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THIN FILMS

and

SURFACES

by
WINIFRED LEWIS



1950

CHEMICAL PUBLISHING CO., INC.

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1950

CHEMICAL PUBLISHING CO., INC.

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Printed in the United States of America

FOREWORD

IF any explanation is called for as to the reason for choosing aluminum as the metal given a prominent place in this small monograph which is concerned with surveying the significant features of research on surfaces and thin films of metal, a glance at the subject matter will show that aluminum has not only played a part as the material used in many different investigations of the fundamental nature of thin films and surfaces, but is a metal which affords the most varied illustrations of the applied physical, electrical and chemical properties discussed. As it was desired to provide something like a unified collection of data which could at least rule out one unknown factor — the influence of the ultimate structure of the metallic elements on what may be called their secondary properties — the best single metal to select for the study of thin films and surfaces seemed to be that which could offer the widest range of properties and applications.

Much of the material in this work was originally prepared for a Memorandum issued by the British Aluminium Company, Ltd., while the author was in charge of their technical intelligence, and her grateful thanks are due to the company for its kind permission to make use of this material. The author also wishes to thank the Aluminium Protection Company, Ltd., for allowing her to do some work on the subject while in their employ. Her interest in the subject of thin films and surfaces dates from the days of some post-graduate research carried out at the Sir John Cass Institute in the years 1932 to 1934 on a comparison between the structures of anodic films formed on aluminum respectively by direct and

alternating currents, and this interest has been sustained and increased by a growing appreciation of the fact that the behavior of thin films and surfaces opens up some pregnant problems in fundamental physics: problems not incompatible with a collateral interest in the still more fundamental issues involved in the philosophic basis on which the whole scientific claim rests.

The first part of this monograph attempts to outline what is known up to the present about the structure and properties of thin films and surfaces in general, for convenience preserving a dichotomy between the two forms. Chapter IV deals with the production of thin films. The last two chapters collect what information is relevant about the properties of aluminum, briefly summarize some comparative data for other metals and refer to some of the rather interesting applications of aluminum films and surfaces.

The bibliography does not pretend to be more than a selected one. Specific researches on thin films have been carried out for the greater part within the last fifteen or twenty years, but much greater difficulty is experienced in collating the work which has been done on surfaces, since much of the important information about this subject is obscured in general treatises under almost every scientific heading.

W.L.

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Chapter I

INTRODUCTORY

THE object of this monograph is to present in a coherent form an outline of the available knowledge on metallic surfaces and thin metallic films, excluding from its scope any discussion of the major problems of surface phenomena in relation to the mechanical properties of metals and to corrosion and radioactivity. Metallic surfaces and thin films are closely interrelated from the physical aspect, since a thin film is defined as having a structure essentially fragmentary, without the ordered arrangement of crystal lattices which is characteristic of massive metal. Thus thin films possess the property of "incompleteness" which is the definite feature of the surface of massive metal, whose structure is abruptly discontinuous on one side. In the case of surfaces the study of the physical problems is rendered extremely difficult by the necessity for taking into account this discontinuity in its far-reaching effects, and the influence of the underlying metal as well as of the atmosphere, or other bounding medium. The study of thin films in conjunction with that of surfaces may help to differentiate the nature and function of the crystalline fragmentary structure if we hold the view that it is characteristic of both.

The special interest which attaches to the conception of surface is aroused by its inherently paradoxical nature. It is the negation of the bounded object as conceived in the physical sense; the "end" of one structure coincident with the "beginning" of

another. Even the dry dictionary definitions^{1*} of "something without depth," "a mere outside," or the more precise mathematical conception of "a two-dimensional locus of points" raise at once the speculative problems of the relation between the finite and the infinite or the positive and the negative in their ultimate senses. When we stop to consider that most of human knowledge of the physical universe is derived from surfaces, it is with something of a shock that we face the fact that in practical terms we have not yet, in the world of the physicist or the chemist or the metallurgist, adequately and clearly sorted out what the specific properties of the surface, as such, are and how far they influence and are in turn influenced by the underlying and the bounding structures; in other words, how far, they are twisting our conceptions of the objective materiality we observe and deal with as scientists. The dilemma that we are defining things in terms of other things which we have not yet defined may, in fact, be unpleasantly close.

To return to metals, it is not so long ago that such an authority as Professor Desch² opened his presidential address to a distinguished international body of scientists with the remark: "When we consider how much of our immediate knowledge of metals is derived from their surfaces, it is rather surprising to find how scanty is our information as to the true properties of the surface of a metal." Professor Desch proceeded to find what comfort he could by accounting for the anomalous behavior of surfaces in terms of their inability to resist contamination, due to the chemical unsaturation of their "incomplete" structure, but this only carries the problem of surfaces as such from their relationship with one bounding medium to their relationship with another. By examining this dual relationship it may be possible to throw light on many of the practical problems which concern the metallurgist in connection with corrosion and its profound in-

*References in the text may be found at the end of the book, whereas the bibliographies inserted after sections and chapters refer to pertinent publications.

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fluence on the mechanical properties of metals which are of material interest, but it leaves the major issues of fundamental metal physics untouched.

We find that every property of metals which is dependent on the ultimate constants of the atomic structure (and it does not seem legitimate to regard as a property anything which is not so dependent) differs in thin films - - the density, the optical constants, the electrical constants, and so on. This opens up two channels of speculation. Firstly, are these variations a characteristic property of the "incomplete" atomic structure of the thin films (ergo, of the "incomplete" atomic structure of surfaces), or do they result from the physical, optical and electrical behavior? Secondly, what is the ultimate meaning to be attached to the constants we obtain for massive metal, since the massive metal always has a surface which is itself an "incomplete" atomic structure and which must intervene as such in all the measurements?

The first problem raises the almost sacrilegious issue as to whether there are any constants in the sense they have been scientifically defined up to the present, or whether the fact of the existence of surfaces in the material world is not the only real "constant" which can be counted on. It certainly implies that a great deal more of clear thinking will have to be done before what have been accepted as the fundamental laws of physics can stand secure. Bridgman,³ for example, claimed to have discovered a deviation from Ohm's Law on the basis of investigations which he carried out on a very thin piece of metallic foil. Fry⁴ and others have toppled over the laws of optical theory which form the basis of most of our practical calculations. The situation is not better with other branches of physics.

The second problem is the offshoot of the first and raises not less fundamental issues - - issues which, in fact, challenge the whole of the assumptions which lie behind the structure of scientific thought and which have not changed so much as the modern

scientist would like to think. While the imposing façade of science has run up to lofty heights, the simple skeleton of logic which forms its core has not changed fundamentally since Aristotle's time, in spite of the attempt of the dialecticians and the exponents of mathematical logic to infuse new life into its bones.

From this long-range speculation to return to so-called practical problems may be drab, but it is the lot of the scientist until the logicians can rub the cobwebs from their eyes.

The first practical problem which arises in the study of thin films and surfaces is the examination of their properties under very clearly defined conditions, with the object of isolating and defining their characteristic behavior in terms of conventional physical theory. Little is known of the boundary, if any, between the properties and behavior of metallic surfaces and of thin metallic films. It has been the usual tendency for physicists to regard them as having many phenomena in common, and justification for this view is evident in some at least of the following chapters. A clarification of the position depends on the careful observation of their respective properties, combined with a record of the whole history of the films or surfaces under discussion and full details of the experimental conditions of examination. It is almost incredible how little attention is paid by skilled research workers to this detailing of all that should be known about the specimens whose properties they discuss. It is, for example, rare for those who have devised methods of examination to state clearly the limits of applicability of the method, such as the limiting thickness of a film which can be examined. It is rare for those who determine physical properties to record the purity and past history of the metals examined, their origin and age, and other physical and chemical data. It is rare, moreover, for research workers to define clearly and precisely what constants they are determining, so that it happens not infrequently that the values derived for the same material are quite discordant: this is very noticeable,

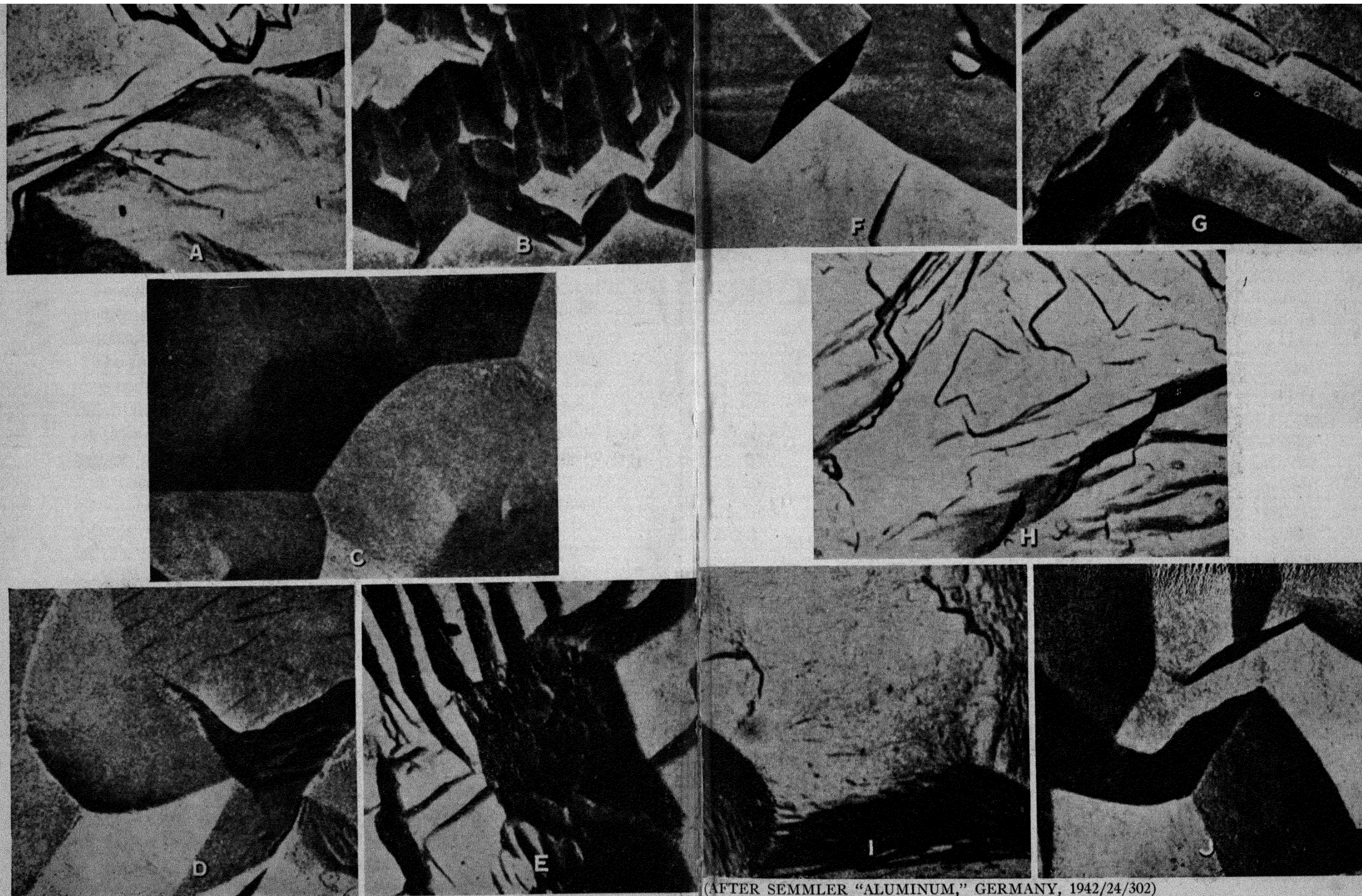


PLATE 1. ELECTRONOPTICAL STUDIES OF ALUMINUM SURFACES

A — Unannealed, hard-rolled high-purity aluminum sheet (equivalent magnification on reproduction = 3,600 diameters); B — Specimen as in A after recrystallization (equivalent magnification in reproduction = 4,800 diameters); C — Cast aluminum without removal of casting skin (equivalent magnification in reproduction = 5,300 diameters); D — Specimen as in C, but showing rounded form of cube face; E — High-purity aluminum, recrystallized as in B, with subsequent hot etching (equivalent magnification in reproduction = 5,100 diameters).

(AFTER SEMMLER "ALUMINUM," GERMANY, 1942/24/302)

F — Specimen as in A, B and E, but incompletely recrystallized; G — Fully recrystallized 99.5 per cent aluminum (equivalent magnification in reproduction = 5,000 diameters); H — Hard-rolled aluminum sheet, 99.5 per cent pure (equivalent magnification in reproduction = 6,900 diameters); I — A fully recrystallized 99.5 per cent pure aluminum as in H, but subjected to different etching treatment (equivalent magnification in reproduction = 3,400 diameters); J — Cast aluminum, 99.5 per cent pure.

