quantitative x-ray measurements.

190°C. Similar estimates have been carried out for θ' by SILCOCK *et al.*⁽¹⁴⁵⁾ The accuracy of GUINIER's G.P. [2] figures is open to question, the diffracted intensities due to the G.P. [2] precipitate are in general

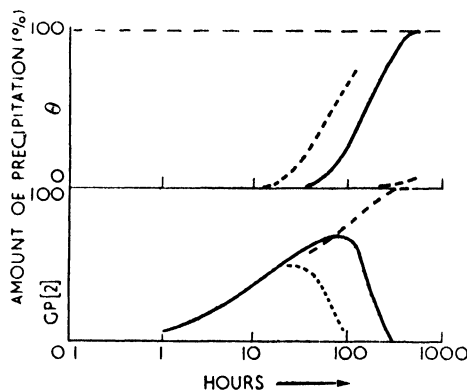


Fig. 62. Variation of the fraction of the θ' and G.P. [2] or θ'' structures precipitated with isothermal ageing time: in aluminium-4-per-cent-copper alloys⁽¹⁶⁸⁾
 Ageing at 190°C
 — „ „ 180°C
 --- „ „ 150°C

modified both by small particle and disorder effects and are not suitable for quantitative measurement.

SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾ have carried out the first really comprehensive examination of the structural changes occurring in an agehardening system. The study has covered a wide range of degrees

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of supersaturation and has included sufficient work on the actual hardness specimens used by HARDY⁽¹⁰¹⁾ to enable the structural findings to be directly related to the hardness curves as in Figs. 63 and 64. Table 2 lists the structures first detected for various copper contents at ageing temperatures from 130°C to 240°C.

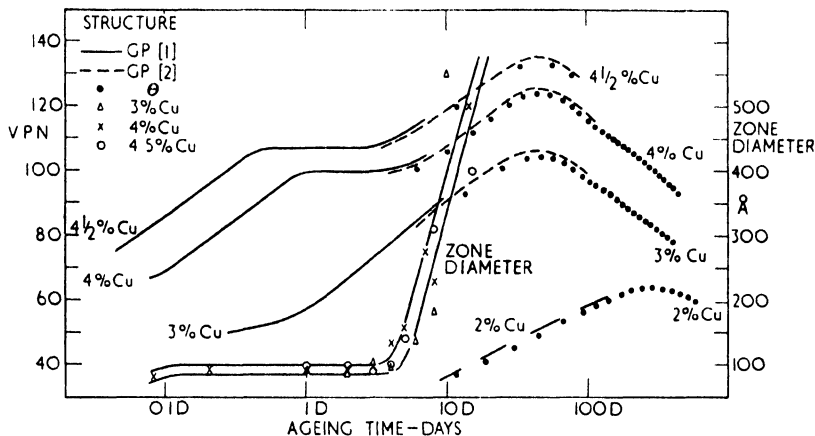


Fig. 63. Structures and zone diameters of aluminium-copper alloys aged at 130°C in relation to the hardness-ageing curves⁽¹⁴⁵⁾

Examination of Figs. 63 and 64 shows that the maximum sequence of intermediate stages in the precipitation process tends to be favoured by a high degree of supersaturation and a low ageing temperature. Thus,

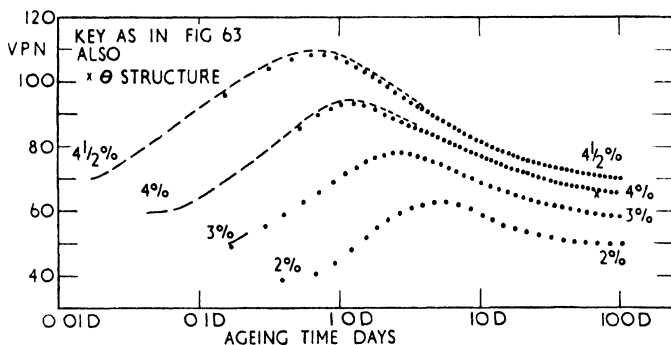


Fig. 64. Structures of aluminium-copper alloys aged at 190°C in relation to the hardness-ageing curves⁽¹⁴⁵⁾

on ageing at 130°C the sequence in which the structures dominate the x-ray pattern is always

$$\text{G.P. [1]} \rightarrow \text{G.P. [2]} \rightarrow \theta' \rightarrow \theta \quad . \quad . \quad . \quad . \quad (97)$$

except in the case of the 2 per cent alloy. As shown in Table 2 results with this alloy were somewhat variable suggesting that the degree of

TABLE 2

Structures first Detected for Increasing percentages of Copper

Ageing Temperature °C	2% Cu	3% Cu	4% Cu	4½% Cu
110	G.P. [1]	G.P. [1]	G.P. [1]	G.P. [1]
130	θ' or θ' and G.P. [2] or G.P. [1]	G.P. [1]	G.P. [1]	G.P. [1]
165		θ' and little G.P. [2]	G.P. [1] and G.P. [2]	
190	θ'	θ' and very little G.P. [2]	G.P. [2] and little θ'	G.P. [2] and G.P. [1]
220	θ'		θ'	θ'
240			θ'	

supersaturation existing is near some critical value. G.P. [1] was never detected on ageing at 190°C. G.P. [2] occurred at the higher degrees of supersaturation but θ' was the first detected structure for the 2 per cent

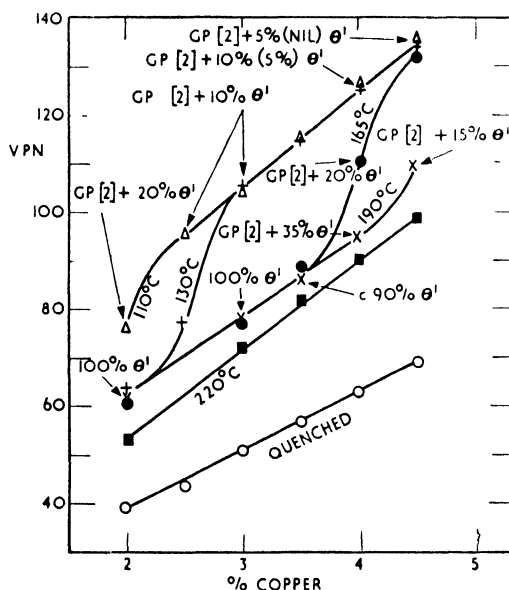


Fig. 65. Quenched and peak hardness values and structures of aluminium-copper alloys aged at different temperatures⁽¹⁴⁵⁾. Percentages of θ' in brackets are for ageing at 110°C

copper alloy. θ' was always the first structure detected on ageing at 220°C and 240°C. These results are in very good agreement with those of GUINIER with one minor exception. GUINIER⁽¹⁶⁸⁾ records that he never detects G.P. [2] without having first detected G.P. [1] whereas ageing at 190°C SILCOCK *et al.* detected G.P. [2] as their first structure for the 4 per cent and 4½ per cent alloys. It was also present initially in the 3 per cent copper alloy (see Table 2).

Figs. 63 and 64 show that the higher peak hardnesses are associated with the G.P. [2] structure,

a fact which is brought out more clearly by Fig. 65.⁽¹⁴⁵⁾ Here the quenched and peak hardness values of alloys aged at different temperatures are plotted against composition and can be seen to fall into two main groups. (The 4 per cent copper alloy aged at 165°C, the 2.5 per cent copper alloy aged at 130°C and the 2 per cent copper alloy aged at 110°C represent an intermediate stage.) The structures associated with each of the hardness points have been added to the original diagram due to HARDY⁽¹⁰¹⁾ and it will be noted that the upper group of peak hardness values occurs in alloys in which G.P. [2] is the dominating structure. The intermediate values and the lower group all contain larger amounts of the θ' structure.

If the interpretation of the x-ray evidence favoured by GUINIER⁽¹⁶⁴⁾ and by SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾, equation (97), be accepted then using this equation in conjunction with Table 2 we have a complete picture of the various structural sequences occurring under all degrees of supersaturation. The only alternative view of the x-ray evidence would be to assume that the streaks interpreted as due to G.P. [1] were in fact due to thin platelets of G.P. [2]. GUINIER has always regarded G.P. [1] and G.P. [2] as distinct structures but has not published direct experimental evidence to support his view. SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾ have recently reported two findings which strongly suggest that the distinction is a valid one.

First, they have applied the small angle scatter method to study in some detail the relationship between the diameter of the G.P. zones [1] and the stage in the two stage hardness curves obtained by HARDY,⁽¹⁰¹⁾ Fig. 63. As this figure shows the G.P. [1] diameter remained substantially constant across the flat of the two stage hardness curves and the diameter of the platelets increased rapidly at the end of the flat concurrently with the appearance of the G.P. [2] or θ'' structure on the oscillating crystal films. If the G.P. [1] regions were merely thin platelets of G.P. [2] there seems no logical reason why their growth process should be so markedly discontinuous.

SILCOCK *et al.* have also studied the development of the sharp G.P. [2] spots in the G.P. [1] streaks in some detail. Their measurements showed that the maxima of the diffuse spots which first developed did not coincide with the position of the sharp spots obtained after longer ageing periods at 130°C. The c parameter of the G.P. [2] structure changed from 7.9 Å to 7.6 Å suggesting an ordering process in which aluminium atoms were being removed from the structure and the degree of misfit with the matrix lattice increased. When G.P. [1] was not detected prior to G.P. [2] during ageing at 190°C the c parameter was constant at 7.6 Å. The weight of the evidence therefore supports the view that G.P. [1] and G.P. [2] can be regarded as separate structures.

KÖSTER^(168a) has very recently reported in brief outline work by KÖSTER and GEROLD on the 5 per cent copper alloy. Their experimental findings are in very good agreement with those of SILCOCK, HEAL and HARDY. Their figure for the value of the c parameter of the G.P. [2] structure (7.68 Å) confirms that of SILCOCK *et al.* and their sequence of structures on ageing at 125°C, 200°C and 230°C are those to be expected from the work of the English authors. KÖSTER and GEROLD state that their calculation of the scattering from various models of the G.P. [1] structure indicate that the best agreement with experiment is obtained by assuming a single plane of copper atoms with the distortion due to this plane falling off linearly through at least fifteen planes of aluminium atoms. They claim that this model provides better agreement with experiment than that suggested by GUINIER and PRESTON, Fig. 60b.

The detailed atomic arrangements of the structures occurring, equation (97), are not all well established. The structure of θ is beyond doubt but both GUINIER⁽¹⁴³⁾ and SILCOCK *et al.*⁽¹⁴⁵⁾ have noted the occurrence of θ' diffraction spots which cannot be explained by PRESTON's structure⁽¹⁴⁷⁾ or that of WASSERMANN and WEERTS.⁽¹⁶⁵⁾ GUINIER'S⁽¹⁶⁴⁾ suggested G.P. [2] structure is not entirely in accord with the more recent and extensive work of SILCOCK *et al.* The G.P. [1] structure is very ill defined. It is clear that copper atoms concentrate in certain preferred {100} planes, but as yet it is not clear (i) to what extent copper atoms have replaced the aluminium atoms, (ii) how many planes are enriched in copper atoms and (iii) the extent of the distortion caused by this concentration of copper in adjacent aluminium lattice planes. When they are published the calculations of KÖSTER and GEROLD may reduce the uncertainty.

Equally the experimental evidence does not always determine whether the sequence of structures arises by a series of allotropic changes or by independent nucleation from the matrix. GUINIER⁽¹⁴³⁾ has shown by the orientation relationships that θ can be formed by an allotropic change from θ' or by independent nucleation from the matrix depending on the degree of supersaturation. SILCOCK *et al.*⁽¹⁴⁵⁾ have shown that G.P. [1], G.P. [2] and θ' in turn can be the first detected structure under suitable conditions of supersaturation which strongly suggests that G.P. [2] and θ' can be nucleated independently.

Before it can be assumed that the preferred mode of formation is always that of independent nucleation due weight has to be given to two other experimental findings of SILCOCK *et al.* They are: (i) the change in the c parameter of G.P. [2] from 7.9 Å to 7.6 Å, when it is preceded by G.P. [1] during ageing at 130°C, whereas a constant value of 7.6 Å is obtained on ageing at 190°C when no G.P. [1] is detected; and (ii) the finding that when first detected the θ' platelets are always thicker than the G.P. [2] platelets concurrently present except when both form

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simultaneously as in the 2 per cent copper alloy aged at 130°C and the 3 per cent copper alloy aged at 165°C.

There can, however, be no doubt that the pattern of precipitation, equation (97), originally due to GUINER, and subsequently confirmed for a wide range of supersaturations by SILCOCK, HEAL and HARDY, Figs. 63 and 64, and Table 2 is entirely correct.

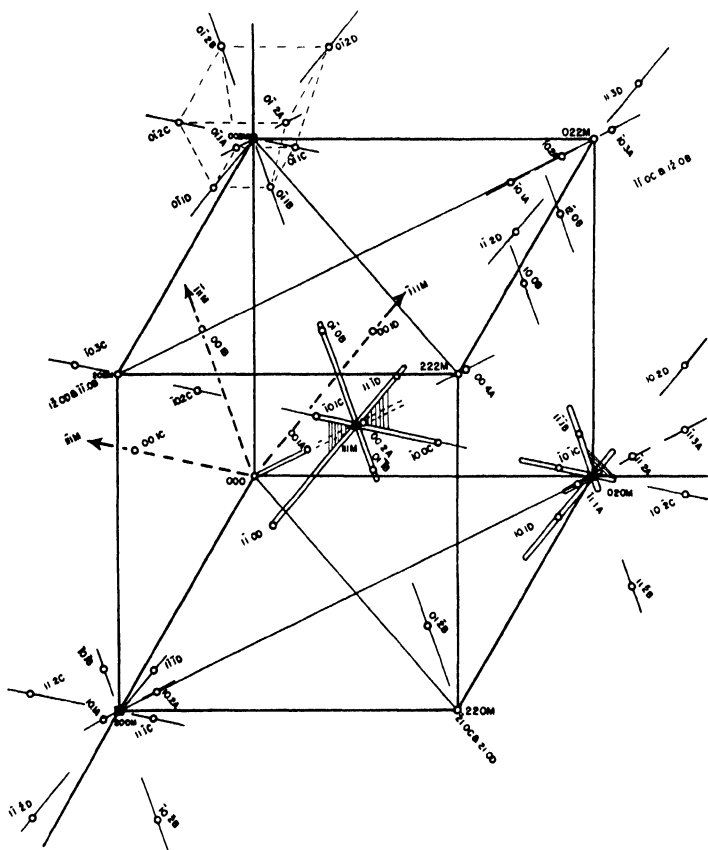


Fig. 66. Portion of the reciprocal lattice for an aluminium-20-per-cent-silver alloy aged 8 years at room temperature⁽¹⁴¹⁾

Aluminium-silver Agehardening Alloys

The early work of BARRETT and GEISLER⁽¹⁴⁸⁾ and BARRETT, GEISLER and MEHL,^{(149), (109)} established the existence of an intermediate transition precipitate γ' of hexagonal structure coherent with the matrix on $\{111\}$ planes: γ' was succeeded by an equilibrium precipitate γ . These authors used the Laue method to study the ageing of a 20 per cent silver alloy. In their view the theory put forward by PRESTON and GUINIER for aluminium-copper alloys involving segregation of solute atoms to

preferred planes of the matrix would explain the findings in the aluminium-silver system. However, they were able to offer an alternative theory which they considered equally satisfactory. They assumed that the silver rich platelets had a structure differing from that of the matrix, the limited thickness of the platelets being responsible for the streaks on the Laüé films. In this case the breaking up of the streaks into well-developed precipitate spots as ageing continued represented purely an increase in thickness of the platelets to a stage where normal three-dimensional diffraction effects were obtained. The Laüé streaks on this point of view are mainly a particle size effect and do not represent a lack of periodicity in the matrix lattice as a new structure has been formed. In 1948 GEISLER and HILL⁽¹⁴¹⁾ extended the American work on this alloy using the modified version of the Laüé method which they have developed. Fig. 66 is a reproduction of their plot of a portion of the reciprocal lattice for an ageing period of eight years at room temperature. Both matrix and γ' points are plotted, thus (220) M is the (220) matrix point and (01 $\cdot\bar{2}$) B the (01 $\cdot\bar{2}$) point of the B orientation of γ' . The observed relrods are plotted as double lines and include a rod through the origin (000). These authors also reported the detection of relplanes and argued that these relplanes and the relrods passed through and bore a closer relationship to γ' precipitate relpoints than to matrix relpoints. This argument is open to question. In actual fact the relrods frequently appear to run from one γ' precipitate relpoint through a matrix relpoint to another γ' precipitate relpoint. This suggests a relaxation of one Laüé condition which is associated with both structures, that is some transition from one to the other. Nevertheless, they interpreted their results as being due to stringlets and platelets (see Fig. 48) of the transition precipitate γ' .

TABLE 3

Time for Appearance of Platelets on Small
Angle Scatter Patterns at Different Ageing
Temperatures, GUINIER⁽¹⁶⁶⁾

<i>Ageing Temperature °C</i>	<i>Time</i>
20	Not observed
100	Not observed (up to 2 months)
140	100 hours
165	22 "
255	18 minutes
300	3 "
342	30 seconds
405	< 15 "

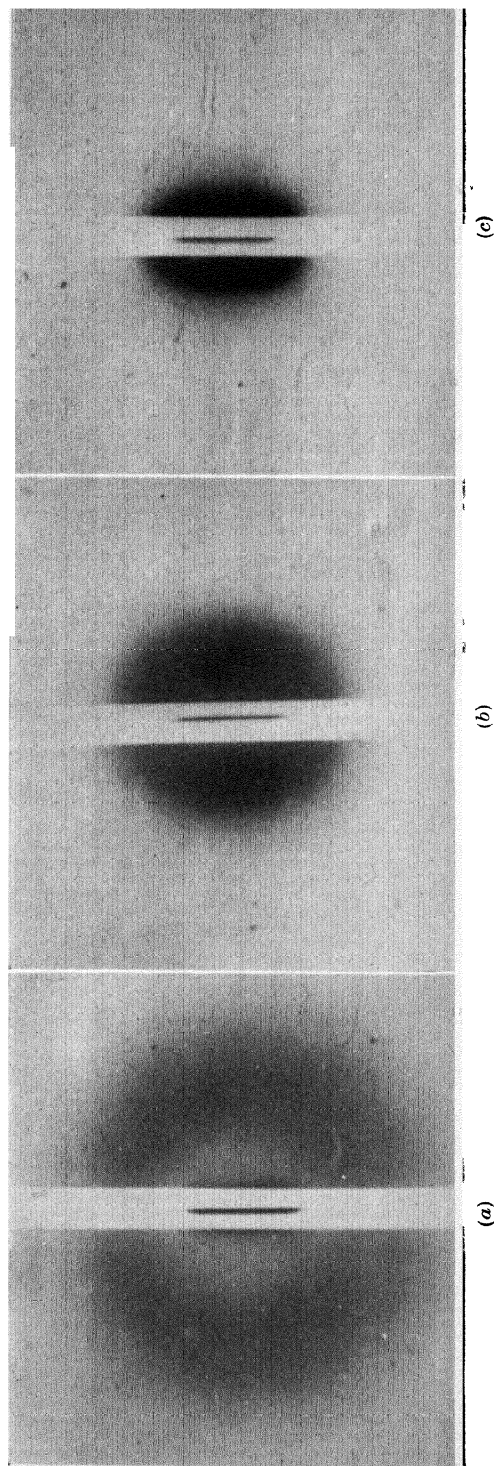
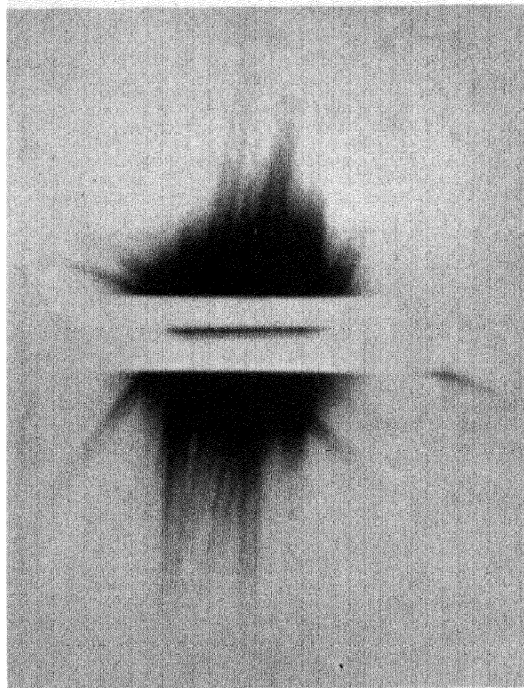
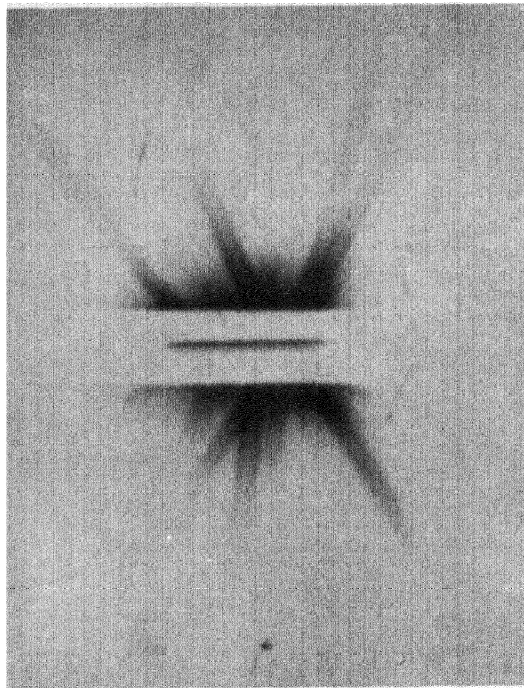


Fig. 59. Small angle scatter patterns of aged aluminium-20-per-cent-silver alloys. CuK_α radiation. (a) as quenched; (b) after 4 ageing at 140°C ; (c) after 1 min. at 342°C (156)



(a)



(b)

Fig. 67. Small angle scatter patterns for an aluminum-20-per-cent-silver alloy (a) aged 3 minutes at 342°C ₍₁₅₆₎ (b) aged 19 days at 140°C .

GUINIER⁽¹⁴³⁾, ⁽¹⁵⁶⁾ has studied an alloy of similar composition by the oscillating crystal, the stationary crystal, and the small angle scatter methods. Using the latter he obtained diffraction patterns which he interpreted as due to roughly spherical solute rich regions.⁽¹⁴³⁾ Subsequent extension of the work⁽¹⁵⁶⁾ enabled him to show that the spherical silver rich nuclei which are first formed are replaced by silver rich platelets after the periods of time given in Table 3. Fig. 67 showing the platelet pattern should be compared with Fig. 59.

JAGODZINSKI and LAVES⁽⁵⁾ in a paper published in 1949 criticized GUINIER's particle size figures and suggested that errors arose from his failure to make due allowance for the closeness of packing of the spherical solute rich regions. They suggested that the formulae for the scattered x-ray intensity should be based on that appropriate to a liquid rather than on the simpler gas formulae. WALKER and GUINIER⁽¹⁶⁹⁾ as a result have developed a new method of interpreting the x-ray results in which they postulate "zones" built up of spherical silver rich cores surrounded by concentric silver poor spherical shells. The excess of silver atoms in the centre is obtained from the shell and hence equals the silver deficiency of the shell. GUINIER⁽¹⁵⁶⁾ has shown that diffraction rings similar to that about (000) also surround matrix Bragg diffractions indicating that the small angle scatter effects are related to the matrix structure. WALKER and GUINIER therefore assume that the atoms remain at the nodes of the matrix. They also assume that their spherical "zones" are distributed haphazardly throughout the matrix. They obtain the Fourier transform of the experimentally obtained diffracted intensity curve as a function analogous to the Patterson function of structure analysis. This function gives the probability $P_{\text{Ag-Ag}}$ of finding an atom of silver at a distance r from a given silver atom. The curves obtained for the 20 per cent silver alloy as quenched from 500°C are reproduced in Fig. 68, *a* and *b*. The broken line in Fig. 68*b* corresponds to $P_{\text{Ag-Ag}} = 0.05$ the value for a random distribution of silver atoms in the solid solution. It can be seen that the intersections of this line with the curve in Fig. 68*b* indicate that the groups consist of silver rich cores of diameter about 16 Å surrounded by silver poor shells of diameter approximately 72 Å. At room temperature these values remain unchanged for many months but 91 hr at 100°C, 4 hr at 140°C, or 10 sec. at 255°C suffice to reduce the diameter of the initial ring on the experimental intensity curve to half of its value. WALKER, BLIN and GUINIER⁽¹⁷⁰⁾ have recently reported a small angle scatter examination of a 20 per cent silver alloy at 525° and 600°C, that is in the solid solution equilibrium state prior to quenching. A Geiger counter was used to record the diffracted intensity and the experimental curves were interpreted in the same manner as that outlined for the paper by WALKER and GUINIER.⁽¹⁶⁹⁾ The results obtained are shown in

Fig. 69, *a* and *b*, and may be compared with Fig. 68, *a* and *b*. The probability $P_{\text{Ag}-\text{Ag}}$ of finding an atom of silver at a given distance r does

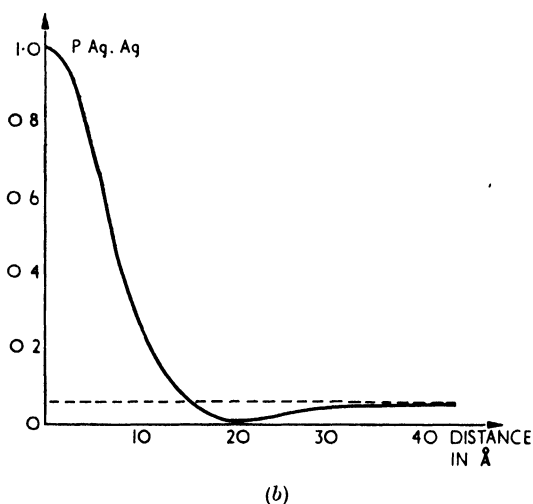
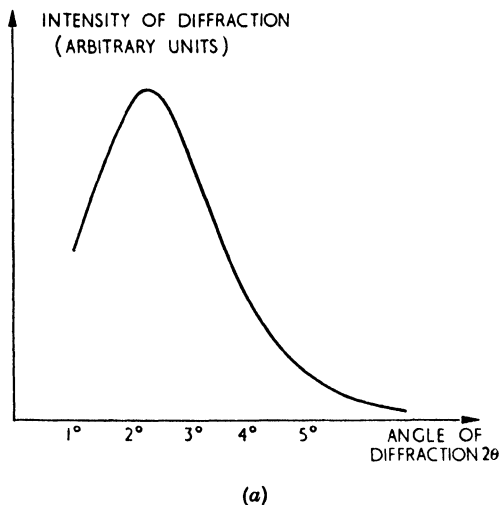


Fig. 68. (a) Diffracted intensity near (000) for an aluminium-20-per-cent-silver alloy "as quenched" from 500°C. (b) Probability $P_{\text{Ag}-\text{Ag}}$ of finding an atom of silver at a distance r from a given silver atom. The broken line corresponds to the value of $P_{\text{Ag}-\text{Ag}}$ for a random solid solution distribution of silver atoms⁽¹⁸⁹⁾

not fall to the random solid solution value of 0.05 until $r \sim 12 \text{ Å}$ whilst it is equal to 0.4 for the closest distance of approach for the aluminium matrix i.e. 2.8 Å . These results suggest that clusters rich in silver atoms exist in the equilibrium solid solution. The clusters become larger as the

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temperature is lowered, cf. 600°C and 525°C. RUDMAN, FLINN and AVERBACH⁽¹⁷¹⁾ have briefly reported that they have obtained results for aluminium-silver alloys at equilibrium above the solubility temperature

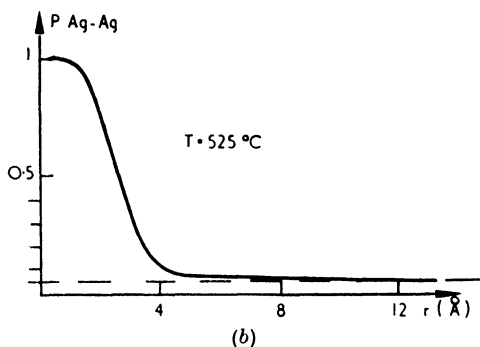
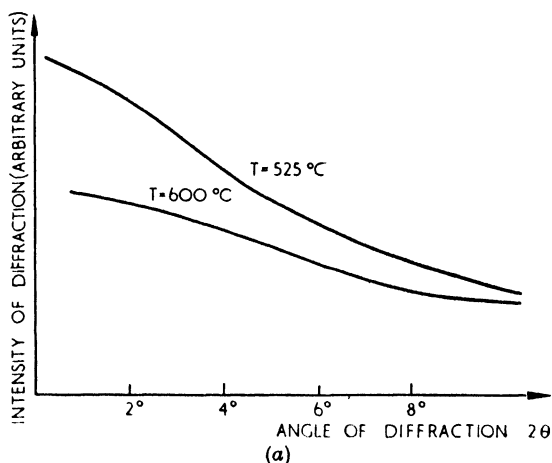


Fig. 69. (a) Diffracted intensity distribution near (000) for an aluminium-20-per-cent-silver alloy at 525° and 600°C. (b) Probability curve $P_{\text{Ag-Ag}}$ versus r obtained from the 525°C intensity plot⁽¹⁷⁰⁾

which are in qualitative agreement with those of WALKER, BLIN and GUINIER.⁽¹⁷⁰⁾

The paper by GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ already referred to in the earlier discussion on x-ray methods and a companion paper by ZIEGLER⁽¹⁷²⁾ appeared concurrently with the paper by GUINIER⁽¹⁵⁶⁾ discussed above. The German workers who used a 38 per cent silver alloy considered that the streaks on their Laüé (Figs. 70-72) and Schiebold-Sauter photographs (Figs. 49-52) were due principally to stacking faults in the successive layers of cubic close packed atoms of the face centred cubic matrix. ZIEGLER⁽¹⁷²⁾ gives a satisfactory explanation of the observed distribution of diffracted intensity in reciprocal

space by postulating the existence of hexagonal lamellae six atom layers thick coherently embedded in a face centred cubic matrix thus ——— ABCABC **ABABAB** ABCABC ———. The lamellae are irregularly spaced at wide intervals. The observed variation and ZIEGLER's calculated intensity variation along the relrod through the (01.0) γ' , (111) matrix, and (01.1) γ' relpoints are shown in Fig. 73 *a* and

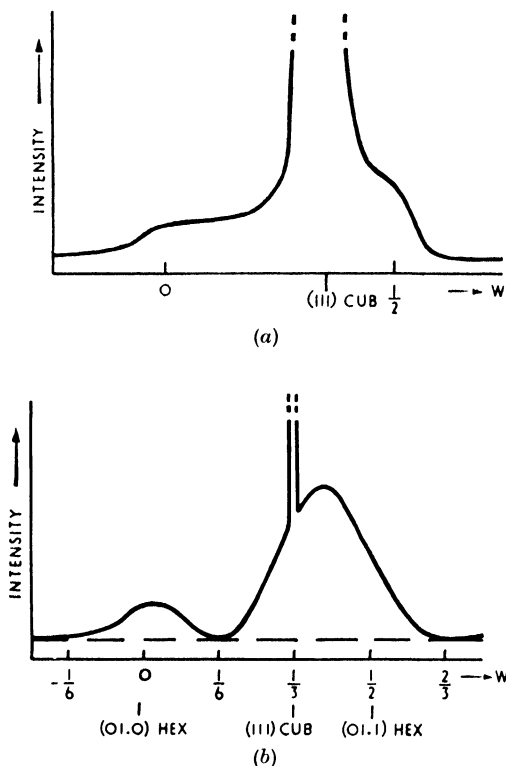


Fig. 73. (a) Observed and (b) ZIEGLER's calculated intensity variation along the relrod through the (01.0) γ' , (111) matrix and (01.1) γ' relpoints for an aluminium-38-per-cent-silver alloy⁽¹⁷²⁾

b. The agreement is fair: as ZIEGLER remarks a better agreement would probably be obtained by a statistical distribution of lamellae of various thicknesses. However, it seems clear that some such distribution of hexagonal lamellae of the potential γ' structure in the cubic matrix can explain the observed diffraction effects.

The paper by GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ considered the variation of the diffraction patterns during reversion of the 38 per cent silver alloy and recorded the surprising fact that the streaks on the Laüé photographs were unaffected by the reversion. Thus the intense streaks present after 6 hr ageing at 150°C (Fig. 71) remained after 2 min. at 220°C (Fig. 72) despite the fact that the

hardness⁽⁷²⁾ (Fig. 103) and the electrical conductivity⁽¹⁷³⁾ had returned to values near those as quenched after solution treatment. Therefore it appears that the hardening during the early stages of ageing in the 38 per cent alloy is not produced by the atomic re-arrangements responsible for the Laüé streaks.

The available x-ray evidence has been outlined. It remains to be seen whether it can be correlated to permit a possible mechanism of precipitation to be deduced.

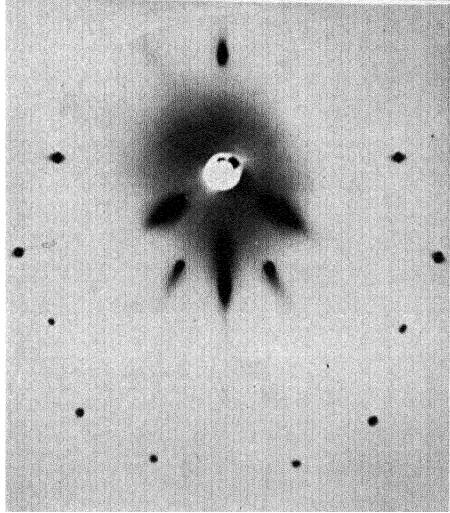


Fig. 70. As quenched from 545°C

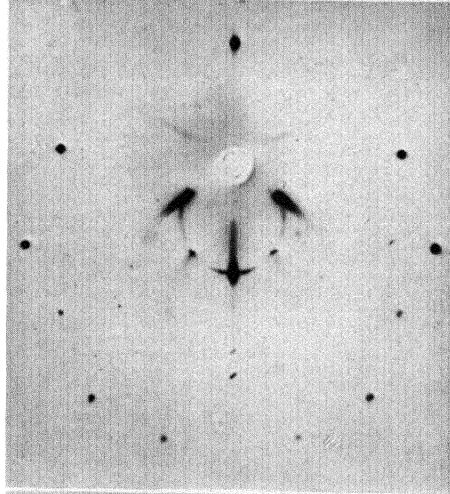


Fig. 71 Aged 6 hr at 150°C

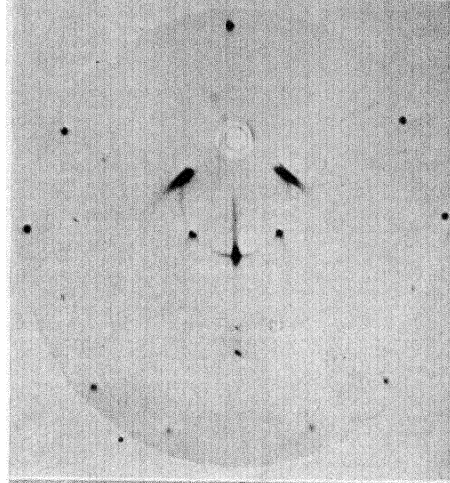


Fig. 72. Aged 6 hr at 150°C, followed by 2 minutes at 220°C then 22 seconds at 260°C

Laue photographs of a single crystal of an aluminum-38-per-cent-silver alloy. X-ray beam along $[331]^{(142)}$

A first question is the significance to be attached to the small angle scatter results obtained by GUINIER and his collaborators. The criticism advanced by JAGODZINSKI and LAVES⁽⁵⁾ of GUINIER's first interpretation of his results has been met by the re-interpretation due to WALKER and GUINIER.⁽¹⁶⁹⁾ There remains the more serious criticism due to GEISLER and HILL⁽¹⁴¹⁾ who suggested that a combination of relrods through both the origin and precipitate relpoints near it (Fig. 66), is actually responsible for small angle scatter patterns of the type shown in Fig. 59 *a, b* and *c*, that is, that the spherical clusters do not exist. Fig. 74 from the paper by GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ shows the relplot due to these authors of the same section of reciprocal space for a 38 per cent silver alloy aged 10 hr at 150°C. Comparison is made difficult by the differences in alloy composition and ageing treatment but both relplots represent states corresponding to small angle scatter patterns of the type shown in Fig. 59 *a, b* and *c*, and it is noteworthy that the German workers did not detect relrods through the origin. As both they and GUINIER used monochromatic radiation it seems probable that GEISLER and HILL are in error in this instance and have been confused by white radiation effects. The uniformity of the rings shown in Fig. 59 is also hardly in keeping with the explanation of GEISLER and HILL.

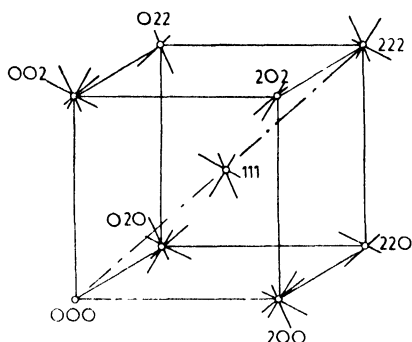


Fig. 74. Reciprocal lattice plot of an aluminium-38-per-cent-silver alloy. Aged 10 hr at 150°C⁽¹⁴²⁾

The discovery by GLOCKER, KÖSTER, SCHERB and ZIEGLER that the Laüé streaks obtained by ageing at 150°C did not disappear on reversion treatment at 220°C while the hardness (Fig. 103) fell to the solid solution value is of considerable significance. If the Laüé streaks are not due to the atomic re-arrangement responsible for the increase in hardness then it seems necessary to postulate the existence of two precipitation mechanisms occurring concurrently. GUINIER's silver rich spherical regions, which would not be detected by the German workers' experimental methods, are clearly a likely explanation of this initial increase in hardness. Examination of the time scale supports this idea: thus comparison of the hardness curves for a 20 per cent silver alloy published by KÖSTER and BAUMANN⁽⁷²⁾ with Table 3 indicates that the spherical regions can be responsible for the first rise of the hardness curve. If the behaviour of the 38 per cent silver alloy is analogous to that of the 20 per cent alloy it follows that the same can be true for this

alloy. If this is so it is necessary for the spherical solute rich regions to re-dissolve on reversion at 220°C to allow the hardness to fall to the "as quenched" value. In contradiction to this assumption GUINIER states⁽¹⁵⁶⁾ "when an alloy aged at room temperature is heated to a high temperature the zones it contains do not dissolve but, on the contrary, they grow rapidly until the platelike precipitate succeeds them." From this and the information given by WALKER and GUINIER⁽¹⁶⁹⁾ it is possible to infer that a reversion treatment of 2 min. at 220°C after 6 hr ageing at 150°C would cause the existing spherical solute rich regions to double in size. GUINIER's inference that the spherical regions do not dissolve but grow rapidly is not necessarily correct, undoubtedly some grow but possibly the majority could equally well dissolve. The small angle scatter films merely record the average size of the zones: if the average size prior to the 2 min. ageing at 220°C is too small for stability at 220°C the bulk of the zones will re-dissolve while a few of favoured larger sizes will grow rapidly. If the zones are the principal source of hardening prior to the second rise on the hardness curve (Figs. 96 and 103) a large number of small zones are likely to cause more interference with slip (see p. 269) than a few large zones so that a loss of hardness could occur on reversion. It may be noted that irrespective of the x-ray patterns the change in electrical conductivity⁽¹⁷³⁾ and the specific heat measurements discussed later (p. 238) prove that re-resolution has occurred on reversion.*

The spherical silver rich regions can thus be regarded as the most likely cause of the first hardness changes at low ageing temperatures. GUINIER⁽¹⁴³⁾ ceases to detect these regions in his 20 per cent silver alloy after 24 hr ageing at 150°C , by extrapolation we can assume from Table 3 that the platelets will appear at 150°C after 30–50 hr.

Recent work by WATANABE and KODA⁽¹⁷⁴⁾ has shown that a 20 per cent silver alloy has a two-stage hardness curve between 140°C and 200°C , therefore the platelets would appear to be associated with the second rise, since the work of KÖSTER and BRAUMANN⁽⁷²⁾ shows that the flat is well advanced after 12 hr. We know that these platelets are silver rich but we have little direct evidence of their structure or potential structure. There is the evidence presented by GUINIER⁽¹⁴³⁾ of diffuse spots (which are most intense "after a long ageing at 140°C ") which indicate a tendency to form a superstructure of the face centred cubic

* WALKER and GUINIER,^{173a} have carried out an examination of the reversion behaviour of a single specimen of an aluminium 20 per cent silver alloy. They report that a visual examination of the x-ray patterns showed little change in the scattering after reversion. The authors pointed out that quantitative measurements are required to determine the extent of any reversion. Assuming that the reversion behaviour of the 20 per cent silver alloy is analogous to that of the 38 per cent silver alloy, this finding is in conflict with the hardness (Fig. 103), specific heat (page 238) and electrical resistance,¹⁷³ results. Further work is required to resolve this anomaly.

matrix. Table 3 shows that platelets appear after 100 hr at 140°C. It is possible therefore that the initial spherical solute rich regions as they increase in size from the "as quenched" value of 16 Å diameter undergo an ordering process, the atoms remaining at approximately the matrix positions. As the superstructure develops the restraints upon growth imposed by the matrix modify the shape of the solute rich regions so that platelets replace spheres. GUINIER has suggested that subsequent movement of the {111} planes of the cubic lattice parallel to themselves

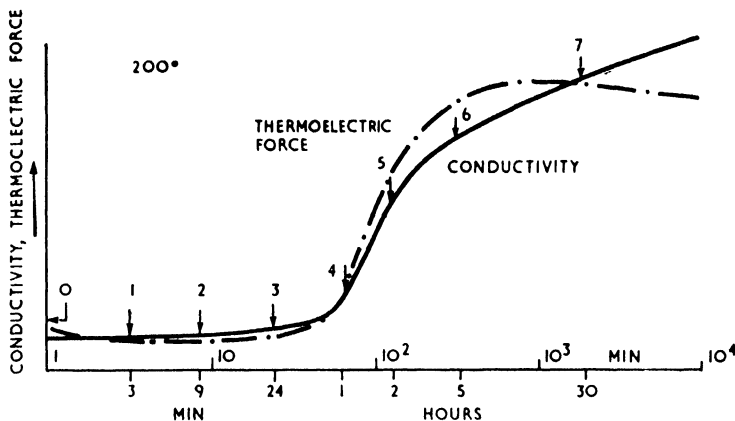


Fig. 75. Variation of conductivity and thermo e.m.f. with ageing time at 200°C for an aluminium-38-per-cent-silver alloy⁽¹⁴²⁾

occur to produce lamellae of the γ' structure. These lamellae grow as ageing continues and in due course transform to the equilibrium γ precipitate.

We still require an explanation of the Laüe streaks observed by GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ during ageing of the 38 per cent silver alloy and of the retention of those streaks on reversion at 220°C. The paper of KÖSTER, STEINERT and SCHERB⁽¹⁷³⁾ and that of KÖSTER and BRAUMANN⁽⁷²⁾ from which Fig. 103 is taken, show that reversion of the 38 per cent silver alloy after ageing at 150°C is complete up to the second rise in the hardness or conductivity curves (16 hr). Reversion after longer ageing times is decreasingly effective in restoring the "as quenched" values. The atomic re-arrangement responsible for the Laüe streaks can have little or no effect on the hardness up to 16 hr because the streaks do not vanish on reversion. Subsequently it could play an increasingly important part in the hardening. Hexagonal diffractions due to three dimensional γ' precipitate appear in the Laüe streaks after 48 hr and peak hardness is reached after 160 hr at 150°C. Thus the γ' precipitate is at least partly responsible for the second hardness peak. At higher ageing temperatures, 200°C and above, the

γ' structure could be responsible for the bulk of the hardening. Thus at 200°C hexagonal diffractions appear in the Laüe streaks after 60 min. but peak hardness is not reached until 5 hr.⁽⁷²⁾ Except for the first rise in the hardness curve at 150°C we can associate major increases in hardness with the appearance of the hexagonal γ' diffractions in the Laüe streaks. This is also true of other physical properties as is shown by comparison of Table 4 and Figs. 75 and 102 taken from the papers by

TABLE 4

Analysis of Laüe photographs of an aluminium—38 per cent Silver Alloy aged at 200°C after Quenching from 545°C⁽¹⁴²⁾

<i>Position Fig. 75</i>	<i>Ageing Time at 200°</i>	<i>Appearance of photographs</i>
0		No streaks
1	3 minutes	Streaks just detectable
2	9 minutes	Weak streaks
3	24 minutes	Intense streaks
4	60 minutes	Hexagonal diffraction on the streaks
5	2 hours	Strong hexagonal diffractions
6	5 hours	Sharper hexagonal diffractions
7	30 hours	Streaks nearly gone. Hexagonal diffractions very strong and sharp

GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ and KÖSTER and BRAUMANN.⁽⁷²⁾ On ageing at 200°C intense Laüe streaks appear before there is any significant change in the electrical conductivity, thermo e.m.f. or elastic limit (Fig. 96) and only with the appearance of the γ' reflections do we obtain changes in these properties.

ZIEGLER⁽¹⁷²⁾ has shown, as we have discussed earlier (p. 204), that the Laüe streaks may be explained by a sequence of stacking faults in the cubic close packed matrix structure. These stacking faults will comprise thin layers of hexagonal close packing but they cannot properly be designated γ' until their silver content is that appropriate to the γ' structure, i.e. 66 atomic per cent silver. Diffusion of silver atoms to these stacking faults will have to occur to permit thin platelets of γ' to form. If, quite independently of the spherical solute rich regions, stacking faults are arising parallel to {111} planes of the matrix by slip of these {111} planes parallel to themselves then Laüe streaks would be obtained on the x-ray photographs and would remain unchanged on reversion if the stacking faults persisted. The stacking faults are thus to be associated with the relief of stress when first formed though subsequent diffusion of silver atoms to the faults resulting in the growth of γ' lamellae would in turn cause hardening. It is not unlikely therefore that stacking faults stable at 150°C should be retained for short

reversion treatments at 220°C. The present authors have earlier (p. 206) found it difficult to accept GUINIER's inference that the silver rich spherical regions grow rapidly on raising the ageing temperature and have preferred to assume that some grow while the majority re-dissolve in order to allow the hardness to return to the "as quenched" value on reversion. An increase in the number of stacking faults on reversion may assist in the reduction of the hardness: the Laue photographs published by GLOCKER *et al.*, Figs. 70, 71 and 72, show streaks which are, if anything, more intense after reversion than before and are therefore not in conflict with this possibility.

It must also be borne in mind that diffusion of silver atoms away from the stacking faults, which is in effect re-resolution of γ' lamellae, may cause some softening and provided that the stacking faults themselves were retained the Laue streaks would be unaffected.

An alternative explanation of the Laue streaks may be hazarded. Diffusion studies⁽¹⁷⁵⁾ have shown that porosity may be generated at the low melting-point side of the interface of a diffusion couple possessing a wide concentration difference. This is associated with a flux of vacancies into the side which has suffered a net loss of atoms. The aluminium-silver alloys examined have a much higher solute concentration than occurs in any of the other alloys which have been thoroughly studied. Diffusion to form the spherical clusters may well involve a vacancy mechanism. If the excess vacancies condense on $\{111\}$ planes they would provide the stacking faults and would probably not be dispersed by the reversion treatments which would generate more vacancies. Dilatometric measurements should prove or disprove this hypothesis.

Attention is currently being given to the mechanism of the allotropic transformation in cobalt between face-centred cubic and hexagonal close-packed lattices using dislocation models.^{(176), (177)} It has been found that rotation of a suitable partial dislocation about a pole can produce a single stacking fault on $\{111\}$ planes of a face-centred cubic lattice. A clear understanding of the cobalt transformation may lead to a new explanation of the stacking faults in the aluminium-silver system.

The silver rich platelets detected by GUINIER⁽¹⁵⁶⁾ could be due to stacking faults in the matrix lattice which have become sufficiently silver rich by diffusion to produce detectable small angle scatter patterns. Alternatively, as suggested earlier, the platelets could be formed by a process of preferred growth of the spherical regions. The relative diameters and thicknesses of the two types of region might assist in choosing between these alternatives but GUINIER has not published the necessary figures.

Thus we can visualize two possible mechanisms of precipitation which singly or in combination can explain the available experimental

evidence. Mechanism A based principally on GUINIER's work on the 20 per cent silver alloy can be written

spherical solute rich regions $\rightarrow$ ordered regions spherical
or flat $\rightarrow \gamma' \rightarrow \gamma$ (98)

Again this is merely a method of expressing the order in which the states become dominant features of the x-ray pattern.

Mechanism B which is derived principally from the German work on the 38 per cent silver alloy can be written

stacking faults in the matrix $\rightarrow$ lamellae of $\gamma' \rightarrow$ three
dimensional γ' precipitate $\rightarrow \gamma$ (99)

The work of GUINIER and his collaborators^{(169), (170)} and of RUDMAN *et al.*⁽¹⁷¹⁾ has shown that aggregates of silver atoms exist in the solid solution prior to quenching and immediately after quenching; it is to be expected therefore that mechanism A will cause hardening from the earliest stages of ageing whereas mechanism B will not cause significant hardening until the third stage is reached.

Aluminium-magnesium-silicon Agehardening Alloys

This is a pseudo-binary system with an equilibrium precipitate of magnesium silicide (Mg_2Si)—the β phase. GEISLER and HILL⁽¹⁴¹⁾ used an alloy containing 1.4 per cent magnesium silicide and found evidence, Fig. 57, of relplanes and relrods, which they interpreted as due to the formation of magnesium silicide stringlets and platelets (cf. Fig. 48). They showed relplots of their films containing relrods passing through and symmetrical about transition precipitate relpoints (Fig. 76). They are not associated with matrix or equilibrium precipitate relpoints and seem to afford definite evidence of lack of periodicity of an intermediate coherent precipitate structure as the cause of the observed diffraction effects. GUINIER and LAMBOT⁽¹⁸³⁾ have also reported the discovery of relplanes in this system. LAMBOT^{(184), (185)} has reported the results of their work more fully and has given a more detailed interpretation. LAMBOT⁽¹⁸⁵⁾ worked on an alloy containing 0.5 per cent magnesium and 0.48 per cent silicon with traces of iron and manganese as impurities. This is equivalent to 0.79 per cent Mg_2Si with an excess of silicon. He took some photographs of four other alloys containing up to 4 per cent Mg_2Si , and claimed that the diffraction patterns were the same as those of the 0.79 per cent Mg_2Si alloy apart from diffraction effects due to the excess of undissolved Mg_2Si . One of these four alloys contained 1.5 per cent Mg_2Si , a concentration close to that used by GEISLER and HILL, but LAMBOT used a solution treatment temperature of 525°C (at which the solubility Mg_2Si is *circa* 1 per cent) so that he never actually investigated a degree of supersaturation as high as that used by

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GEISLER and HILL. Serious differences exist between the replots of the two groups of workers which may, in part, be due to the fact that their alloys are not of the same composition. There is agreement on the fact that the first detected effects are due to relplanes parallel to $\{100\}_{\text{Al}}$ planes but LAMBOT⁽¹⁸⁴⁾ merely observed that the diffraction on these relplanes ceased to be uniform. Local intensifications occurred

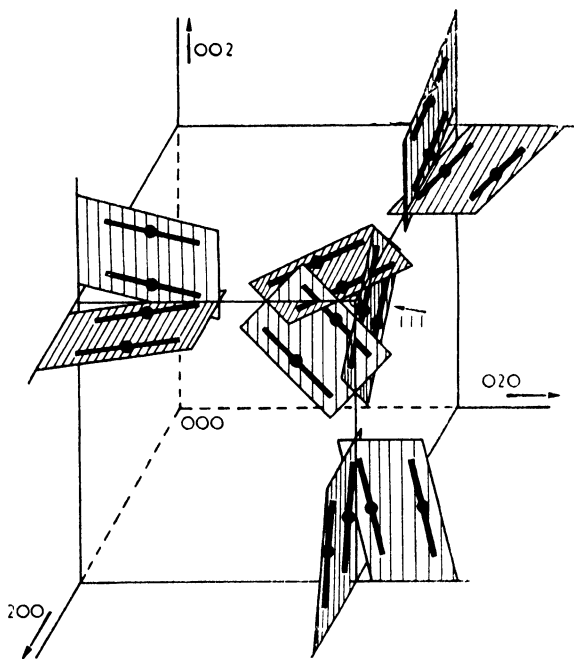


Fig. 76. Portion of the reciprocal lattice for aged crystals of aluminium-1.4-per-cent-Mg₂Si alloy. This is a composite drawing for three different stages in the ageing process showing the relplanes which contract to form relrods and then precipitate relpoints⁽⁶⁾

which he has described as a “checker board” structure. LAMBOT and GUINIER interpret this non-uniformity of diffracted intensity as a sign of the progressive ordering in groups of the previously independent parallel rows rich in magnesium and silicon atoms which were responsible for the uniform relplanes. LAMBOT does not at any time detect the well-defined relrods of GEISLER and HILL.⁽¹⁴¹⁾ The replots published by GEISLER and HILL are, if they are entirely correct, convincing evidence of the existence of an intermediate precipitate. Their plots also indicate the formation of platelets on $\{100\}_{\text{Al}}$ and $\{110\}_{\text{Al}}$ planes and possibly also on $\{120\}_{\text{Al}}$, $\{130\}_{\text{Al}}$ or $\{140\}_{\text{Al}}$ planes which infers that the platelets are forming on a series of different habit planes, which in turn suggests that the platelets have more than one structure. This seems unlikely and

leads to the view that the relrods are not all as well defined as the authors would have us believe.

LAMBOT obtained the equilibrium precipitate Mg_2Si after 30 min. at 300°C . Under the same conditions, GEISLER and HILL found platelets of their transition precipitate. After 4 hr ageing at 220°C GEISLER and HILL found relplanes parallel to $\{100\}$ matrix planes: LAMBOT's "checker board" on these $\{100\}$ relplanes was readily visible after 12 hr. It is questionable whether GEISLER and HILL using their experimental method could detect the variations in diffracted intensity on $\{100\}$ relplanes which LAMBOT found and they have, in any event, only recorded the two ageing treatments mentioned above in their paper. It is therefore possible that the American workers have missed the "checker board" structure development of the initially uniform relplanes.

The French workers in papers^{(144), (185)} published subsequently to that of GEISLER and HILL, infer the existence of a transition precipitate developing by a process of ordering of the spacing and atomic arrangement between the lines rich in magnesium and silicon atoms, thus now confirming the finding of GEISLER and HILL.

In the former paper⁽¹⁴⁴⁾ GUINIER reported the results of small angle-scattering experiments designed to obtain evidence of the early stages in the ageing process. The scattering factors of magnesium and silicon are very close to that of aluminium. GUINIER⁽¹⁴⁴⁾ ingeniously tried to overcome this difficulty by working on the very similar aluminium-magnesium-germanium alloy, in order to introduce an atom with a distinctive scattering factor. His failure to obtain a small angle scattering pattern can be explained in several ways: (i) no solute rich regions have formed, (ii) the explanation which GUINIER himself advances, that the solute rich regions rapidly became too large to be detected, (iii) GUINIER was perhaps somewhat optimistic in hoping that the presence of germanium would result in patterns of detectable intensity. The ratio of the scattering factors of solute rich regions to that of the matrix would in any event be less than 7 : 5. The absence of any experimental evidence of regions rich in magnesium and silicon atoms thus does not justify the assumption that such regions do not exist.

The experimental evidence strongly suggests that an intermediate transition precipitate, which we can term β' , is formed in this system but the lack of knowledge of the β' structure greatly handicaps any attempt to devise a sequence of structural changes. Fig. 77 shows the atomic arrangement in the (110) Mg_2Si plane superimposed on the (100) matrix plane, the group of magnesium and silicon atoms ABCD can fit with little distortion on to the matrix lattice sites, and this fit can be continued in the $[100]_{\text{A1}}$ direction with increasing, but small distortion. In the $[010]_{\text{A1}}$ direction the fit cannot be continued. In the $[001]_{\text{A1}}$

direction perpendicular to the plane of the paper the respective spacings are $2.24 \text{ \AA}$ and $2.02 \text{ \AA}$, a 10 per cent mis-fit. If the $(100)_{\text{Al}}$ plane of Fig. 77 is rich in magnesium and silicon atoms, there will obviously be a tendency for chains of these atoms to form along $[100]_{\text{Al}}$ and the equivalent $[010]_{\text{Al}}$ direction, but little tendency for the chains to develop in directions perpendicular to their length. Such chains running in the two possible directions will disrupt periodicity in the $(100)_{\text{Al}}$ planes without materially affecting the spacing between them. That is periodicity

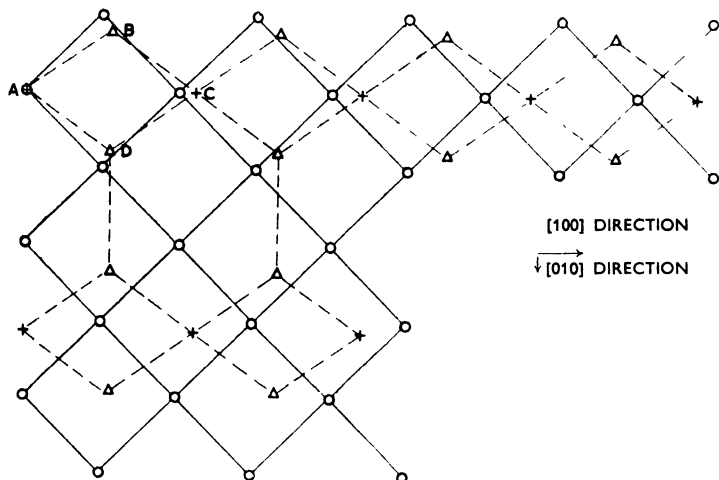


Fig. 77. Illustration of the fit of the atoms in the (110) plane of Mg_2Si on the (100) plane of the aluminium lattice
 O Al atoms Δ Mg atoms + Si atoms

will be maintained in the $\langle 100 \rangle_{\text{Al}}$ direction only and the result will be the observed relplanes. Following GUINIER it is now possible to visualize that such parallel chains in the $(100)_{\text{Al}}$ planes could take up a preferred spacing perpendicular to their length to develop an ordered arrangement which would include aluminium atoms. Alternatively, growth of a considerably modified Mg_2Si structure could occur from the chains as nuclei in directions outside the $(100)_{\text{Al}}$ plane. If the β' structure contains aluminium atoms the ordering process in the $(100)_{\text{Al}}$ planes could lead to the development of β' , and since the re-arrangement is essentially the ordering of a disordered β' precipitate, it would be expected to give diffraction patterns corresponding to relrods through β' relpoints. This would be in accordance with the findings of GEISLER and HILL.⁽¹⁴¹⁾ More systematic ageing treatments are required to allow a determination of the β' structure. For the present we can write the possible precipitation sequence as:

G.P. zones (rich in Mg and Si atoms) on $\{100\}_{\text{Al}}$
 planes $\rightarrow$ ordered zones of β' structure $\rightarrow \beta$. . . (101)

Aluminium-copper-magnesium Agehardening Alloys

Two authors, BAGARYATSKII^{(186), (187)} and LAMBOT^{(184), (185)} have reported investigations of this system using monochromatic radiation methods. The Russian author examined an alloy containing 3 wt. per cent of copper and 1.15 wt. per cent of magnesium while LAMBOT's alloy contained 4 wt per cent of copper and 1.28 wt per cent of magnesium with traces of silicon and iron.

BAGARYATSKII's findings can be summarized as follows:

Alloys aged at room temperature, and for limited times at temperatures up to 150°C had x-ray patterns showing relplanes parallel to $\{100\}_{\text{Al}}$ planes. After longer times and at higher ageing temperatures, relrods could be detected along $\langle 012 \rangle_{\text{Al}}$ directions. Concurrently, fairly sharp relpoints due to a phase differing from the equilibrium S phase appeared. Finally, the S phase relpoints appeared.

BAGARYATSKII claimed that the diffraction spots due to the intermediate phase corresponded to an orthorhombic structure with

$$a' = 4.04 \text{ \AA}, b' = 9.04 \text{ \AA}, c' = 7.2 \text{ \AA} \quad . \quad . \quad (102)$$

This is closely analogous to the S phase (Al_2CuMg) which has a similar structure⁽¹⁸⁸⁾ with

$$a = 4.00 \text{ \AA}, b = 9.23 \text{ \AA}, c = 7.14 \text{ \AA} \quad . \quad . \quad (103)$$

He terms the intermediate phase S' as a parallel to θ' and θ in aluminium-copper alloys, and γ' and γ in aluminium-silver alloys.

BAGARYATSKII interpreted the relplanes parallel to $\{100\}_{\text{Al}}$ planes as due to a destruction of periodicity in the $\{100\}$ planes of the solid solution, their inter-planar spacing being preserved. He rejected the alternative of needle-shaped, i.e. stringlet, nuclei of the S' phase. He assumed that groups of magnesium and copper atoms of concentrations corresponding to the S' phase collect on the $\{100\}_{\text{Al}}$ planes and adopt one of the twelve possible $\langle 031 \rangle_{\text{Al}}$ directions in which they have a close fit with the solid solution lattice. This destroys periodicity in the $\{100\}_{\text{Al}}$ planes since no long-range order of the potential S' nuclei exists, periodicity is however preserved in the $\langle 100 \rangle_{\text{Al}}$ directions. The precipitation process proceeds no further at room temperature: at higher temperatures ordering of the groups rich in copper and magnesium atoms allows nuclei of S' to develop whose (100) planes fit closely on the $\{021\}$ planes of the matrix. Extensive growth of the S' phase is possible in the a' and b' directions, since $a' = 4.04 \text{ \AA}$ is the matrix spacing along $\langle 100 \rangle$ directions, and $b' = \sqrt{5} \times 4.04 \text{ \AA}$ is the matrix spacing along $\langle 012 \rangle$ directions. Growth is limited in the c' directions where a fit is obtained with the matrix at c' , $5c'$, $10c'$, etc. only. Thus the S' nuclei are periodic in two directions and relrods are found along $\langle 021 \rangle_{\text{Al}}$ directions. Growth continues until relpoints are obtained when the

extent of the misfit with the matrix lattice in the c' direction causes loss of coherence and the formation of the equilibrium S phase. The interpretation BAGARYATSKII advances is in accord with his experimental results and the physical picture of the sequence of changes is plausible. He has no direct evidence of the segregation of copper and magnesium atoms on to $\{100\}_{\text{Al}}$ planes and the relplanes could be interpreted in terms of "stringlets" of S' (cf. Fig. 48). In the aluminium-copper alloys segregation of small copper atoms on to $\{100\}_{\text{Al}}$ planes causes a contraction of the interplanar spacing of these planes. In the aluminium-copper-magnesium system segregation of groups of equal numbers of small copper and large magnesium atoms could be expected to maintain the interplanar spacing of the $\{100\}_{\text{Al}}$ planes. This consideration supports BAGARYATSKII's interpretation.

We now have to consider the bearing of LAMBOT's work on that of the Russian author. Of importance are the small angle scatter experiments of the Belgian author which can be interpreted as due to the segregation of copper atoms on $\{100\}_{\text{Al}}$ planes and which therefore support BAGARYATSKII's interpretation of his evidence. The presence or absence of magnesium atoms cannot be determined ($f_{\text{Al}} \sim f_{\text{Mg}}$) but the small copper atoms would create conditions favourable to the segregation of the large magnesium atoms on to these planes.

The other observations made by LAMBOT can be explained by the simultaneous operation of two precipitation processes, that operating in binary aluminium-copper alloys and that suggested by BAGARYATSKII for aluminium-copper-magnesium alloys. What may be termed the "binary aluminium-copper effects" are of weak intensity compatible with the assumption that only a small proportion of the copper atoms are involved. BAGARYATSKII did not observe these latter and it is noteworthy that LAMBOT's alloy contains 0.80 wt per cent copper in excess of that required to combine with the magnesium to form the S phase. Both authors observed initial relplanes parallel to $\{100\}_{\text{Al}}$ planes but LAMBOT did not find the relrods along $\langle 021 \rangle_{\text{Al}}$ directions nor the relpoints due to the intermediate S' phase. LAMBOT reported a linear orientation relationship only, viz. $[100]_S \parallel [100]_{\text{Al}}$, but the Russian author claimed that a planar orientation relationship existed between the matrix and the S phase, namely

$$[100]_S \parallel [100]_{\text{Al}}; [010]_S \parallel [012]_{\text{Al}}; [001]_S \parallel [021]_{\text{Al}} \quad . \quad . \quad (104)$$

which permits twelve crystallographically identical orientations of the S and S' phases. He qualified this claim with the statement that only the relationship

$$[100]_S \parallel [100]_{\text{Al}} \quad . \quad . \quad . \quad (105)$$

was rigidly adhered to at all stages in the ageing process, the scatter of S' phase orientations in the planes $\{100\}_{\text{Al}}$ he attributed to a second

possible set of habit planes for the S' phase, the $\{035\}$ matrix planes on which the $\{011\}_S$ planes can match. This further type of coherence requires a greater distortion than the alternative previously considered and accounts for an angular scatter of 4° in the $\{100\}_{Al}$ planes. BAGARYATSKII did not give his experimentally determined scatter; he associated the maximum scatter with peak hardness and claimed that with over-aging the indications of scatter almost disappeared. Thus inferring that the greater distortion due to matching on the $\{035\}_{Al}$ planes causes increased hardness and leads to earlier loss of coherency.

BAGARYATSKII presented his experimental findings in outline only. It is not clear for instance whether the lattice constants of the S' phase (equation (102)) are well established by precise measurements, or whether these are values deduced from the requirement of coherency on $\{021\}$ matrix planes supported by measurements of unsharp diffraction spots yielding values not in conflict with those assumed.

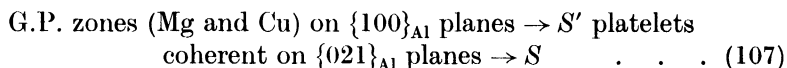
LAMBOT's work suffers from the disadvantage that the increased copper content has led to two precipitation mechanisms proceeding concurrently with the possibility that the diffraction effects due to the mechanism associated with the aluminium-copper binary alloys have obscured those due to the precipitation of the S phase. It appears that precipitation occurred more rapidly in the alloys examined by the Belgian author. Thus the eight diffuse diffraction spots near the origin detected by both authors persists unchanged after 65 hr at 150°C according to BAGARYATSKII, while LAMBOT records that they sharpen prior to disappearing in less than 10 hr at 150°C . BAGARYATSKII was able to show a photograph taken after 30 min. at 218°C in which relatively sharp S' reflections had appeared in these diffuse spots, LAMBOT never detected them at all at 200°C .

LAMBOT accepted the views of OGINATA and MUTUZAKI⁽³⁵⁰⁾ that the S phase was tetragonal with

$$a = 5.71 \text{ \AA}, c = 7.94 \text{ \AA} \quad . \quad . \quad . \quad (106)$$

and formulae $\text{Al}_5\text{Cu}_2\text{Mg}_2$, a structure and formulae not in accordance with single crystal work of PERLITZ and WESTGREN⁽¹⁸⁸⁾ in 1943.

The available evidence suggests that BAGARYATSKII's views are correct and the precipitation mechanism may be written



There is as yet no evidence to suggest that the ordering reaction in the G.P. zones leads to the formation of a further intermediate phase such as the G.P. [2] phase obtained in the aluminium-copper system. But a more systematic investigation of the aluminium-copper-magnesium system may reveal further information. It may also be noted that the

metallographic observations on the plane of precipitation (GAYLER^(188a)— $\{100\}_{\text{Al}}$ at 350°C; NISHIMURA and MURAKAMI^(188b)— $\{100\}_{\text{Al}}$ and $\{110\}_{\text{Al}}$ at 250°C) have yet to be reconciled with the x-ray work.