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for instance, in the case of certain optical properties, such as so-called reflectivity values. Much of the incompatibility between the views held by different research workers is due quite simply to the fact that they have in practice derived not the same but essentially different constants, or dealt with not the same but essentially dissimilar materials. A glance through the following chapters on the structure and properties of films and surfaces will show that the structure, for example, may be crystalline or amorphous at different stages of its career; it may be influenced by the chemical, physical and mechanical conditions of the substrate; it will be profoundly influenced by the nature of the gas adsorption or absorption it has undergone during its formation or subsequently, and so on. The factors which operate to interfere with the results of observations are almost overwhelmingly numerous, and it is often a thankless task to try to correlate the results of different research workers in any field of investigation.

Once having collated what may be termed roughly the life history of a film surface with whatever property or group of properties has been observed, another problem presents itself. The question should be asked how far the experimental method used will have itself raised difficulties in arriving at a correct observation. It is by no means impossible that the method, by its nature, may have altered the property which it sought to determine. For instance, it has been shown that electronic rays split up homogeneous amorphous thin films into individual crystalline particles, so that electron-ray methods of examination may actually induce modifications of the structure which they purport to observe. In all cases of true thin films or surfaces the dimensional problem will also be of particular interest, since the order of dimension of the observational error — or, in some instances, of the observational unit (such as a wavelength) — will not be incomparable.

Having disposed of these problems, the next problem — perhaps the most thorny one — is that of interpretation. Until recently

the investigation of the properties of metals concerned itself little with theoretical considerations of the relationship between the problems which the investigation raised and surface conditions or phenomena except in the case of what have been regarded as obvious "surface properties." There is now general recognition that the study of thin films and surfaces is not only linked with the problems of what may be regarded as academic metal physics, but has undoubtedly a bearing on many of the practical problems of the metallurgist and of the chemist which have not yet been attacked from this angle. For instance, it has been suggested recently⁵ that the study of thin films can throw light on the problems of intermetallic diffusion. The main problem of interpretation will, however, be concerned with inferring from the results of correlated observations, how far the conventional physical laws can be accepted and how far the so-called anomalies which have been observed with thin films and surfaces are in fact characteristic of the films and surfaces or are part and parcel of the laws of electronic physics, optical transmission, electrical conductance, etc., involved. This is the main problem on which the far-reaching scope of the subject has a bearing and which, so far, has scarcely been noticed by the majority of research workers who have been attracted by the study of thin films and surfaces, though it has been adumbrated by a few.

As in many branches of physics and chemistry in the last half-century's somewhat chaotic development of scientific theory and thought alongside — and not infrequently, in slightly undignified manner, behind — the inventive genius which an industrial age has thrust upon us, the attraction to the study of thin films and surfaces has often been the outcome of some practical application of their properties which have up to a point forged ahead of theory. The qualification "up to a point" is necessary, since apparently sturdy practical applications have all too often been seriously frustrated or completely aborted by the premature enthusiasm of the so-called practical producer, who is quite unable

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to foresee the technical pitfalls which inadvertency may produce. Great interest has been centered, for example, on the field of electrodeposited coatings (which, because of their greater thickness, are outside the proper scope of this monograph), and this has led to the development of other types of metallic films and coatings, such as sputtered and evaporated films, which are referred to in detail in the following study. The prevention of oxidation and tarnishing of the universally used domestic silver and silver-plated ware by depositing an extremely thin protective film has been the subject of considerable investigation, and there is no doubt that a commercially acceptable process would almost revolutionize the silversmith's market.

A major application of some form of surface treatment of massive metal is connected with the production of reflectors of all types for the optical and heating and allied industries. Other metals may compete in this application, but aluminum has a strong position. Aluminum in the form of thin films deposited by evaporation or sputtering on glass or on a metallic substrate has been found to provide optical mirrors with extremely valuable properties for astronomical use. Some years ago the Astronomer Royal⁶ drew attention to the potentialities of films of aluminum alloys for the production of astronomical mirrors.

More recently attention has been called to the use of sputtered light metals to replace nickelplating or substitute zincplating⁷ and, alternatively, it has been suggested⁸ that articles of iron, steel, copper and brass and particularly light metals can be coated with extraordinarily resistant metal or metal-alloy layers equal to all chemical and technical stresses. Another angle of approach has been suggested in connection with the provision on non-conductors of fastly adherent conducting coats of such metals as ruthenium or rhodium, preferably pure, but possible in the form of alloys, to serve as key deposits for an outer coating of a good conductor, which can be deposited either by chemical reduction or by physical methods. Examples of the applications of such

intermediate thin films produced by cathode sputtering are condensers, resistances of any size, contacts and incandescent resistance bodies. The great advantage of the cathodically deposited film as compared with the commonly used flux material, such as speculum metal solutions (liquid bright gold, silver or platinum) used in glazing, is the greatly increased adhesion. Glazing coatings consist of grains lying loosely on one another. The denser structure of the cathodically deposited film improves the conductivity of the intermediate layer, and its increased adhesive power prevents the tendency to peel when high-frequency currents are used.

In electrical apparatus provided with these deposited intermediate films, not only can all the mechanical requirements met with in practice be satisfied, but the electrical properties are also more constant and there are no disturbances of the nature of rustling effects.

Microphonic material can be produced by depositing platinum, irridium or other metal on particles of non-conductive material by cathodic atomization in vacuo.⁹

Other actual and suggested practical applications of thin films are speculum metal gratings, films for X-ray targets, rectifiers, and the gilding and silvering of silks and fabrics. Some work has been done on the replacement of electrodeposited copper films by thin aluminum films produced by evaporation for the preservation of gramophone records.

Research has also been carried out on the silvering of light-alloy pistons by means of cathodic disintegration and on the working up of valuable constructional parts which have become unusable owing to excessive wear. The material lost by wear can be readily replaced by locally deposited films without changing the unitary nature of the foundation body.⁹

Van Voorhis¹⁰ has proposed the coating of aluminum with thin films of uranium and thorium, in connection with the studies of the effective cross-sections to observe fissions induced by neutrons

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and of the energy of the fission fragments. The essential requirement is the production of films so thin that the energy losses of the fragments shall be only a small fraction of the total energy.

The production of condenser coatings on mica for high ohmic resistances was early recognized¹¹ as one of the potential applications of very thin metallic films. Another interesting application – in a very different field – which was among the earliest suggested, is the production of oligodynamic effects for medical benefit, for example, by the silvering, followed by special after-treatment, of catgut and sutures for surgical use.

Chapter II

THE STRUCTURE OF METAL SURFACES AND OF SURFACE FILMS

INTEREST in the structure of metal surfaces has chiefly been centered in the nature of polished surfaces. Beilby,¹² some 20 years ago, published the results of a comprehensive series of microscopic investigations of the changes produced in the nature of a surface during the polishing process and of the converse set of changes as the polish was removed by etching the surface. From his researches he concluded that polishing causes the surface to flow and that the final polished surface is covered by a "vitreous" or amorphous layer. This view of the nature of polished surfaces has been widely accepted by other workers, who have not in all cases, however, subscribed to Beilby's liquefaction theory in its entirety. It has been opposed by Benedicks,¹³ Tammann¹⁴ and Kirshner.¹⁵ With the advent of electron diffraction, additional evidence of the existence of the amorphous flowed layer has been accumulated.¹⁶ The thickness of the Beilby layer is considered to be of the order of 30 Å. Lees¹⁷ considers the Beilby layer to be separated from the non-oriented polycrystalline interior of the metal by a layer, 150-500 Å. in thickness, of oriented crystals.

The Beilby polish layer on metals has been found to have the remarkable property, not shared by the corresponding crystalline surface, of dissolving metal films deposited thereon. Thus, at room temperature, zinc dissolves rapidly in polished copper and somewhat less readily in polished mild steel surfaces, but it is insoluble in either of these surfaces after the Beilby layer has been

removed by etching. After a certain stage of deposition has been reached, the Beilby layer becomes saturated and further deposited layers retain their structure indefinitely.

The mechanism of heterogeneous gas catalysis is considered by some physicists¹⁸ to be possibly associated with diffusion of the reacting gases into the metal surface where the electrical field of the surface atoms activates them.

Electron and Electron Scan Microscopes and the Study of Surfaces by Electronoptical Photographs. Although the electron microscope -- in its present stage of development, at least -- is chiefly a tool for the investigation of thermionic emission and related phenomena, it has been used experimentally to a limited extent for the study of the crystalline structure of metal surfaces.

In the ordinary high-power glass optical microscope, useful magnification is limited by diffraction effects and other factors to about 1,000 diameters. The range of the electron microscope is, in most cases, within about ten times this magnifying power, though its performance may be considerably greater in some instances. The actual electronic magnification for ordinary work is of the order of 500 diameters, and this is coupled with an eight-power glass optic in the usual type of instrument, giving a total magnification of about 4,000. The image is obtained on a fluorescent screen and can either be viewed directly, as optically magnified, or photographed with an ordinary camera provided with a special Bausch and Lomb lens which gives about eight diameters of magnification.

The lens system in an electron microscope may be either electrostatic or electromagnetic. There are certain advantages and disadvantages associated with each type. Apart from the fundamental difficulty connected with the interpretation of electron-optical observations in relation to the surfaces of massive metal that, since the penetration is of the order of one-tenth, the wavelength of light and the thickness of the specimen should be

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of a very small order, there is a serious mechanical difficulty arising from variable electron intensity, which produces marked chromatic aberration. The electron speed changes as it emerges from the specimen, due to inhomogeneities in the thickness. Von Ardenne¹⁹ attempted to overcome the problem of chromatic aberration by introducing a scanning system, but the electron scan microscope does not appear yet to have been used to any great extent as a metallurgical tool.

For the examination of metallic surfaces, in the case of most metals, the thermionic emission is insufficient to allow of the production of electron images without prior activation of the surface. At very high temperatures and for very rapid electron acceleration, as in the case of tungsten, tantalum, molybdenum and platinum-rhodium above about 1,250° C., the energy of the electrons is sufficient to yield an electronograph without special activation.

Activation is carried out with barium salts, and, among other workers, Burche²⁰ has investigated the structural transformations which occur in metallic surfaces in connection with different gas discharges and stages of oxidation of the metal underlying the barium layer at the grain boundaries and surfaces of the crystallites. Ruska,²¹ using an electromagnetic lens system, obtained images of ruptured aluminum foils.

Some research workers have dispensed with direct observations which involve the unknown factors connected with activation and have approached electron-optical investigation by the application of the principle of "replicas." Mahl's²² work on these lines has been followed, in the case of aluminum, by Semmler's²³ attempts to examine the replica of the surface offered by very thin, evenly thick valve films of aluminum oxide formed anodically in a weak electrolyte under controlled conditions and removed by the mercury method. Some electron-optical photographs of aluminum surfaces are shown in plate 1. Stransky²⁴ used different etching methods in place of anodic oxidation. Such structural

changes as recrystallization have been demonstrated by both these and by other workers.

Magneto-metallographic Method of Examining Surfaces. Reference may be made to a new magnetic method of examining the surface of magnetic metals which may be capable of extension. It has been developed by Eremin²⁵ in the Tziitmach Laboratory for examination of the macro- and microstructure of steels. Magnetic colloids, with a particle size of the order of 10^{-4} mm., are deposited on the section, which is previously magnetized. By suitably varying the direction, strength and distribution of the magnetic field or by superimposing different fields, the distribution of the magnetic colloid layer may be made to delineate accurately the crystalline structure.

The Structure of Surface Films. The formation of natural surface films is essentially connected with the phenomena of solution by and diffusion into the surface metallic layer of gases, the most common of which is, of course, atmospheric oxygen. On exposure to air, an oxide film is formed on the surface of many metals. The nature of the growth presents many complex problems. The ordinary rate of growth in thin films follows a parabolic law

$$x^2 = \text{const. } t$$

where x is the thickness of the oxide film, but the process of formation depends also on the pressure and temperature of the oxygen or gas, the extent to which it diffuses through the film, the solubility or insolubility of the oxygen at the forming-oxide-film/gas interface, the structural nature of the surface film, the concentration of dissociated atoms in the layer next to the metal and other factors.

Wagner and Grunewald²⁶ examined the parabolic growth in the case of the oxidation of zinc and developed the theory that the metal atoms go into solution in the oxide at the metal/oxide interface and dissociate into interstitial ions and free electrons until

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equilibrium is reached. This applies only to true thin films, where the space charge set up by the diffusing ions and electrons is negligible. Taking the concentration of dissolved atoms as n at the metal/oxide interface and zero at the oxide/gas interface, the concentration gradient becomes $\frac{n}{x}$ and the volume V of the oxide formed per ion of metal is derived as

$$\frac{1}{2}x^2 = 2V Dnt$$

where D is the diffusion coefficient of the ions which determine the rate of flow, the electrons being freely mobile.

Straightforward growth by the parabolic law does not, however, hold good for all metals. Aluminum forms a notable exception, along with certain other metals such as chromium, mercury and various steels, where the parabolic law is followed only up to a critical thickness of the order of 100 Å., after which its growth is interrupted.

Mott²⁷ has suggested a theory to account for this cessation of growth, based on quantum mechanics. He suggests, by analogy with the quantum-mechanical tunnel effect, that the electrons can penetrate only a distance of the order of 50 Å. into an insulating layer (aluminum oxide, for example, is stoichiometric and non-conductive) without receiving external energy of excitation. In order to pass through thicker layers, they would require to receive energy from heat motion as in the case of thermionic emission.

This theory gives results which agree fairly well, as regards the order of magnitude of the thickness of the film when it reaches a constant state, with those of Tronstad,²⁸ Steinheil²⁹ and other workers³⁰ who have investigated the same problem.

The temper colors of surface films have been the subject of much study and controversy. A permanent temper-color sequence is observed with those metals which form compact oxide films in accordance with the parabolic growth rate law. Tammann³¹ was the first investigator of the colors of oxide films, which he assumed to be interference colors, due to diffraction phenom-

ena, and which he used to determine the thickness of the films. Evans³² analyzed the theoretical conditions necessary for the production of temper colors, and Hinshelwood³³ studied temper phenomena in detail. Constable³⁴ settled any doubt as to the nature of the phenomena by demonstrating the actual existence of absorption bands in the spectra of light reflected from surfaces showing interference colors and he compared the relationship between the color and the film thickness of various oxide films. The results of his comprehensive study of the subject are reproduced in table I.

TABLE I. *Colors and Corresponding Thicknesses of Oxide Films*
(Constable)

Metal	Order of Color	Color of Film by Reflected Light	Thickness of Homogeneous Film of the Same Color
Copper	I	Dark brown	0.38 x 10 ⁻⁵ cm.
		Red brown	0.42
		Very dark purple	0.45
		Very dark violet	0.48
		Dark blue	0.50
		Pale greenblue	0.83
	II	Pale silvery green	0.88
		Yellowish green	0.97
		Full yellow	0.98
		Old gold	1.11
		Orange	1.20
		Red	1.26
Nickel	I	Pale brown	0.49 x 10 ⁻⁵ cm.
		Dark brown	0.54
		Purple	0.57
		Very dark violet	0.60
		Very dark blue	0.76
	II	Silvery green	1.12
		Yellowish green	1.20
		Yellow	1.26
		Straw	1.35
		Yellowish brown	1.62
Iron	I	Dark brown	1.72
		Straw	0.46 x 10 ⁻⁵ cm.
		Reddish yellow	0.52
		Brownish red	0.58
		Purple	0.63
		Violet	0.68
		Blue	0.72

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Miley³⁵ compared the thickness of oxide films measured by an electrical method with Constable's values, obtained electro-photometrically, and found the good agreement shown in table II.

TABLE II. *Corresponding Thickness of Oxide Films as Determined by Optical and Electrical Methods (Miley)*

Color	Method	
	Electrical Å	Optical Å
1st Order		
Dark borwn	370	380
Red brown	410	420
Purple	460	450
Violet	485	480
Blue	520	500
Silver green	800	880
2nd Order		
Yellow	940	980
Orange	1,170	1,200
Red	1,240	1,260

Oxide films formed on aluminum or chromium do not give interference colors. Mott³⁶ has suggested that this is probably because they are not thick enough.

Where the oxide films grow continuously to considerable thicknesses, say, of the order of 500 Å., they sometimes, as in the case of zinc which has been studied, inter alia, by Vernon and his co-workers,³⁷ exhibit a granular structure which is possibly due to recrystallization. This type of film is very sensitive to temperature and appears to follow a logarithmic law of growth, due to recrystallization.

The effect of lowering the pressure has been studied by Gulbransen,³⁸ who investigated the formation and stability of oxide films on ferrous materials, including stainless steels.

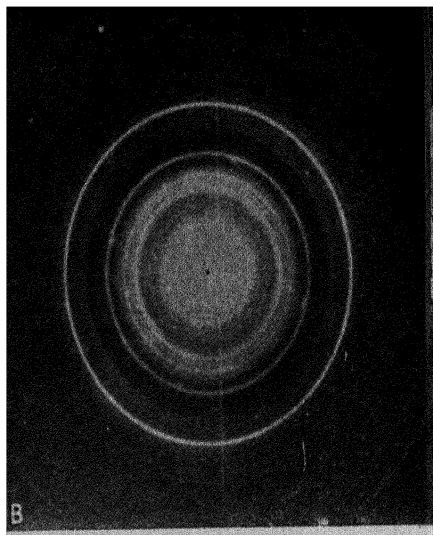
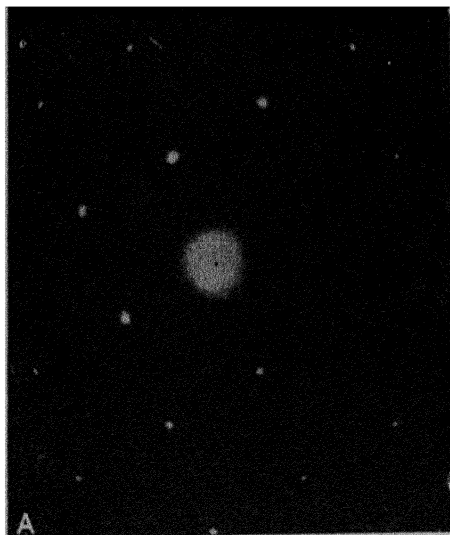
As regards the influence of the composition of the film on the interference colors, Miley showed in the case of copper that oxides of different stages of oxidation may be present. The characteristic interference color is only formed when a layer of one oxide sufficiently thick to behave as a single film is formed.

The problems which arise in the case of naturally formed oxide and surface films become still more complex in the case of films formed artificially by chemical treatment and, particularly, in the case of those formed by anodic oxidation. There is extensive literature on the subject, more especially on anodic films on aluminum, which have attained great commercial and scientific importance. Several theories on the mechanism of the growth of the anodic oxide films have been advanced. It seems to be fairly generally agreed that a primary or basis film is first formed by the interaction of oxygen atoms derived from the electrolyte with the metallic aluminum. The older theory of hydrolysis and electrophoretic deposition has been largely discarded. The first-formed film may or may not be hydrated by the water present in the electrolyte, depending on the conditions of electrolysis. In either case, it reaches a critical thickness at which, in consequence of the increased resistance, the voltage becomes so high that breakdown occurs and brings about the formation of pores in the primary film which admit of fresh contact between the electrolyte and the basis metal. The film then recommences to grow at the foot of the pores.

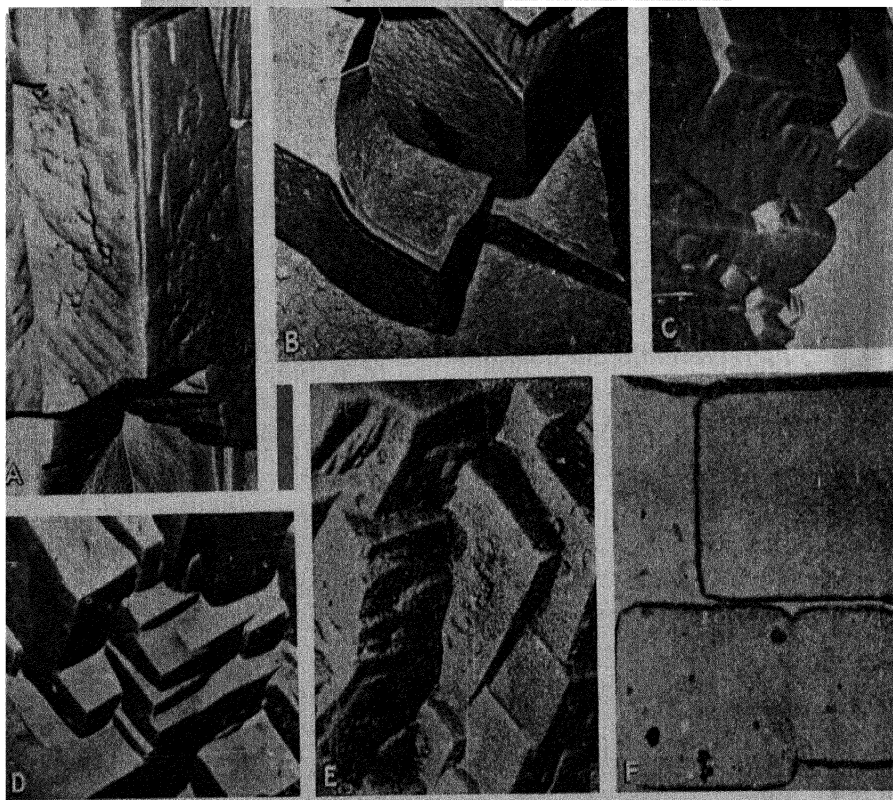
Among recent workers who have supported this theory, Mahl³⁹ and Fischer and Kurz⁴⁰ have shown the existence of breakdown pores in supermicrographs. Semmler,⁴¹ however, attributes the pore formation to re-solution of the metal at characteristic structural points.

The fact that processes of dissolution of the oxide film and re-solution of the basis metal are superimposed on these electrolytic growth processes, in addition to other factors connected with the complex phenomena of strong electrolytes, makes a complete interpretation of the mechanism of growth of anodic films extremely difficult.

Considerable divergences are also to be noted in the accounts of the physical structure of the formed anodic films, both on aluminum and on other metals. Apart from the fact that the anodic



Two electron diffraction patterns (A and B) of oxide films of aluminum.



Electronoptical micrographs (A to F), characteristic of anodic films on aluminum (compare with structures shown in Plate 1).

oxide films probably undergo aging from an initially predominantly hydrated amorphous state to a crystalline modification, in the same way as thin films of metal (see page 23), it would appear from the conflicting evidence of X-ray diffraction patterns¹² and electron-optical photographs¹³ that the structure of the film varies throughout its depth. Harrington and Nelson¹⁴ have reported that under certain conditions anodic films formed on tantalum and titanium are at least partly crystalline, and under other conditions they are probably amorphous.

In commercial production of anodic films on aluminum, sealing or heating treatments or both are usually given to stabilize the film. Hot-water sealing probably transforms at least a portion of the amorphous film to a crystalline substance.

Chemical surface treatments of aluminum produce definitely crystalline substances, which give sharp diffraction rings — in contrast to the usual case for anodic films — although it is not always possible to identify the compound formed with an aluminum compound of known structure.

Plate 2 reproduces some electron diffraction patterns of oxide films of aluminum and some electron-optical photographs of the anodic film, which may be compared with the electron-optical photographs of the surface of aluminum reproduced in plate 1.

The Properties of Oxide Films. It is not possible within the scope of this monograph to enter into a detailed discussion of the properties of oxide films or other surface films, which would require a volume to itself. Reference to their behavior, which is obviously differentiated from that of metal, either massive or in the form of thin films — for example, non-metallic films of oxide, etc., are dielectric — will be found in the chapters concerned with the properties of metallic films and surfaces. However, it may be simply indicated here that thin films of oxide behave anomalously as compared with massive oxide, in the same way as thin films of metal behave anomalously as compared with massive metal. Taylor and Edwards⁴⁵ have shown, for example, that the optical

reflectivity or emissivity of oxide films on aluminum approaches that of the massive oxide only when the film thickness reaches a value comparable with the wavelength of the radiation which is reflected or emitted.

Chapter III

THE STRUCTURE OF THIN FILMS

General Observations on Thin Films. It may be desirable to emphasize the significance of the term "thin films." The terminology regarding coatings and films of metals is lacking in coherence and clarity and metal films have been variously defined on the basis of their actual thickness. Lustman⁴⁶ tried to clear up the situation by defining a surface film as having a thickness not less than 2,000 Å. (or 20,000 m μ or 2×10^{-4} mm.), in contradistinction to scale, which he defined as having a thickness not in excess of 2,000 Å., but these definitions are applied to surface films, principally oxide films. Thin films of metal, properly called, are of dimensions smaller than Lustman's limiting thickness. From the standpoint of pure theoretical considerations, the thickness of metallic films which justify the designation of "thin films," distinguishable from massive metal by anomalous physical properties, never exceeds the order of colloidal dimensions, with a practical limiting thickness of the order of 100 Å. (or 10 m μ). All the theory of the physical structure and of the optical, electrical and chemical behavior of films discussed in this monograph relates to true thin films of such dimensions. In the upper ranges of thickness down to 1 m μ the film can be observed with the ultramicroscope. In the lower ranges of thickness which come within the order of molecular dimensions, down to monoatomic layers of metal, they are not visible under the ultramicroscope, but they can be examined by the electron microscope, by electron diffraction, or by other methods.