Aluminium-zinc Agehardening Alloys

BARRETT, GEISLER and MEHL⁽¹⁸⁹⁾ investigated this system using a 25 wt per cent zinc alloy. GUINIER⁽¹⁵⁷⁾ reported work on a 34 wt per cent zinc alloy but added that he investigated alloys in the range 20–50 per cent zinc and found these to differ only in the rate of reaction. Using his small angle scatter method GUINIER found evidence of spherical solute rich regions immediately after quenching and on ageing for up to 44 hr at 78°C. On ageing at 100°C GUINIER detected platelike zinc rich regions. The American workers found streaks on their Laüé films after 8 days at 100°C in good agreement with GUINIER's findings. Neither group of workers succeeded in detecting an intermediate precipitate although the American authors infer that one exists. The equilibrium precipitate, pure zinc, has a hexagonal structure. RUDMAN, FLINN and AVERBACH⁽¹⁷¹⁾ have recently reported the results of measurements of the intensity of the x-radiation scattered at small angles from an aluminium 20 atomic per cent zinc alloy at temperatures above the solubility temperature. They interpreted their results as evidence of small zinc-rich clusters in the solid solution. Each zinc atom had 3.7 zinc nearest neighbours instead of the 2.4 to be expected in a random solid solution. The system thus is similar in many ways to the aluminium-silver agehardening alloys and further investigation should seek to find whether stacking faults occur during the precipitation process.

Aluminium-magnesium Agehardening Alloys

FINK and SMITH⁽¹⁹⁰⁾ and LACOMBE⁽¹⁹¹⁾ examined polycrystalline specimens of alloys containing approximately 10 per cent of magnesium. They detected an intermediate precipitate β' in addition to the equilibrium precipitate β (Mg_2Al_3). Later PERRYMAN and BROOK⁽¹⁹²⁾ carried out an examination of a 10 per cent magnesium alloy by the Debye-Scherrer method using monochromatic radiation. They found evidence of at least one intermediate precipitate.

This system is of interest because it has often been argued that it provides evidence of the validity of the particle size explanations of the relplanes and relrods obtained with agehardening alloys, that is the stringlets and platelets of GEISLER and HILL⁽¹⁴¹⁾ shown in Fig. 48. GEISLER, BARRETT and MEHL⁽¹⁸⁹⁾ examined a single crystal of an aluminium-10-per-cent-magnesium alloy and obtained streaks on Laüé photographs corresponding to relrods. Their argument followed the line that in the aluminium-silver system the atomic sizes are so little different that case (i) (p. 184) is not satisfied whereas in the aluminium-magnesium

system the x-ray scattering factors of aluminium (f_{Al}) and magnesium (f_{Mg}) are nearly identical so that case (ii) is not satisfied. The similarity of the anomalous diffraction patterns in all agehardening systems examined suggested to them that they should have a common origin which could only be case (iii) i.e. small structurally perfect precipitate particles. However, an examination of the micrographs, the hardness curves, and the Laue photographs, published by these authors shows that the diffraction effects in aluminium-magnesium alloys are first detected in the region of, or well after, peak hardness, and that concurrently the microstructures show well formed visible precipitate platelets. Calculations of the thickness of the platelets from the micrographs give figures which should, in a fully periodic or perfect precipitate structure, yield relpoints and not relrods. The diffraction effects can best be interpreted as due to a structurally imperfect magnesium rich precipitate, the imperfections resulting from a disordered arrangement of large magnesium (atomic diameter 3.20 Å) and small aluminium (atomic diameter 2.86 Å) atoms with a consequent departure of some of the atoms from the ideal precipitate structure positions.

The ageing time relationship between the single crystal work of GEISLER *et al.*, and that on polycrystalline specimens by FINK and SMITH, LACOMBE, and PERRYMAN and BROOK is not clear and further work is required before a mechanism of precipitation can be suggested.

Copper-beryllium Agehardening Alloys

Papers by GUINIER and JACQUET^{(178), (155)} in 1943 and 1944 described work on a 2.3 per cent beryllium alloy which showed the ageing process to have some similarity to the aluminium-copper system. Small angle scatter films indicated the presence of beryllium-rich platelets on {100} planes in the early stages of ageing. Their thickness increased more rapidly relative to their diameter during ageing compared with the copper-rich platelets in the aluminium-copper system. Oscillating crystal films of alloys aged at 190°, 220°, 300° and 420°C suggested that the platelets developed directly into the equilibrium precipitate γ . In 1948, GUY, BARRETT and MEHL⁽¹²⁸⁾ published the results of work on the 1.73 per cent beryllium alloy, which were in very good agreement with those of GUINIER and JACQUET. They assumed, without evidence, the existence of an intermediate transition precipitate coherent with the matrix lattice. In the discussion of their paper, GEISLER produced evidence he attributed to thin platelets of a transition precipitate coherent with the matrix on {100}_{Cu} planes. In 1949, ELISTRATOV, FINKELSHTEIN and PASHILOV⁽¹⁷⁹⁾ found evidence of relplanes. Later ELISTRATOV⁽¹⁵²⁾ reported that the relplanes were parallel to {100}_{Cu} planes and that relrods were found in $\langle 100 \rangle_{\text{Cu}}$ directions. In 1951, GRUHL and WASSERMANN⁽¹²¹⁾ reported the results of an examination by

the Debye-Scherrer method of polycrystalline samples of the 1.8 per cent beryllium alloy. On ageing at temperatures above 325°C they found the equilibrium precipitate γ immediately present, below this temperature they obtained evidence of an intermediate precipitate γ' . Thus after 22 hr ageing at 200°C the α solid solution lines which had been sharp became diffuse and three lines due to γ' appeared. The γ' lines increased in strength with further ageing. GRUHL and WASSERMANN attributed the diffuseness of the α solid solution lines to lattice strain caused by coherency of the γ' precipitate on the $\{100\}$ planes, pointing out that the loss of sharpness of the α lines was associated with the presence of γ' . They considered γ' to be ordered α with a body-centred tetragonal structure since the new lines were at locations for matrix superlattice lines. The orientation relationship they found for γ was

$$(100)_{\gamma} \parallel (100)_{\alpha}; (010)_{\gamma} \parallel (011)_{\alpha} \quad . \quad . \quad . \quad (100)$$

In 1952, GEISLER, MALLERY and STEIGERT⁽¹⁸⁰⁾ reported work on the 1.73 per cent beryllium alloy aged for 1, 3 and 18 hr at 300°C. They observed five diffraction spots on their oscillating crystal films of the alloy aged 18 hr, which could not be attributed to the matrix or the equilibrium precipitate γ . They attempted the interpretation of the diffraction evidence by postulating a number of intermediate structures involving simple atomic movements. It was found necessary to assume the existence of a prior structure γ'' coherent on the $\{100\}$ planes of the matrix in order to obtain a γ' structure which would fit the x-ray evidence. Their assumptions involved conditions which specified the structure and lattice parameter of γ'' although they had no actual evidence of its existence. GEISLER and his co-workers also found relrods in $\langle 100 \rangle_{\text{Cu}}$ and $\langle 112 \rangle_{\text{Cu}}$ directions and relplanes parallel to $\{100\}_{\text{Cu}}$ planes. They were able to explain both their own experimental findings, and those of the other investigators^{(178), (155), (128), (179), (152)} by the sequence of structures γ'' , γ' , γ having matrix habit planes $\{100\}$, $\{112\}$, and $\{111\}$ respectively. The conclusion that the habit planes of the γ structure were $\{111\}_{\text{Cu}}$ was based on a metallographic investigation. This is supported by the work of DAHL, HOLM and MASING⁽¹⁸¹⁾ who found on ageing wire specimens that the γ crystals had a fibrous structure with $[110]_{\gamma}$ along the axis of the wire, while the matrix crystals had the usual fibrous structure with $[111]_{\text{Cu}}$ along the axis. The orientation relationship given by GUY *et al.*,⁽¹²⁸⁾ by GUINIER *et al.*,^{(178), (155)} and by MIYATANI,⁽¹⁸²⁾ differs from this and is in accord with that of GRUHL and WASSERMANN⁽¹²¹⁾ (equation (100)). GUY *et al.* and GUINIER *et al.* have stated that the relationship given by them was approximate. The evidence obtained by GEISLER and his co-workers suggests that the precipitates γ'' , γ' and γ , appear in that order with increasing ageing time. They have no evidence to enable a choice to be

made between independent nucleation of γ'' , γ' and γ , or some consecutive reaction $\gamma'' \rightarrow \gamma' \rightarrow \gamma$, although they do suggest that as the three habit planes (100), (112) and (111) have a [110] direction in common, a series of allotropic changes may be possible.

GEISLER and his co-workers have undoubtedly put forward an ingenious explanation of their experimental findings. Their ideas must, however, be treated with some reserve until supporting evidence is available. Summing up, we can say that GUINIER has produced evidence of the formation of beryllium-rich regions on {100} planes of the matrix in the early stages of ageing. Both GEISLER, MALLERY and STEIGERT, and GRUHL and WASSERMANN have each established the existence of a transition precipitate. Their proposed structures are different, the interplanar spacings on which these are based are not in agreement and there is a remarkable discrepancy in the lattice constants which they assume for the solid solution (3.59 Å and 3.54 Å) and the equilibrium precipitate (2.70 Å and 2.67 Å). It is only possible to conclude that there is at least one transition precipitate whose structure is at present uncertain.

Iron-carbon Alloys

During the last ten years work on this system has been carried out by British, Russian and American workers. Prominent amongst the most recent published papers are those of JACK whose present views will be stated and used as a basis for discussing both his results and those of other workers. Quenched martensitic steels possess an already hardened structure consisting of tetragonal martensite (α') and retained austenite (γ). ANTIA, FLETCHER and COHEN⁽¹⁹³⁾ state that high carbon steels undergo three structural changes during low temperature tempering or ageing, and define these stages as that occurring from 80–160°C accompanied by an increase in hardness, that occurring from 230–280°C accompanied by slight softening, and finally, that occurring at 260–360°C accompanied by marked softening. It is stressed that the underlying phase reactions are time dependent.⁽¹⁹³⁾

As stated by JACK,^{(151), (194)} there is general agreement that the second tempering stage corresponds to the transformation of retained austenite. He confined his attention to the first and third tempering stages which are associated with the decomposition of martensite to form the equilibrium structures ferrite (α) and cementite (orthorhombic Fe_3C). The experimental work was limited to polycrystalline aggregates which he investigated using the Debye-Scherrer powder method. JACK employed crystal reflected monochromatic x-radiation thus obtaining a low and uniform background and greatly increasing the sensitivity and accuracy of the method. On tempering at 120°C JACK noted that the martensite pairs of reflections were replaced by broader

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ferrite lines. No decomposition of the retained austenite was apparent. Fig. 78 taken from JACK's paper⁽¹⁵¹⁾ shows the "as quenched" condition, (a), and photographs after 5 and 40 days at 120°C, (b) and (c). Certain very faint and diffuse extra lines which were observed are marked on (b) and (c). These lines increased in intensity with increased ageing time and are shown by JACK to be possible diffractions of a close-packed hexagonal phase which he terms ϵ iron carbide. The unit cell dimensions were similar to those previously reported by HOFER, COHN and PEEBLES⁽¹⁹⁵⁾ which they attributed to Fe_2C , and were also similar to the values associated with a hexagonal carbide detected as a fine dispersion by HEIDENREICH, STURKEY and WOODS^{(196), (197)} in their electron diffraction investigation of martensitic steels tempered at 200°C. The relative intensities of JACK's lines were not the same as those of HOFER or HEIDENREICH's carbides nor were they similar to those given by any usual close packed hexagonal arrangement of metal atoms. JACK's results are given in Table 5.

TABLE 5

X-ray Diffractions from the Close-packed Hexagonal Iron-carbide Transition Phase (ϵ - Fe_3C) of Martensite Tempered at 120°C⁽¹⁵¹⁾

Intensities	Indices <i>hkl</i>	Interplanar Spacings, <i>kX</i>					Calculated for <i>a</i> = 2.729 <i>kX</i> <i>c</i> = 4.326 <i>kX</i>
		Observed after					
		ϕ min.	5 days	7½ days	40 days	40 days	
m	100	28°	2.36	2.40	2.38	2.37	2.36
vw	002	61°	2.12	2.15	—	—	2.16
*	101	0	—	—	—	—	2.07
ms	102	18°	1.60	1.60	1.60	1.60	1.60
w	110	41°	1.36	1.36	1.37	1.36	1.36
m	103	30°	1.23	1.23	1.23	1.23	1.23

* Masked by $\gamma_{(111)}$ and $\alpha_{(110)}$ reflections

He observed that the angular distance ϕ min. between any (hkl) plane normal and the (101) plane normal was roughly proportional to the relative weakening of the usual intensity of the (hkl) diffraction required to give the observed value. Any plane which was not parallel to the (101) plane gave rise to a diffraction line of reduced intensity the reduction being a function of the angle ϕ_{min} . The intensities were estimated visually and hence can be said to be peak and not integrated intensities. The quoted intensities were therefore inversely proportional to the line widths.⁽¹⁹⁸⁾ Thus the line widths were a function of ϕ_{min} and from this JACK argued that the ϵ phase precipitate particles were sufficiently large, or had sufficiently developed periodicity, to satisfy

the Laue conditions in one direction only, normal to the (101) planes. The interplanar spacing of the (101) planes of ϵ carbide (2.07 kX) is almost identical with that of the (101) planes of tetragonal martensite (2.06 kX). JACK suggested that ϵ carbide forms from martensite (α') with (101) _{ϵ} parallel to and coherent with (101) _{α'} . JACK was in effect arguing that because of the almost identical spacing of the (101) planes in the two structures, periodicity was maintained along the normal to these planes, i.e. in the [101] _{ϵ} direction whereas in other directions varying degrees of disorder arose because of the lack of fit of the two structures. This is analogous to the early stages of precipitation in aluminium-silicon-magnesium alloys where the aluminium lattice spacing of $4.04 \text{ \AA}$ is maintained in one $\langle 100 \rangle$ direction but periodicity is disrupted in perpendicular directions. If JACK is correct, single crystal investigations should detect replanes arising from lack of periodicity in all directions in the (101) _{ϵ} planes. His explanation of his results is ingenious and the physical picture so obtained is probable but the actual evidence itself is extremely slight. The five diffraction lines, Table 5, are so broad and diffuse that photometric measurements are not feasible. The visual intensity estimates of such lines must be very approximate and the line widths deduced from them even more so. It is unfortunate also that the (101) line which in JACK's view should be unaffected, and should serve as a standard of intensity for the weakened lines, is itself masked by the austenite (111) and the ferrite (110) diffractions.

On ageing at 160°C and 250°C the diffraction lines due to the retained austenite disappear slowly as do the ϵ iron carbide lines. Concurrently a new set of lines appears and increases in strength: they occupy the positions of some of the cementite lines but the relative intensities are completely different. Included amongst the strongest of these lines are the previously identified diffractions observed on x-ray photographs of tempered martensite by ARBUSOV and KURDJUMOV⁽¹⁸⁶⁾ and ascribed by them to a new iron carbide. JACK explained the anomalous intensities by assuming cementite was being precipitated as thin plates parallel to the (001) planes (of cementite) and that in the [001] direction the Laue condition is relaxed. With sufficiently thin plates only ($hk0$) diffractions occur⁽¹⁸⁷⁾ and JACK shows that his observed line intensities fit in with his postulate if he assumes also the existence of a small proportion of thicker platelets capable of giving three dimensional diffraction.

CRANGLE and SUCKSMITH⁽¹⁸⁸⁾ carried out magnetic saturation intensity measurements on, and hence determined the Curie points of, martensitic steels. They obtained results which differ from those of JACK in that iron percarbide is supposed to form as an intermediate phase between the ϵ iron carbide and the cementite.

CRANGLE and SUCKSMITH⁽¹⁸⁹⁾ make the point that failure to observe diffraction lines from a complex structure like iron percarbide (*g*), Fig. 77, when it is in the form of small particles embedded in a ferrite matrix does not necessarily prove its absence. JACK⁽²⁰³⁾ attempted to discount the magnetic measurements by arguing that the magnetic properties of the thin coherent plates of cementite as it is first formed will differ from those of cementite crystalites due to the effects of strain and small size.* In reply CRANGLE and SUCKSMITH pointed out that there is no experimental evidence that attainable stresses can directly influence the Curie point of a ferro-magnetic. McLEAN⁽²⁰⁴⁾ drew attention to the fact that if the final product of tempering is Fe_3C it seems unlikely that at some earlier stage a phase richer in carbon (iron percarbide Fe_{20}C_9) should form as it would require a higher rate of diffusion. COHEN and ROBERTS⁽²⁰⁵⁾ reported findings in good agreement with JACK as did ARBUZOV.⁽²⁰⁶⁾ CALNAN and CLEWS^(206a) have provided valuable support for the more general features of JACK's views. They extracted electrolytically the platelike precipitate reported by TROTTER and McLEAN⁽²³¹⁾ in a plain 0.6 per cent carbon steel after 1 hr at 250°C, and examined the result by both x-ray and electron diffraction techniques. The x-ray examination yielded the cementite structure with modified intensities as reported by JACK, whereas the electron diffraction pattern was that of cementite with the normal intensities. The equivalent wavelength of the electron beam would be of the order of 0.05 Å, i.e. one-thirtieth of that of the x-rays. Calculation shows that the carbide platelets could possibly be as thin as 30 Å and still yield normal intensities in the electron diffraction patterns (the limiting figure depends on the effective voltage of the electron diffraction unit which has not been given by CALNAN and CLEWS). Platelets of this order of thickness would cause broadening of certain lines in the x-ray diffraction pattern and could lead to the apparent disappearance of some lines and much reduced intensities for others. Strictly two-dimensional platelets (thickness ≥ 10 Å) as suggested by JACK are not consistent with the normal electron diffraction pattern. This point of view has also been taken by FOLKE^(206b) whose work is quoted by LEMENT, AVERBACH and COHEN.^(206c) The latter authors report work on a 1.4 per cent carbon alloy the electron micrographs indicating platelets of a few hundred angstroms thickness while the x-ray diffraction patterns remain those of modified cementite. LEMENT, AVERBACH and COHEN give no details of the x-ray work and FOLKE's thesis is still unpublished. Without knowledge of what these authors mean by modified cementite patterns it is not possible to comment on their finding. KURDJUMOV

* DIJKSTRA and WERT^(203a) have shown how the coercive force may reach a maximum value when the particles are of the same size as the thickness of the domain wall, see p. 243.

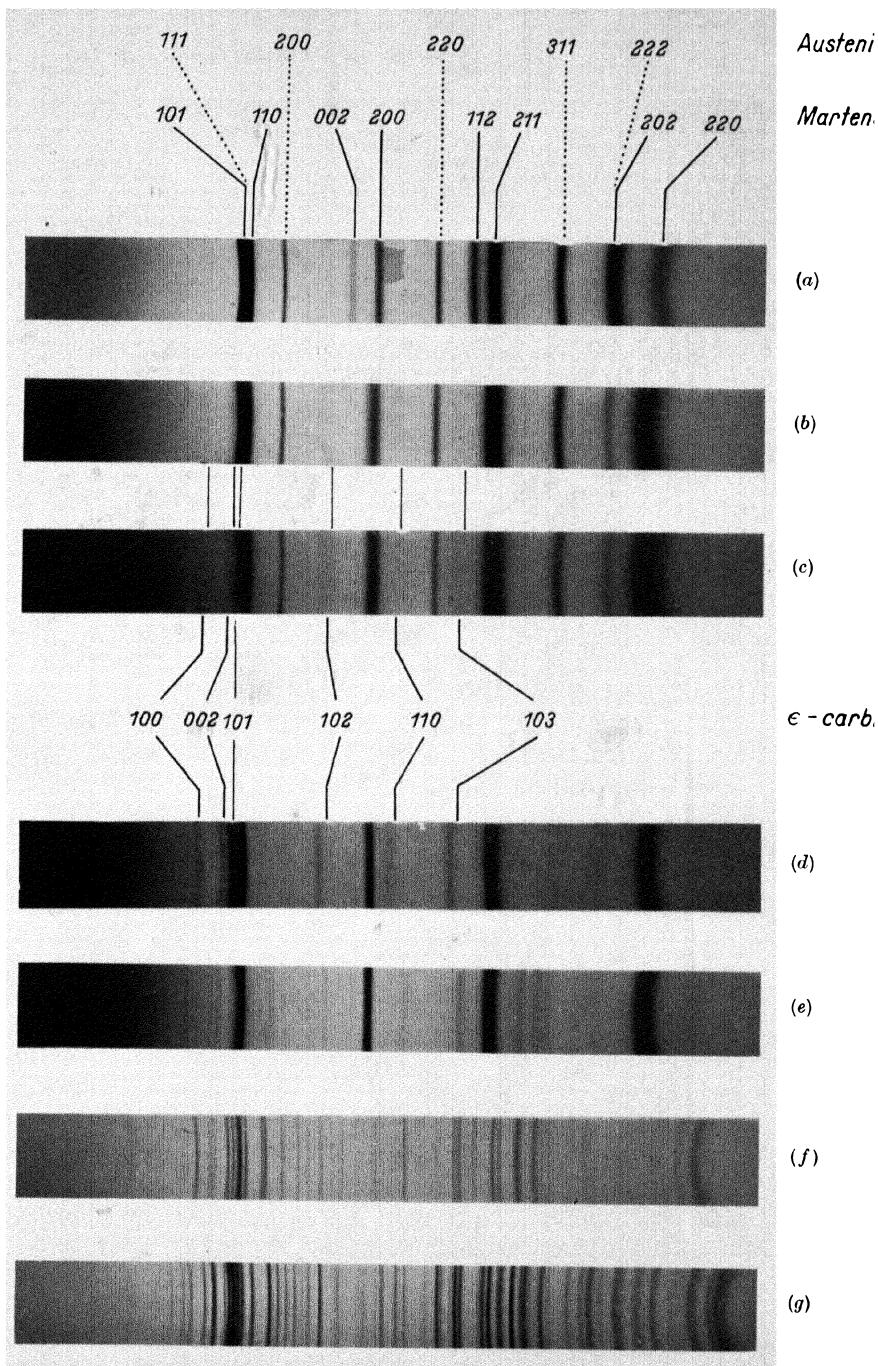


Fig. 78. X-ray powder spectra of martensitic steel (1.3 wt per cent of carbon) tempered at 120° and 250°C. Taken with crystal reflected monochromatic FeK α radiation.⁽¹⁵¹⁾ (a) As quenched; (b) Aged 5 days at 120°C; (c) Aged 40 days at 120°C; (d) ϵ -iron carbide plus ferrite (α -iron); (e) Aged 12 days at 250°C; (f) Crystalline cementite; (g) Iron percarbide⁽¹⁵¹⁾

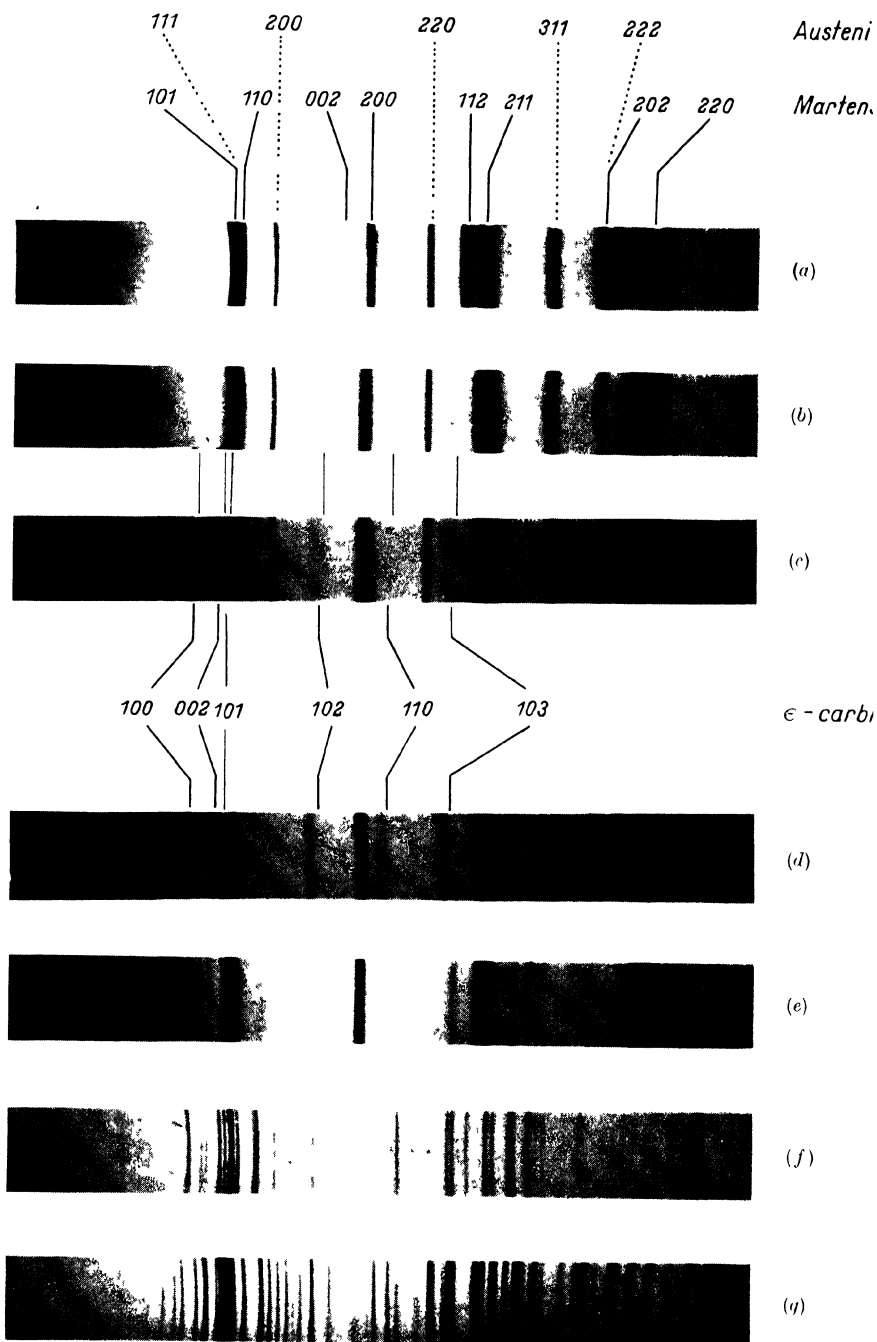
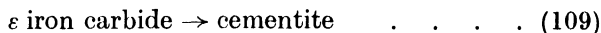


Fig. 78. X-ray powder spectra of martensitic steel (1.3 wt per cent of carbon) tempered at 120° and 250°C. Taken with crystal reflected monochromatic FeK α radiation.⁽¹⁵¹⁾ (a) As quenched; (b) Aged 5 days at 120°C; (c) Aged 40 days at 120°C; (d) ϵ -iron carbide plus ferrite (α -iron); (e) Aged 12 days at 250°C; (f) Crystalline cementite; (g) Iron percarbide⁽¹⁵¹⁾

In the case of supersaturated ferrite the limited information available suggests that the sequence of precipitates is



Iron-nitrogen Alloys

JACK has shown ⁽²¹⁶⁾ that the γ -phase of the iron-nitrogen system (nitrogen austenite) is structurally isomorphous with the carbon austenite of the iron-carbon system. When quenched, nitrogen austenite transforms to nitrogen martensite (α') with a similar structure to that of carbon martensite (α'). After tempering the nitrogen martensite below 200°C JACK⁽²¹⁷⁾ identified a new iron nitride, the existence of which had been suggested by DIJKSTRA⁽²¹⁸⁾ and WERT.⁽⁹¹⁾ Although this is a transition phase in the decomposition of nitrogen martensite to ferrite and Fe_4N (γ') it is also a martensite in which the ordering of the interstitial nitrogen atoms is complete. JACK therefore termed it α'' . The unit cell contains eight distorted and expanded body-centred tetragonal units of the original martensite and has an increased tetragonality with an ideal formulae of Fe_{16}N_2 . This may be thought of as the Fe_4N (Fe_{16}N_4) structure⁽²¹⁹⁾ in which the removal of alternate nitrogen atoms causes considerable distortion. α'' can therefore be regarded as a transition structure between α' and γ' .

In JACK's view the tempering of nitrogen martensite consisted in an ordering of the interstitial nitrogen atoms so that the filled and expanded iron atom octahedra were distributed regularly throughout the lattice. He claimed that the $\alpha' \rightarrow \alpha''$ change was a disorder $\rightarrow$ order change of a novel type. The increased tetragonality of α'' is in contrast to the reduction in tetragonality of martensite₂ (α'') as compared with martensite₁ (α') in the iron carbon system and supports JACK's view that the change is due to ordering. The subsequent formation of the ordered Fe_4N structure from the α'' phase required the diffusion of nitrogen atoms so that a regular array of filled octahedra sharing corners only was produced.⁽²¹⁹⁾ Consideration of the potential matching planes of the three structures suggests that α'' will form with (200) and (020) planes parallel to {100} planes of the matrix (spacings 2.86 and 2.87 Å respectively). The misfit of the (002) α'' planes with the {100} matrix planes is large (3.15 and 2.87 Å respectively). JACK therefore suggested that α'' will form as thin platelets, with (001) α'' parallel to {100} planes of the matrix and coherent with the matrix in the directions $[100]\alpha''$ and $[010]\alpha''$. This surmise on JACK's part, seems reasonable although he has presented no specific experimental evidence to support the idea.

JACK's calculated and observed α'' intensities are given in Table 6, p. 226. The agreement supports his suggested α'' structure.

JACK and MAXWELL⁽²²⁰⁾ have investigated the ageing behaviour of supersaturated nitrogen ferrite (about 0.05 per cent nitrogen) and their

PROGRESS IN METAL PHYSICS

x-ray evidence shows that the first formed precipitate is the transition α'' nitride and not the equilibrium Fe_4N (γ') phase. The same sequence of phases thus appears to occur for both high and low degrees of supersaturation and the behaviour is very similar to that of the iron carbon system in this respect.

TABLE 6
X-ray Diffractions from α'' (9.4 N Atoms/100 Fe Atoms)⁽²¹⁷⁾

Indices	Intensities		Indices	Intensities	
	Calculated	Observed		Calculated	Observed
101	2	—	323	8	5
110	< 1	—	224	37	37
002	< 1	—	332	< 1	
200	< 1	—	105	3	—
112	2	vvw	314	7	113
211	2	vvw	422	106	
*202	131	—	413	8	—
*220	75	80	215	6	vw
103	9	vw	431	< 1	—
301	< 1	—	501	< 1	—
310	< 1	—	510	< 1	—
222	< 1	—	404	51	53
213	11	8	512	2	
004	13	15	305	4	—
312	< 1		006	5	—
321	< 1	—	521	< 1	—
114	4	—	334	5	—
*400	36	33	*116	23	88
303	4	—	*440	65	
204	3	—	*433	17	26
411	< 1	—	*503	9	
330	< 1	—	424	17	—
402	< 1	—	325	17	78
420	< 1	—	206	61	

* Overlapping with α or γ reflections

The available evidence suggests therefore that nitrogen martensite decomposes to form Fe_4N via an intermediate transition phase α'' for both high and low degrees of supersaturation. JACK⁽²¹⁷⁾ has suggested probable orientation relationships between α' and α'' and between α'' and γ' but does not appear to have justified assumptions of thin plates of α'' coherent with α' .

The Magnetic Hardening Alloys

Grouped together under this heading for convenience are the alloys of composition approximately 53 per cent copper–11 per cent iron–36 per cent nickel studied by BRADLEY,^{(221), (222)} DANIEL and LIPSON,^{(223), (224)}

DANIEL,⁽²²⁵⁾ and HARGREAVES,^{(226), (150)} and the commercial alloys Cunico (50 per cent Cu, 21 per cent Ni, 29 per cent Co) studied by GEISLER and NEWKIRK.⁽²²⁷⁾ Both groups of alloys have a single phase face-centred cubic structure at high temperatures but enter a pseudo-binary miscibility gap at lower temperatures. BRADLEY⁽²²¹⁾ showed that his alloy breaks down to two face-centred cubic lattices passing through a transition state of two tetragonal face-centred lattices coherent with the parent cubic lattice. He further showed that, prior to the appearance of the lines due to the coherent tetragonal lattices, broad but quite intense side bands appeared flanking each parent lattice line on the Debye Scherrer films. The parent lattice lines remained sharp and well defined. The two equilibrium face-centred cubic structures formed are respectively copper-rich and copper-poor in composition relative to the original single phase. The two tetragonal coherent transition phases have axial ratios slightly greater than, and slightly less than unity and are also copper-rich and copper-poor relative to the matrix. This system was investigated by DANIEL and LIPSON⁽²²³⁾ who advanced the view that the side bands were due to regular deformation of the cubic lattice caused by the segregation of matrix atoms to form regularly spaced copper-rich and copper-poor regions prior to the formation of the tetragonal phases. The theory of a modulated lattice developed by DANIEL and LIPSON satisfactorily accounted for the positions of the observed side bands but not for their intensities. Later work by the same authors⁽²²⁴⁾ showed that the intensities can be considered to be modified in a systematic manner by extinction effects and after introducing a somewhat large and arbitrary extinction correction their earlier theory accounted for all the experimental findings. In the type of structure they postulated there is a periodic sinusoidal variation of lattice parameter throughout the body of the crystal, concentration gradients are set up in the alloy at regular intervals while the single phase structure is retained. The wavelength of the periodicity is of the order of 10^{-6} cm, i.e. 100 Å. After longer times the diffraction pattern of the periodic state gradually changes into another pattern which can be explained by tetragonal lamellae or a periodic structure with a range of longer periods.