A thin film must be regarded as a fragmentary metallic structure, whose atoms are in a condition quite different from that in a crystal lattice. Complete crystal lattices are only gradually built up as the number of atom layers increases.

Every property of metals which is dependent on the constants of the lattice may, therefore, be expected to differ in a thin film and in massive metal. Where the surface of massive metal possesses, for any reason, such as mechanical working or chemical action, a distorted or decayed crystalline fragmentary structure, the surface film may then be regarded as if it were a thin film deposited on a base of the same metal, and the same anomalous behavior will give rise to so-called surface effects. Thus, for example, there are special optical conditions dependent on surface treatment, etc. In considering the surface of a metal, however, since no question of basal-plane pseudomorphism or allied phenomena can arise, the surface film of a metal does not necessarily behave as a film of equal thickness of the same metal when deposited on another substrate.

Two theories have been suggested to explain the characteristic irreversible changes in thin films: one depends on the decay of the lattice distortions and the other depends on recombination of the interstitial atoms and lattice vacancies. Vand⁴⁷ believes that the former hypothesis gives the more consistent results. David⁴⁸ has suggested that certain of the anomalous properties of thin metallic layers can be accounted for quantitatively in terms of the dipole vibrations of the individual metallic grains, which are assumed to have the same constants as the massive metal.

Thin metal films, in contradistinction to thin liquid films, possess mobility even when several atoms or tens of atoms thick, and such films still simulate the properties of a gas.

Andrade has shown that there are various stages of surface stability in thin metallic films.⁴⁹ The most freely mobile part is the surface layer which is originally amorphous,⁵⁰ and which is responsible for the first stages of crystallization at the temperature

at which aggregation first occurs. At higher temperatures, a very thin film of the order of thickness of ten atoms exists in a stable state, anything between this and the full thickness of the film being unstable. At still higher temperatures, the surface layers of the thin film become mobile and allow spherulites to form as the earliest steps of crystallization. This structural change can be followed with the electron microscope.^{51, 52}

In some cases, it has been observed that the fibres of the spherulitic aggregate, on account of their small transverse dimensions, do not have the usual crystal spacing in directions normal to the axis, so that optic anisotropism may occur.

At a later stage, isotropic crystals are formed and, in the case of films on a solid substrate, these have a preferred orientation. In the case of aluminum, which has a cubic lattice, the orientation has been found by Dixit⁵³ to be on the 111 plane at low temperatures but on other planes at and above 300°.

The Structure of Thin Metallic Films. The question as to whether thin films are, structurally, amorphous or crystalline, has been the subject of prolonged controversy.

One of the contributory causes for this continued doubt has been the diversity in the methods of investigation and in the nature and composition of the films investigated, due to different methods of production or varying conditions in the same method. As regards the methods of investigation, direct observations are made with the ultramicroscope, the electron microscope, by selective reflection, by the Debye and Bragg methods, or by means of electron-diffraction observations. Indirect methods depend on interpretation of the behavior of films or of any of their properties. There is value in the fact that such variety of investigatory methods exists, but it has also accounted for much contention.

Moreover, the conditions under which observations have been made are not always clearly or adequately defined by the investi-

gators. As there are many factors which can operate to upset or modify the normal behavior of thin films or their properties, or to change the interpretation of such behavior or properties, it is definitely essential to know all the conditions.

Apart from these complications, which all too often sidetrack the arguments for or against a particular hypothesis, the main reason for conflicting statements lies undoubtedly in the fact, which emerges implicitly from research in this field, that thin metal films are subject to modifications of state both during and after their formation. To some extent these modifications of structure are inherent in, and a direct function of, the thinness of the films and the consequently increased mobility of the metal atoms; to some extent they are also dependent on the external conditions of formation or aging.

There is the further point that in the ultimate limit, there is no sharp distinction between the amorphous state and the crystalline state.

The theory of Andrade regarding the surface stability of thin films has been discussed under the heading "General Observations on Thin Films." Estermann⁵⁴ and Hamburger⁵⁵ were two of the earliest workers to demonstrate the discontinuous structure of thin films. They were able to show, by means of ultramicroscopic investigations, the variation in particle size, which was found to fluctuate between 30 and 500 Å. for different film thicknesses. These workers assumed that the metal atoms which impinged on the surface (the method of thermal evaporation was used in both cases) do not remain fixed in position on the underface, but are mobile until larger individual crystallites are formed. According to Estermann, the free path of the atom on the underface may be as great as 300 Å. Rama Swamy⁵⁶ and other workers assume that a thin film exists in the earliest stage in a two-dimensional gaseous state, which is non-conducting and non-metallic. The next stage seems to be the formation of a predominantly colloid or amorphous film. Hamburger and Rein-

ders⁵⁷ were able to confirm the existence of such an amorphous film on the basis of their measurements of the electrical conductivity and by ultramicroscopic observations. Smakula,⁵⁸ who based his conclusions on optical observations in the visible and infrared regions of the spectrum, and on electrical resistance measurements, and Suhrmann and Barth,⁵⁹ who also worked on optical and electrical resistance measurements, support this hypothesis. Goetz⁶⁰ also demonstrated the existence of an amorphous film by microscopic observation.

The final stage is the transformation into "metallic electrons" of the weakly bound and more firmly bound electrons successively, and the aging to a crystalline layer of metallic properties, at first unorientated, then becoming orientated, the existence of which has been demonstrated by a host of investigators using a wide variety of methods.⁶¹ Some of these have maintained, principally on the basis of electron diffraction observations, that in the case of sputtered films, the deposits are *ab initio* crystalline, but some doubt seems to exist about the influence of internal heating effects during examination on the aging of the film. Was⁶² has suggested that the effect of the electronic rays is to split up the homogeneous amorphous thin films into separate particles which become crystalline. This would explain why electron-ray diagrams show the normal metal pattern in many instances.

The progression of these stages of formation is influenced by a multitude of factors. It depends on the nature of the metal of the film; on the nature of the deposition, its rate and the temperature of the evaporating coil or sputtering electrode; on the conditions of vacuum during deposition, or, alternatively, on the gas employed; on the chemical, physical and mechanical conditions of the substrate; on the changes in temperature undergone by the film during formation and aging; and finally, on external influences.

Thus, by cooling the surface on which the film is being produced, the ultimate crystallization of the film is delayed until a

certain critical thickness is reached.⁶³ This critical thickness, representing the boundary conditions between the amorphous and crystalline states, is influenced by the gases in the carrier layer more than by the actual nature of the substrate.⁶¹ By slowing down the evaporation, crystallinity can be prematurely induced.⁶⁵ The physical condition of the substrate has some influence on the crystalline structure which the deposited film takes up until a certain thickness, not necessarily equal to the so-called critical thickness, is reached; thus, basal plane pseudomorphism has been shown to occur in very thin films of aluminum deposited on a platinum underface.⁶⁶ Gas layers absorbed from the underface also influence the nature of the film.

Cartwright⁶⁷ has described an interesting phenomenon which he calls "frosting" of glass surfaces on which thin speculum films of gold were being produced: when the surface of the glass was not preheated, the gold surface appeared "blistered," as if explosions have occurred between the surface of the glass and the metal film. He suggested that this behavior might be due to electrostatic repulsion.

The actual particle size of thin deposited films may be very much smaller than the grains in thicker films. Hass⁶⁸ has shown that aluminum is much finer-grained than silver in films of equal thickness and that thin aluminum films are composed of very fine granules of diameter less than 100 Å. which grow in thickness as the film thickens. The lattice constant for thick films was found to be the same as that for massive aluminum, that is to say, 4.05 ± 0.01 Å. Oliver⁶⁹ has compared the structure of films of chromium and aluminum.

Examination of Thin Films by the Electron Microscope. The electron microscope is, as has been indicated, a comparatively new tool — interest in which has been chiefly orientated in other directions — and its application to the study of thin films has barely yet been explored. Von Ardenne⁷⁰ has developed a scan-

ning instrument, primarily intended to overcome the difficulty of chromatic aberration, which he considered as specially valuable for the examination of thin films. The problem of examining thin metallic films electronoptically is roughly analagous to that of dealing with semiopaque sections in optical microscopy, since with high enough electron velocity and thin enough films, the specimens are at least partially transparent. Transmitted illumination can be used, the beam of electrons being focused either electrostatically or with a magnetic objective. Behne⁷¹ has described the use of an instrument of the electrostatic type and Ruska⁷² examined images of thin foils of aluminum by means of 60 Kv. electrons transmitted through the foil, using a magnetic microscope. Borries and Ruska⁷³ also reported on the results of examining colloidal gold and silver films with the electron microscope.

These workers have only concerned themselves with the macrostate of foils of metal which were of the order of 1μ in thickness. Pinholes in the foil were observable and sharp images could be obtained of the jagged edges of ruptures. The foils in question were, of course, of a much higher order of dimensions than thin films properly called.

Determination of the Thickness of Thin Films. It has been pointed out at the beginning of this chapter that the thin films discussed in this book are of a very small dimension, with a practical limiting thickness of the order of 0.00001 mm. Most of the methods described in the literature for the measurement of the thickness of metallic coatings are concerned with films of a higher order of thickness than this and many of the methods cannot be applied to the determination of the thickness of thin films properly called.

“Thickness” requires some definition. If the film is not uniform, or if it is on a substrate which is not perfectly plane, the thickness which is measured may be either the mean thickness,

that is, the average of a large number of values of the thickness measured at different points perpendicular to the surface; or it may be the thickness at any given point.

The available methods for measuring thickness may be classified under five headings:

1. Mechanical Methods — weighing, quantitative stripping.
2. Magnetic Methods — magnetic force exerted, variation in magnetic intensity.
3. Chemical Methods.
4. Electrical Methods — measurement of resistance, electrostatic capacity measurements, etc.
5. Optical and Photoelectric Methods — measurements of interferences and intensity.

The mechanical method of weighing, which is usually done by the indirect method of weighing the evaporation apparatus before and after,⁷⁴ is limited by the sensitivity of the balance and is applicable only to films of thickness greater than $40\text{m}\mu$. The stripping method, which has been described *inter alia* by Brenner,⁷⁵ is again dependent on weighing, and it also fails when the metal of the film contains an element present also in the basis metal. It cannot in any case be counted on to give accurate results for films of a thickness less than about 0.004 mm. , even when anodic stripping is employed.

The magnetic methods depending on the force required to detach a magnet from the surface, which have been developed by a number of workers⁷⁶ and which include the magnetic meter and induction methods, are again no precision methods. Even where fine microscopic control is provided in the technique, they are only applicable to coatings of a thickness greater than about 0.0005 mm. Eremin's apparatus, which is based on the differential measurement of the variation in the intensity of magnetization of a high-remanence body, has a high sensitivity for coatings of the order of thickness of $1\text{m}\mu$ and may be capable of extension in principle to thinner coatings.

The chemical methods are based either on the time taken for the coating to be dissolved by a specific reagent or on spot tests. They can only be regarded as approximate methods even for films of considerable thickness, and it does not appear that their sensitivity could be developed to a point where they would be applicable to measuring the thickness of thin films.

The only methods which can give results of any value in determining the thickness of thin films proper are the optical and electrical methods. In general, these methods are only capable of measuring the mean thickness and do not extend to the measurement of the thickness at a given point. A more serious objection is that they are subject to all the difficulties associated with the anomalous behavior of thin films, with their age and stage of growth, with the complications due to adsorbed gases and the presence of embryo surface films formed by combination with the atmosphere in which they are produced or in which the measurements are made. It is usually desirable to use a combination of the methods referred to in Chapter V to eliminate some of the uncertain factors. Odenbach⁷⁷ has shown that measurements of the thicknesses of thin films made by means of the optical constants⁷⁸ agree fairly well with the values derived from the X-ray interferences above a certain critical thickness. X-ray reflection methods are rendered unreliable if the film contains defects or discontinuities such as pores.

In the case of electrical methods, the difficulty with resistance measurements is the uncertainty regarding the constancy or otherwise of the value derived. Measurements based on electrostatic capacity⁷⁹ are at present only applicable to insulating layers. Those depending on change of potential following anodic dissolution of the coating film⁸⁰ have not been very far developed.

Chapter IV

THE PRODUCTION OF THIN METALLIC FILMS

METALLIC films and coatings may be produced by:

1. Mechanical Methods:
 - (i) Rolling
 - (ii) Beating
 - (iii) Spraying
2. Chemical and Electrochemical Methods:
 - (i) Electrodeposition
 - (ii) Reduction
 - (iii) Thermal decomposition
3. Physical Methods:
 - (i) Thermal evaporation
 - (ii) Cathodic sputtering

Films of the reflector metals, including aluminum, are in practice produced in the form of foil [1(i)], as sprayed films [1(iii)], and by the two physical methods of thermal evaporation and cathodic sputtering. Other methods are available for the production of small films for experimental purposes. Thus, aluminum foil can be thinned down by suitable etching and mounted on gauze. If the film is wanted free from its base, it is deposited in vacuo on different materials, which may either be dissolved away or volatilized; celluloid or crystalline rock salt may be used in the first case, or high-purity naphthalene in the second case. A good technique for aluminum, taking account of its great affinity for oxygen,

has been described by Howe and Purcell⁸¹ and Larkins and Yearian.⁸² A method of producing wedge-shaped films of metal, with linear variation of thickness from zero at the centre to maximum at the periphery, by vacuum deposition, using a rotating sector shutter of Archimedean spiral shape, is described by O'Brien and Russell.⁸³

The minimum thickness of aluminum foil obtained by rolling is of the order of dimension of 10^{-3} mm., which excludes it from the category of a thin film. The sprayed films, of the type produced by the Schoop method, have their practical utility chiefly in the field of corrosion protection, the discussion of which is outside the scope of this monograph; and in any case, their thickness would exclude them from the true category of thin films.

The method of chemical reduction has not been very far developed, but some interesting suggestions were made recently at a Corrosion Conference in Moscow.⁸⁴

The films which form the subject proper of this study are those produced by thermal evaporation and cathodic sputtering. Production of thin films by either of these methods involves three essential stages:

1. The production of the gaseous phase of metal
2. The distribution of the metallic gaseous phase
3. Condensation

The gaseous phase is produced in thermal evaporation by the application of heat, and in cathodic sputtering by the action of a spark discharge.

The distribution of the metallic gaseous phase is, in the case of thermal evaporation, chiefly in accordance with the laws of space radiation, while in cathodic sputtering, up to a certain discharge level, it is chiefly a diffusion phenomenon.

It is sometimes stated that cathodic sputtering has an advantage over the thermal evaporation method in that the object coated may, with careful technique, be kept practically cold,

while a rise of temperature necessarily results from coating by thermal evaporation. In practice, however, the time during which the heater system is actually energized in the thermal evaporation is very small, and with proper apparatus, the rise of temperature may be regarded as negligible. It is not, in any case, established with certainty whether a rise of temperature does or does not occur in the case of sputtering also: von Hippel⁸⁵ advanced the theory that sputtering really consists in local boiling, and, without accepting this hypothesis in detail, Ditchburn⁸⁶ has pointed out that the kinetic energy of a positive ion of 2,000 volts must be converted into heat very close to the surface; the extent to which this heating may affect the deposited film depends on the rapidity with which the heat can be conducted away.

Thermal Evaporation

General. The simplest form of evaporation consists in heating a metal wire *in vacuo* to near its boiling point by the production of Joule's heat or in an electric furnace; or an electric arc or glowing cathode may sometimes serve as the source of evaporation.

The distribution of the gaseous metal phase from the emitting to the receiving surface depends only on the conditions of vacuum.

Where the vacuum is sufficiently high, the atoms direct themselves linearly in the same way as light waves, Lambert's Cosine Law* being directly applicable.⁸⁷

If, in addition to the vaporized metal, there is any residue of gases in the so-called vacuum, the distribution of the metal vapors depends on diffusion laws.

The presence of gases, i.e., inadequate conditions of vacuum, may have far-reaching effects on the products of condensation, affecting not only the chemical nature but also the physical condition and adherence of the deposit.

* i.e., the number of atoms received per unit of area is proportional to:

$$\frac{c I \cos \theta \cos \phi}{r^2}$$

These properties are also influenced by other factors, among which are the distance between the evaporating source and the receiving surface, and temperature.

In regard to the former factor, it has been found that for proper adherence, the atoms of the metal deposited should pass directly from the source to the place where they impinge on the surface to be coated without meeting molecules of the residual atmosphere of the gas contained in the vessel; that is, their mean free path should be greater than the greatest distance from the source to the surface of the mirror.⁸⁸

The temperature of the source has also to be taken into consideration. Too high a temperature of the metal being evaporated gives rise to deposits which are pulverulent and non-adherent. This is due to the fact that the vapor density of the gaseous metal becomes too great. It has been found possible to prevent premature condensation by ionizing the gaseous metal by means of auxiliary electrodes, which are charged to a sufficiently high potential; by charging the metal atoms in the same way, even for high gaseous metal densities, adherent and specular coatings may be obtained.

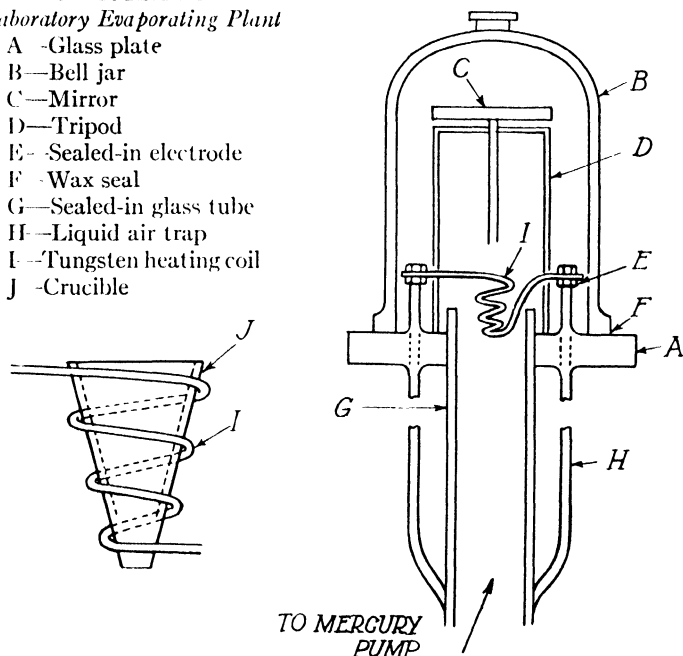
Under ideal conditions of vacuum, disposition of source and temperature, there still remains the problem of obtaining a deposit of uniform thickness. With a single source of heated metal whose size is small in relation to its distance from the different points on the surface to be coated, and where this distance is not the same for all these points, the coating deposited during a given time will not be of the same thickness everywhere - particularly in the case of larger mirrors.⁸⁹ This difficulty is overcome in practice by using a number of sources geometrically so distributed as to give a coating of uniform thickness, or by using a moving source or sources. In some cases the coating on a given mirror may be desired to follow a particular figure, and this can be arrived at by screening.

PRODUCTION OF THIN METALLIC FILMS

The shape of the source also affects the deposition. In the case of a U-shaped element of an evaporation unit formed with tungsten wire (as used in the American apparatus), it has been shown⁹⁰ that far more vapor comes from the sides of the U than from the drop, due to migration of the aluminum to the regions of highest temperature. Therefore, with such a U-source, evaporation takes place not from a point source but from small line sources, the greater part of the vapor being projected laterally if the U-source is vertical.

The exploitation of the evaporation process dates back to the time of Edison, who, in 1890, obtained patents in connection with it.

DIAGRAM 1
Laboratory Evaporating Plant



All early attempts at the evaporation of metals in vacuo were made in apparatus constructed on the general principle of that shown in diagram 1.

A large glass bell jar was supported on a flat glass base connected by pipe work surrounded by a liquid air trap to a mercury condensation pump. Inside the bell jar were arranged a support system for the mirror and a heater system consisting of a tungsten spiral enclosing and supporting a crucible of refractory material. The metal to be evaporated was put into the crucible.

Where the boiling temperature of the metal to be evaporated exceeds $1,000^{\circ}\text{C.}$, the method fails because of the difficulty of heating the metal up to the necessary temperature; and considerable modifications in method and apparatus have been made since the thermal evaporation method of depositing metals has been developed for technical and commercial purposes.

Preparation of the Surface for Evaporation. In order to produce a successful mirror surface of aluminum, or of any other metal, it is essential that the surface to be treated shall be absolutely clean. When the mirror to be coated is sufficiently clean, the "breath test" should be passed, i.e., the surface should show no breath figure, the breath condensing to form a structureless gray film on the surface. In the case of small mirrors, cleaning is not especially difficult, but with large mirrors wax and dirt are frequently retained in the small faults and the mirrors have been found very difficult to clean, as the foreign material works out to the surface. It is inadvisable to use a rouge pad, as the figure of the mirror may be altered. The best method for preparing the premirror surface is to preclean as thoroughly as possible with ordinary detergents and then to submit the surface to the action of an electrical discharge. Good results are obtained by degreasing with caustic potash and concentrated nitric acid alternately as the preliminary step. For the second stage of the treatment, an electrode, insulated in a capillary tube, is passed into the bell jar used for the evaporation through the axis of the switch mechanism. While the jar is being evacuated, a discharge

from the electrode causes the jar to be completely filled with ions. This process cleans the disc more efficiently than any other.

Deposition of Aluminum by Thermal Evaporation. Several methods, differing somewhat in detail, have been developed for the condensation of aluminum. The following are typical:

(a) *American Method.* Dr. Strong⁹¹ has elaborated a method which is extensively used both in America and also in England. The technique is described as follows: A tungsten-wire heater coil of fairly thick wire is used, since it has been found that the tungsten does not affect the purity of the deposited aluminum, in which it is not detectable by analysis. The wire, 0.030, in. in diameter, is wound on an eightpenny finishing nail to form a coil 1 inch long with eight turns. If the pitch of the helix is shorter, the aluminum will short the heater and will not itself be properly heated, whereas if the diameter is too great, the ratio of aluminum to tungsten becomes too great and the coil burns out. If wire of larger diameter is employed, it is too brittle. Tungsten has only a limited solubility in aluminum and if the sizes are right, the aluminum can become saturated with tungsten before the wire is dangerously reduced in diameter. The tungsten dissolved by the aluminum is redeposited on the helix as evaporation proceeds. It may be sintered to the helix by a final heating of the empty coil. One coil of tungsten lasts for twelve charges of aluminum. The aluminum is cut in the form of a cylinder of thin sheet which fits easily in the helix.

For coating large mirrors, several coils are employed and a more elaborate vacuum chamber and pumping system are necessary. The principal features of Dr. Strong's apparatus for coating mirrors up to 38 in. in diameter are shown in diagram 2.

Larger mirrors are prepared by the same method in a suitably enlarged and adapted apparatus.

(b) *Metropolitan-Vickers Method.* The Metropolitan-Vickers Electrical Co., Ltd.,⁹² has developed a method which differs some-

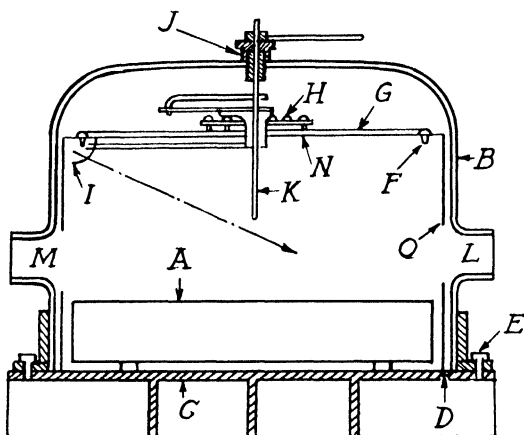


DIAGRAM 2

Dr. Strong's Evaporating Plant

- | | |
|---|---|
| A --Mirror to be aluminized (36 in. diameter) | II-- Switch |
| B--Bell jar (39½ in. inside diameter) | I--Baffle |
| C--Baseplate | J-- Packing gland for switch control |
| D--Groove for lead fuse-wire gasket | K--Electrode for cleaning the mirror face |
| E--Bolts to fasten bell jar to baseplate | L--Observation window |
| F--Filaments of tungsten wire from which aluminum is evaporated | M--Pump connection |
| G--Conductors to supply current to filaments | N--Plate to carry filaments and switch |
| | O--Removable brass cylinder to carry N |

what in the type of apparatus used from that employed by Dr. Strong. In the Metro-Vick apparatus, the relative positions of the surface to be coated and of the heaters are changed, the mirror or other article being arranged face downward over the heater system, which consists of strips of molybdenum about 0.005-0.01 in. thick. These strips are supported between terminal blocks and are bent transversely so as to form shallow trays. They are connected to the terminals of a heavy-current low-voltage transformer which supplies the heating power. The aluminum or other metal to be evaporated is placed on the heater trays in the form of a fine powder and is spread evenly over the heater surface. It is claimed that the use of the metal in powder

form minimizes the heater perforation which is caused if short lengths of wire or small lumps of metal are employed.