GEISLER and NEWKIRK⁽²²⁷⁾ investigated the commercial magnetic alloy Cunico (50 per cent Cu, 21 per cent Ni, 29 per cent Co) and discovered its behaviour to be analogous to that of the copper-iron-nickel alloy in the occurrence of two coherent intermediate tetragonal phases during decomposition. The diffraction patterns published by GEISLER and NEWKIRK show the tetragonal phases already present in the "as quenched" alloy so that their work has no bearing on the earlier stages of the decomposition process. Nevertheless, they dismiss the theory advanced by DANIEL and LIPSON as unnecessary and explain the

presence of lines flanking the parent lattice lines as due to "the coexistence of parent lattice and decomposition products." Their work is of interest in the relationship they show between magnetic and mechanical

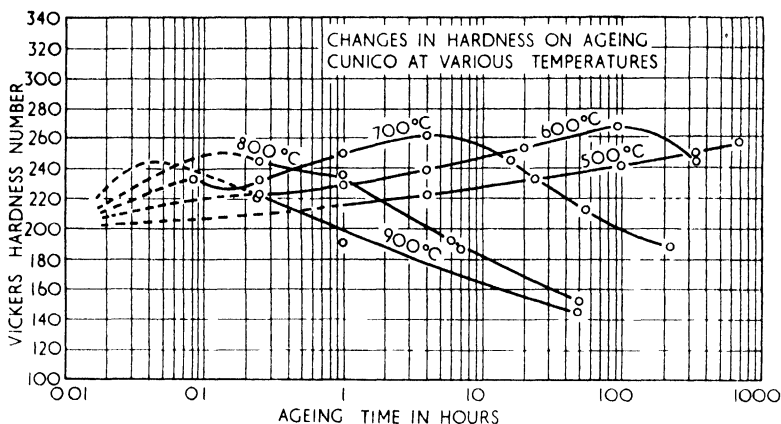


Fig. 79. Hardness of aged samples of cunico⁽²²⁷⁾ (50 per cent copper, 21 per cent nickel, 29 per cent cobalt)

hardness and the stage in the precipitation process. Thus they find maximum hardness ageing at 600°C after 100 hr, Fig. 79, when their diffraction patterns show the precipitate is still predominantly coherent tetragonal lamellae. If the stage corresponding to the side bands in

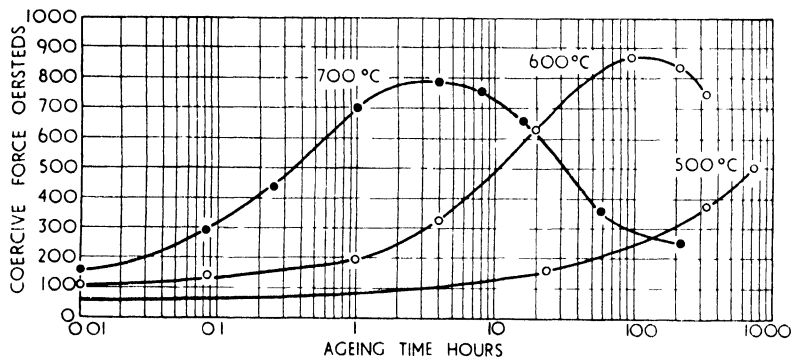


Fig. 80. Coercive force of aged samples of cunico⁽²²⁷⁾

BRADLEY'S alloy, exists in Cunico it has been swamped by the rapid formation of the tetragonal decomposition products which are responsible for the peak hardness. The magnetic properties are shown, Fig. 80, to reach a peak at 600°C at the same time as the hardness. Anomalous upward inflections occur in their electrical resistivity curves at much shorter times, e.g. 1 hr at 650°C and 10 hr at 600°C.

Recent work by HARGREAVES^{(226), (150)} has shed further light on the early stages of the precipitation process in the copper-iron-nickel type alloys. HARGREAVES used strictly monochromatic radiation; the $K\alpha_2$ component was eliminated in order to obtain maximum sensitivity of detection of faint diffraction effects. He examined alloys close to the composition selected by BRADLEY in the field⁽²²⁸⁾ in which the tie lines correspond to approximately constant Ni : Fe ratios so that the separation of the two face-centred cubic equilibrium phases involves chiefly the diffusion of copper atoms. The alloy chosen by HARGREAVES for the bulk of this work was of composition (52 per cent Cu, 14 per cent Fe and 34 per cent Ni) but he carried out experiments on alloys of composition (62 per cent Cu, 9 per cent Fe, 29 per cent Ni) and (45 per cent Cu, 13 per cent Fe, 42 per cent Ni) amongst others. HARGREAVES extended the theory of a modulated lattice developed by PRESTON⁽¹⁴⁶⁾ and by DANIEL and LIPSON.⁽²²³⁾ He made the fundamental assumption that adjacent pairs of tetragonal lamellae of the two phases are formed which retain complete coherence with the matrix and merely cause modulations: the whole group therefore diffracts coherently. This arrangement constitutes a periodic modulation of the structure with a rectangular wave form. He calculated the diffraction to be expected by such a modulated structure for a number of cases of which the most important two are:

- (i) A number of pairs of lamellae in contact with each other with no unchanged matrix in the group considered.
- (ii) Adjacent pairs of lamellae separated by unchanged matrix but equally spaced.

Both (i) and (ii) were calculated for modulation of spacing and for a simultaneous modulation of spacing and scattering power. He shows Fig. 81 that the relative amplitudes of the first and second order side bands is comparable when δ , the fraction of the period occupied by the lamellae, is small but that as δ increases to unity the first order side bands predominate. δ equal to unity is of course case (i). The predictions of HARGREAVES' theory are in good agreement with his experimental findings and enable him to suggest that the lamellae retain complete coherence with the matrix until a maximum disregistry of one third of a unit cell is reached: independent tetragonal lamellae are then formed coherent with the matrix on the basal plane only.

HARGREAVES' views differ from those of DANIEL and LIPSON in the assumption of a rectangular (and local), as opposed to a general sinusoidal wave form for the modulation. The fully coherent tetragonal lamellae can be regarded as a "precipitate" or as part of a segregation process prior to precipitation, they appear to have certain features in common with both processes. Thus HARGREAVES assumes (i) that the net effect of the lamellae is to modulate the matrix lattice which still

papers should be consulted for the detailed results. The appearance of a visible precipitate has been correlated with the ageing curve. The study has, in general, been markedly less successful in detecting and differentiating between the various metastable structures except by indirect inference—the difficulty is due chiefly to the fineness of the precipitate. The early stages of decomposition produce mottling effects in both the visible⁽²³⁰⁾ (Fig. 82) and electron micrographs^{(102), (231)} (Fig. 83). Rippling of the surface is also noted occasionally when large volume changes occur, as in the copper-beryllium system.^{(155), (232–234)} No precipitate was detected in this system by the electron microscope at ageing times which had produced appreciable hardening.⁽²³⁵⁾

GAYLER^{(110), (127)} has observed a change in etching characteristics during the ageing of aluminium-copper alloys which could be associated with a change in the nature of the precipitate. Although CASTAING⁽¹⁰⁷⁾ observed mottling of the replica at an early stage in the ageing of an aluminium-4-per-cent-copper alloy, the earliest precipitate detected by POLMEAR and HARDY⁽¹²³⁾ could be identified as θ' by comparison with x-ray work (SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾). No precipitate was observed at 130°C at ageing times shorter than the time to peak hardness (see Fig. 63) when significant property changes had already occurred.

Studies with the electron microscope which gave reliable structures have indicated particle sizes in aluminium-alloys from fifty to several thousand angstroms, depending on the ageing treatment.^{(106), (107), (123), (236–243)} The particle shape has also been observed with the electron microscope. TROTTER, MCLEAN and CLEWS⁽²⁴⁴⁾ interpreted their results on iron-carbon alloys aged at 250°C as plates. On the other hand, RADAVIDH and WERT⁽²⁴⁵⁾ ageing in the same temperature range reported plates in iron-nitrogen alloys but spheres in iron-carbon alloys. TSOU, NUTTING and MENTER⁽²¹⁵⁾ claimed plates in iron-carbon alloys aged at 300°C. Using a rotary shadowing technique. LEMENT, AVERBACH and COHEN^(206c) found elongated films at the sub- and martensite plate boundaries whilst globular particles occurred within the martensite plates of iron-carbon alloys. There can, however, be no doubt about the needle-like shape of the precipitate in aluminium-Mg₂-Si alloys, which is illustrated by Fig. 84 due to CASTAING.^{(107), (242)}

VI. PROPERTY CHANGES

Measurements for quantitative interpretation should depend on only one particular aspect of the precipitation process, for example the amount of solute remaining in solution. Most of the physical and technical properties integrate effects from the matrix and the precipitate and their interaction with one another. The account such property changes give of the precipitation behaviour varies from the semi-quantitative, through the qualitative and descriptive, to the proof of

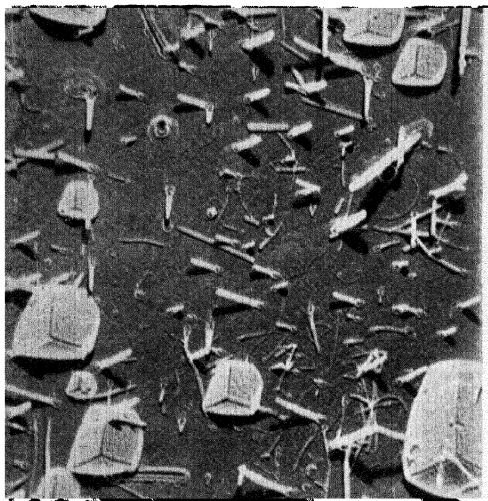


Fig. 84. Needle-like particles in aluminium-
1.5-per-cent- Mg_2Si alloy aged 16 hr at 250°C .
($\times 12,000$)^{(106), (242)}

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and the two values of τ_1 and τ_2 were interpreted as due to different aspects of the decomposition.

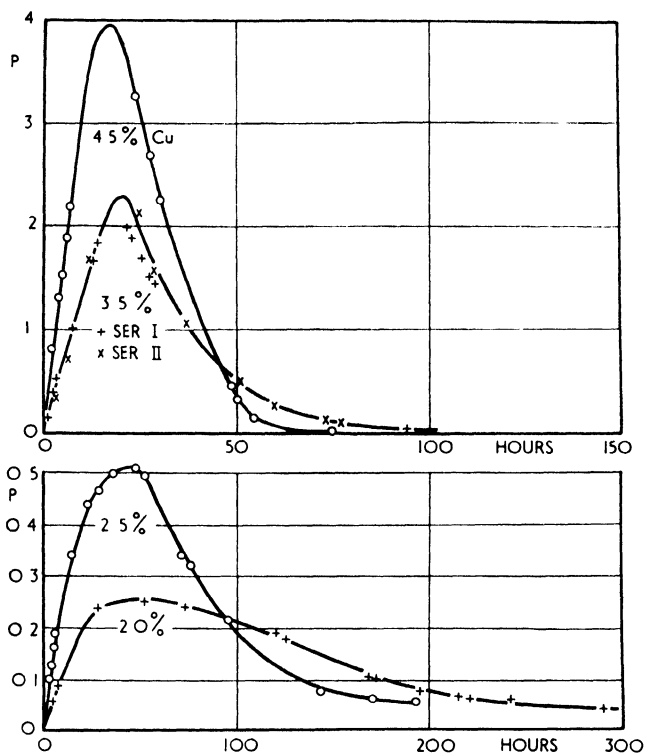


Fig. 85. Evolution of heat during precipitation in aluminium-copper alloys at $225^{\circ}\text{C}^{(246)}$ (P is the rate of heat evolution at time t)

TABLE 7

Experimental and Calculated values for the Heat Evolved by Aluminium-copper Alloys when aged at $225^{\circ}\text{C}^{(246)}$

Wt % Cu	Q meas.	Q calc.	Σ
2.0	43	45	2.1
2.5	47	59	2.0
3.5	75	85	2.0
4.5	111	110	2.2

BORELIIUS, BERGLUND and AVSAN⁽²⁴⁹⁾ have reported calorimetric measurements on iron-nitrogen alloys but they did not study the precipitation process.

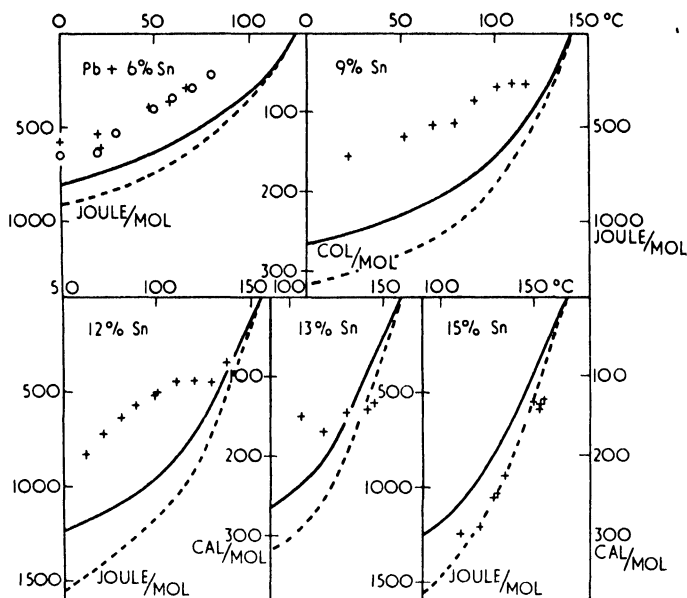


Fig. 86. Evolution of heat during precipitation in lead-tin alloys⁽²⁴⁸⁾

○ BORELIUS and SÄFSTEN⁽²⁴⁷⁾, + NYSTROM⁽²⁴⁸⁾

— calculated from the two-phase boundary

--- values obtained by means of a simplified formula and the experimental points for the 15 per cent tin alloy

Property Changes as Evidence of Metastable States

Thermal Measurements—Differential heating curves on quenched and aged alloys have frequently shown an absorption of heat prior to the evolution associated with general precipitation. The effect was noted by KOKUBO⁽²⁵⁰⁾ on aluminium-Mg₂Si alloys, and by FRAENKEL⁽²⁵¹⁾ on a number of aluminium-copper alloys with and without magnesium and manganese. LUZHNIKOV and BERG⁽²⁵²⁾ found that the heat absorption of aluminium-copper and aluminium-copper-magnesium alloys increased with the ageing time at room temperature.

More precise information was given by the measurements of instantaneous apparent specific heat of SWINDELLS and SYKES⁽²⁵³⁾ whose results on an aluminium-4-per-cent-copper alloy are shown in Fig. 87. Curve (c) applies to the quenched alloy during re-heating. The part between A and B which lies above the calculated curve in the absence of transformations (b) corresponds to an absorption of heat. The dip BCD is due to heat evolved on precipitation and the remaining high

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temperature part results from heat absorbed by the re-solution of the precipitate. Curves (f) and (g) were obtained on alloys aged 15 hr at

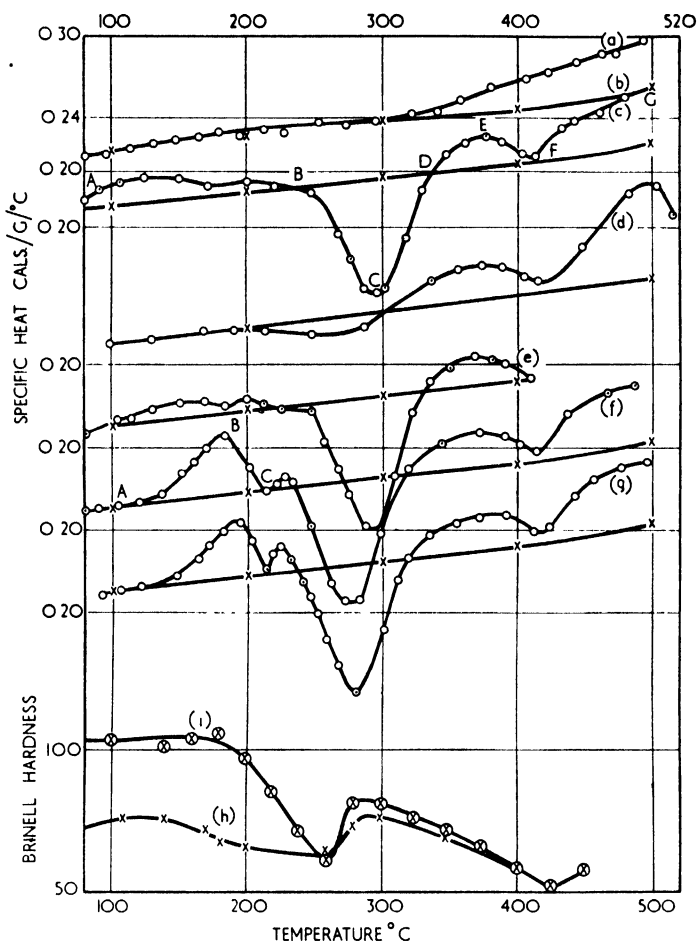


Fig. 87. Changes in the instantaneous specific heat and hardness of an aluminium-4-per-cent-copper alloy on heating⁽²⁵³⁾. Curve (a) slowly cooled 4 per cent copper alloy; (b) calculated specific heat/temperature curve; (c) specimen quenched from 525°C, aged 32 days at room temperature; (d) specimen heated to 380°C and water quenched; (e) similar to curve (c), but aged 3 days at room temperature; (f) specimen quenched and aged 15 hr at 110°C; (g) specimen quenched and aged 22 hr at 140°C; (h) Brinell hardness curve on material treated as curve (e); (i) Brinell hardness curve on material treated as for curve (g)

110°C and 22 hr at 140°C. The first absorption of heat starts at a higher temperature than in curve (c), and is succeeded by a second very small absorption at C in curve (f). The dip at F in curve (c) also appears

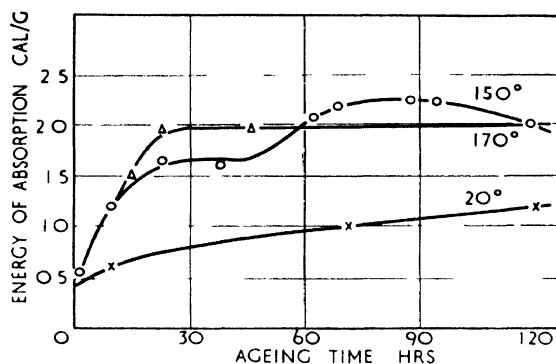


Fig. 88. The energy required to re-dissolve a low temperature decomposition product as a function of the ageing treatment (e.g., the area ABC of curve f in Fig. 87) of an aluminium-4.3-per-cent-copper alloy⁽²⁵⁴⁾

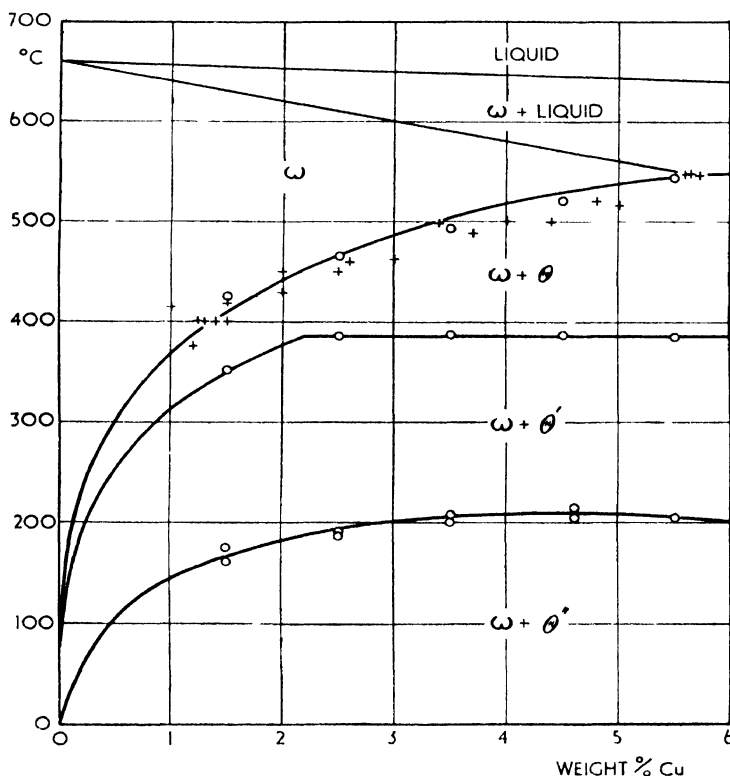


Fig. 89. Stable ($\omega/(\omega + \theta)$) and metastable ($\omega/(\omega + \theta')$, $\omega/(\omega + \theta'')$) solubility curves for aluminium-copper alloys⁽⁶⁷⁾. (Note: θ'' here represents the copper-rich clusters and does not necessarily have the structure of θ'' or G.P. zones [2]).

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to be real. SUZUKI⁽²⁵⁴⁾ has studied more completely the effect of different ageing treatments on the early part of the specific heat/temperature curve. The area under the curve *ABC* of curve (*f*) Fig. 87 is due to the

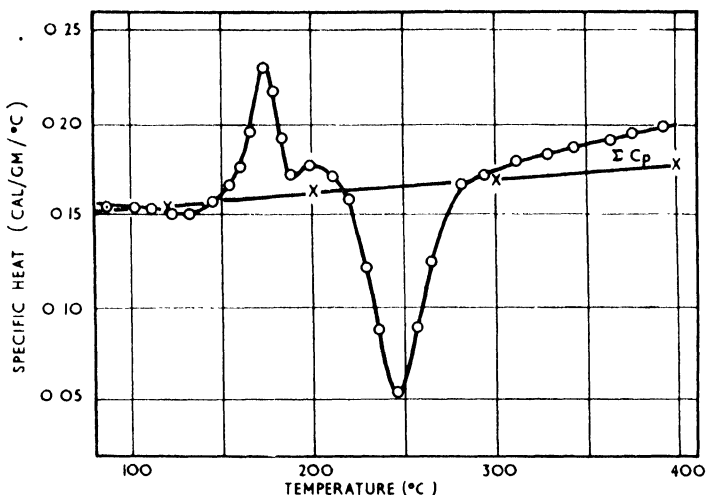


Fig. 90. The instantaneous specific heat curve for an aluminium-40-wt-per-cent-silver alloy aged 7 days at room temperature⁽²⁵⁵⁾

re-resolution of a decomposition product formed at lower temperatures (see the section on Reversion, p. 168) and is thus an inverse measure of the heat evolved during the low temperature ageing. SUZUKI plotted the energy for reversion as a function of the ageing time prior to the specific

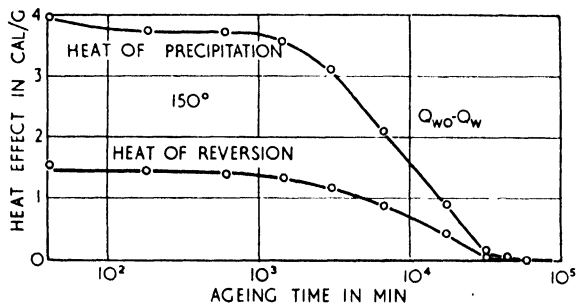


Fig. 91. Dependence of the thermal effects in an aluminium-38-per-cent-silver alloy on the ageing period at 150°C prior to testing⁽²⁵⁷⁾

heat measurements. His results are given in Fig. 88, and were markedly similar in shape to his hardness ageing curves at the same temperatures. For example, both methods give two stage curves at 150°C. The reversion temperatures, that is the point *B* on curve (*c*) of Fig. 87 have been obtained by differential thermal analysis on alloys of different

copper content, and are plotted against composition in Fig. 89 due to BORELIUS, ANDERSSON and GULLBERG.⁽⁶⁷⁾ The plot for θ' comes from points similar to F on curve (c) of Fig. 87.

JONES and LEECH⁽²⁵⁵⁾ and KÖSTER⁽²⁵⁶⁾ found an appreciable heat absorption in aluminium-silver alloys, see Fig. 90, which also shows the secondary small absorption. A more complete account has been given by KÖSTER and SCHELL⁽²⁵⁷⁾ who measured both the heat of precipitation (the area BCD of curve (c) in Fig. 87) and the heat of reversion (the area ABC of curve (f) in Fig. 87) as a function of the ageing time at 150° and 250°C, as shown in Fig. 91. The heat of reversion remained

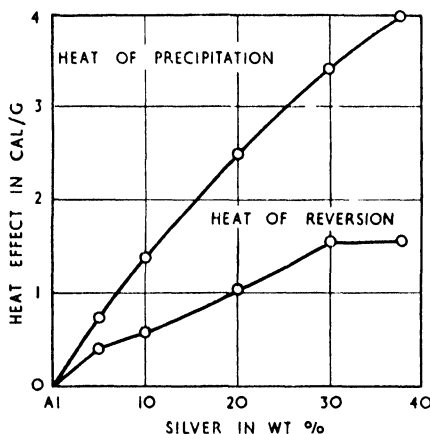


Fig. 92. The heat evolved on precipitation and absorbed by reversion in aluminium-silver alloys⁽²⁵⁷⁾

nearly constant until an ageing time at 150°C corresponding to the second rise in strength (Fig. 97) and then fell smoothly, which is contrary to the results of SUZUKI, Fig. 88. Almost all the heat had been evolved by the aluminium-silver alloy after an ageing time at 150°C equivalent to the time to peak strength. Fig. 92 gives the maximum values of the heats of precipitation and reversion as a function of composition.

The total heat of precipitation reaches about 140 cal/gm atom at 38 wt per cent silver, whilst the heat absorbed on reversion is then about 53 cal/gm atom. It is not possible to relate the heat of precipitation to the free energy of solution of silver in aluminium as this is not known and could be calculated only through the method of equations (37–39), since the solubility curve of silver in aluminium does not give a straight line when plotted logarithmically against $1/T$. The reversion temperature (point C on curve (f) of Fig. 87) has already been shown plotted against composition in Fig. 23 and is of slightly different shape from the curve for $w/(w + \theta'')$ in Fig. 88.

An independent investigation of the aluminium-38% silver alloy by HIRANO^(257a) has confirmed the specific heat curves of KÖSTER and SCHELL. HIRANO paid more attention to an initial evolution of heat before the heat absorption associated with reversion although this was not large in relation to the experimental accuracy. He also showed that the heat absorption (area similar to *ABC* on curve *f* of Fig. 87) could be plotted, merely by changing the scale, on the same curve as the hardness in the case of an aluminium-20% silver alloy aged for periods up to 10h at 160°C.

SWINDELLS and SYKES⁽²⁵³⁾ observed a small heat absorption in the specific heat temperature curve of an aluminium-Mg₂Si alloy, but did not find similar effects in quenched silver-copper and copper-beryllium alloys, where the first change was the evolution of heat due to precipitation. JONES and LEECH⁽²⁵⁸⁾ also studied copper-beryllium alloys and observed weak absorptions after short ageing treatments which they suggested to be due to reversible transformations in the precipitate.

The details of the specific heat temperature curve have not yet been satisfactorily explained on a quantitative basis, and in any event will be somewhat dependent on the rate of heating used. The absorption of heat could result from the solution of nuclei which were below the size for stability at the higher temperature. A stronger case can be made for the view that the heat absorption represents the energy to re-dissolve a metastable precipitate when its solubility curve has been crossed. x-ray work generally shows no evidence of the low temperature decomposition product above a certain ageing temperature. The thermal measurements suggest metastable states occur in aluminium-copper, aluminium-copper-magnesium, aluminium-silver, aluminium-Mg₂Si (less sure) alloys, they do not occur in silver-copper alloys, and their existence from this evidence is uncertain in copper-beryllium alloy.

Magnetic Properties

The measurement of magnetic properties on binary alloys has only rarely provided information not obtainable from other experimental techniques. BITTER and KAUFMANN⁽²⁵⁹⁾ and GORDON and COHEN⁽²⁶⁰⁾ observed that the initial general precipitate in copper-iron alloys was paramagnetic. The latter found that the precipitate in the grain boundaries (discontinuous precipitation) was always ferromagnetic. The former workers and SMITH⁽²⁶¹⁾ reported that the paramagnetic phase could be transferred to the ferromagnetic condition by cold work, in substantiation of the results due earlier to TAMMANN and OELSEN.⁽²⁶²⁾ The first precipitate was considered to be metastable face-centred cubic iron in registry with the matrix lattice, whilst the ferro-magnetic phase was the stable body-centred cubic iron.

Significant magnetic measurements have been carried out on ternary

and more complex alloys. SNOEK⁽²⁶³⁾ studied the iron-12 wt per cent cobalt-18 wt per cent molybdenum and the iron-26.5 wt per cent nickel-13.3 wt per cent aluminium alloys. Both alloys consist of ferromagnetic and non-magnetic phases at room temperature but are single phased at elevated temperatures. The iron-cobalt-molybdenum alloy precipitates a ternary phase on ageing⁽²⁶⁴⁾. The iron-nickel-aluminium alloy is in a pseudo-binary miscibility gap separating two body-centred cubic solutions, one based on α -iron and the other on NiAl so that the nickel and aluminium are in equiatomic proportions.⁽²³⁰⁾ The important measurements made by SNOEK were of the coercive force and "internal

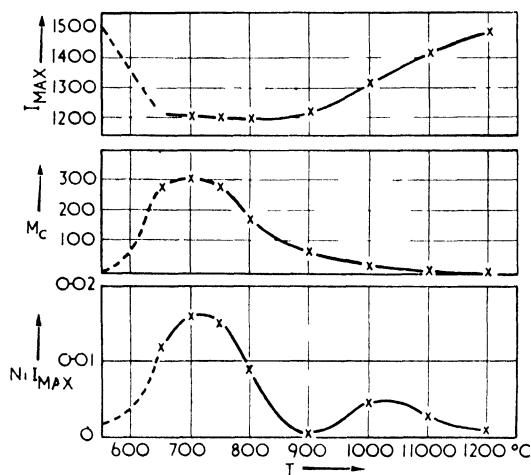


Fig. 93. Saturation magnetic intensity (I_{max}), coercive force (M_c) and the "internal demagnetization factor" (N_i) for an iron-12-per-cent-cobalt-18-per-cent-molybdenum alloy aged 5 minutes at successively higher temperatures; the second maximum in N_i is related to the $\alpha \rightarrow \gamma$ transformation⁽²⁶³⁾

demagnetization factor" which is closely related to the ratio between the volume of non-magnetic material and the total volume of the specimen. The results in Fig. 93 show that the coercive force and the "internal demagnetization factor" change towards their peak values simultaneously in the iron-cobalt-molybdenum alloy. In the iron-nickel-aluminium alloy, the coercive force changed much earlier than the "internal demagnetization factor" and, on isothermal ageing (Fig. 94) passed through its peak before the latter had changed significantly. Results were also obtained by SNOEK⁽²⁶⁵⁾ on a series of alloys along the section from iron to NiAl phase and were taken to support the view that although iron-cobalt-molybdenum alloys gave "dispersion hardening" (i.e. precipitation) iron-nickel-aluminium alloys gave "diffusion hardening" (i.e. the initial decomposition did not involve true precipitation). It has been known for some time that Alnico magnetic materials

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(iron-nickel-aluminium plus cobalt, titanium, etc.) show their highest coercivity combined with a useful remanence when the quenching and re-heating to the ageing temperature is replaced by a controlled rate of cooling. Results due to SNOEK are shown in Fig. 95 from which it will be seen that the "internal demagnetization factor" is also much increased so that only part of it is truly non-magnetic. BURGERS and

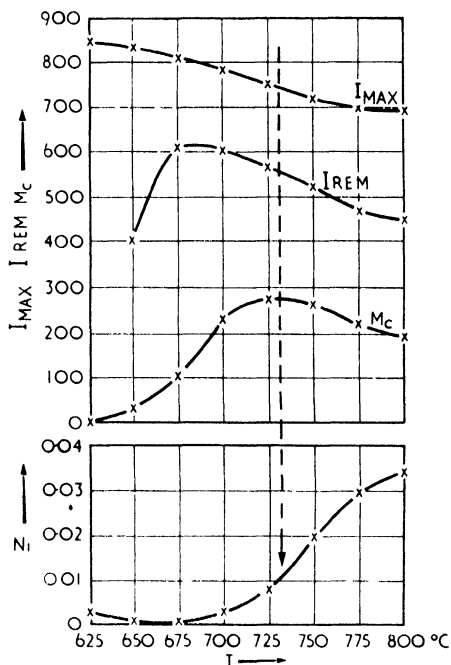


Fig. 94. Saturation magnetic intensity (I_{max}), coercive force (M_c) and the "internal demagnetization factor" (N_i) for an iron-26.5-wt-per-cent-nickel-12.3-wt-per-cent-aluminium (22.5-atomic-per-cent-nickel-22.5-atomic-per-cent-aluminium) alloy aged 15 minutes at successively higher temperatures⁽²⁶³⁾

SNOEK⁽²⁶⁶⁾ had earlier failed to detect a new phase by Debye-Scherrer x-ray methods except after extremely slow cooling.

The behaviour of the iron-nickel-aluminium alloys can be explained by the segregation of nickel and aluminium atoms over small regions of composition without the formation of a new phase. HARDY⁽²⁶⁷⁾ has shown analytically the existence of a spinodal curve in systems similar to iron-NiAl. The high coercive force is taken to result from the lattice strain and the small size of the regions involved. GEISLER⁽²⁶⁸⁾ has preferred the view that a high coercivity is due to high coherency strains in the lattice or magneto-striction of opposite sign in the matrix and precipitate. He has suggested⁽⁶⁾ that a controlled rate of cooling

provides a more constant or narrower distribution of particle size of the coherent precipitate.