The vacuum technique is standard. The plants in use have been designed with a view to commercial production. The pumping systems are accordingly arranged for ease of maintenance, and all vacuum joints are designed so as to give the minimum trouble in making and breaking.

Large mirrors are handled by means of specially designed lifting tackle, and the evaporation of metal on a large surface or surfaces is effected from a number of suitably placed heaters.

(c) *French Method.* A method has been developed in France by Dunoyer⁹³ which is based on the use of a moving source of evaporation or, alternatively, of a fixed source and moving receiving surface. In the first form of the apparatus, the crucible containing the coating metal is suspended by flexible or rigid conductors which carry the heating current, and is given an oscillating or rotating motion, in the second form, the crucible is fixed while the surface to be coated is maintained on a moving carriage on rails and is set in motion by an oscillating movement, the carriage being, if necessary, connected to the containing vacuum apparatus by release springs.

Other apparatus, with slight modifications or minor differences, have been suggested, but the three referred to above embody the main principles of modern vacuum deposition technique.

There is a considerable literature on the subject.

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Cathode Sputtering

General. In cathode sputtering, the material of the cathode is dislodged by high-speed positive gaseous ions. The processes of cathode sputtering are still unexplained, and it is not certain whether the particles emitted are of atomic or of molecular magnitude. The surface of the vacuum chamber has to be within the positive column of the electrical discharge, and in order to maintain the spark discharge, a certain gas pressure must be maintained in the sputtering vessel.

The cathode fall of potential is constant and independent of the current through the gas and of the pressure, provided:

- (a) no chemical action occurs between the cathode and the gas.
- (b) the negative glow does not cover the whole of the cathode and is not interfered with by the walls of the sputtering vessel.

The Laws of Cathodic Sputtering are as follow:

(1) Up to a cathode drop of the order of 1,000 volts, the diffusion laws are valid even near the cathode: at higher cathode drops of the order of 3,000 volts, there is in the case of most metals no normal diffusion up to 37 cm. from the cathode.

(2) The rate of deposition increases linearly with the voltage above a certain critical voltage.

(3) The rate of deposition increases rather more than linearly with the current.

(4) The rate of deposition decreases exponentially with increasing the distance of the mirror from the cathode.

(5) The rate of deposition is increased by sputtering in a heavy gas.

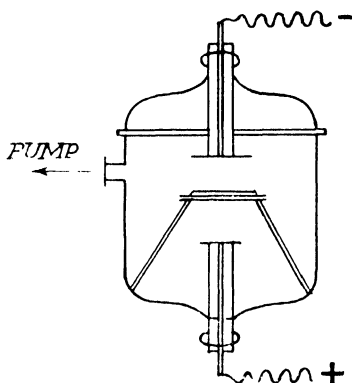
(6) The rate of deposition differs for each metal.

According to Meyer and Guntherschulze,⁹⁴ the quantity of metal deposited cathodically is a function of the specific weight. The sputtering in this case was carried out in mercury vapor.

The Apparatus for Deposition by Cathodic Sputtering. A simple sputtering apparatus described by Richter⁹⁵ is shown in diagram 3.

It is formed from two bell jars, in the upper of which a disc-form electrode is inserted with a gas-tight connection. This electrode may be either of the metal to be sputtered or it may be coated with this metal. A small compensating electrode, usually of aluminum, is positioned in the lower bell jar. The jars have to be suitably sealed.

DIAGRAM 3
*Sputtering Apparatus
According to Richter*



A limiting vacuum of at least 10^{-2} mm. is required from the evacuating pump. In order to achieve a pressure of 0.1 to 0.01 mm. the upper electrode is connected with the negative pole, and the compensating electrode is connected with the positive pole of a variable, high-tension current supply of 1,000-2,000 volts. This may suitably be a transformer or a high-tension battery.

This laboratory type of apparatus has been improved by various workers, such as Beach,⁹⁶ Cartwright,⁹⁷ and Darbyshire,⁹⁸ and others. It is essential that the apparatus shall be clean, and for this object, it is advisable to remove contaminating gases between the pump and the sputtering chamber with a liquid-air trap. Darbyshire has described improvements in the method of cooling the cathode. Richter⁹⁹ advocated the use of thin wire electrodes

with diameter of the same order as the free path of the gaseous atoms to diminish back diffusion. Cartwright introduced the idea of heating the support in vacuo to about 200°C. in order to prevent "frosting," which occurs in the case of some metals such as gold.

One of the primary difficulties in the commercial application of sputtered films has been to obtain good adhesion adequate for the technological requirements, and the processes intended for commercial operation have been developed with a view to overcoming the tendency of the coating metal to strip off when exposed to service conditions. This difficulty is associated with insufficient union with the foundation material, and in plant designed for commercial production, provision is normally made for heating the article which is to be coated to a fairly high temperature, with the object of bringing about diffusion or alloy formation. Berghaus¹⁰⁰ has taken out a number of patents for an apparatus of the type shown in Diagram 4.

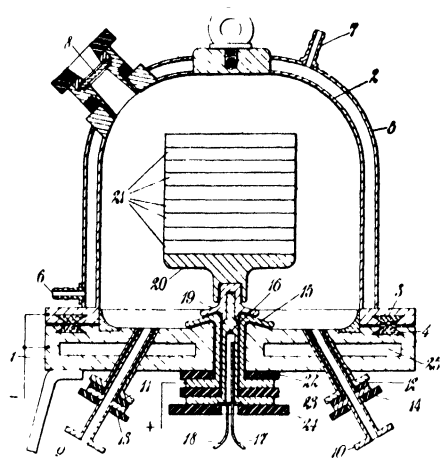
The article is heated either by a gas discharge or by a glow current to a temperature not lower than that of the eutectic alloy of the sputtered metal and the metal being coated. The metal applied by disintegration is periodically melted by adjustment of the current supply, to facilitate alloying in the intermediate zone. The cathode disintegration is carried out in a reducing gas or gas mixture, such as hydrogen or hydrogen-nitrogen, at subatmospheric pressures, ranging from 10^{-6} to 3 mm., according to the metal and gas atmosphere employed.

In an alternative form of apparatus intended for high output, Berghaus constructs the vessel wall of the disintegrating chamber of the cathode material, in order that the discharge energy applied to the cathode shall be as large as possible. The vessel is surrounded by a cooling jacket, water, oil or air being used as cooling medium. The filling gas in this apparatus may either be an inert or reducing gas, or it may be a gas or vapor intended to have some chemical action on the material. The pressure is usually kept between 5 and 0.1 mm. of mercury.

PRODUCTION OF THIN METALLIC FILMS

DIAGRAM 4

Commercial Sputtering Plant



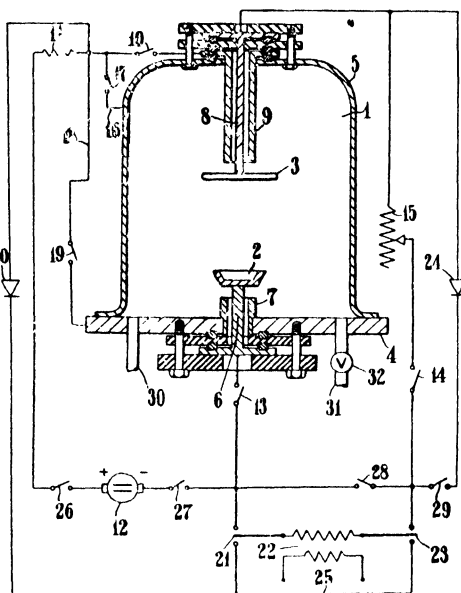
- 1—Lower part of sputtering vessel
- 2—Removable upper part of sputtering vessel
- 3 and 4—Seals, jointly forming cathode
- 5—Cooling jacket
- 6—Lead
- 7—Outlet
- 8—Viewing window
- 9—Insulated pipe connection (to pressure indicator and gas-filling apparatus)
- 10—Insulated connection to vacuum pump (not shown)
- 11 and 12—Insulating rings
- 13 and 14—Insulating and pressing-on rings
- 15—Anode
- 16—Hollow lead-through element
- 17—Lead for coolant
- 18—Lead
- 19—Insulating screen pin
- 20—Quartz support plate for object being sputtered
- 21—Material to be metallized
- 22 and 23—Insulating rings
- 24—Insulating and pressing-on ring
- 25—Cooling duct

In some of the later models the cathodes are of thick wires or strips, in some instances with a core of a metal which fuses at a higher than the outer sheathing temperature, since it has been found that the speed of disintegration, which is normally rather slow and is one of the disadvantages of cathode disintegration as a method of coating for commercial purposes, can be greatly increased by raising the temperature of the cathodes to the point almost of melting. Berghaus states that the cross-sectional dimensions have no influence on the amount disintegrated per

DIAGRAM 5

*Another Type of Commercial
Sputtering Plant*

- 1—Cathode disintegrating chamber
- 2—Crucible-shaped cathode
- 3—Article to be metallized
- 4—Lower part of chamber
- 5—Removable upper part of chamber
- 6—Cathode holder
- 7—Screen
- 8—Insulating holder for the article to be metallized
- 9—Screen
- 10—Switch
- 11—Protective resistance
- 12—d-c source (or may be rectified a-c)
- 13 and 14—Switches
- 15—Regulating resistance (controls glow-current heating)
- 16—Lead
- 17—Switch
- 18—Lead
- 19—Switch
- 20—Check valve
- 21—Two-way switch
- 22—High-tension a-c transformer
- 23—Two-way switch
- 24—Check valve



- 25—Lead to screen 9
- 26, 27, 28, 29—Switches
- 30—Lead to vacuum pump
- 31—Supply lead for reducing gas atmosphere
- 32—Regulating valve for reducing gas mixture

square centimeter surface of the cathode if the energy of disintegration per unit surface is kept comparatively constant. His results are listed in Table III.

The General Electric Company¹⁰² has described a method of stabilizing the sputtering film by heat-treating it to a temperature below the sintering point of the metal deposited, e.g., 110-150°C. Phillips Gloeilampen¹⁰³ establishes a magnetic field between the cathode and the anode, and applies a sufficiently high voltage to cause ionization of the gaseous atmosphere, the magnetic and electric fields intersecting each other. The

PRODUCTION OF THIN METALLIC FILMS

Heraeus Company¹⁰¹ has described a process specially suited to the sputtering of such metals as ruthenium, rhodium or palladium on non-conducting materials.

TABLE III. *Cathodic Sputtering Amount Disintegrated*
(Berghaus¹⁰¹)

Cathode			Electrical energy of disintegration		Amount disintegrated		Current yield
Diameter in mm.	Length in cm.	Surface in cm. ²	Total in watts	Specific in W/cm. ²	Total mg/h.cm. ²	Specific mg./h	mg./amp.h.
Cathode material Cu							
0.3	10	0.95	2.1	2.2	0.6	0.63	275
3.0	10	9.5	2.1	0.22	0.61	0.064	275
3.0	10	9.5	21	2.2	5.8	0.61	370
5.0	10	16	35	2.2	9.4	0.60	390
Cathode material Ag							
0.3	10	0.95	2.1	2.2	2.2	2.3	1,540
3.0	10	9.5	2.1	0.22	2.6	0.27	1,540
3.0	10	9.5	21	2.2	25.6	2.7	2,600
5.0	10	16	35	2.2	39.2	2.4	2,800

Metals Commonly Deposited by Sputtering. Silver and copper are among the easiest metals to sputter. Rhodium, palladium, irridium and similar metals can be fairly readily sputtered, as can also tungsten. There is no special difficulty in sputtering any of the metals of the iron group, such as iron, cobalt, nickel, manganese; of the zinc group, such as cadmium and zinc; or of the arsenic group. Aluminum is one of the most difficult metals to sputter, others in the difficult category being lithium, magnesium, chromium and beryllium.

The difficulty in the case of aluminum and the other light metals is probably associated with the oxide film. Aluminum sputters less than any other metal in any of the gases usually employed in the sputtering chamber, such as hydrogen, helium, nitrogen,

oxygen or argon. The normal average cathode fall in aluminum in different gases, measured up to the instant of the appearance of glow, has been determined by various workers whose values are listed in volts in Table IV.

TABLE IV. *Normal Average Cathodic Fall for Aluminum in Different Gases, Measured to Appearance of Cathodic Glow According to Various Investigators*

Gas	Air	O ₂	H ₂	N ₂	He	Ne	Ar	H ₂ O Vapor
Voltage	229,302	311	171	179	141	120	100	321
Reference	(105) (106)	(107)	(105)	(105)	(108)	(109)	(105)	(110)

Guntherschulze¹¹⁰ gives the threshold values for the sputtering of aluminum electrodes as 350 volts.

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Chapter V

THE PROPERTIES OF METALLIC FILMS AND SURFACES

IT should be noted that this chapter does not include any account of the problems of surface characteristics in relation to the mechanical properties of metals, and also excludes reference to corrosion and radioactive phenomena.

The Mechanical Properties of Thin Films

Hardne ss. "Hardness" is not a very closely defined term, and its measurement, which is more of technological than scientific interest, is usually made in terms of an arbitrarily selected combination of factors which may or may not be true constants. If hardness is considered as mechanical resistance to plastic deformation, the grain size and the distortion of the lattice are the ultimate controlling physical values involved, and Wood¹¹ has pointed out that, in the case of very small grain size, these are physically equivalent, since the smaller the grains the greater the volume occupied by the distorted surface layer.

The lattice deformation is accompanied by broadening of the X-ray spectral lines. Although no dependable technique has yet been evolved for the quantitative application of this effect, it would appear to be a basis of approach to the problem of measuring the hardness of thin films. Electron diffraction and electron scan microscopy may also be able to throw light on the problem when the difficulties of interpretation are further understood. Mechanical tests, depending on the use of a thrusting instrument, are not feasible, since it is not possible to make the thrusting

instrument so small as to prevent any deformation of the base underneath the coating, and scratch tests are unreliable even for thick coatings. Optical tests, based on the loss of reflectivity after the surface has been submitted to some mechanical treatment intended to resist its so-called hardness -- which would seem, however, to be more strictly its abrasion-resistance -- such as bombardment with small particles, have been proposed,¹¹² but they fail in any case where the films concerned are thin enough to be transparent or semi-transparent, because of the uncertainties involved in the double reflections from the outer film face and the underlying metal face (see next section on the optical properties of thin films).

Surface Tension. Different workers¹¹³ have reported on the "crumpling" of thin foils which has been observed to take place at high temperatures and which is a surface tension phenomenon. Measurements have been carried out on silver and gold.

Resistance to Pressure. It has been experimentally shown¹¹⁴ that a silver membrane of 300 Å. thickness can withstand an external pressure of 8 mm. mercury. By cautiously blowing on such a film, definitely audible vibrations arise.

Cohesion. Metal films of as small a thickness as 50 Å. have been found to possess complete cohesion and to be free from pores.

Resonances. Wolter¹¹⁵ has explained the existence of resonances in silver, gold, platinum, potassium and sodium films by the assumption that the density of the metal in the thin layer is less than that in the massive state and that it varies from place to place in the layer.

The Optical Properties of Metallic Films and Surfaces

Examination of the optical properties of metallic surfaces and thin films of metals is of importance from two points of view: from that of their own interest and possible exploitation and because

of the information which they are capable of giving about the structure and nature of surfaces and thin films and about the processes of formation and changes which the latter undergo.

Optically, thin films behave in a different way from compact metal. With increasing film thickness, the reflectivity increases whereas the refractive index decreases, until, on reaching a certain thickness, which is critical for each metal and which is equivalent to the limiting thickness for transparency, the constants approximate to the values which apply to the massive metal.

In the following, the general theory of optics is reviewed briefly in its relation to metallic films and surfaces considered as homogeneous, isotropic, crystalline media.

Propagation of Light through Metals. The subject of plane light waves is one which necessitates a great deal of pure physical theory. It has been dealt with comprehensively by such workers as Drude¹¹⁶ and Wood.¹¹⁷ So far as metals are concerned, however, although the propagation of light is a perfectly determinate problem, the results of optical theory differ in many respects from anything contained in the usual reference works and textbooks on optics, and they are by no means common knowledge. The application of Maxwell's electro-magnetic theory is, of course, fundamentally involved, although much valuable information was obtained before its genesis. The form of solution of Maxwell's equations appropriate for plane waves contains a large number of constants which must satisfy certain relations because of purely mathematical requirements, and consideration of the mathematical irrelations reveals some interesting physical interpretations of the distinction between dielectrics and metals, considered as homogeneous, isotropic, crystalline media. Some of these may be referred to here:

In metals, the electric and magnetic vectors are not in phase as is the case with dielectrics.

Fry¹¹⁸ has shown that within a metal the "absorbed" light is

always of a hybrid type, in which one vector is always rotating and both are sometimes rotating, except in the extremely special case of normal incidence.

As the wave front of a plane wave progresses in a metal, the amplitude decreases, and it also varies from point to point. The wave front is not at right angles to the planes of equal amplitude, both the wavelength within the metal and the extinction coefficient varying with the angle of incidence.

The relationship $\epsilon_1 = 1 - r_1 = 2\sqrt{\nu_p}^{119}$ developed by Drude holds good only for the long infrared waves for metals. In the near infrared, the optical constants vary with the temperature and are, therefore, very much influenced by the thermal vibrations of the solid. In the visible and ultraviolet portions of the spectrum, the optical constants are approximately independent of the temperature.

Reflection and Refraction of Metals. The phenomena of reflection and refraction, in connection with light incident upon a surface, are explained in terms of the electromagnetic theory by the reasoning that if two media are in contact, their electromagnetic fields must be definitely related, so that certain boundary conditions must be satisfied when a wave of light moves through the first medium. These conditions concern the continuity of the normal and tangential components of the electric and magnetic vectors. In dielectrics, there are no surface charges or currents to interfere with continuity, but in metals, conduction currents do give rise to surface charges, and probably to negligibly small surface currents. The mathematical solution of the conditions shows that the incident light wave gives rise to two other waves, one the reflected beam in the same medium and the other the reflected beam in the second medium. The relationships which exist between the various constants that characterize the three waves must be considered separately for the cases of the surfaces of massive metal and thin films.

In the case of simple reflection at a plane boundary of massive metal, the principal points to be noted are that the velocity and damping vectors are not at right angles as in a dielectric, so that there is a component of damping in the direction of propagation; that the velocity and damping change very little with increasing angle of incidence -- which means that light impinging obliquely upon a metal travels farther in it than light which impinges normally; and that both the magnetic and electric vectors are kept as nearly as possible parallel to the surface no matter what the angle of incidence is.

In the case of reflection from a thin film, five beams in all are involved: the incident and reflected beams; the refracted and internally reflected beams within the film; and the transmitted beam in the base, considered a dielectric. The relationships between these beams indicate certain peculiarities of reflection from metallic films. In the first place, an interference phenomenon gives rise to the fact that there is a certain thickness of film which absorbs more light than does massive metal, even though the film is still comparatively transparent. In the second place, films which are still so thin as to be virtually transparent exhibit marked selectivity as to plane of polarization, particularly at high angles of incidence, with the result that the state of polarization of reflected light differs materially from that of the incident light.

Absorption by Metals. When a beam of light shines upon a metallic plate, the electric intensity inside the plate is proportional to the intensity in the incident beam. The factor of proportionality, however, is not an *absolute* constant. This is obvious since it differs for different metals, and depends upon the medium (air or glass, for example) through which the light reaches it. It is not even an *intrinsic* constant of the metal, for if the intensity of the incident beam were kept fixed, the electric intensity inside the metal would be different for different planes of polarization,

or for different angles of incidence, or for different wavelengths. Moreover, even if the intensity, color and plane of polarization of the incident are all kept fixed and only the angle of incidence is allowed to change, the curves which relate the intensity inside the metal to the angle of incidence will be of different shapes at different depths below the surface, due to the fact that light is extinguished the more rapidly the more oblique its angle of incidence.

The rate at which energy is absorbed by a metal is, according to the Maxwell theory, directly proportional to the electric intensity *at the place where the absorption takes place*, that is, inside the metal. The constant of proportionality is, in this case, an intrinsic property of the metal. It does not vary with the plane of polarization or angle of incidence of the incident light, nor does it vary from place to place within the metal.

This "intrinsic absorbing power" is based upon the electric intensity *inside* the metal. It is not what is commonly called the "absorbing power" of the metal. The latter is the ratio of the rate of absorption to the intensity of the incident beam and contains not only the intrinsic factor but also the other factor of proportionality referred to before varying, therefore, with almost every conceivable change in the incident beam. This "bulk absorbing power" is not primarily governed by the ability of a substance to absorb energy, but is in reality a phenomenon of refraction. Whatever succeeds in passing the bounding surface is absorbed sooner or later, if the lower medium is opaque, or passes out of the system if it is transparent. The amount "absorbed" is, therefore, determined solely by the reflecting power of the metal, not by its subsequent disposal of the refracted portion.

In considering the above facts in relation to thin films of metal, it becomes apparent that while the presence of the base will not affect the "intrinsic absorbing power," it may profoundly affect the light intensity within the film and, therefore, may cause the

amount of energy absorbed to vary with wavelength, plane of polarization and angle of incidence, in a way quite different from that observed with only two media. This is particularly true if the layer is so thin that the results of multiple internal reflection are important. In such cases, the "lamellar absorbing power" of a very thin layer will have to be differentiated from the "bulk absorbing power" of an opaque layer. The "lamellar absorbing power" of very thin, virtually transparent films is found to be dependent upon the intrinsic absorbing power, the ratio of the total intensity just above the surface of the film to the intensity of the incident beam and the rate at which energy is carried to the film by the incident beam. In the case of thicker films which are no longer transparent nor yet quite opaque, the optical behavior involves many complex factors whose physical interpretation is not clear.

It should be noted that this theory is concerned with the simplest case of homogeneous isotropic crystalline media. The metallic surfaces and thin films met with in practice, however, rarely satisfy these conditions. In the case of surfaces, these are usually polished and, therefore, remain no longer crystalline. In the case of films produced by thermal evaporation or cathode sputtering, the structure is initially predominantly colloidal (amorphous) and only slowly ages to crystalline form. The presence of impurities and of adsorbed gases may also have far-reaching effects. Both surfaces and films are also frequently optically anisotropic, even in the cases of metals, such as aluminum, which crystallize regularly. Zocher¹²⁰ has shown that dichroism is produced by polishing thin films of aluminum. This is due to atomic displacement and is positive. Finally, internal stresses, such as may be, for example, set up by changes of temperature in the surface layer or thin film, may greatly influence the optical behavior. .

It should also be pointed out that no allowance is made for the effect of surface films, principally oxide films, so far as the theory

is concerned. Drude developed the subject theoretically, but his work depended on the contemporary knowledge of oxidation phenomena, which has been greatly modified since his time, and certain of his fundamental assumptions have been questioned by later workers.¹²¹ In the most general case, a surface film must be regarded as an anisotropic absorbing medium. Formulae have been constructed to indicate the influence of the surface film on the phase difference and on the amplitude ratio of the principal components.

Selective Color Absorption. Metals, in the same way as other inorganic and organic substances, exhibit characteristic selective color absorption, which may vary considerably over the whole spectrum range.

Interference Colors of Thin Metallic Films. If the transmission factor (see page 53) of a particular metal is high enough to allow a substantial proportion of the incident light to pass through a thickness of at least unit wavelength in a thin film, interference colors are produced in the same way as with certain oxide films (see page 16). Prosad and Ghosh¹²² showed that colored rings formed in sputtered films of platinum, these rings being due to interference fringes. Nathanson¹²³ utilized the interference colors of sputtered aluminum and manganese films to measure their thickness. Overbeck¹²⁴ examined the interference colors on tin. Edwards¹²⁵ carried out a comprehensive investigation of the conditions necessary for the formation of interference colors in thin sputtered metal films: he showed that the film had to be thin enough to be transparent, the actual thickness depending on the material of the substrate, and the colors being most definite when the film is on a "white" substrate. Several orders of interference fringes may be formed with monochromatic incident light. The actual color depends on the angle of incidence, but the color cycle is more or less constant for different metals. Gale¹²⁶ confirmed

the theory of interference colors by reducing the thickness of the film and producing appropriate color changes.

The theory of the formation of interference colors is rather complex, depending on the five preliminary phase changes which take place at each reflection and refraction before the final phase change which determines the color-thickness relationship. Edwards has given a theoretical discussion of the subject, but Chalmers¹²⁷ in a recent treatise points out that the treatment is not complete, because Edwards has not taken into account the different behavior of the two polarized components at high angles of incidence. Chalmers also discusses some other objections to the interference theory.

Emissive Power of Metals. The emissivity is defined as the ratio of the emissive power of the metal to that of a black body at the same temperature.