It may be noted in passing that suitable compositions of the Alnico magnetic materials, particularly those containing cobalt and copper, are also affected if the cooling be carried out in a magnetic field so that the precipitation occurs preferentially in the direction of the magnetic

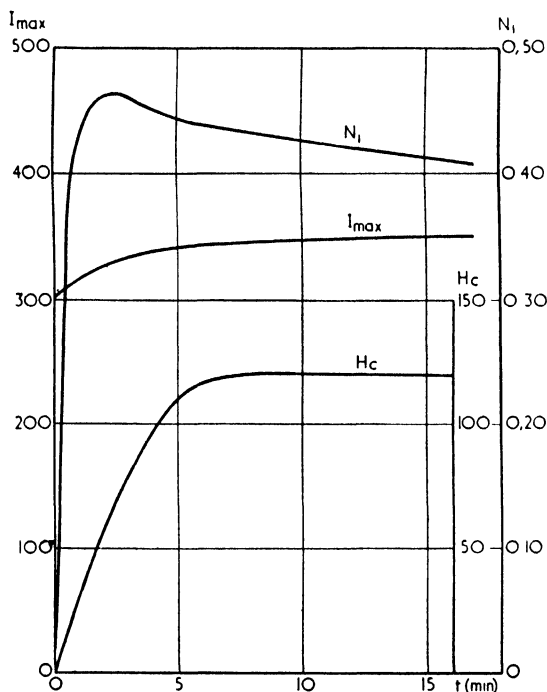


Fig. 95. Saturation magnetic intensity ($I_{\max}$), coercive force (H_c) and the "internal demagnetization factor" (N_i) for an iron-35-atomic-per-cent-nickel-35-atomic-aluminium alloy as a function of the cooling time from 1200–500°C. The very high values of N_i show that the alloy is not homogeneous⁽²⁶⁵⁾

field^(269–273) but the discussion of this phenomenon lies beyond the scope of the present work.

The x-ray results of DANIEL and LIPSON,^{(223), (224)} DANIEL⁽²²⁵⁾ and HARGREAVES⁽²²⁶⁾ on the copper-iron-nickel system can be interpreted as due to micro-segregation of the elements over small regions (further details are given on page 229). However, it is not certain whether these alloys (which are cold-rolled in commercial practice) show the anomalous changes in magnetic properties observed in the iron-nickel-aluminium system. The significance of the x-ray results can only be determined if similar effects are observed in another system where they can be correlated with the magnetic ageing curves. GEISLER and NEWKIRK⁽²²⁷⁾

have examined the copper-nickel-cobalt system, which possesses a pseudo-binary solubility gap like the copper-iron-nickel system, and concluded that a simple mechanism involving a coherent precipitate explained both the magnetic and precipitation phenomena in all systems;^{(268), (274)} a point of view which has been discussed above in relation to the x-ray work. This view is probably satisfactory when no anomalies occur in the ageing curves or structural data. In the case of a gold-30-per-cent-nickel alloy aged at 500°C, the curves for the electrical resistance, hardness, coercive force, magnetization and remanence all change simultaneously.⁽²⁶⁸⁾ However, GEISLER's conclusion does not appear able to dispose satisfactorily of SNOEK's curves for the "internal demagnetization factor" in iron-nickel-aluminium alloys, Fig. 95.

DIJKSTRA and WERT^(203a) suggested that the coercive force should be a maximum when the particle size was the same as the thickness of the domain wall. An iron-0.02-per-cent-carbon alloy gave its maximum coercive force after about 95 per cent precipitation when aged at 250°C. On ageing at 200°C, the maximum value of the coercive force was not reached until precipitation, judged by internal friction measurements, was complete. The effect was thought to be associated with coagulation of particles still below the critical size at the end of precipitation. When the precipitate was taken as spheres of Fe_3C the critical diameter was calculated to be 1200 Å.

Ageing Curves

Property changes with ageing time which occur in several stages or which are not predicted by simple considerations may provide valuable evidence of the existence of metastable states. Changes in hardness giving small inflections on a hardness/time curve and results on complex alloys are better neglected but GAYLER and PARKHOUSE⁽¹²⁷⁾ and later HARDY⁽¹⁰¹⁾ have clearly demonstrated two stage ageing curves in aluminium-copper alloys. The latter's results at 130°C have already been given in Fig. 63 together with the structural states observed. Two stages separated by a flat were also found at 110°C but the plateau becomes less evident as the ageing temperature is raised. Fig. 65 has shown how the peak hardness values fell into two groups when plotted against composition. The upper group were associated with the two stage ageing curve and were due chiefly to the G.P. zones [2] (θ''). At 130°C θ' occurred from the peak onwards so that the replacement of the G.P. zones [2] by θ' must cause a softening. On the other hand, the formation of θ' in a matrix not stiffened by G.P. zones [2] led to hardening and the lower group of peak hardness values in Fig. 65 were associated with θ' . It may be noted here that the time to peak hardness at 130°C was almost independent of concentration. This is a most unusual occurrence because the rate of precipitation is invariably increased and

the time to peak hardness is usually reduced by increasing the super-saturation. HARDY⁽¹⁰¹⁾ also found that the curves for the incubation values of his hardness ageing curves formed a set of intersecting *C*-curves Fig. 96 (cf. Fig. 26) allowing good correlation with the initial incubation products observed by x-ray methods.⁽¹⁴⁵⁾

LANKES and WASSERMANN⁽¹²²⁾ studied both the hardness and volume changes accompanying the ageing of the aluminium-4-per-cent-copper

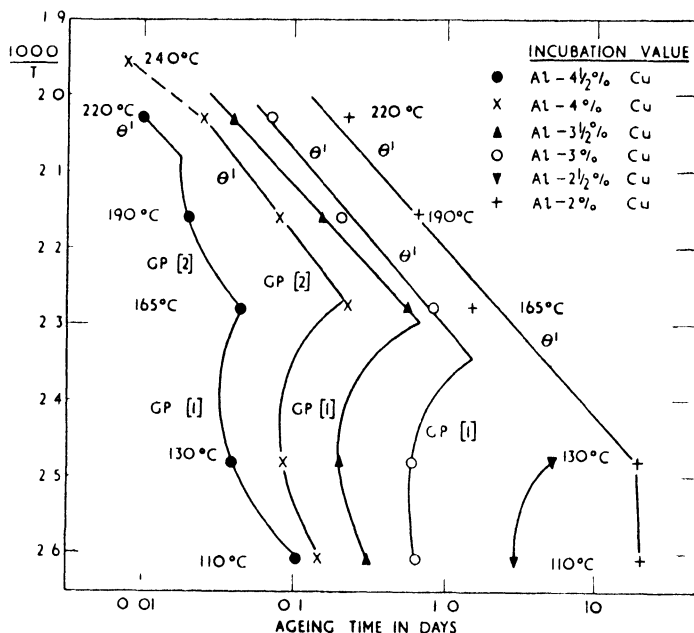


Fig. 96. Temperature/incubation value relationships with the decomposition products first detected by x-ray investigation

alloy. They found an initial contraction (also observed by KOKUBO and HONDA⁽²⁷⁵⁾) was replaced by an expansion due to general precipitation. At higher temperatures there was a subsequent contraction (also observed by KEMPF and HOPKINS⁽²⁷⁶⁾) which was associated with the transformation of θ' to θ . No initial contraction took place at ageing temperatures above 200°C. Anomalous dilation curves are also found on aluminium-copper-magnesium alloys, the pseudo-binary aluminium-*S* phase (Al_2CuMg) alloy gives a large expansion at room temperature which is subsequently followed by a contraction.⁽¹⁰⁵⁾ It has been noted by several workers^{(277), (278)} that the electrical resistance of aluminium-copper alloys passes through a maximum on ageing at room temperature whereas the simple concept of rejection of solute from the matrix predicts a fall in resistance. The effect is much more pronounced on the aluminium- Al_2CuMg alloy.⁽¹⁰⁵⁾

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A very similar pattern of results has been found on aluminium-silver alloys by KÖSTER and his co-workers^{(72), (173), (279)} who obtained clearly defined two-stage ageing curves. Fig. 97 shows the elastic limit with two-stage curves below 185°C for the aluminium-38-per-cent-silver

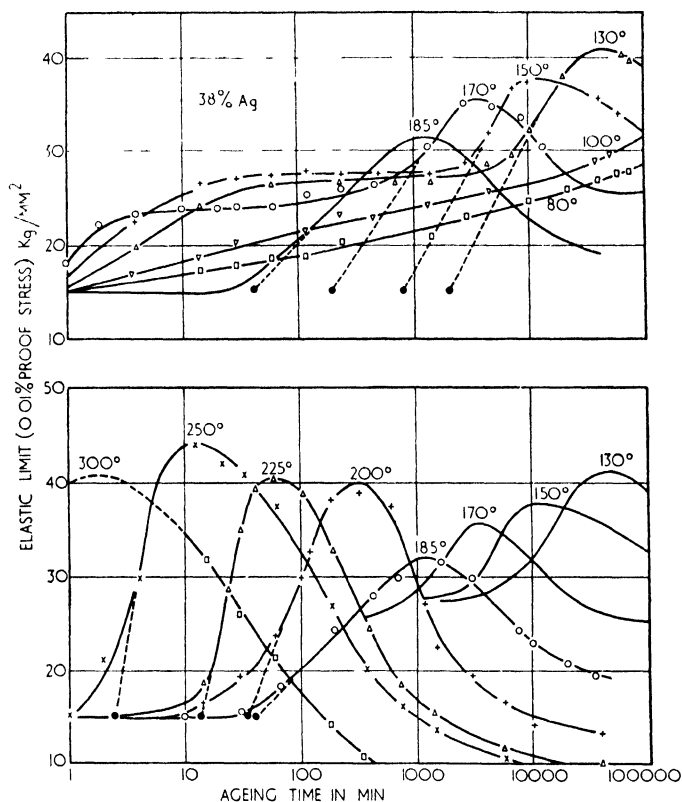


Fig. 97. The elastic limit of an aluminium-38-wt-per-cent-silver alloy aged at various temperatures⁽⁷²⁾

alloy. Isochronal plotting in Figs. 98 and 99 for the hardness and electrical conductivity bring out the same point. Fig. 23 has already given the compositional dependence of the temperature above which only single stage ageing curves were obtained. GEISLER, BARRETT and MEHL⁽¹⁰⁹⁾ also found irregularities in the resistance curves of aluminium-silver alloys, and WATANABE and KODA⁽¹⁷⁴⁾ have presented evidence of two stage hardness ageing curves in aluminium-20-per-cent-silver alloys. It is evident from Fig. 97 that the incubation value/temperature plot for the aluminium-38-per-cent-silver alloy will also show evidence of two intersecting *C*-curves. For example, the incubation times lengthen as the ageing temperature is increased to 185°C and then decrease at higher temperatures.

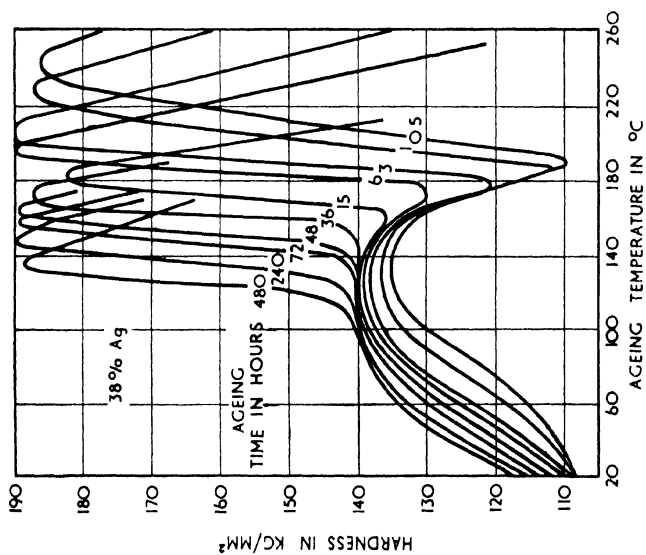


Fig. 98. Isochronal curves for the hardness of an aluminium-38-wt-per-cent-silver alloy aged at various temperatures (72)

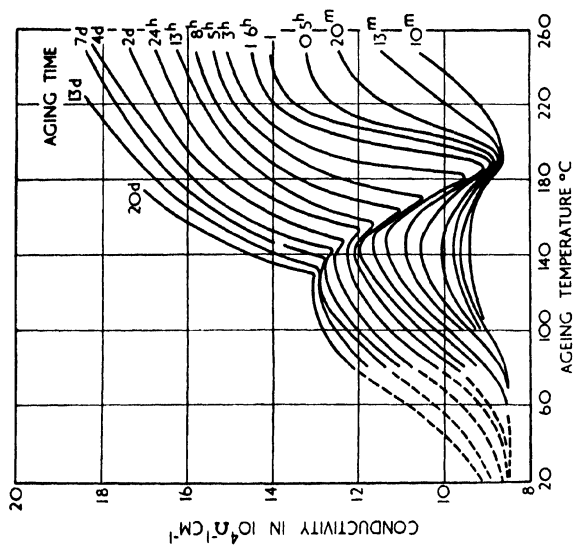


Fig. 99. Isochronal curves for the electrical conductivity of an aluminium-38-wt-per-cent-silver alloy aged at various temperatures (72)

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Anomalous changes have been observed in other alloy systems. For example, LACOMBE⁽¹⁹¹⁾, ⁽²⁸⁰⁾ reported an expansion in the lattice parameter of aluminium-13.5-per-cent-magnesium alloys aged at 200°C prior to the reduction expected to accompany precipitation. JOLIVET and ARMAND have also observed dilation anomalies in these alloys.⁽²⁸¹⁾ COHEN⁽²⁸²⁾ found small additional ageing peaks on the hardness curves

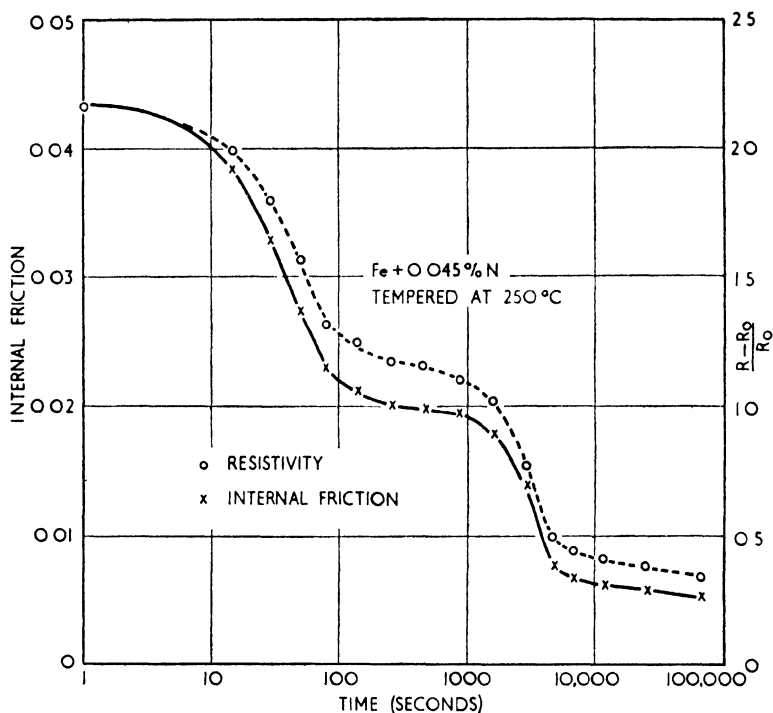


Fig. 100. Resistivity and internal friction during precipitation of nitrogen at 250°C⁽⁹²⁾

of silver-8.7-per-cent-copper alloy and also a slight increase in volume before the contraction on precipitation. Copper-beryllium alloys give an increase in resistance on ageing⁽²⁸³⁾ which GRUHL and WASSERMANN⁽¹²¹⁾, ⁽²⁸⁴⁾ interpreted as evidence of the formation of Guinier-Preston zones as the first decomposition product. This is supported by the accompanying rise in hardness.⁽¹²⁸⁾ Forms of two-stage ageing curves are also found in aluminium-zinc alloys.⁽¹¹¹⁾, ⁽²⁸⁵⁾ Both DIJKSTRA⁽²¹⁸⁾ and WERT⁽⁹²⁾ observed a two-stage curve in the ageing of iron-nitrogen alloys and the latter's results are shown in Fig. 100. Both iron-carbon⁽²⁸⁶⁾ and iron-nitrogen alloys are normal in that the rise in hardness and change in other properties occurs at the same time as the fall in resistance and damping capacity.

Regular changes are observed in other systems although this may result partly from the lack of a complete investigation or from the inability to obtain a sufficiently high degree of supersaturation. Effects due to discontinuous precipitation also show up, for example Fig. 101 due to PERRYMAN and BROOK⁽¹⁹²⁾ and WEIL⁽²⁸⁷⁾ gives the lattice parameter changes in aluminium-7-per-cent-magnesium alloys. The co-existence of the new and old solid solution with different lattice parameters is evidence of discontinuous precipitation. It will be noted that the new solid solution continues to deposit solute after it has been

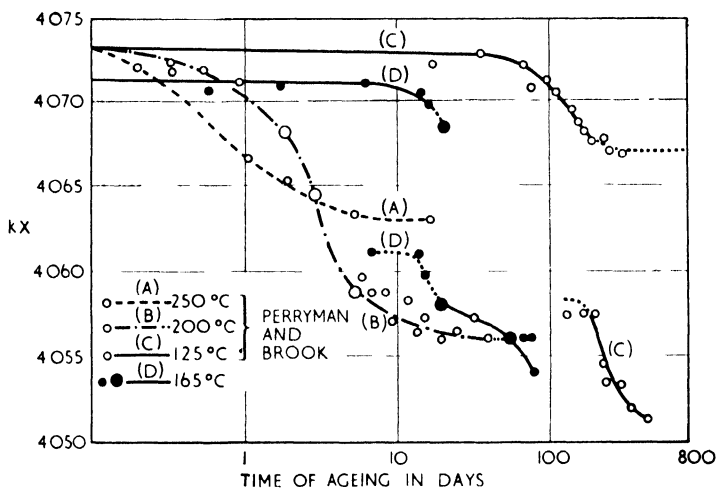


Fig. 101. Lattice parameter measurements of PERRYMAN and BROOK⁽¹⁹²⁾ and WEIL⁽²⁸⁷⁾ on aluminium-7-per-cent-magnesium alloys aged as indicated

formed. However, there appears to be no evidence in the literature to support the conclusion (p. 154) that the composition of the initial nucleus becomes more rich in solute during the ageing process. Such information would be difficult to obtain because a very small quantity of a new phase is very difficult to detect on Debye-Scherrer films.

Anomalous property changes have provoked much discussion. The increase in resistance has been associated with lattice strains due to a coherent precipitate out-weighing the fall in supersaturation. An alternative view suggests the particles should have an abnormally high resistance when their size corresponds approximately to the wavelength of the conducting electron, about four atom distances.⁽²⁸⁸⁾ An increase in resistance can only be accepted as direct evidence of a metastable precipitate if the former view holds.

The anomalous change in volume (and lattice parameter) is generally associated with coherency strains between the particle and matrix or

with the relief of quenching strains. The former view allows the change to be accepted as evidence of a metastable precipitate since the equilibrium precipitate will generally possess a true interface.

FINK and SMITH⁽¹⁹⁾ and GEISLER^{(6), (124)} have taken strong exception to the view that the two-stage ageing curves represent evidence of a change from one metastable decomposition product to another. GEISLER prefers to believe that the initial rise in aluminium-copper alloys is due to rapid precipitation of θ' in localized regions whilst general precipitation accounts for the second rise to peak hardness. It is completely true that the first rise is greatly dependent on the rate of quenching (severity of the quenching strains) but the x-ray work illustrated by Fig. 63 and Fig. 64 disposes of GEISLER's view because a sequence of decomposition products has been observed. It is quite possible that the G.P. zones [1] may be more favoured by the quenching strains than the G.P. zones [2] and thus accentuate the flat plateau. But this could be taken to favour the argument for a distinction between the two structures. The x-ray results on aluminium-silver alloys leave little doubt that the two stage ageing curves reflect the formation of the spherical clusters as the cause of the first stage and γ' as the cause of the second stage even though the process appears rather complex (see page 199 *et seq.*).

Reversion

It was first noted by GAYLER⁽²⁸⁹⁾ that an aluminium-copper-magnesium-silicon alloy which had been aged at room temperature softened before hardening when it was aged at an elevated temperature. Reversion may be defined as the loss of hardness or other properties produced by heating for very short times to temperatures above the ageing temperature. The alloy will be capable of re-hardening at the lower temperature. It is a general experience that the re-ageing is slower than on the quenched alloy and this is regarded as due to the relief of quenching strains. Fig. 102 shows the repeated reversion of iron-carbon alloys.^{(290), (291), (292)}

The subject has been extensively studied on aluminium-copper alloys^{(293), (294), (295)} and on duralumin-type alloys.⁽²⁹⁶⁻²⁹⁹⁾ Similar results have been found on aluminium-zinc,^{(300), (301)} aluminium-magnesium-silicon,^{(302), (303)} and other aluminium alloys.⁽³⁰⁴⁾ In aluminium-silver alloys the first stage of the hardness curve shows complete reversion, see Fig. 103, whilst only part of the second stage is recovered,⁽⁷²⁾ similar results applied to the electrical conductivity.⁽¹⁷³⁾ PRESTON⁽¹⁶²⁾ and GUINIER⁽¹⁶⁸⁾ reported that reversion redissolved the precipitate formed on the natural ageing of aluminium-copper alloys, but GLOCKER, KÖSTER, SCHERB and ZIEGLER⁽¹⁴²⁾ noted no change in the x-ray pattern of aluminium-silver alloys after reversion because

they were only detecting the stacking faults or incipient γ' precipitate (see page 203 *et seq.*). In the discussion of the x-ray work on this system

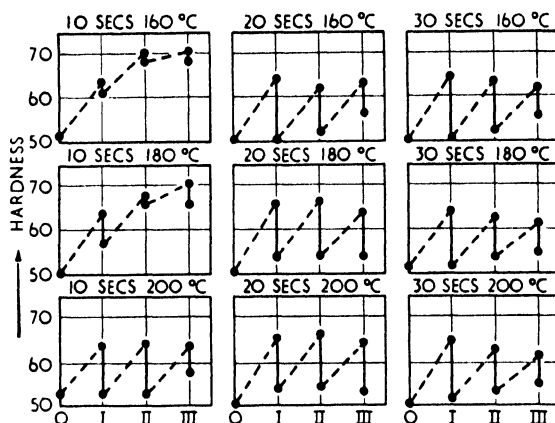


Fig. 102. Reversion treatments repeated three times after intervals of seven days at room temperature on quenched 0.043 per cent carbon steel⁽²⁹¹⁾

the conclusion has been reached that the silver clusters would be redissolved. SAULNIER⁽²⁹⁵⁾ and AVAKYAN and LASHKO⁽³⁰⁵⁾ found that

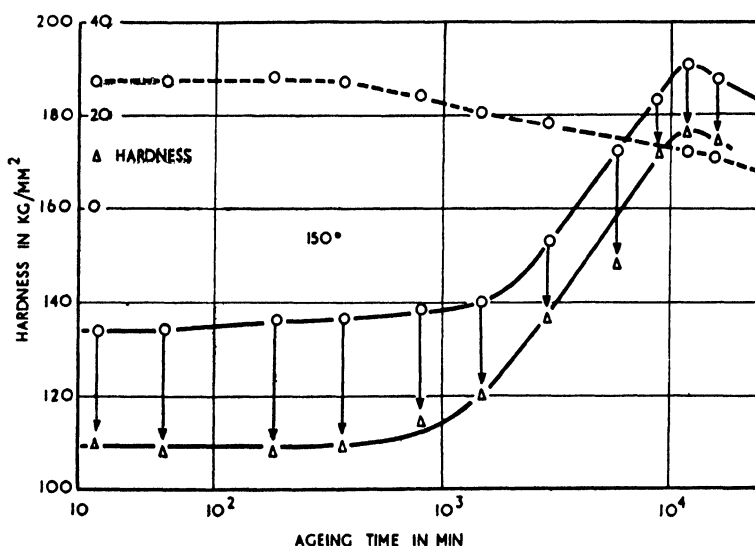


Fig. 103. Reversion of an aluminium-38-wt-per-cent-silver alloy after ageing for various times at 150°C⁽⁷²⁾

the reversion treatment caused susceptibility to intercrystalline corrosion in aluminium-copper alloys and argued that the process depended on the precipitation of the θ' nuclei developed at room temperature.

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This ignored the repeatability of the process; the corrosion properties suggest that a distinction should be made between the behaviour of the grain boundaries and grain centres. A very short treatment at an

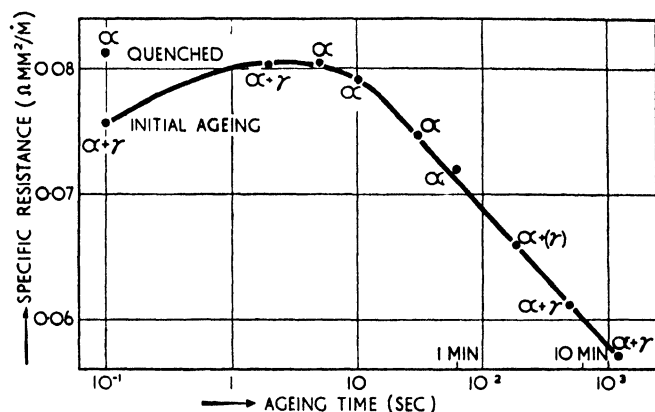


Fig. 104. Resistivity curve for a copper-1.8-per-cent-beryllium alloy quenched and aged 1100 hr at 200°C and then aged at 420°C⁽³⁰⁸⁾

elevated temperature may give re-solution of the majority of the precipitate in the grains and yet be long enough to cause precipitation in the grain boundaries.

Reversion also occurs in copper base alloys⁽³⁰⁶⁻³⁰⁸⁾ but may be less complete. Fig. 104 gives results due to GRUHL⁽³⁰⁸⁾ on a copper-beryllium alloy. The x-ray investigation showed that the γ' precipitate formed at 200°C was redissolved, and later replaced by the equilibrium γ precipitate. GRUHL and WASSERMANN^{(121), (284)} had earlier found that only γ was formed at ageing temperatures in excess of 325°C.

As described previously, the absorption of heat shown by the enhanced specific heat on heating (Figs. 87 and 89) is to be associated with the re-solution of a low temperature decomposition product. The only point for discussion is whether the solution is caused because the particles are below the critical size for growth at the new ageing temperature, or whether the alloy has been taken above the solubility curve for the metastable precipitate. Both factors will occur in practice and reversion studies do not in themselves allow a choice to be made without recourse to other experimental information. The solubility curves of BORELIUS (Fig. 89) may be compared with

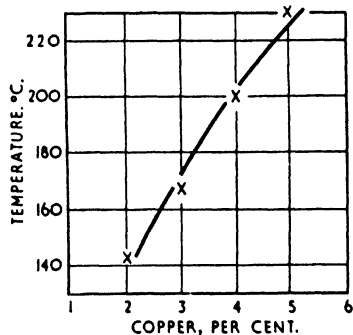


Fig. 105. Reversion temperatures for aluminium-copper alloys (PETROV)⁽⁷⁹⁾

those of PETROV for reversion (Fig. 105 from KONOBEEVSKI⁽⁷⁹⁾). Aluminium-silver alloys are compared in Fig. 23.

Property Changes as Evidence of the Rate of Precipitation

Time Dependence at Constant Temperature

Little attention has been given to the Austin-Rickett equations for the course of the decomposition (equations (67-70)) except by some

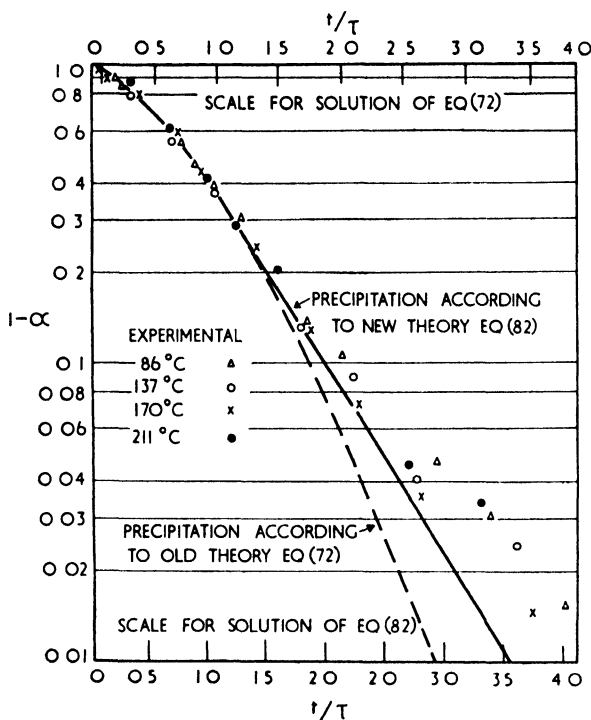


Fig. 106. Curves which show the fit of precipitation data to the two methods of taking into account the interference of adjacent particles during the growth of spheres of precipitate in iron-carbon alloys ⁽⁹²⁾

Japanese workers. According to MISHIMA⁽⁸³⁾ the equations can be used to account for data on aluminium-copper ($p \simeq 1$ two dimensional precipitate, $p \simeq 2.6$ three dimensional precipitate), copper-beryllium ($p \simeq 1$), copper-silver ($p \simeq 1$), iron-copper ($p \simeq 1$, $p \simeq 1.9$), iron-carbon ($p \simeq 1$), iron-molybdenum⁽⁸⁴⁾ ($p \simeq 4.0$) and nickel-tin alloys ($p \simeq 4.0$). WATANABE and KODA⁽¹⁷⁴⁾ found the initial rise in hardness of aluminium-25-per-cent-silver alloys aged at 50°, 70° and 90° followed equation (67) with $p \simeq 1$. It would be interesting to have the same data plotted according to equation (75).

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WERT^{(91), (92)} has followed the precipitation of iron-carbon and iron-nitrogen alloys by damping capacity measurements which depend only on the amount of solute left in interstitial solution. The results in Fig. 106 show how equation (75) fits the data up to 80 per cent decomposition whilst equation (82) fits it up to 95 per cent. m was found to be 1.45 for iron-carbon alloys, see Fig. 107, and 2.45 for iron-nitrogen alloys corresponding to precipitation of spheres and discs respectively (equation (74)). It was concluded that a large proportion of the nuclei

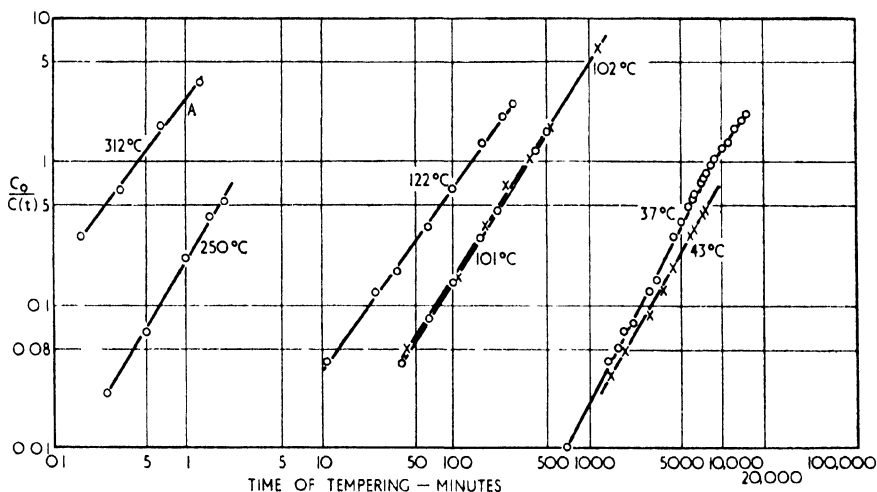


Fig. 107. Precipitation data for iron-carbon alloys plotted according to equation 75.⁽⁹¹⁾ The carbon initially in solid solution was about 0.016 wt per cent for all curves except A which refers to 0.019 wt per cent. The ordinate is $\ln (c_0 - c_f)/(c - c_f)$ and the lines have a mean slope of $m = 1.45$

must be present when the specimen was quenched or very shortly afterwards. SEEMANN and DICKENSCHIED⁽³⁰⁹⁾ repeated WERT's experiments using resistance measurements and found $m = 1.2$ for iron-carbon alloys. ROBERTS, AVERBACH and COHEN⁽⁹⁸⁾ obtained $m = 0.3$ for the first stage in the decomposition of martensite (precipitation of ϵ carbide) which they presumed to grow by the thickening of quenched nuclei so that the ideal value would be 0.5.

WERT^{(91), (92)} and WERT and ZENER⁽⁹⁶⁾ calculated the number of particles of precipitate from equations (79) and (80), and obtained the results in Table 8, p. 254.

HARDY⁽¹⁰¹⁾ found that the first rise in the hardness-ageing curves of aluminium-copper alloys could be represented by an equation similar to equation (75), but with $m = 1.5$. The dilation curves of LANKES and WASSERMANN⁽¹²²⁾ at 200°C produced the same value of $m = 1.5$,⁽¹⁰⁰⁾ although GUINIER⁽¹⁶⁸⁾ has calculated a value of $m = 1.8$. x-ray work

shows that platelets are being formed so that m should be 2.5 if the assumptions of ZENER and WERT apply fully. Possibly the particles do not all start to grow at the same time or their edge-wise growth cannot be proportional to the time as in the case of iron-nitrogen alloys. GUINIER⁽¹⁶⁸⁾ has suggested that the departure from the ideal value of m is a consequence of the range of the ratio thickness : radius observed with the electron microscope.

TABLE 8

The number of Particles of Precipitate in aged Iron-carbon Alloys
(WERT)

% C	Ageing Temp. °C	No. of Particles per c.c.	Dist. Apart Å	Equation
0.016	27	2×10^{15}	800	(79)
0.016	102	10^{14}	2000	
0.016	312	3×10^{12}	7000	
0.016	86	3.9×10^{13}	(80)	
0.013	137	2.6×10^{13}		
0.018	170	1.7×10^{13}		
0.012	211	9×10^{12}		

Temperature Dependence

The type of reciprocal rate curve predicted by theory is essentially a straight line at low temperatures when plotted against $1/T$ and curving to longer times as the temperature approaches the (meta-)solubility curve. This effect is clearly shown in the C -curves for the isothermal sub-eutectoid transformation of γ -iron to pearlite⁽³¹⁰⁾ and of other eutectoid systems such as copper-aluminium^{(311), (312)} and copper-beryllium.⁽³¹³⁾ The initial reaction in a eutectoid decomposition involves the formation of a nucleus of a new phase and is identical with precipitation. The subsequent formation of a second phase adds its own complexities and the eutectoid decomposition will not be dealt with here. It is worth noting, however, that the decomposition rates have been analyzed,^{(85), (314-316)} and that several decomposition products may be formed successively.

C -curves have also been observed experimentally in gold-platinum,⁽⁵²⁾ gold-nickel,⁽⁴⁷⁾ lead-tin^{(46), (49)} and aluminium-zinc.⁽⁵³⁾ Fig. 108 and 109 show the results for gold-platinum and lead-tin alloys, and the arrows give the temperature above which $\partial^2 F / \partial x^2$ becomes positive according to calculations on the Borelius pattern. There is a rough correlation between this temperature and that at which the plot diverts appreciably from the straight line. The change is more abrupt at the platinum-rich than at the gold-rich side, see Fig. 108. SMOLUCHOWSKI⁽¹⁰⁾ has

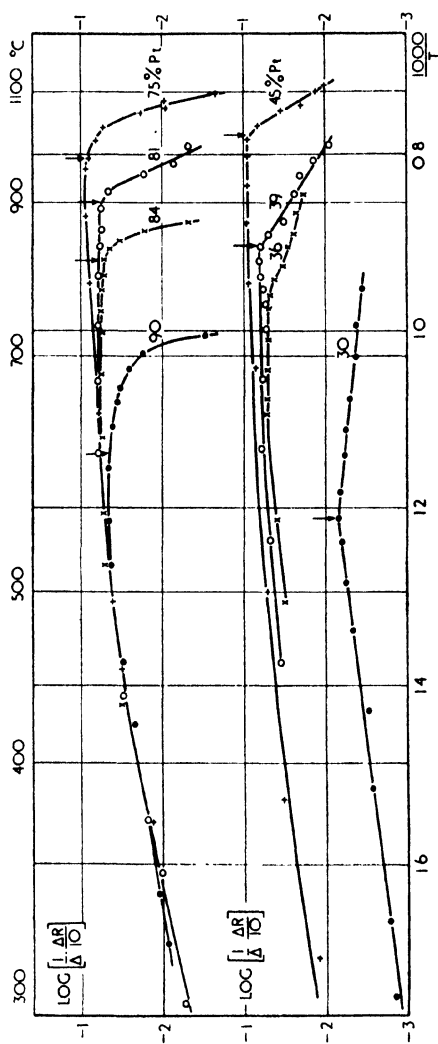


Fig. 108. The rate of precipitation (the fraction of the resistance change in the first minute) of gold-platinum alloys as a function of composition (WICTORIN⁽⁵²⁾)

associated this with a higher value of $\partial^3 F / \partial x^3$ (see equation (34)). Plotting the logarithm of the time to half the reaction against the composition of gold-platinum alloys also showed changes of direction at points which could be associated with the spinodal curve according to JOHANSSON and HAGSTEN⁽³¹⁷⁾ and WICTORIN.⁽³¹⁸⁾ The dashed lines in Fig. 109 for the lead-tin alloys are for the initial rate of precipitation matched to the straight line portion and calculated by HARDY⁽⁸⁾ using the Becker model.

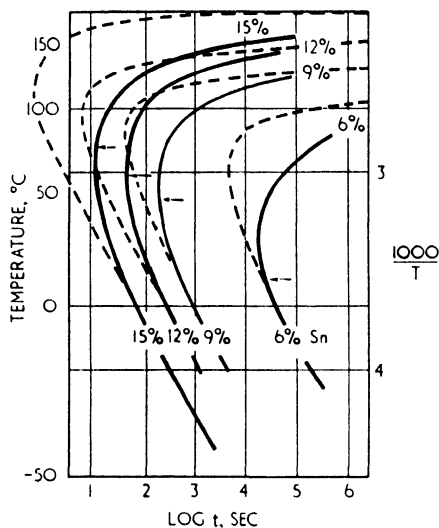


Fig. 109. Comparison of BORELIUS' experimental curves (full lines) for the time to half the resistance change for lead-tin alloys on ageing, plotting against $1000/T$, and curves (dashed lines) calculated from nucleation theory based on the original calculations and fitted to the straight line portion of the experimental curves.

$Q = 10,400$ cal/g-atom.

t = time to half resistance change

← denotes the temperature for a change from a positive to a negative value of $\partial^2 F / \partial x^2$

The agreement is reasonably good. Similar reciprocal rate curves were found by SCHEIL and STADELMAIER⁽³¹⁹⁾ below the solid solubility curve of NaCl-KCl. The temperature of the maximum rate of precipitation, that is the nose of the C -curve, is plotted in Fig. 110 and shows no relation to the spinodal curves calculated either by the authors or HARDY.

The sequence of C -curves with increasing temperature when a series of precipitates occur (predicted in Fig. 26) is well illustrated by the bainite reaction in alloy steels.^{(320), (321)} As discussed above, indications of this type of plot are to be found in aluminium-copper alloys (Fig. 96) and aluminium-silver alloys. Minor but apparently reliable divergences

from a straight line may be seen in the reciprocal rate plots of aluminium-silicon alloys.⁽¹⁰⁰⁾

A considerable amount of data has been obtained showing a straight line plot between the logarithm of the time to various stages of the ageing curve and the reciprocal of the absolute temperature. It is not unusual to find that the activation energy obtained from the slope of the curve ($\partial \ln t / \partial 1/T'$) is less than the activation energy for diffusion

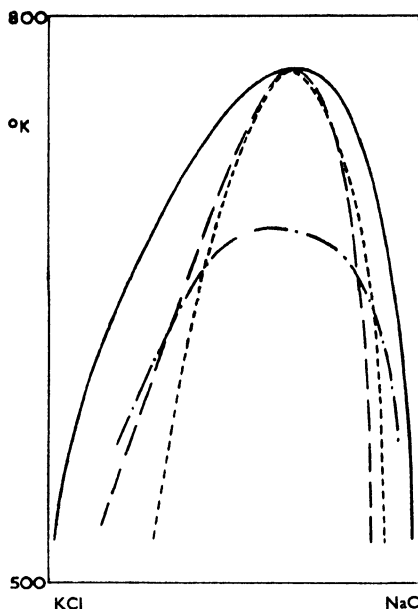


Fig. 110. The solubility data and spinodal curves for solid solutions of KCl-NaCl. The dashed spinodal curve was calculated from HARDY's sub-regular solution model. The dotted spinodal curve was calculated by SCHEIL and STADELMAIER⁽³¹⁹⁾ who found the maximum rate of reaction along the chain curve

obtained by measurements at more elevated temperatures. The discrepancy depends on the system and tends to get less when the property being measured occurs at a later stage of the ageing curve. GEISLER⁽¹²⁵⁾ has presented data for an aluminium-copper-magnesium alloy which brings out this point, see Table 9, p. 258. However, his interpretation of the first reactions as being due to localized precipitation was quite hypothetical.

As an example of the discrepancy, the relation between the logarithm of the time to peak hardness and $1/T$ for aluminium-copper alloys gives an activation energy of 24,000 cal/gm atom⁽³²²⁾ compared with 34,000 cal/gm atom obtained from diffusion measurements at elevated temperatures.⁽³²³⁾ The diffusion coefficients calculated from x-ray measurements of the particle size are several orders of magnitude less

than those obtained by extrapolation from diffusion studies,^{(5), (101)} The discrepancy is so large that no hardening could occur in aluminium alloys if the high temperature activation energy for diffusion applied to room temperature. A different diffusion mechanism at low temperatures might be operative and account for the lower activation energy.

TABLE 9
Activation Energies for various Properties on Precipitation in
Aluminium Alloy 24S*(125)

<i>Property</i>	<i>Activation Energy Calories per gramme atom</i>
10 per cent of first increase in strength	11,900
50 per cent of first increase in strength	14,600
90 per cent of first increase in strength	16,400
Start of decrease in corrosion resistance	23,400
Start of decrease in elongation	26,400
50 per cent of decrease in corrosion resistance	28,700
Minimum corrosion resistance	27,000
Start of second increase in strength and hardness	30,400
Maximum hardness and tensile strength	30,400
Full recovery of corrosion resistance	30,400
50 per cent of second increase in yield strength	32,700
50 per cent of change in solution potential	33,900
50 per cent of decrease in elongation	35,300
Minimum elongation	36,200
Maximum yield strength	36,200
Average for volume diffusion in Al-Cu alloys	33,900
Average for volume diffusion in Al-Mg alloys	32,200

* Aluminium—4.5 per cent copper—1.5 per cent magnesium—0.6 per cent manganese.

KÖSTER and SPERNER⁽²⁷⁹⁾ have reported that the logarithm of the time to peak hardness at ageing temperatures between 150° and 300°C was a rectilinear function of silver content with up to 0.2 atomic fraction (50 wt per cent) in aluminium-silver alloys. The rate of precipitation increased with increasing silver content. The slopes of the reciprocal rate curves gave "activation energies" which decreased linearly with the silver content in accordance with the equation

$$\text{"activation energy"} = 32,600 - 560 (\text{at } \% \text{ silver}) \quad . \quad (113)$$

The danger of taking activation energies from the reciprocal rate curves has been pointed out in Section III (p. 176) since the measurement is only accurate if the distance between the particles (number of particles) does not change over the temperature range involved. This point is so serious that it renders pointless any discussion of the various activation energies obtained for different stages of the ageing curves. The effect may be illustrated by the values in Table 10 due to WERT.⁽⁹¹⁾ He studied the ageing of an iron-carbon and iron-nitrogen alloys. The

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normal ageing curves gave activation energies appreciably lower than those for diffusion. However, the values obtained when the material was nucleated at 27°C and then aged between 31 and 66°C were much closer to the activation energies for diffusion.

TABLE 10
Activation Energies for Iron-carbon and
Iron-nitrogen Alloys⁽⁸¹⁾

Source	Iron-carbon Alloys cal/mole	Iron-nitrogen Alloys cal/mole
Diffusion	18,400	20,000
Reciprocal Rate Plot	13,000	14,000
Reciprocal Rate Plot (Nucleated)	17,500	18,000

Very little attempt has been made to measure the temperature dependence of K_4 in equation (94). ROBERTS, AVERBACH and COHEN⁽⁸⁸⁾ obtained a value of 8000 cal/mole from the tempering of martensite.

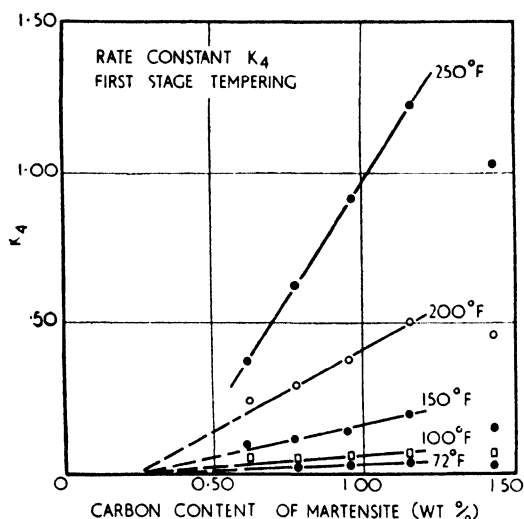


Fig. 111. Compositional dependence of the rate constant K_4 (equation 72) for the first stage in the tempering of martensite⁽⁸⁸⁾

This may be compared with 9200 cal/mole for half ($m = 0.5$) the value of Q for diffusion in Table 10. K_4 was also found to be a linear function of carbon content (see Fig. 111). The zero values of K_4 indicates a metastable solubility limit of 0.25 wt per cent carbon. The precipitation reaction in the tempering of martensite is not greatly different

from normal precipitation except that the lattice strain energy probably facilitates the nucleation process. This may tend to give a more constant number of particles than in normal precipitation and consequently accounts for the better agreement with theory.

VII. GENERAL DISCUSSION

Experimental Techniques

Experience gained since 1940 allow the minimum experimental techniques to be stated which are necessary to establish an accurate descriptive theory of a complicated precipitation process, and to provide information for the testing of kinetic theories. The most appropriate techniques will, of course, depend on the particular system under investigation.

Ageing curves are required for a physical property, such as electrical resistance, lattice parameter or internal friction, which is closely related to the amount of solute in solution and independent of the precipitate. Ageing curves are also required for at least one other physical or mechanical property dependent on the precipitate or the inter-relation of the precipitate and matrix and which is most likely to show anomalous behaviour. A reasonably wide range of alloys and supersaturations must be included in order to seek evidence of anomalies. The analysis should examine the isothermal and temperature dependent relationships between the stages in the ageing process for comparison with the x-ray structural data on the pattern of precipitates. A check must be made for discontinuous precipitation.

X-ray structural investigations are essential; the realization that a sufficient volume of reciprocal space must be accurately surveyed forms the most important single general concept of the last decade. Hence single crystal methods are preferred. The experimental methods chosen must be such that the interpretations in terms of a reciprocal lattice plot (of the diffractions from both the matrix and the precipitate) are subjected to the minimum degree of uncertainty. This necessitates the use of monochromatic radiation or of proportional counters arranged to record the characteristic K_{α} radiation only. The moving film methods, particularly that due to BUEGER,⁽¹³³⁾ provide a very elegant means of obtaining some of the essential information, though the more simple oscillating crystal method can serve equally well. In both cases, stationary photographs are desirable to check for one dimensional diffraction effects ("relplanes"—see Fig. 48). Diffuse regions very close to the nodes of the reciprocal lattice are best studied by small angle scatter patterns of the intensity distribution near the origin. The Laue method can be used for rapid surveys when the precipitation pattern has been established.

Many of the recent advances in x-ray technique have not yet been applied to precipitation study. Major disadvantages of the use of monochromatic radiation are the loss of intensity and the asymmetry of the diffraction patterns due to the height of the line focus it is necessary to adopt in order to minimize this loss. GUINIER⁽³²⁴⁾ has partially overcome these difficulties by the use of the increased intensity (4–10 times) of a rotating anode x-ray tube. Very recently a point focus doubly curved monochromator has been constructed⁽³²⁵⁾ yielding intensities sixteen times as great as the Johansson type⁽³²⁶⁾ used by GUINIER⁽¹⁵³⁾ and SILCOCK *et al.*⁽¹⁴⁵⁾ Such enhanced intensities greatly enlarge the field of practicable investigations.

Any improvement in the quantitative measurements of intensities requires a concurrent development of existing diffraction theory. Recent work by LIFSHITZ and ROSENVEIG⁽³²⁷⁾, WILSON,⁽¹³⁴⁾ MERING⁽¹⁶⁷⁾ and JAGODZINSKI⁽³²⁸⁾, ⁽³²⁹⁾ has enabled progress to be made. Further advances are needed so that the structural states and shapes assumed can be expressed accurately as reciprocal lattice plots and intensity distributions for comparison with the experimental results.

Experimental Precipitation

The completeness of our information on the precipitation process will be discussed for a number of alloy systems. The results of the x-ray analysis show that the structural changes are frequently complex and only for the aluminium-copper alloy may a qualitative understanding of the decomposition be taken as **proved**. The x-ray techniques of PRESTON and GUINIER have been applied systematically by SILCOCK, HEAL and HARDY,⁽¹⁴⁵⁾ and it is established that the dominant structure in the pattern of precipitates follows the sequence

$$\text{G.P. zones [1]} \rightarrow \text{G.P. zones [2]} \rightarrow \theta' \rightarrow \theta \quad . \quad . \quad (114) \\ (\text{or } \theta'')$$

Apart from the change $\theta' \rightarrow \theta$ it is not yet known whether the preferred path of the transformations is allotropic or whether the new decomposition product arises in the matrix by independent nucleation. Successively more stages of the precipitation sequence are omitted as the supersaturation is reduced. There is also a close correlation between the form of HARDY'S ageing curves in this system and the precipitates observed experimentally (see Figs. 63 and 64). The peak hardness results (Fig. 65) and the incubation values (Fig. 96) neatly interlock with the structural investigation. The changes of the other physical properties on ageing are fairly well established. The G.P. zones [1] are associated with a small volume contraction followed possibly by a slight expansion and with a small increase in electrical resistance followed by a slight fall. The formation directly from the

matrix, of the G.P. zones [2] or θ' is accompanied by a large volume expansion and a large decrease in electrical resistance. The experimental work may be described convincingly in terms of the precipitation pattern above. Effects arising from localized precipitation will inevitably be present but, although they produce a change of emphasis, they do not significantly influence the picture presented here.

More quantitative aspects of our knowledge of the precipitation process in aluminium-copper alloys are less satisfactory. For example, although the structure of θ has been adequately determined, the accepted structure of θ' cannot be entirely correct whilst the structure of the G.P. zones [2] (θ'') is known with even less certainty. Information on the sizes of the particles throughout the ageing process is limited and often subject to uncertainties. As is the case for most alloy systems, accurate quantitative measurements on the kinetics of the decomposition are hard to come by. This arises chiefly because the number of particles of precipitate is temperature dependent and often indeterminate.

The aluminium-silver system shows some confusion in the structural results which is due partly to the diversity of the alloys studied by the different workers. Nevertheless, the first decomposition product can be described as spherical silver-rich clusters which may later undergo an ordering process. The formation of stacking faults appears to occur independently early in the ageing process. Both are stages in the development of the γ' precipitate. The ageing curves of KÖSTER *et al.* give clear evidence of two stages, only the first of which vanishes completely on reversion. The first stage did not occur above 185°C whilst the incubation value/temperature relationship indicates two C-curves meeting at this temperature. Complete ageing curves on alloys of lower silver content and x-ray work by different techniques on several alloys would go far to eliminate the anomalies and set up a reliable pattern of precipitates. On the other hand, only the aluminium-silver system has been studied fully by specific heat measurements. The experimental technique is essentially athermal, so that the temperatures to which the measured energy values apply is rather indeterminate. There is a clear indication from the energy absorption that the majority of the first decomposition product is re-dissolved by reversion, even though the largest clusters may be capable of growth at the reversion temperature. WALKER and GUINIER⁽¹⁶⁹⁾ observed spherical aggregates on short treatments well above 185°C which is the upper limit put forward by KÖSTER *et al.* as the temperature above which two-stage ageing curves were not obtained. The experimental results are not necessarily in conflict. The spherical clusters at the higher temperatures and above the solubility limit^{(170), (171)} could represent a statistical distribution of fluctuations as opposed to a metastable distribution formed on ageing at low temperatures with a fall in free energy.

The structures postulated by JACK for the precipitation reactions in iron-carbon and iron-nitrogen systems and martensites seem reasonable in view of the limited choice of distribution of the atoms in the interstitial sites. Nevertheless, in view of his free use of strictly limited experimental evidence, his suggestions must be treated with some reserve until further support is forthcoming. If JACK's interpretation be accepted it becomes necessary to account for the differences between the two systems and to justify the marked freedom of the decomposition processes from the usual compositional dependence. As shown in Fig. 112, a self-consistent set of free energy/compositional curves may be

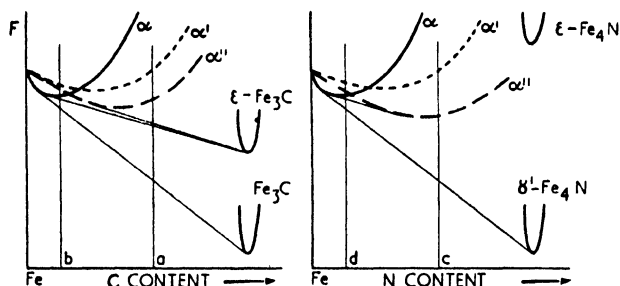


Fig. 112. Hypothetical free energy/structural/compositional curves (not to scale) for iron-carbon and iron-nitrogen systems undergoing decomposition.

put forward for this purpose. Quantitative agreement is not to be looked for as the pattern of precipitates is not completely clear; the coherent Fe_3C has been omitted from Fig. 112. Alloy (a) will transform from γ to the partially ordered α' iron-carbon martensite on quenching. Decomposition to the fully ordered α'' is accompanied by the formation of ϵ carbide which requires a carbon content of 0.25–0.3 per cent in the α'' in metastable equilibrium.⁽⁹⁸⁾ The formation of Fe_3C either from the ϵ carbide or directly from the matrix leads to body centred cubic iron with carbon atoms in random solution. The free energy curves have been drawn to agree with the finding that martensite cannot be retained in low carbon steels. Ageing of alloys quenched from the α solid solution range, e.g. alloy (b) may reasonably give ϵ carbide rather than α'' provided the rate of nucleation be greater.

Only a slight difference is needed to explain the behaviour observed by JACK in the iron-nitrogen system—namely that the intermediate precipitate has an appreciably higher free energy so that it is not normally formed. Under these conditions (Fig. 112) alloy (c) will form partly ordered α' nitrogen martensite on quenching which can transform without compositional change to the ordered α'' nitrogen martensite. Precipitation of the disordered random body centred cubic

solution and γ' (Fe_4N) will occur as the second stage. The observation that α'' is precipitated from the supersaturated random solution (alloy (d)) is also a consequence of the high free energy assigned to ϵ -nitride.

The divergence between the x-ray and magnetic measurements on the decomposition of carbon martensite has not been satisfactorily explained and requires further investigation. Two stage ageing curves have been found in iron-nitrogen alloys (Fig. 100) and may occur in iron-carbon alloys. These systems are also important because of the correlation made by WERT and ZENER between the ageing process and the theoretical equations for the isothermal decomposition obtained from the growth law for an individual particle. They deduced that spheres occurred in iron-carbon alloys and platelets in iron-nitrogen, but there is a divergence between the particle shapes reported by different workers using the electron microscope.

Many systems are known where the changes accompanying precipitation appear relatively simple and all the properties change simultaneously (e.g. gold-30-per-cent-nickel alloy). The apparent simplicity may arise in three ways. The system may be truly simple and show no intermediate coherent precipitates or anomalous clusters of solute atoms. Secondly, the degree of supersaturation attainable may not be great enough to allow such complications to occur. For example, Fig. 14 shows that the spinodal curve will not be crossed by supersaturated copper-silver or silver-copper alloys until the temperature is too low for appreciable atomic movements. Thirdly, very few systems have been thoroughly investigated by all the techniques of structural analysis so that many new facts must await discovery. It has been shown above that complications have often been observed in the precipitation process and the details are still unresolved in several systems. For example, G.P. zones and an intermediate precipitate occur in aluminium-copper-magnesium alloys, spherical clusters are present in aluminium-zinc alloys aged at low temperatures, an intermediate precipitate and possibly G.P. zones occur in aluminium-magnesium-silicide alloys, copper-beryllium alloys have so far defied an adequate explanation of the pattern of precipitates, and the plane of precipitation has not been established unambiguously in the silver-copper⁽³³⁰⁾ systems. Diffraction effects occur in the copper-iron-nickel magnetic alloys whose interpretation is not yet entirely certain. The iron-NiAl alloys, which show major anomalies in the ageing behaviour of their magnetic properties, still have to be investigated by x-ray structural methods. The conclusion is thus justified that only in the aluminium-copper system can a qualitative account be given of the ageing process at all degrees of supersaturation with anything remotely approaching rigorous certainty.

Thermodynamics of Precipitation

It is hardly possible to go beyond the conclusion that the agreement between the theoretical predictions and the experimental observations is satisfactory only in a general sense. Both agree that the maximum number of stages occurs at high supersaturations and that a metastable equilibrium involving an intermediate decomposition product may produce an apparent pause in the course of the precipitation whilst the next more stable phase is being nucleated. The observation that each initial decomposition product produces a separate *C*-curve on the plot of the reciprocal rate against temperature affords only general agreement.

BECKER'S theory of the initial rate of nucleation is satisfactory when extended to include the conception of a "steady-transient" distribution of embryos with the lattice of the new structure. The limitation lies in the inability to calculate the activation energy and sizes of stable nuclei because of the absence of information about the free energy/compositional relationships, the lattice strain energy and interfacial energy terms. The same ignorance makes it very unlikely that the more sophisticated nucleation theories based on statistical mechanics would be any more informative than the Becker treatment. Apart from the observation of SILCOCK, HEAL and HARDY⁽¹⁴⁵⁾ that the G.P. zones [2] of aluminium-copper alloys show a continuous change in spacing and probably increase in copper content, there has been little experimental confirmation of the prediction that the initial precipitate becomes richer in solute and may show a fall in volume fraction (p. 154).

The approach of BORELIUS must be held to represent an oversimplification because it neglects the surface energy terms. Furthermore, the number of atoms in a fluctuation cannot be calculated *ab initio* and forms an arbitrary parameter conveniently providing a fit with the experimental data. However, it must be admitted that the number of atoms in a fluctuation obtained in this manner is of a reasonable order of magnitude. The appeal of the theory lies in the relatively good agreement between the calculated spinodal curves and the lowest temperature of retardation (Fig. 16) which has been recorded for a number of systems, e.g. gold-platinum, aluminium-zinc, gold-nickel and lead-tin alloys as shown in Figs. 10-12 and 15. The agreement may be partly fortuitous since the alloys can usually be examined over only part of the spinodal curve. Where a full check could be made, as in the KCl—NaCl system in Fig. 110, there was no agreement between the spinodal curve and the lowest temperature of retardation (which will be lower than the temperature of the maximum rate of reaction plotted) across the centre of the diagram. The trend of the experimental points at the higher temperatures in the gold-platinum system tends to support this conclusion as, particularly at the platinum side, they are

directed inside the spinodal curve (Fig. 10). The apparent agreement between the experiment and theory may lie not in the accuracy of the simple fluctuation theory but in the fact that the free energy per gramme-atom of precipitate is greatest at the spinodal point (equations (5) and (6)). In any case, it must be remembered that the experiments usually apply to the time for an appreciable part of the precipitation process whereas the theory is limited to the initial rate of reaction.

The combination of the Borelius-Becker fluctuation and nucleation theories on page 160 and in Fig. 17 is on sounder grounds but the same difficulties apply to the direct calculation of the rate of precipitation. As set out in Fig. 18, there is no reason why a statistical distribution of segregates may not be preferred in certain systems to a "transient-steady" distribution of embryos with the lattice structure of the new phase. The observations^{(170), (171)} that silver-rich clusters exist above the solubility limit of silver in aluminium may fall into this category.

Most of the theories would agree with the prediction that alloys quenched into a region where $\partial^2 F / \partial x^2$ is negative should show decomposition without nucleation. On the other hand there is a marked dearth of experimental results to support this conclusion. This may arise partly because the segregation may be swamped by nucleation. The magnetic alloys of the copper-iron-nickel system may behave in this manner but the interpretation of the x-ray evidence is not completely unambiguous. HARGREAVES' work⁽²²⁶⁾ implies some process halfway between fluctuation and nucleation and may illustrate an extreme case of the compositional changes predicted in the nuclei. Supporting evidence is required and the iron-NiAl system should be worthy of investigation from this point of view.

It has not proved possible to calculate the free energy of the intermediate precipitates and therefore the number of decomposition products cannot be predicted for a given system. Aluminium base alloys have proved a fruitful source of data on complex ageing processes. This may stem partly from the fact that aluminium atoms have a relatively small x-ray scattering factor and are well suited to allow a determination of the distribution of most species of solute atoms. MEIJERING⁽⁶⁴⁾ showed that an inflected free energy/compositional relationship may apply to the aluminium-copper solid solution and has thus provided some theoretical justification for the view that the first decomposition product is a disordered copper-rich face-centred cubic phase. DEHLINGER and KNAPP⁽⁶⁵⁾ tacitly assumed an inflected free energy/compositional curve for aluminium-silver alloys. Their work represents an attempt to account theoretically for a metastable distribution of the silver-rich clusters found on ageing aluminium-silver alloys. The argument is generally satisfactory but the numerical results are not completely theoretical as they are based partially on experimental

findings. MEIJERING⁽⁶⁴⁾ suggested that an inflected free energy/compositional curve in aluminium-copper alloys originated in a change of valency of the aluminium atoms across the phase diagram. The same effect may exist in aluminium-silver alloys and may be present in aluminium-zinc where no intermetallic compounds are present. An alternative explanation of the solubility gap in this system is due to LEIGH^{(331), (332)} but may apply to other aluminium alloys. LEIGH showed that the shear constant $\{\frac{1}{2}(c_{11} + c_{12})\}$ of aluminium solid solutions passes through a sharp maximum at an electron atom concentration of 2.67 which implies a peak at this point in the free energy/compositional relationship. Irrespective of the cause, an inflected free energy/compositional curve for aluminium base solid solutions seems a reasonable theoretical assumption on which to build a qualitative interpretation of the initial decomposition process.

There is a strong need for reliable thermodynamic data on solid alloy systems such as the results of SEIGLE, COHEN and AVERBACH⁽³³³⁾ on gold-nickel alloys. The possibility of a knowledge of the interfacial energies between the matrix and a particular precipitate seems more remote but is no less important to the quantitative test of the nucleation theories. In view of this basic ignorance there would be little quantitative advantage to be expected from further theories of nucleation. Effort could more profitably be directed to calculations of the metastable solubility curves, the entropy contributions from clusters of solute atoms and the relative free energies of intermediate precipitates with interstitial atoms.

Kinetics of Precipitation

The equations for the course of precipitation based on the growth laws of ZENER frequently provide an excellent fit with the experimental data although it would be interesting to plot the same results using the Austin-Rickett formula. The constant in ZENER's equation should indicate the shape of the particles and clear distinctions have been found between different systems. However the success is not always complete as other experimental methods do not always confirm the particle shape predicted by the experimentally obtained growth constant. The discrepancy in aluminium-copper alloys ($m = 1.5-1.8$ instead of the theoretical 2.5 for platelets) may reflect the limitations of the initial assumptions and the difficulty of specifying the concentration distribution about the edge of a growing platelet. The latter is particularly important since it will control the ratio of radius to thickness.

The analysis of the temperature dependence of the reaction rate emphasizes the danger of calculating the heat of reaction from the slope of the reciprocal rate/ $(1/T)$ curves unless great care is taken to ensure the number of particles of precipitate be independent of the temperature.

This factor is so serious that it must be held to nullify many of the previous arguments about the difference between the heat of reaction and the activation energy for diffusion and also the dependence of heat of reaction on the different stages in the ageing process. For similar reasons there would be little merit in discussing the frequency factors (outside the exponential term—equation (19)) obtained experimentally from the initial rate of precipitation.

Criticisms that the diffusion coefficient calculated from the sizes of the precipitate particles are not commensurate with the values obtained by extrapolation from high temperature measurements^{(5), (101)} are more soundly based. Even if errors in the sizes assigned to the particles by x-ray methods cannot be excluded it does not seem possible to escape the conclusion that ageing occurs in aluminium alloys at such low temperatures that the extrapolated diffusion coefficients would suggest that no reaction could occur. It is possible that the decomposition process at low temperatures is limited to re-arrangement of the solute atoms in very small regions of appropriate concentration or that there is a change in the diffusion mechanism. A satisfactory solution to this discrepancy between theory and experiment is still awaited.

Strain Energy Considerations

Intermediate precipitates can be reasonably accounted for qualitatively since a coherent precipitate of small size will have a lower strain and interfacial energy than the non-coherent equilibrium precipitate. Attempts to make this quantitative have not proved very satisfactory; more success has attended the discussion of the preferred shape of the particles. According to NABARRO^{(23), (24), (73)} the elastic energy due to a difference in volume between the precipitate and the matrix can be reduced by a change of shape from spheres (with minimum interfacial energy) to plates. GUINIER⁽³³⁴⁾ has reconciled the shape of the G.P. zones (or segregates) determined by the small angle scatter method with the difference between the atomic diameters of the solvent and solute and his results are given in Table 11.

The re-calculated values have been obtained using the apparent atomic diameters in the relevant solvent metal as given by AXON and HUME-ROTHERY.⁽³³⁵⁾ An equiatomic ratio of copper to magnesium was assumed for the ternary alloy.

It will be seen that a spherical shape is only permissible when the difference in atomic diameter is very small. Differences greater than about 2 per cent lead to platelets.

OPINSKY and SMOLUCHOWSKI^{(336), (337)} suggested that the form taken by the precipitate would be such that the grouping of the solute elements minimized the strain energy. This factor has not been examined theoretically for ternary alloys but the structural results on some

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systems, e.g. aluminium-copper-magnesium,⁽¹⁸⁴⁻¹⁸⁷⁾ show clear evidence that the grouping of the solute atoms in the initial decomposition product is such as to retain the lattice spacing of the matrix. The effect will probably be most apparent when the atomic diameters of one of the solute elements is larger, and the other smaller, than that of the solvent atoms. This relation occurs in aluminium-copper-magnesium alloys.

TABLE 11
Effect of the Difference between the Atomic Diameters
of the Solute and Solvent on the Shape of the Initial
Solute Rich Region⁽³³⁴⁾

<i>Alloy</i>	<i>Relative difference in Atomic Diameter</i>		<i>Form of Nucleus</i>
	<i>GUINIER %</i>	<i>Recalculated %</i>	
Al-Ag	+ 0.7	0	Spherical
Al-Zn	- 3.0	- $\frac{1}{2}$	Spherical
Al-Cu-Mg		+ $2\frac{1}{2}$	Flat
Cu-Be	- 20	- 9	Flat
Al-Cu	- 11	- $11\frac{1}{2}$	Flat
Al-Mg		+ 14	Not known

As pointed out by MOTT⁽³³⁸⁾ it is difficult to see why the hardening during ageing should be associated with a decrease in the active lengths of the Frank-Read sources.⁽³³⁹⁾ The local strain energy in the lattice about the precipitate is regarded as an important element in increasing the mechanical strength of the alloy. It is thought that a flexible dislocation cannot move readily through the regions of localized strain and tends to "hang up."^{(23), (340-342)} Increased strength results from a finer dispersion of particles because of the higher stress required to push the dislocation through the barrier. Hardening will also occur when the precipitate produces no strain energy. Studies of the plastic properties of ductile materials have shown that the flow stress increases with decreasing mean free path between the particles^{(343), (344), (345)} and curved slip bands can occur in such materials. The strain field around a dislocation may repel it from, or hold it up at, particles with different elastic constants from the matrix even though in the extreme case, they may be coherent and have an identical lattice spacing, e.g. as occurs in the silver rich clusters of aluminium-silver alloys and G.P. zones of the aluminium-copper-magnesium system. Recent work by FISHER, HART and PRY⁽³⁴⁶⁾ considers also the resistance to deformation (back stress) offered by the steady state number of closed dislocation loops supported by the particles.

The relation between dislocations and the precipitation reaction must be very intimate and the exact mode by which the different types of dislocations^{(347), (348)} provide sites for nuclei would form a worthwhile investigation. The growth of certain lattice structures can be explained by an arrangement of dislocation lines forming a generating node between two lattices^{(348), (349)} but the origin of the nuclei still has to be considered.

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SOLIDIFICATION OF METALS

Ursula M. Martius

INTRODUCTION

THIS article will deal with our present state of knowledge of solidification, which will be defined for the purpose of this review as the growth of an existing crystal nucleus into its own melt.

After a comparative stalemate in this field since the early thirties, the problem of crystal growth from the melt has recently attracted more attention and the influx of new information from neighbouring fields of research is beginning to influence our views on solidification problems. There is on the one hand the rapid progress made in the clarification of nucleation problems⁽¹⁾ and the recent strong interest in lattice imperfections⁽²⁾ that will stimulate new attacks on solidification problems; on the other hand, metal single crystals are being used more and more frequently in fundamental research, and improved techniques for the growth of single crystals from the melt have been devised.⁽³⁾ Their increased use furnishes additional information as to the mechanism of crystal growth under these conditions.

Our fundamental ideas on crystal growth from the melt go back to the work of TAMMANN⁽⁴⁾ and his school. To him we owe much of our basic experimental information and its interpretation.

Since TAMMANN's days considerably more has been added to our knowledge of interatomic forces in crystalline solids and the work of STRANSKI⁽⁵⁾ KOSSEL⁽⁶⁾ and others⁽⁷⁾ implemented this knowledge into the general theory of growth of a crystal from vapour or dilute solution.

Very recently, the incorporation of new ideas on crystal imperfections gave new stimulation to these problems and justified a number of the assumptions of the earlier theory.⁽⁸⁾

As far as growth of a crystal from the melt is concerned, there exists as yet no consistent general theory which would explain all the phenomena observed during the solidification process. Most of the experimental evidence on the mode of solidification of the melt was not obtained as the result of research on solidification as such, but as a by-product of other studies. One of the sources of information is the investigation of ingots mainly undertaken to improve the technical quality of castings. Other relevant material was obtained during the development of different methods for the production of metal single crystals. The study of crystal imperfections and mosaic structures provides another source of information on crystal growth.

Part I of this review contains a brief outline of the basic thoughts and theories of crystal growth from the melt, while in Part II the known experimental facts pertinent to the problem of solidification are compiled. In Part III the question is discussed as to how far the presently available theories can account for the experimental data. This part may be read separately for a brief survey of the field.

This method of presentation inevitably involves cross references and repetition. However, in a field where there exists such lack of balance between experiment and theory and where the experimental evidence is so heterogeneous in character and origin, it was felt that the duty of the reviewer is not only to compile critically what is known, but also to indicate the gaps in our knowledge and clearly distinguish between experiment and interpretation. For this reason this method of presentation was finally adopted.

The article will treat only the solidification of a single phase and no attempts are made to review work on alloys. Much is still lacking in our knowledge of the simple case of solidification of a pure metal and only when these phenomena are fully understood should one extend into more complicated systems.

PART I. BASIC CONSIDERATIONS AND PREVIOUS THEORIES

Any attempt to develop a general theory of crystal growth must start from the basic considerations of the variables that determine the change of state: melt to crystal. At a given pressure, there exists one temperature T_m at which the solid is in equilibrium with its melt. A decrease in temperature causes the solid phase to grow at the expense of the liquid phase and in solidifying L_m the latent heat of solidification is liberated. If no heat is extracted externally, the latent heat of melting will raise the temperature of the system and growth of the solid phase stops when T_m is reached again. Hence, continuous growth of the solid requires the presence and maintenance of a temperature gradient. This means that any problem of crystal growth is essentially a non-equilibrium problem and any interpretation of crystal-growth phenomena arrived at by equilibrium considerations should only be applied with extreme caution. This applies specially to growth from the melt, while equilibrium conditions can be better approximated in the case of growth from vapour or dilute solution. The growth process from the melt shows certain characteristic differences from the growth from vapour or dilute solution. While in the latter case the supply of material for the growth of the solid phase is an important factor and the concentration gradient usually determines the speed of the transition, there are no problems of supply in the case of growth from the melt. In this case, it is usually the speed of dissipation of the latent heat of solidification which determines the speed at which the solid grows.

If we consider the growth of a pure metal into its own melt as pictured schematically in Fig. 1, then there are two possibilities of how the latent heat can be extracted: (a) The heat conduction can take place entirely through the solid, while all the liquid is at a temperature above T_m (the temperature of the region immediately adjacent to the growing solid-liquid interface will be discussed later). In this case the magnitude of the temperature gradient in the solid and the heat conductivity of the solid determine the speed of growth; (b) If the liquid is supercooled it can take up the heat of solidification and thus permit continuous growth of the solid, which will prevail as long as the melt remains supercooled. Under these conditions the heat transfer is very rapid and phenomena associated with higher rates of growth, as described in IIC occur when the liquid is supercooled appreciably.

TAMMANN⁽⁴⁾ already pointed out that extraction of heat through the melt can maintain the process of fast solidification. However, it was

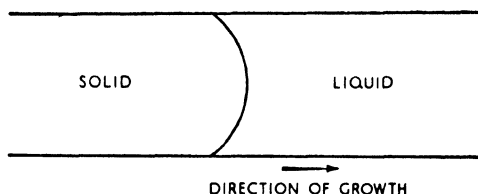


Fig. 1. Schematic representation of the solidification process

realized already in the early periods of the study of crystal growth, that in addition to the thermal factors outlined above, there are certain crystallographic factors that determine the mode in which the crystal solidifies.

The first systematic investigations of growth from the melt (rather than from dilute solution or vapour) were carried out by G. TAMMANN and his co-workers.⁽⁴⁾ Working with transparent organic melts, they measured the speed of growth as a function of the degree of supercooling and as functions of the heat transfer characteristics of liquid and solid. On the basis of numerous experiments of this kind TAMMANN arrived at the concept of nucleation and crystal growth as the two main processes in solidification. He clarified for the first time the dependence of these phenomena on the degree of supercooling and realized fully the influence of the liberated heat of solidification on the course of the phase transformation.

As a consequence of this experimental work TAMMANN formulated the concept of the "linear velocity of growth," an idea which had considerable influence on the subsequent thinking in this field. The linear velocity of growth, as defined by TAMMANN, is the rate at which a crystallographic plane is propagated parallel to itself during solidification.

It is a vector quantity and its magnitude is a function of the degree of supercooling and of the crystallographic orientation. At the melting point, i.e. at the equilibrium temperature, the growth velocity is zero for all crystal faces. With increasing supercooling of the melt the experimentally measured growth velocities increase until a maximum is reached at a certain degree of supercooling. It was found for many organic substances that further supercooling of the melt did not change the growth velocity, which remained at its maximum value until at very large amounts of supercooling (only obtainable in case of organic melts) the velocity of growth decreased. Both the absolute value of the velocity and the temperature where the maximum was reached are in this picture different for different crystallographic planes.

Fig. 2 shows the generalized result of the experimental work of TAMMANN'S school. TAMMANN explained that in the range AB, the

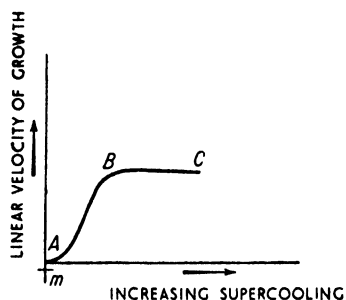


Fig. 2. TAMMANN'S generalized picture of the growth process

latent heat of solidification is dissipated through the container walls or through the solid; this is a slow process and determines the speed of growth of the solid. In the region BC, the strongly supercooled melt takes up the latent heat of solidification. In this range of "adiabatic" solidification, the measured velocities of growth are true constants of the material. It is interesting to note from the original papers that crystallization under these adiabatic conditions is always dendritic or columnar. The

observers point out that the melt does not solidify with a continuously advancing interface, but that parallel crystal arms advance, leaving some of the melt between them. The maximum linear growth velocities are of the order of magnitude of several millimetres per second and were measured as the advance of these crystal arms. All the experiments were carried out on transparent organic melts.

The anisotropy of the growth velocity was always stated by TAMMANN as an experimental fact and he made no attempt at an explanation on the basis of the crystallographic or atomic properties of the crystal. He reasoned that if the velocities of growth were not vector quantities, a crystal, growing unrestrictedly from the melt, would always be a sphere.

More recently BORELIUS⁽⁵⁴⁾ obtained very similar results in an interesting investigation of the crystallization of supercooled selenium. He measured, for instance, the rate of dendritic crystallization directly under the microscope (thin layers of selenium are transparent to red light). In some of his experiments a supercooled selenium melt of a

given temperature was inoculated with small selenium crystal needles obtained by sublimation of selenium vapour. The observed rate of crystallization at a given temperature depended strongly on the crystallographic orientation of the seeds, varying as much as 52 mm per hour and 0.70 mm per hour at 147°C for crystal needles presenting to the melt crystal faces parallel or normal to the hexagonal axis.

Much of the work on crystal growth from dilute solution or from the vapour was concerned with the reasons for the preferential development of certain crystallographic faces during growth, and with the persistence or disappearance of these faces in the equilibrium form (i.e. the form which the crystal takes when it is in equilibrium with its vapour). STRANSKI⁽⁹⁾ and others dealt with the problem of the equilibrium form and with the question of growth close to equilibrium conditions and discussed these problems in relation to the interatomic forces in the solid. The theory emerging from these considerations, pictures the growth process as an atom by atom addition on to an already existing crystal nucleus, and considers the binding energy of the different sites of the crystal lattice. The lattice positions which have the largest number of nearest neighbours are the energetically most favourable sites and hence will be filled up first. This process leads first to the completion of existing high index planes and then to the subsequent growth of the low index faces which will—in this picture—grow out and leave the crystal bounded by close packed planes. The theory of growth from the vapour⁽¹⁰⁾ shows that growth of a new plane of atoms on to a completed crystallographic face requires either a “two-dimensional nucleus,” (i.e. the formation of a little island of new atoms on the completed face) to start a new plane, or the presence of a step (“re-entrant step” or “re-entrant corner”) which can provide a favourable low energy position for the addition of the first atoms to form the new plane. It is obvious that this picture furnishes a good approximation only under conditions not too far from the equilibrium where slow atom by atom addition is a permissible assumption. This theory of growth of perfect crystals under near equilibrium conditions was recently extended to the growth of imperfect crystals under the same conditions.⁽⁸⁾

FRANK⁽¹¹⁾ was the first to point out that crystal imperfections, for instance dislocations could furnish a self perpetuating re-entrant step which would eliminate completely the necessity for any two-dimensional nucleation.

As far as the problems of crystal growth from the melt are concerned, these concepts are only partially applicable. There is, to the writer's knowledge, no direct experimental evidence for the existence of equilibrium forms of a metal crystal in contact with its own melt, nor is there any information on the detailed structure of the solid-liquid

interface during growth*; nevertheless, on an atomic scale the basic phenomena will be the same during growth from the melt as they are during growth from vapour or dilute solution. However, the influence of the interatomic forces of the already existing solid on the growth process will be modified by the thermal factors outlined above and by the influence of the structure of the liquid. This has not yet been taken fully into account, but recent progress in the theory of nucleation as well as in investigations into the structure of liquid metals should soon permit a new and fruitful approach.

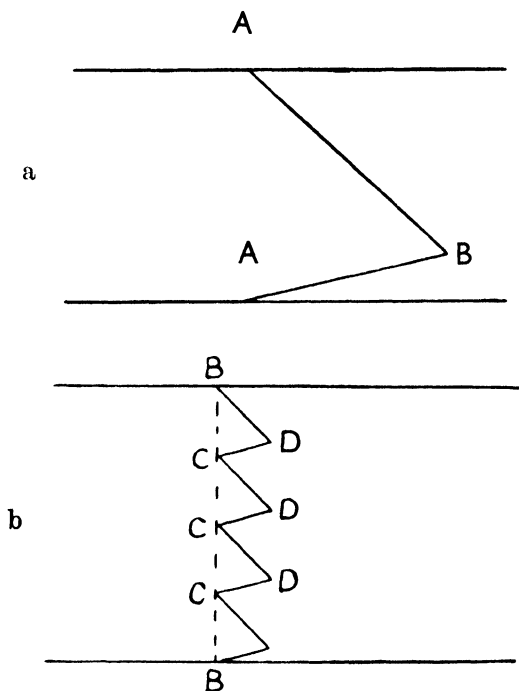


Fig. 3 (a). Solid-liquid interface. Zero temperature gradient.
(b) Solid-liquid interface. Finite temperature gradient⁽¹²⁾

As to the influence of the thermal factors, it is necessary to distinguish clearly between conditions under which the heat conduction takes place through the solid only and conditions where the liquid phase is appreciably supercooled and the latent heat of solidification is conducted into the liquid. The former case corresponds roughly to what the literature

* However, recently communicated work by ELBAUM and CHALMERS⁽⁶⁸⁾ presents experimental evidence of what could be the structure of the interface. The authors observed a steplike structure on interfaces exposed by rapid separation of liquid and solid during growth. The observed structure was strongly dependent on the crystallographic orientation of the growing solid.

calls "slow growth," while the latter corresponds approximately to conditions of "fast growth." The necessary conditions for continuous growth as outlined in the theory of crystal growth from vapour or dilute solution were sometimes thought to be applicable also to slow growth from the melt; however, CHALMERS and MARTIUS⁽¹²⁾ showed that for instance the presence of a temperature gradient in the liquid might produce a growing solid-liquid interface as shown in Fig. 3*b*. It is assumed that the solid is growing by the propagation of close-packed planes which, on account of the temperature gradient in the liquid do not grow out into the position AB, in Fig. 3*a*, but form a pyramid-shaped interface with close-packed planes as walls of these "growth pyramids" (Fig. 3*b*). The position C can serve as re-entrant corner for further growth, if the shape of the interface does not change during growth. As long as the temperature gradient in the liquid does not change, the interface will only move parallel to itself on growth of the solid. Depending on the crystallographic orientation of the solid, the "growth pyramids" may or may not be symmetrical. The heights of the individual pyramids and their spacing on the interface will depend on the temperature gradient in the liquid. Growth from the melt under various external conditions can be pictured by considering the influence of thermal factors and crystallographic orientation on the shape and size of the "growth pyramids." Although this picture is, of course, highly idealized it is consistent with the available experimental evidence on the mechanism of growth. An application of this hypothesis to the mechanism of dendritic growth is suggested in IIIC.

The considerations outlined above apply to ideally pure metals only. The presence of impurities, even to the minute extent found in highly purified materials has considerable influence on the solidification process. Two cases can be distinguished. Conditions can either be such that the diffusion in the liquid is complete at any time and hence the composition of the liquid is uniform at all times, or incomplete diffusion during solidification results in the formation of regions of higher concentration of impurities in the liquid. Impurities change the liquidus temperature of the melt. RUTTER and CHALMERS⁽¹⁴⁾ used the term "constitutional supercooling" to denote the change of solidification temperature of the melt resulting from the change of composition of the residual melt due to concentration of solute. RUTTER and CHALMERS⁽¹⁴⁾ have discussed the implication of these phenomena on the formation of substructures.

The way in which impurities segregate during solidification or resolidification has recently been treated theoretically by various authors. PFANN⁽¹⁵⁾ recently discussed the principles of "zone melting." In contrast to normal freezing (i.e. transition liquid→solid), zone melting is defined as the traverse of a small molten zone through a long solid

charge. This molten zone is small with respect to the total length of the solid. PFANN showed how differently conducted zone melting procedures can either produce a nearly complete separation of solute and solvent or a homogeneous distribution of the solute.

In the case of normal freezing PFANN derived the following equation

$$C = C_0 k(1 - g)^{k-1} \quad \quad (1)$$

where C and C_0 are the impurity concentrations in the solid and in the initial melt. g is the fraction of the melt which is solidified and k is the distribution coefficient, i.e. the ratio of the impurity concentration on either side of the growing interface under equilibrium concentrations. Equation (1) is only applicable if (i) the diffusion in the solid is negligible (ii) the diffusion in the liquid is complete at all times, and (iii) k is a constant.

TILLER, JACKSON, RUTTER and CHALMERS⁽¹⁶⁾ conducted a quantitative theoretical analysis of the redistribution of solute during solidification, taking the diffusion in the liquid into account. This treatment shows that the assumption (ii) in the above mentioned derivation of equation (1) cannot be reconciled with the current data on diffusion in liquid metals and hence diffusion in liquid and solid cannot be neglected. If the diffusion is taken into account the distribution of solute is strongly influenced by the speed of solidification. This applies to both zone melting and normal freezing.

PART II. EXPERIMENTAL FACTS

A. Ingots

The earliest and most extensive evidence for the mode in which a metal solidifies from the melt came from the examination of structures of ingots. The first and very important fact emerging from these studies was that, under whatever conditions a melt solidifies, the resulting metal is always crystalline. Under no conditions of temperature or pressure has it been possible to obtain metals in vitreous form although a number of attempts have been made throughout the years. Furthermore, it was found that grain size and relative grain orientation of a cast polycrystalline metal may vary over a wide range, depending on the thermal conditions under which the ingot solidifies.

The following facts, bearing on our problem, emerged from the study of the structure of ingots. If a molten metal or alloy solidifies, starting at the cold walls of the container, a thin layer consisting of small equiaxed crystals of random orientation is formed first. Adjacent to this "skin" a zone of large columnar grains of strongly preferred orientation develops which either fills the rest of the casting completely, or is followed by another layer of small equiaxed crystals, again of random

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orientation, the core. The relative thickness of the layers can vary with varying thermal conditions of the freezing process, and with the composition of the melt. Since the technical properties of the metal are directly related to these three zones of the ingots, the empirical conditions for their appearance, and their modification with external conditions have been investigated frequently.⁽¹⁷⁾ In pure metals the core does not appear at all, and the thickness of the outer layer depends on the temperature gradient through the container. The preferred crystallographic orientation of the columnar zone has been investigated by various authors.^{(18), (19)} The texture of this zone can be regarded as a fibre texture, with the majority of the grains lined up along the fibre axis, which is always normal to the cold surface of the mould from which the freezing starts. In face-centred cubic and in body-centred cubic metals, the fibre axis is the cube axis. In hexagonal metals the basal plane tends to be normal to the cold surface, while no very definite evidence is available as to any preferred direction within this plane. In white tin, which is body-centred tetragonal, the [110] direction is the fibre axis, while in bismuth, as far as present results indicate, the body diagonal was found to be normal to the walls of the mould. Table 1⁽²⁰⁾ summarizes these results.

TABLE 1
Textures of Cast Metals

<i>Structure</i>	<i>Metal</i>	<i>Directions [uvw], or Planes (hkl) Normal to Cold Surface</i>
B.c.c.	Fe-Si (4.3% Si)	[100]
	β -Brass	[100]
F.c.c.	Al	
	Cu	
	Ag	[100]
	Au	
	Pb	
	α -Brass	
C.p.h.*	Cd($c/a = 1.885$)	Columnar grains, (001)
		Columnar grains, [210]; chilled surface, [001]
	Zn($c/a = 1.856$)	Columnar grains, (001)
		Columnar grains, [210]; chilled surface, [001]
	Mg($c/a = 1.624$)	Columnar grains, [100]
		Columnar grains with (205) surface
Rhombohedral	Bi	[111]
Tetragonal	β -Sn	[110]

* Three-indices system; equivalent indices in four-indices systems are as follows: (001) = (0001) = basal plane; [100] = [2110] = diagonal axis of type 1 = close-packed row of atoms in basal plane; [100] normal to the surface = (210) parallel to surface; [210] normal to surface = (100) parallel to surface.

B. Single Crystal Techniques

Many significant observations on the properties of metals grown from the melt were made in the course of the development of methods for the

production of single crystals. Everyone who has ever attempted to grow single crystals from the melt has soon found that it largely depended on the speed of solidification, on the purity of the metal and on thermal factors, whether or not the melt would solidify as a single crystal.

Numerous empirical rules for obtaining the optimum conditions for the growth of single crystals of various metals were given by different authors.⁽³⁾ Not all of them realized the importance of the temperature gradient as a thermal variable, which CHALMERS stressed again recently.⁽¹³⁾ However, in some cases, even in the earlier literature, the optimum conditions of growth are expressed as functions of speed of solidification and of the temperature gradient.^{(21), (22), (23)} In the course of these attempts to find the optimum range for single crystal growth a considerable amount of information was accumulated as to growth irregularities, substructures in single crystals and the conditions for nucleation of new crystals. In the following paragraphs some of these observations, which have a bearing on the fundamental problem of solidification will be mentioned.

At this point it is necessary to define the term "single crystal" which is not always used in the same sense in the various investigations. In this review "single crystal" means a crystalline solid of coherent lattice structure in contrast to a polycrystalline material. In the latter, regions of one crystallographic orientation join on to regions of completely different crystallographic orientations, with no systematic relationship between the orientation of neighbouring grains. This definition of a "single crystal" permits the inclusion in this term of the substructures that occur during growth. Although the substructures are characterized by a change in crystallographic orientation, these changes are systematic. Neighbouring regions show a definite orientation relationship and, looking at the total volume of the single crystal, the small changes of orientation tend to average out, leaving the overall crystallographic orientation of the "single crystal" unaltered. This is, of course, not a very strict definition, and whether certain substructures are regarded as large deviations from perfect single crystals, or as polycrystalline material with a very strongly preferred orientation, is purely a matter of terminology.

BRIDGMAN^{(24), (25)} published a number of observations on the properties and crystallographic orientations of metal single crystals grown from the melt by slowly moving the molten metal through a temperature gradient. Over a large number of experiments he found that certain crystallographic orientations were much more likely to occur among the single crystals obtained by this technique than other orientations. He found that in zinc the basal plane tends to be parallel to the axis of the specimen, i.e. parallel to the direction of heat flow, while he

found no preferential orientation in cadmium. In antimony, which is "easy to grow, the principal cleavage plane is parallel to the specimen axis," and in tin, "the axis of the four-fold symmetry prefers either to be parallel or perpendicular to the length of the rod."

The conditions for single crystal growth in zinc as a function of the temperature gradient (G) and the rate of growth (R) have been investigated rather thoroughly by various authors.^{(21), (23)} They found that the melt would only solidify as a single crystal at specific values of R and G (often only the ratio of these quantities is quoted) although the absolute values of G and R in various experiments differ considerably. All early investigations were carried out at very slow rates of growth, but later work showed that it is sometimes advisable to use higher growth rates.

If and when a single crystal of Zn is formed by random nucleation, its orientation is likely to be such that the normal to the basal plane tends to be at right angles to the axis of the specimen. This orientation occurs over a wide range of G/R values, while other orientations are much more sensitive in their propagation to external conditions, i.e. changes in R or G . Fig. 4 shows a plot of the results of CINNAMON and MARTIN⁽²¹⁾ which is quite representative for the results in this group of investigations. Their G/R value, though, is more than one order of magnitude larger than the value recommended by ANDRADE and ROSCOE.⁽²³⁾

Realizing the importance of the speed of growth and of the temperature gradient for the successful growth of single crystals, GOSS and WEINTROUB⁽²⁸⁾ recently investigated the influence of these variables on the crystallographic orientations and substructures of single crystals of metals of low melting point. The authors used a horizontal travelling

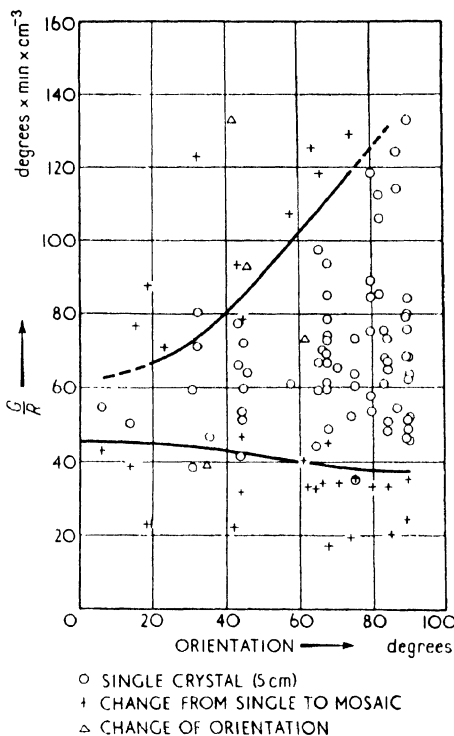


Fig. 4. Graph showing the effect of the temperature gradient (G) and the rate of growth (R) on the propagation of single crystalline structure (orientation denotes the angle between the normal to the basal plane and the axis of the specimen)⁽²¹⁾

furnace and obtained by random nucleation specimens of 12 mm diameter and approximately 60 mm in length. Various temperature gradients and speeds of growth could be imposed upon the melt. The authors investigated tin, lead, bismuth and zinc, at rates of growth from 0.06 to 30 mm/min. and temperature gradients from $2^{\circ}\text{C}/\text{cm}$ to $65^{\circ}\text{C}/\text{cm}$.

They found that these temperature gradients had little influence on their experiments. At high speeds of growth, larger than 5 mm/min, tin and lead grew as single crystals from a very small polycrystalline beginning of the specimen. The orientation of these single crystals with respect to the direction of heat flow was random. Single crystals of the same metals could also be obtained at low speeds of growth (smaller than 5 mm/min.); the orientation was again random in lead, while the tin single crystals showed a tendency to grow with the [110] direction close to the axis of the specimen. At medium speeds of growth (around 5 mm/min.) it was more difficult to obtain single crystals and substructures were more prominent. Single crystals of zinc could only be obtained at low speeds; at high speeds groups of crystals with very similar orientation, all of them tending to have the direction of heat flow as close to the basal plane as possible, were obtained. Bismuth single crystals were produced at all speeds and the orientation was usually such that the [111] axis was at about 80° to the axis of the specimen.

The conditions under which a single crystal can grow from the melt were recently generalized by CHALMERS⁽¹³⁾ in terms of the fundamental variables such as speed of growth, temperature gradient, degree of supercooling. With his technique crystals are grown from "seeds" of predetermined crystallographic orientation by progressive solidification of the melt using a horizontal travelling furnace, and speeds of growth varying from 1 to 25 mm/min. (seed crystals were first used by GOETZ,⁽²⁷⁾ but were also suggested in one of the early BRIDGMAN papers.⁽²⁴⁾)

Bicrystals, consisting of two crystals growing simultaneously side by side, can also be produced by CHALMERS' technique using two separate seeds. The way in which the boundary between these two crystals grows is of considerable general interest. According to the experiments of CHALMERS and co-workers, the direction of the boundary between two single crystals of different orientation growing simultaneously side by side depends on the crystallographic orientation of both crystals as well as on the speed of growth. This relationship can be expressed in

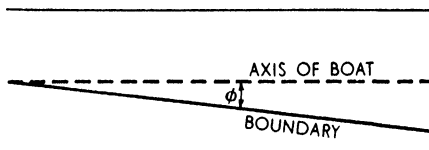


Fig. 5. Bi-crystal with sloping crystal boundary schematical⁽¹³⁾

terms of the angle ϕ , as illustrated in Fig. 5. At low speeds of growth (that is below 2 mm/min.) the boundary tends to be parallel to the direction of heat flow; hence $\phi = 0$. At intermediate rates of growth, the observed angle is the resultant of both the influence of the thermal conditions of the experiment—which tend to bring the boundary parallel to the direction of heat flow—and the crystallographic factors which will cause ϕ to increase with increasing difference in orientation. In the range of fast growth the crystallographic factors govern the direction of boundary growth. There does not yet exist a complete explanation of these crystallographic factors. But from these experiments it can be concluded that there are certain crystallographic orientations which could be called the “preferred directions of growth” and if in one of the crystals these directions are parallel to the direction of heat flow, the boundary will always slope into the neighbouring crystal of different orientation. During growth the latter decreases in width at the expense of its neighbour. The process is faster, the larger the difference of orientation and, for a given orientation difference, the higher the speed of growth. Hence, between crystals of random orientation, the one in which the “preferred direction of growth” is closest to the direction of heat flow, will be bounded by divergent grain boundaries. The experimental material presently available does not yet permit the formulation of a general relationship between the observed “preferred directions of growth” and the crystal lattice of a metal. From the evidence available, CHALMERS concludes that for face-centred cubic metals, the cube axis is the preferred direction of growth; for hexagonal close-packed lattices it is the $[10\bar{1}0]$ direction and for tin, which is body-centred tetragonal, it is the $[110]$ direction.

Successful growth of a single crystal requires that only the existing nucleus grows and no new crystals (“strays”) are produced during the freezing process. In order to achieve this, it is necessary either to avoid nucleation of new crystals, or to suppress the growth of any new crystal nucleus. CHALMERS⁽¹³⁾ discussed in detail the possibility of nucleation and subsequent growth of stray crystals. “Strays” may either nucleate on the walls of the container, or on fine particles on the surface, etc., and they may become stable because of existing supercooling of the liquid. Supercooling of the liquid may arise from local heat losses, from the depression of the liquidus temperature due to impurities, or from a finite rate of freezing. Whether a “stray,” once formed, survives, depends on the direction of the boundary between the stray and the matrix. If the boundary slopes into the stray the latter will grow out (or never come into existence) while it will survive and expand if its boundaries are divergent.

The considerations outlined above lead to the confirmation of the generally accepted rule, that a low speed of growth, a steep temperature

gradient and a pure metal are the best prerequisites for growing single crystals.

C. Dendrites

Observations on dendritic growth are another source of experimental evidence of the mode in which a metal solidifies and of the dependence of this mode on external factors. It has long been observed that under conditions of fast solidification all metals tend to form tree-like skeletons of the type shown in Fig. 6. Forms of this type are usually called "dendrites" and although this term is often used rather loosely, it does nearly always mean that in the course of solidification a tree-like skeleton is formed ahead of the coherent solid-liquid interface, and the space between the "dendrite arms" is filled in later. The distinction between

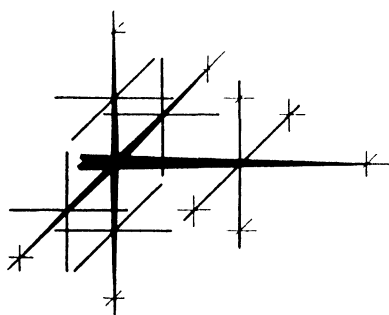


Fig. 6. Dendrite skeleton schematical⁽²⁸⁾

primary and secondary dendrite arms originates from this concept; the primary arms are parallel to the overall direction of growth. Many crystallographers were attracted by the beautiful regularity of the dendrites and their very frequent appearance on polished sections of cast metals make them a familiar picture to the metallurgist. Nevertheless, it is only recently that scientists have started to understand the laws governing the formation of dendrite

structures.^{(28), (29)} The very striking feature of dendritic growth is its crystallographic regularity. This regularity is so very pronounced that the dendrite directions are used to determine crystallographic orientations in ingots.⁽³⁰⁾

WEINBERG and CHALMERS^{(28), (29)} recently investigated the laws governing dendritic growth; single crystals of lead were grown at high speeds of growth from seeds in a horizontal travelling furnace. The crystallization was interrupted at a certain stage by pouring off the remaining liquid very quickly. The dendritic structure of the solid was then examined microscopically and by means of x-rays. The authors found that in lead the dendrites always form along the cube axis, regardless of the direction of growth of the crystal or the overall direction of heat flow (see Fig. 7). WEINBERG and CHALMERS also showed from directly measured cooling curves that supercooling of the liquid directly adjacent to the solid-liquid interface during growth is a necessary condition for the appearance of dendrites. Although this necessary condition is mentioned in various earlier works, there does not seem to be any direct experimental evidence available prior to WEINBERG and

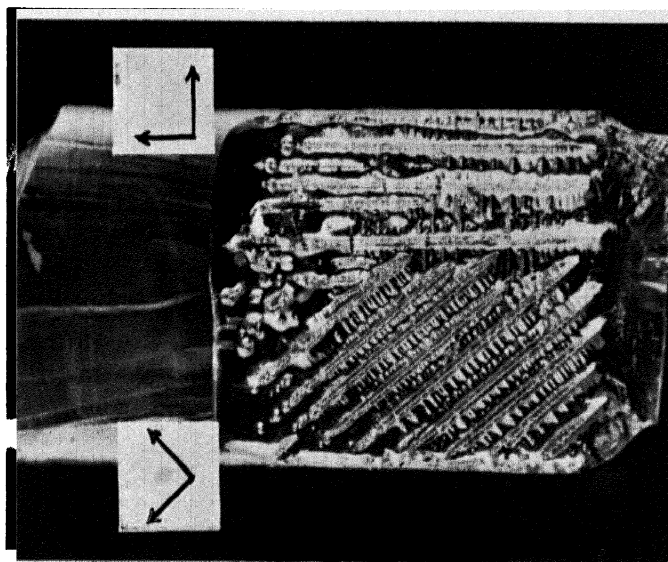


Fig. 7. Dendritic pattern of a bi-crystal of the indicated orientation⁽²⁸⁾

CHALMERS. The actual growth of a dendrite is very fast, much faster than the speed of advance of the coherent solid-liquid interface from which the dendrites start out. Various authors observed that the dendritic skeleton is formed first and that the space between the dendrite

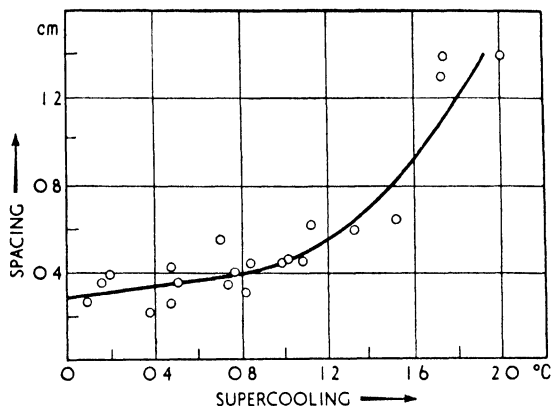


Fig. 8. Average separation of the dendritic rows of lead crystals as a function of the super cooling of the liquid metal⁽²⁹⁾

arms is filled out only later. WEINBERG and CHALMERS found that the spacing of the primary dendrite arms in lead depended on the degree of supercooling of the liquid (Fig. 8) while the spacing of the secondary arms did not seem to be affected by different amounts of supercooling.

ALEXANDER and RHINES⁽³¹⁾ measured the spacing of dendrites in a large number of non-ferrous alloys, cast into circular moulds under identical conditions. They observed that the dendrite spacing of an alloy increased with increasing solute content, and was, within the range of these experiments, independent of the grain size of the casting. The spacing of the dendrites varied with the distance from the walls of the mould, and since the rate of freezing decreases from the wall of the mould to the centre in a systematic manner, ALEXANDER and RHINES concluded from their data that the dendrite spacing is inversely proportional to the rate of freezing. Fig. 9 shows a representative graph of their results. However, the observations of the dendrite spacing of WEINBERG and CHALMERS and of ALEXANDER and RHINES cannot be compared directly.⁽³²⁾ The spacing of dendrites will be some function of the degree of supercooling. In the experiments of WEINBERG and CHALMERS supercooling of the liquid was caused by external heat losses, while in the experiments of ALEXANDER and RHINES the supercooling of the liquid was caused by the change in composition of the alloy during freezing. The amounts of supercooling obtainable under these two

conditions are quite different and hence the resulting spacing of the dendrites cannot be compared directly.

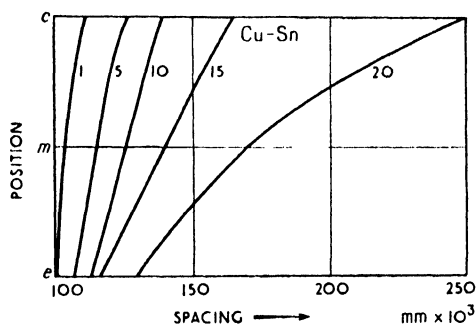


Fig. 9. Dendritic spacing versus position in the ingot (e = edge, m = mid-distance, c = centre) for copper tin alloys. Curves identified by the percentage of tin⁽³¹⁾

GRAF⁽³³⁾ has described observations on the crystallography of dendrites in the course of his work on "lamellar" substructures and his theory of crystal growth from the melt; both will be discussed in detail later. He pointed out that observations of various authors showed that dendrites in face-centred cubic metals are formed as pyramids of closest-packed planes. The cube direction, in which the dendrite arms extend, is the axis of a pyramid of four $\{111\}$ planes; in sodium chloride, grown from supersaturated solutions, the dendrites are reported to consist of $\{110\}$ pyramids with a $[100]$ axis.

Simultaneously and independently of GRAF'S work WEINBERG and CHALMERS also showed that the observed directions of the primary dendrite arms could be interpreted as the axis of a pyramid formed by the closest-packed planes of the lattice, not only in face-centred cubic metals, but also in tin (body-centred tetragonal) where the dendrite axis is $[110]$ which is the corresponding direction for the pyramids of the four closest-packed planes. In hexagonal metals, the direction of the primary dendrite arms is $[10\bar{1}0]$. This direction is the axis of the pyramid of $\{11\bar{2}0\}$ planes. These planes are the second closest-packed planes in the close-packed hexagonal structure. The closest-packed planes, $\{0001\}$, do not intersect.

Another peculiar feature of dendrite growth, which was observed by several authors and discussed in detail by GRAF,⁽³³⁾ is that the dendrite tips often appear rounded off. Fig. 10 from GRAF'S work gives a good example of this phenomenon which has been noted rather frequently.

Dendrites have been observed in nearly all metals and alloys grown from the melt as well as in salts grown from supersaturated solutions.

D. Substructures and Impurities

The study of dendrites is closely linked with the investigations of other crystalline substructures formed in metals during growth from the melt. Large metal crystals grown from the melt are never ideally perfect single crystals. When examined optically or by means of x-rays, they turn out to consist of a "mosaic" of "ideal regions," which are slightly disoriented with respect to the crystallographic orientation of their neighbours. The size of these regions and their orientation difference can vary considerably. All these substructures formed during growth can change their appearance with changing conditions of solidification. Substructures on large single crystals grown from the melt have been noticed by nearly everyone who has grown single crystals. Many experimental observations on these substructures are available and it has been claimed again and again that, although the appearance of these substructures may vary considerably they are not just "imperfections," which could be eliminated by suitably improved techniques of crystal growth, but that their presence has a fundamental significance. Substructures are said to reflect the mechanism by which the crystal grows and hence are necessary consequences of the growth process. In the opinion of some authors, they represent the smallest thermodynamically stable region of perfect single crystals, etc.

The subject of the fundamental significance of substructures was once hotly discussed without a really conclusive solution being reached;⁽³⁴⁾ but regardless of what the theoretical verdict on the thermodynamic necessity of a substructure in a crystalline solid may be, the experimental evidence is that substructures do occur in all large single crystals grown from the melt.^{(13), (21), (22), (25), (26), (33), (35), (36)} Any general theory of solidification has to explain their presence and the variation of their appearance with external conditions.

In spite of a large number of experimental observations, it is difficult to assess the evidence for the presence of substructures and their detailed properties. Only a few systematic experiments were conducted with the aim of studying substructures, and even there it is hard to assess how far the results can be generalized. The lack of adequate terminology is another handicap.

For our purpose it is convenient to distinguish (according to GRENINGER,⁽³⁶⁾) between "*macro-mosaics*," i.e. all structure irregularities which cause splitting of the Laue spots in back reflection photographs under standard conditions, and "*micro-mosaics*" which cause only broadening of the x-ray reflections under the same conditions.

In the course of the discussion on the theoretical significance of substructures, BUEGER⁽³⁵⁾ introduced the concept of a "lineage structure" and regarded a single crystal as grown continuously, though branched

into lineages. Each lineage of a single crystal grows from a common nucleus and its orientation is only slightly different from that of the neighbouring lineage. This concept was formed to embody all substructures in single crystals which may appear either as filled-in dendrites or as imperfections of smaller angular difference, as, for instance, in slowly grown single crystals. BUEGER though does not elaborate on the growth mechanism of the lineage structure which he regards as more or less universal.

GRAF describes in a number of publications⁽³⁷⁾ the appearance of a layer or lamellae substructure with lamellar spacings of approximately 10^{-4} to 10^{-3} mm, and advances a theory to explain their universal appearance. This theory will be discussed later. In his latest experiments,⁽³³⁾ he obtains the substructures by rapid solidification of a larger melt or by solidification of small metal droplets, where the whole droplet solidifies within a fraction of a second. Dendrites which show a lamellar substructure were formed in both cases. There are no exact data available as to the speed of solidification, temperature gradient, etc.

GOSS and WEINTROUB⁽²⁶⁾ reported on the appearance of substructures which they observed during their work on the growth of single crystals of metals of low melting point and on the prominence of these substructures under certain growth conditions. They found that the speed of growth had a considerable influence on the appearance of macro-mosaics.

Recently, CHALMERS and his co-workers undertook a systematic investigation of substructures formed during growth from the melt, using single crystals of predetermined orientation and the technique described in ⁽¹³⁾. As mentioned earlier, WEINBERG and CHALMERS^{(28), (29)} investigated dendrite formation while TEGHTSOONIAN and CHALMERS^{(40), (41)} studied the formation of a macro-mosaic structure in tin. This structure consisted of "striations" similar to those studied by GRENINGER⁽³⁶⁾ and those mentioned by GOSS and WEINTROUB⁽²⁶⁾ and others.⁽²²⁾ These "striations" are macro-mosaics with a difference of crystallographic orientation of between 0° and 5° as shown in Fig. 11. The authors studied the conditions under which "striations" appear in high purity tin (striations were also observed in copper, lead, zinc, silver, aluminium and nickel) as a function of the speed of growth and crystallographic orientation. They also investigated the range and the systematic relation of the orientation differences in these striations. The following results were obtained:

Striations, which partition the crystal into regions of different crystallographic orientation, extend throughout the whole crystal which can be pictured as being built up like a bundle of rods. Their widths, although subject to statistical fluctuations within any one crystal grown at a

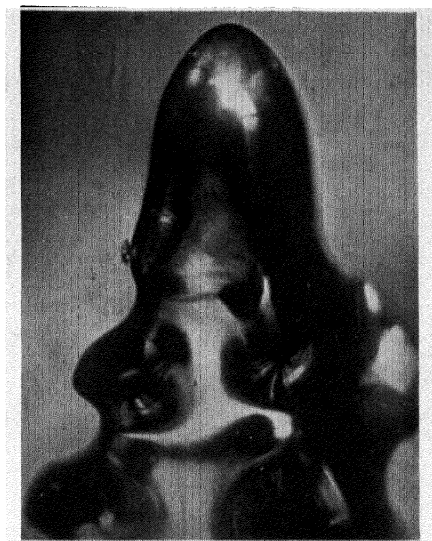


Fig. 10. Copper dendrite grown from the melt.⁽³³⁾ ($\times 100$)

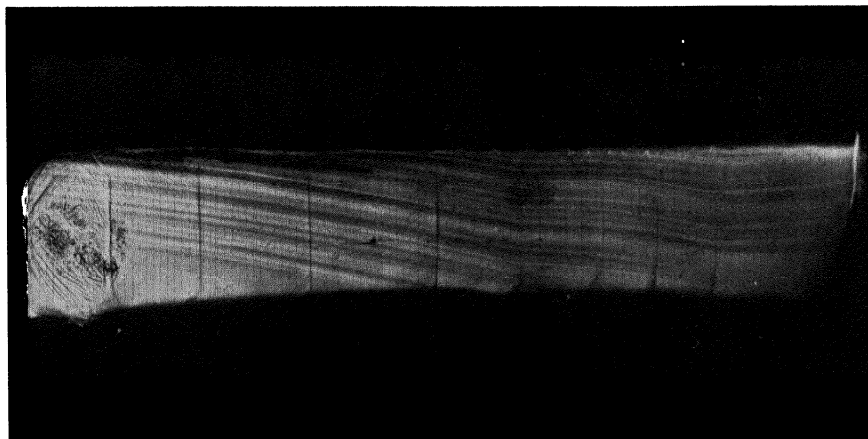


Fig. 11. Striated single crystal of tin⁽⁴⁰⁾

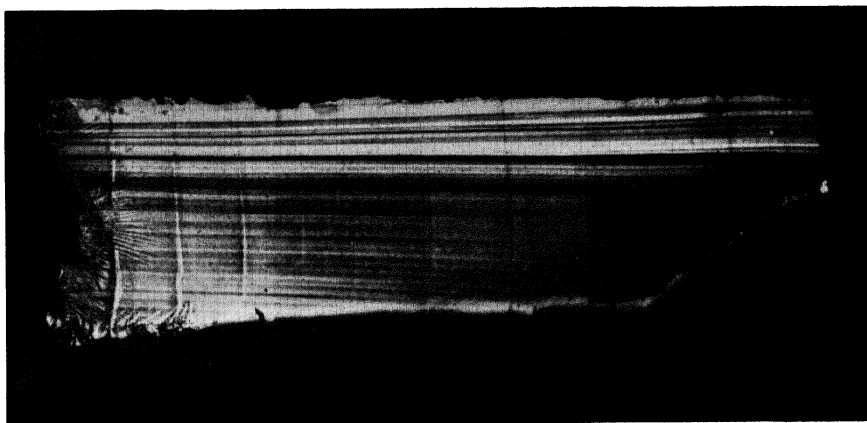


Fig. 13. Striated single crystal of tin showing striation-free edge⁽⁴⁰⁾

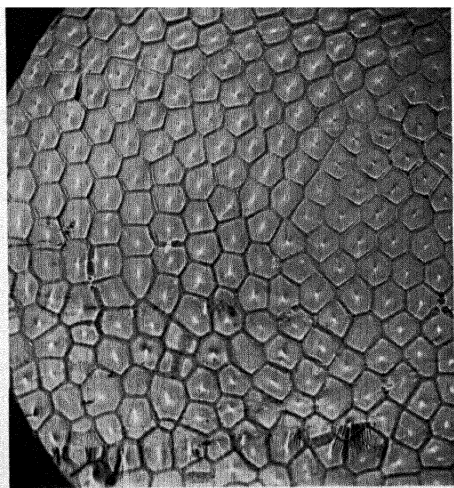


Fig. 16. Decanted interface 'hempur tin'
Speed of growth 3.8 mm. per minute.⁽¹⁴⁾ ($\times 75$)

given rate, decrease with increasing rate of growth. Varying the rate of growth from approximately 1 mm/min. to 10 mm/min., the average striation width in single crystals of tin of the same size and crystallographic orientation varies from 1.20 mm to 0.25 mm. At the same time the difference in crystallographic orientation between neighbouring striations also changes. At a speed of growth of 0.85 mm/min., the average orientation difference was 2.0° , compared with 1.2° at

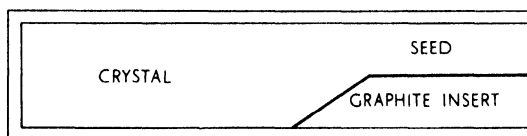


Fig. 12. Schematic diagram of the crystal arrangement in the boat⁽⁴⁰⁾

9.6 mm/min. Hence, wider striations exhibit larger differences in crystallographic orientation. This difference in orientation was found to consist of a pure rotation of the striations around a common axis.

The same work contains very significant experiments on the generation of these striations. Fig. 12 shows schematically how a single crystal in these experiments was grown from a "seed." For the purpose of these investigations the crystal is grown wider than the seed and a graphite insert next to the seed assures a smooth junction. Fig. 13 shows a tin crystal obtained by this method; the seed has been removed.

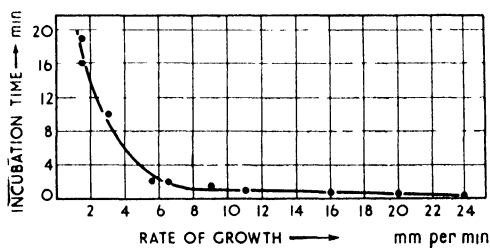


Fig. 14. Curve relating incubation period and growth rate⁽⁴¹⁾

If the original seed is striated, the substructure will grow into the new crystal. In the portion of the crystal which is in front of the graphite insert, new striations form; however, they do not form immediately, but only after a certain incubation period. The portion of the crystal close to the graphite insert is striation-free. During the detailed study of this phenomenon, it was found that the length of the incubation period depends on the rate of growth as shown in Fig. 14. For slow rates of growth (approximately 2 mm/min.) it takes longer for the striations to appear than for fast rates of growth. It also takes a certain amount of time after the striations have appeared (i.e. became visible) before they

reach the final difference in orientation with which they will continue throughout the rest of the crystal. This relationship is shown in Fig. 15.

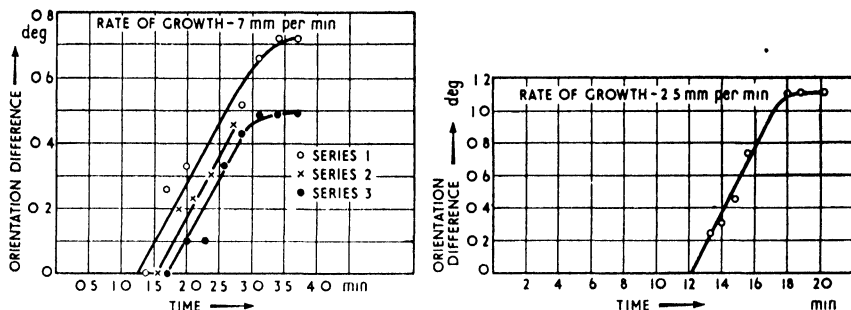


Fig. 15. Curves showing the increase in orientation difference with time across one pair of striations in the region of incubation⁽⁴¹⁾

The observed dependence of the direction of the striations on the speed of growth and on the crystallographic orientation in which the single crystal of tin is grown can be summarized as follows:

The direction in which the striations are formed is a function of both the speed of growth (i.e. the thermal conditions of the solidification process) and the crystallographic orientation of the growing crystal. If a tin crystal is grown with the (001) plane as the plane of the top surface and the specimen axis parallel to the [110] direction, the striations visible on the surface run parallel to [110] under all conditions of growth. In other words, the bounding planes between the striations appear to be (110) planes, which are in the above mentioned orientation parallel to the direction of heat flow. When the orientation of the crystal is changed in such a way that these planes are inclined at some angle to the direction of heat flow, the striations remain parallel to the direction of heat flow at low speeds of growth, but deviate towards the [110] direction at high speeds.

In the course of the above mentioned series of investigations, RUTTER and CHALMERS⁽⁴²⁾ studied, also in tin and with the same experimental set-up, a hexagonal cell substructure. This is a *micro-mosaic* and the regions of this substructure are approximately one order of magnitude smaller than the striations. On a vertical section of the crystal or on the interface exposed by decantation during growth, this substructure manifests itself as a network of hexagonal cells shown in Fig. 16. The projection of these cells appears on the top surface of the crystal as a set of parallel ridges which the authors call "corrugations." In a crystal which shows both striations and corrugations, the two types of substructures appear parallel to each other on the top surface of the crystal. The distance between the corrugations, which is equal to the average

cell diameter, decreases with increasing speed of growth. At low speeds (less than 1 mm/min.) the distance between the corrugations becomes larger, the cells on the decanted interface increase in size, turn into a system of vertical and parallel bands and gradually lose their identities. Striations still exist at this speed. At medium rates of growth, the corrugation distance decreases with increasing speed of growth. At a speed of about 5 mm/min. the hexagonal cells are very regular with an average diameter of 0.05 mm. The detailed examination of the cells on the decanted interface reveals that the centre of each cell is higher than the cell boundaries and the centres of the cells on the growing solid-liquid interface seem to project into the melt during growth. At high rates of growth it was found that a small percentage of the cells enlarged considerably and their projection extended farther into the melt. Further observations indicate that these enlarged cells are the beginnings of dendrites forming at these speeds of growth. Corrugations and striations show exactly the same dependence of the direction of growth on the crystallographic orientation of the growing crystal, but corrugations do not show an incubation period.

In order to assess the influence of impurities (which are present even in "pure" metals) on the formation of these substructures, RUTTER and CHALMERS added small quantities (0.1 per cent wt.) of radioactive antimony to a lead melt before the specimens were grown. The hexagonal cell structure was found to be very sensitive to small quantities of impurities. The presence of impurities caused an increase in cell size and a decrease in cell regularity. When a crystal, containing radioactive impurities, was placed on a nuclear track plate, the corrugations appeared as dark lines indicating that the radioactive impurities had segregated between the cells. These lines disappeared after twenty-four hours annealing. Subsequent experiments showed that during this annealing process the impurities were distributed evenly throughout the whole volume of the crystal.⁽⁴²⁾

RUTTER and CHALMERS observed furthermore that the formation of the hexagonal cell substructure could be suppressed not only by a slow rate of growth, but also by a steep temperature gradient (larger than approximately 75°C/cm).

Earlier, POND and KESSLER⁽⁴³⁾ had also studied this type of substructure, both on the top surface of a solid polycrystalline metal and on the interface which was exposed when after partial solidification the liquid metal was rapidly sucked off. Parallel lines were observed on the top surface, which corresponded to GRAF's "lamellar" lines or to RUTTER's and CHALMERS' corrugations. On the interface, the hexagonal cell structure was found and studied in detail. The substructures appeared in 99.997 per cent pure tin, 99.998 per cent pure bismuth, 99.999 per cent pure indium, and 99.8 per cent pure antimony as well as in 99.997

per cent pure aluminium and 99.99 per cent pure lead. POND and KESSLER observed, in the same way as RUTTER and CHALMERS, a decrease in cell size with increasing speed of solidification, although the data on the absolute dimensions of the cells in the two papers differ considerably.

In the course of nearly all the investigations on substructures as well as on the growth of single crystals, investigators reported a marked influence of impurities on the result of the experiments. In impure metals or in alloys, substructures become "more pronounced." Mosaics occur under growth conditions where few or no visible irregularities are observed in pure metals; some authors even went so far as to claim that all substructures disappear in spectroscopically pure metals, a statement which led to considerable controversy.

The way in which impurities are distributed during the solidification process has recently attracted considerable attention.

Goss⁽³⁹⁾ added known amounts of cadmium, zinc, lead, silver, indium and antimony to 99.997 per cent pure molten tin from which he grew single crystals. He found that the influence of these impurities on the possibility of obtaining single crystals as well as on their substructure depended on the relative amount of the alloying element. If it was present to an amount of 0.1 per cent of the solid solubility limit, it was not possible to obtain single crystals at high rates of growth, but stray crystals occurred (a result which can easily be understood from CHALMERS' observations⁽¹³⁾), while at the slower rates of growth the resulting single crystals showed very marked substructures. Foreign material of approximately 0.01 per cent of the solid solubility limit, did not seem to influence the ease of obtaining single crystals of tin, although an influence could still be seen on the substructures. In experiments with high impurity content, the spectroscopic examination of the solid showed segregation of the foreign components in the parts of the metal that solidified last. The concentration of the solute in the melt increased during fast solidification, a well known result of all examinations on ingots. Using radioactive isotopes STEWART, THOMAS, WAUCHOPE, WINEGARD and CHALMERS⁽⁴⁴⁾ observed the segregation of "bands" of high solute concentration which occurred at intervals in the course of the growth of a single crystal under certain conditions.

DOWD and ROUSE⁽⁴⁵⁾ studied the distribution of radioactive indium in germanium and found the concentration of the impurity in the ingot obeyed the relation

$$C = C_0 k(1 - g)^{k-1} \quad (\text{see Eq. 1, p. 286})$$

The experiments were carried out on germanium ingots and the concentration of indium was 0.0164 per cent. Fig. 17 shows the graph of their results.

Summary

From the experimental material discussed in the previous paragraphs, a number of facts and questions emerge which any theory of solidification will have to explain.

The evidence from the study of ingots shows that even when a large number of crystals nucleate at the beginning of the solidification process, only those with favourable crystallographic orientations with respect to the direction of heat-flow "survive." The atomic and thermodynamic interpretation of these "preferred directions of growth" is one of the open questions in this field. From all experimental evidence, it seems that this "preferred direction of growth" is also the direction in which

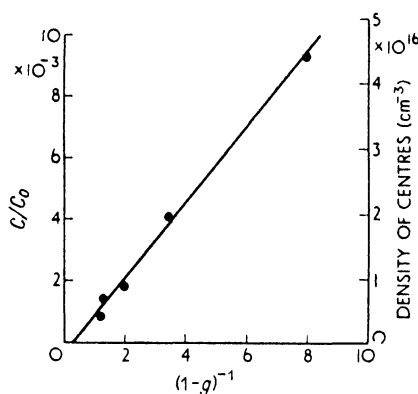


Fig. 17. The concentration of traces of indium in a germanium ingot⁽⁴⁵⁾

single crystals are likely to grow in cases of random nucleation and are easiest to grow in experiments using seeds of known orientation (see p. 291 on boundary growth). It is not too easy to assess the material on dendritic growth in relation to this problem, but it does suggest very strongly that the direction of the primary dendrite arms is the same as the "preferred direction of growth" mentioned above. It is necessary that any interpretation of these phenomena must not only explain the thermal conditions of the appearance of dendrites, but also these

crystallographic features as well as the relationship between dendritic and coherent forms of growth.

The occurrence of substructures as a consequence of the mechanism of growth from the melt, their dependence on impurities as well as on crystallographic and thermal factors, is another group of problems where the present experimental material shows the questions, but not all the answers.

PART III

THE INTERPRETATION OF THE OBSERVED PHENOMENA

In Part I some general thoughts on the phase transformation melt→crystal were compiled. To what extent can these ideas explain the experimentally observed solidification phenomena as described in Part II? This question will be discussed in the following paragraphs which will repeat the sequence of Part II.

A. Ingots

A rather complete explanation of the structure of ingots in terms of nucleation and preferred crystal growth was already given by TAMMANN in 1929.⁽⁴⁶⁾ He interpreted the three zones of a casting as follows: If molten metal is poured into a cold container, then the extraction of heat will take place through the container walls. The layer of the melt closest to the wall will solidify first and a large number of grains which nucleate at random along the walls start to grow into the melt.

On account of the anisotropy of the velocity of growth, grains in which the direction of maximum "linear velocity of growth" is parallel to the direction of heat-flow will grow faster and hence farther into the melt. In so doing they crowd out the grains of different orientation and form the second zone of the ingot with its strongly preferred orientation.

In the case of a pure metal there are only these two zones. Since heat can only be extracted through the solid there is no possibility of supercooling of the residual melt and hence no nucleation of new grains. If, however, impurities are present they will accumulate in the residual melt and change its solidification temperature. The resulting supercooling will permit nucleation of new grains in this centrezone of the ingot.

WINEGARD and CHALMERS⁽⁴⁷⁾ recently reviewed the explanations of the structure of castings in the light of recent work.^{(42), (13)} They discussed the conditions for the stability of a coherent solid-liquid interface, and for the formation of "spikes" ahead of the interface and explained, basically in the same terms as TAMMANN, the centrezone and the conditions of its appearance in alloys and impure metals.

B. Single Crystal Experiments

TAMMANN's explanation of the preferred orientation in the second zone of the ingot, i.e. the "crowding out" of certain crystals by those whose "preferred direction of growth" is close to the direction of heat flow, was also applied to explain the occurrence of certain preferred orientations in single crystal experiments; but no interpretation has ever been given as to the relationship between the crystal lattice of the solid and these directions. GROSS and MÖLLER,⁽⁴⁸⁾ who discussed these phenomena first, explained them as a consequence of the anisotropy of the growth velocity. In this picture the favourably oriented nuclei grow "faster," and hence "farther" into the melt. But this concept is not without ambiguity if we consider the temperature distribution in the melt and at the solid-liquid interface. If, for instance, during growth three crystals in a tube are arranged as in Fig. 18 then we can either assume that the temperature at the solid-liquid interface, a -, b -, c -, d -, e is the same, T_m , or that the point " c ," advancing farthest

into the melt, has a higher temperature; the latter concept would lead to the conclusion that different crystal faces have different solidification temperatures.

However, recent observations of CHALMERS⁽¹³⁾ on the direction of the boundary between two crystals which are growing simultaneously side by side into the melt, may furnish a new and different interpretation of the "crowding out" effect in single crystal experiments and ingots. As discussed in Part II, CHALMERS found that the direction of the crystal boundary in a bicrystal depended on the crystallographic orientation of the neighbouring crystals as well as on the speed of solidification. At very low speeds of growth, the boundary tends to run normal to the interface, i.e. parallel to the direction of heat flow, while at higher speeds of growth the boundary tends to slope away from the crystal which has the "preferred direction of growth" closest to the direction of heat flow. This means that a crystal of this orientation is

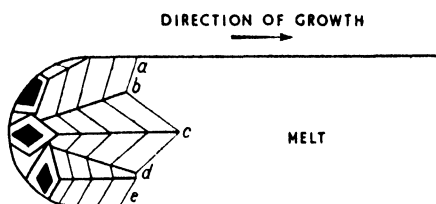


Fig. 18

bounded by divergent boundaries, while a crystal of unfavourable orientation is enclosed by convergent boundaries and hence eventually is "crowded out." The crystals with favourable orientations will survive and continue to grow with parallel boundaries between them.

These considerations of boundary growth would explain how certain crystallographic orientations occur very frequently when single crystals are grown from the melt, and would also explain the observed orientation relationship in the second zone of an ingot.

This explanation is not subject to the difficulties concerning the temperature distribution which an explanation on the basis of the anisotropy of growth velocities encounters, nor does it at all depend on the vector properties of the velocities of growth. However, we do not yet have an atomic or thermodynamic interpretation of *why* certain crystallographic directions always appear as the "preferred directions of growth," or in other words *why* the boundary is convergent or divergent.

C. Dendrites

From all available experimental evidence, it seems as if the above mentioned "preferred directions of growth" are the same crystallographic directions as those in which the dendrite arms develop, and it may be that a correct interpretation of dendritic growth will also furnish the explanation of these "preferred directions of growth." The necessary condition for the dendritic growth as discussed in IIC is that the liquid

phase is sufficiently supercooled to take up the latent heat of solidification. It was pointed out quite early⁽⁴⁹⁾ that since heat can be conducted away more rapidly from a corner or from the tip of a thin needle than from a plane surface, the dendrites, once formed, will grow ahead because of their favourable thermal constitution wherever growth occurs far from thermal equilibrium. These thermal considerations, however, do not account for the crystallographic nature of the dendrites. Why do the dendrite arms in face-centred and body-centred cubic metals always develop parallel to the cube axis and in hexagonal metals always parallel to the $[10\bar{1}0]$ direction? WEINBERG and CHALMERS⁽²⁹⁾ pointed out that the observed dendritic directions in all metals can be pictured as the axis of a pyramid formed by the closest-packed planes of the

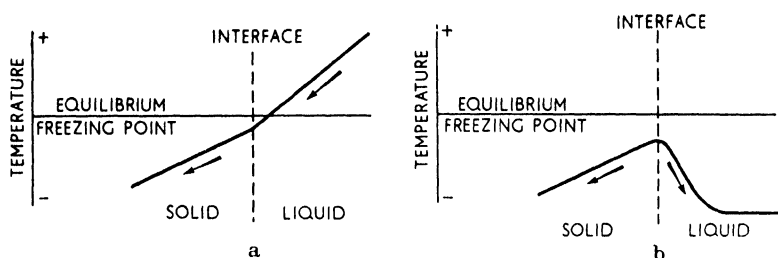


Fig. 19 (a). Temperature distribution during slow growth.
(b) Temperature distribution during fast growth⁽²⁹⁾

crystal lattice under consideration, and suggested the following interpretation of the phenomena of dendritic growth. The authors assumed that growth of dendrites proceeds by two-dimensional nucleation and tangential growth. They first discussed the temperature distribution in the neighbourhood of the growing solid-liquid interface. Fig. 19a shows the temperature distribution as assumed for the case of continuous growth. The liquid immediately adjacent to the interface is slightly supercooled, the temperature of the interface is below the equilibrium freezing temperature T_m but the bulk of the liquid is above T_m ; the dissipation of heat takes place entirely through the solid. If, however, the liquid phase is supercooled, the latent heat of solidification can be conducted away through both the liquid and the solid; the corresponding temperature distribution is pictured in Fig. 19b.

WEINBERG and CHALMERS then considered how the hexagonal cell structure of the interface would be influenced by the temperature distribution in the region around the interface and suggested that in the case of an appreciably supercooled liquid (Fig. 19b) certain enlarged cells will reach into regions of larger supercooling and there they will grow faster on account of the increase in the probability of two-dimensional nucleation with increasing supercooling. Furthermore, it

was suggested that the crystallographic regularity of the dendrites is due to the fact that the growing dendrite is formed as a pyramid of close packed planes and that in the supercooled liquid, growth proceeds by two-dimensional nucleation on these planes. Since dendrites grow parallel to the axis of this pyramid, it is necessary to assume that two-dimensional nucleation always takes place at equal rates on all four walls of the pyramid, an assumption which the reviewer finds not too easy to reconcile with the high speed of dendritic growth and with the thermal conditions during this process.

Since no direct experimental data on the temperature distribution of a growing solid-liquid interface of a metal are as yet available, these ideas have to be regarded as hypotheses and more experimental information will be needed in order to prove or disprove them. Microscopic observations of dendrites show that their tips are very frequently rounded rather than pointed. GRAF⁽³³⁾ based a new purely crystallographic interpretation of dendrites and of the lamellar substructure on these rounded forms. He stressed that the STRANSKI-KOSSEL conceptions of crystallization by tangential growth *in* the plane and two-dimensional nucleation *normal* to the plane only apply under conditions of slow growth, i.e. in a near equilibrium configuration. For the case of fast growth, i.e. conditions far from equilibrium, GRAF postulates another mechanism. From his optical observations that dendrites are bounded by rounded faces and close-packed crystal planes, he concluded that fast growth proceeds normal to all but the closest-packed planes. In contrast to the slow growth phenomena, the high index planes are not completed and do not grow out but normal growth on all high index planes proceeds more or less randomly; this results in rounded forms, with only the closest-packed planes as distinguishable crystal faces.

GRAF advances furthermore the hypothesis that the shape of the first nucleus of the solid is spherical. Only when the solid nucleus grows and the influence of the surface tension of the solid-liquid interface is compensated and exceeded by the mechanical stability (measured as the maximum shear stress) do definite crystallographic faces develop. From these two hypotheses, GRAF developed a picture of how dendrites and growth lamellae are formed during the growth of a spherical nucleus on all but the closest-packed planes. There are, as yet, no controlled experiments available to support or disprove this theory. However, without going into details it should be pointed out that, for instance, according to this picture, hexagonal metals could not form dendrites which they nevertheless do.

Hence one must conclude that there exists at the moment no completely consistent and convincing explanation for the crystallographic aspects of dendritic growth.

would also suppress the formation of hexagonal cell structures, and RUTTER and CHALMERS were able to verify this prediction experimentally.

POND and KESSLER⁽⁴³⁾ who had described the hexagonal cell structure prior to RUTTER and CHALMERS, based their explanation on purely thermal arguments. Heat transfer in the plane of the interface was suggested as the sole reason for the occurrence of the substructure, which the authors regard as a manifestation of the dendritic form of growth. The explanation was criticized by RUTTER and CHALMERS⁽⁵³⁾ who claim that under the conditions specified by POND and KESSLER an interface of the suggested shape would not be stable.

CONCLUSIONS

The fundamental problems of crystal growth from the melt are far from being solved. However, recent work has shown clearly some of the variables that determine the mode in which a metal solidifies. It will now be possible to derive new and simple experiments which can provide experimental information obtained under unambiguous conditions. Such material is needed before it will be possible to prove or disprove the current interpretations of growth phenomena. But it has already become quite clear that solidification has to be treated as a non-equilibrium process.

I would like to acknowledge gratefully the stimulating discussions with Professor B. CHALMERS and with my colleagues at the Department of Metallurgical Engineering at the University of Toronto. Thanks are also due to all those whose papers I was privileged to read prior to publication and to all those who gave me the benefit of their advice and criticism.

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