Little coherence is found in the literature on the subject of the emissivity, or emissive power, of metals, even the definitions being confused. It is common to find the term emissivity loosely described as the amount of energy radiated per unit surface in unit time, the radiation being measured either normally or integrated over the whole surface exposed. Price and Lowery¹²⁸ have pointed out that such a definition is rendered valueless in practice by the difficulties of measuring the exact temperature and of maintaining the temperature constant for the minimum period of time to measure it. They prefer the following definition: "If the amount of energy radiated per second per unit area by a perfect black body at a specified temperature over an infinitesimally small wavelength range be taken as unity, then the amount of energy radiated in a specified direction under the same conditions by any other body is known as the emissivity of the body."

Kirchhoff's Law states that the emissivity of any substance is exactly equal to its absorptivity under the same conditions. Since the sum of the absorptivity and reflectivity under the same

conditions is equal to unity if no energy is lost or gained, the classical theory requires a rigid relationship:

$$E + R = 1$$

between the emissivity and the reflectivity, and utilizes Drude's calculations to arrive at the equation:

$$E = 1 - R = \frac{4n}{n^2 + k^2 + 1 + 2n}$$

in which n is the refractive index and k is the absorptive coefficient. Applying Maxwell's theory, an approximate series:

$$E = 0.365 \sqrt{\frac{\rho}{\lambda}} - 0.067 \frac{\rho}{\lambda} + 0.009 \left(\frac{\rho}{\lambda}\right)^{3/2}$$

has been derived by Hagen and Rubens¹²⁹ for radiation of long wavelength. For most metals, for wavelengths greater than 10μ , the first term is sufficient. Beyond this, the three terms of the series give an approximate value up to 4μ , but Price and Lowery have pointed out that the equation fails completely to give any representation of the emissivity curve in the near infrared and visible due to the resonance of the electrons of the metals at higher frequencies giving rise to selective emission and reflection. In their paper, they give expressions derived from the classical electron theory for the dispersion curves corresponding to the selective emission.

Krönig¹³⁰ has worked on the application of the quantum theory to the dispersion of light in metals, and his work has been experimentally tested by Hurst¹³¹.

The results of some workers would suggest that there is a zero temperature coefficient for all substances at a specific wavelength in the infrared region.

Barnes and Czerny¹³² and Goos¹³³ have investigated the emissivity of thin films of metals, basing their measurements on reflectivity tests.

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Methods of Determination of Optical Constants

The optical constants usually determined are the refractive index, the absorption index and the specular or the total reflectivity. It should be noted that in the case of metallic reflection, strictly speaking, there is no total reflection as in the case of dielectrics, since the wave propagates into the metal. The diffuse reflectivity may also be measured, and in this connection it should be noted again that the ordinary laws of optics do not exactly apply; Lambert's Law is not completely fulfilled. In the case of thin films, the transmission factor may also be occasionally determined.

Definitions of these optical constants are given below in conjunction with the values of the constants for aluminum and other reflector metals, as found by different investigators.

The majority of the earlier work on the determination of the optical constants relates to the surface of massive metal. The methods available, respectively, for investigating surfaces and films are here considered separately.

Determination of the Optical Constants of Massive Metal. In all methods for measuring the optical constants of metals, it must be recognized that in an absorbing medium the incident and the reflected rays penetrate about half a wavelength, so that the presence of any surface film or films may interfere with the results¹³¹. To make allowance for this, the refraction and absorption indexes have to be determined for different angles of incidence. In the case of polished metallic surfaces, the presence of

the Beilby layer has also a modifying effect, though this is of a smaller order than that of a surface film with different optical properties. Again, the microscopic roughness of the surface, which greatly increases the specific surface dimension, and the effect of scratches and their orientation are factors which influence the values obtained.¹³⁵

The following principles are made use of in determining the optical constants of metals:

(i) *Azimuth Angle.* The azimuth angle is defined by:

$$\tan \psi = \frac{R_p}{R_s}$$

where R_p and R_s are the components parallel and perpendicular to the plane of incidence. The angle of incidence for which the phase difference:

$$\delta = \frac{\pi}{2}$$

is known as the principal angle of incidence and the corresponding azimuth is known as the principal azimuth. By determining ψ and δ for given angles of incidence or from the principal angle of incidence and the principal azimuth, the coefficients of refraction and absorption and the specular reflectivity at right angles to the surface can be calculated.

(ii) *Change in Polarization of the Reflected Light.* This method is due to Drude¹³⁶ and may be outlined as follows:

By resolving the electric vector of the incident polarized light into components parallel and perpendicular to the plane of incidence, the state of polarization may be conveniently defined by the two components. On reflection at a metallic mirror, the two components are retarded in phase and reduced in amplitude to different extents. The relative phase retardation and the ratio of the absorption coefficients can be determined with a high degree of accuracy by suitable experimental methods, e.g., with the Babinet compensator.

Goldhammer¹³⁷ gives a simple formula for determining the optical constants of aluminum from polarization measurements.

The method cannot, of course, be applied to the infrared, and it may be noted that an upper limit is imposed in the visible region by the amount of light reflected.

Other methods have been proposed, for example, the direct measurement of the refractive index using a very thin prism of metal.¹³⁸ In this case, however, in order that the law which applies to a dielectric prism shall hold good in the case of refraction through a metal prism, it is necessary for the prism to be so thin that the metallic structure is that of a thin film and the optical method, therefore, belongs properly to those dealing with thin films.

Measurements of Reflectivity. In the case of metals, the simple methods involving the use of the optical wedge or disappearing-filament optical pyrometer as adjuncts to the photometer and optical bench are unsuitable. Special reflectometers have, however, been designed, among which may be mentioned the integrating sphere reflectometer,¹³⁹ for which it is claimed that the results obtained are independent of the diffusion characteristics of the surfaces under examination. Other methods involve a variety of physical principles.

(iii) Determination of the Total Reflectivity of the Surface. This principle may be applied in two ways: either by measuring the ratio of the sum of the intensities of the light reflected in different directions to that of the incident light; or by illuminating the surface homogeneously and measuring the reflected light in one direction only.

The second method has definite advantages compared with the first method, since the total reflectivity may be determined in one single experiment, and the accuracy of the observations is quite independent of the form and condition of the surface. The method is applicable to the infrared.

(iv) *Photoelectric Methods.* The function of the photoelectric cell is to transform variations in luminous energy into variations in an electric current by utilizing the property of metals in general and the alkali metals in particular of emitting electrons under the action of light. Different forms of reflectographs or reflection meters¹¹⁰ have been designed to utilize the photoelectric cell, and a photocolorimeter¹¹¹ has also been constructed.

(v) *Photographic Intensity Measurements.*¹¹² This method depends on the relative intensities of given spectrum lines before and after metallic specimens are interposed in front of a spectrograph slit.

(vi) *Methods Depending on Thermal Effects.* Coblenz and Emerson¹⁴³ have described a method depending on the use of a vacuum thermopile in conjunction with a mirror spectrometer and fluorite prism.

Determination of the Optical Constants of Thin Metallic Films.

In determining the optical properties of thin films, in addition to all the factors which influence the optical properties of surfaces (which, of course, operate equally in the case of films), the question of the thickness of the film must be considered in connection with multiple reflection at both boundaries. The state of polarization of the reflected light is a periodic function of the film thickness for thick films of the order of 200-400Å. The nature of the interfacial surface and the extent of homogeneity and uniformity of thickness of the film must also be taken into account, since the methods in general assume ideal conditions to apply in this connection. The nature of the molecular orientation and distribution and the occurrence of anisotropy may also affect the values obtained.

Several methods have been devised for determining the optical constants of thin films.

(vii) *Change in Polarization of Reflected Light* (cf. method (ii) for massive metal). Drude¹¹¹ investigated the modification of

the reflection formulae in the presence of surface films — more particularly those formed in air — in which the optical properties change gradually from those of the surrounding medium to those of the bulk metal. The equations he developed are capable of generalization to any media and have been extended by various workers.¹¹⁵ Quantitative investigations are, however, limited to films of the order of 20-100 Å., which are fairly uniform in thickness and optical density, and which are deposited on such a substrate that there is a perfectly sharp interface between the different media (which the method assumes).

(viii) *Direct Measurement.* By using a very thin prism of metal¹¹⁶ and orienting the prism so that the angles of incidence and emergence are equal but on opposite sides of the normal, the refractive index can be directly measured. The ordinary formula for dielectrics hold to a near approximation within the limitations imposed by the necessity for extreme thinness (order of 1° apical angle).

The method does not, of course, apply to the infrared.

(ix) *Determination of the Total Reflectivity of the Surface.* The method described under (iii) is directly applicable to metal films deposited on another metal or substrate.

(x) *Measurement of the Light Transmitted by Films of Different Thickness.* This method has recently been developed by Veenemans¹⁴⁷ at Utrecht and Hartzler¹⁴⁸ in America, and has been used for the investigation of evaporated films of tungsten. It depends on the relationship between the thickness of the film, its refractive index and absorption coefficient. It is a complicated numerical problem but can be solved graphically from absorption determinations on films of different thicknesses. For visible light, a spectral pyrometer is employed; for work in the red and near infrared, a monochromator combined with a thermopile and galvanometer is used.

Determination of Constants in the Ultraviolet. Various methods have been devised for determining the reflectivities in the ultraviolet by means of modified reflectometers¹¹⁹ or the ultraviolet microscope.¹⁵⁰

(xi) *Photographic Method.*¹⁵¹ The ultraviolet transmission is measured photographically with a quartz spectrograph and a Martin *densiometer* by determining the relative “densities” of given spectrum lines before and after the metallic specimens are interposed in front of the slit.

The ultraviolet reflectivity may be determined in the same manner by taking spectrograms with and without the metallic reflector surface.

Determination of Optical Constants in the Infrared. Again, modifications of spectrographic methods are available for making measurements in the infrared. A spectrometer with Sylvén prisms may be used for direct measurements.¹⁵² The methods described under (iii) and (x) are also applicable to the infrared.

High-temperature Measurements. At high temperatures, the emissive power of metals in the visible region is considerably greater than in the case of space radiation.

Measurements of the optical constants at high temperatures are principally concerned with the direct determination of the emissive power by comparing the filtered metal radiation with that of the surrounding space.¹⁵³

The method can be extended to the ultraviolet.

Measurement of Diffuse Reflectivity. The diffuse reflectivity of a metal may be indirectly determined by measuring its total reflectivity¹⁵⁴ and its direct reflectivity.

To determine the diffuse reflectivity directly, properly speaking, it is necessary to measure the reflectivity in all directions and construct a solid diagram, the volume of which is proportional to the

diffuse reflectivity. Usually, however, readings are taken in one plane, a curve is plotted and the area enclosed by this is measured. This method gives approximate results only; it makes no allowance for optic anisotropy or other sources of error.

A simplified procedure sometimes employed is to take a number of readings in one plane on either side of the directly reflected ray, the specimen then being turned through 90° and the measurement repeated. An empirical formula relates the values obtained to the percentage of light reflected other than directly.

Measurement of Surface Polish. Measurements of reflectivity are sometimes carried out on metals with the object of determining surface polish. These methods are not concerned with the absolute specular reflectivity or with the absolute diffuse reflectivity, but with an arbitrarily selected empirical expression involving both factors. Different methods are described in the literature.¹⁵⁵

The Magnetic and Electrical Properties of Metallic Films and Surfaces

The interest in the magnetic and electrical properties of thin films and surfaces is, as in the case of the optical properties, twofold. These properties also can throw valuable light on the structure and nature of thin films and surfaces in so far as the theories of magnetism and electricity are established, and they are applied in scientific and commercial inventions.

The theories in connection with the electric properties of metals are still incomplete and transitional, but it may now be considered established, as the result of both experiment and theory, that the conduction process takes place in such a way that the free paths of the electrons are large compared with the interatomic distances. That this fact has a bearing on the electrical properties of metallic films and surfaces will be clear from a consideration of the earlier-discussed nature of the structure of thin films and surfaces. Little can be said of the magnetic or electrical

behavior of surfaces without entering a very uncertain ground, but an interesting phenomenon which has been observed in the case of aluminum may be noted in passing. Accurately machined surfaces of aluminum are found in some instances to undergo distortion during anodic oxidation, and it has been suggested that this distortion may be due to internal stresses set up by electrical forces. The available information regarding the behavior of thin films is summarized in the following sections.

The Magnetic Properties of Thin Films of Ferromagnetic Metals. The magnetic properties of thin films of iron and nickel have been investigated by several workers. Sorensen¹⁵⁶ examined the relationship between the magnetic properties and the film thickness. He found that, other conditions being equal, there is a critical film thickness below which the coercive power falls off very abruptly. For thicknesses greater than this critical value, a decrease in thickness is accompanied by a reduction in coercive power, while the remanence is approximately constant. The critical film thickness for iron was found by Sorensen to be about $55\text{m}\mu$. and that for nickel to be about $200\text{m}\mu$.

Ingersoll and de Vincy¹⁵⁷ carried these results a stage further by demonstrating that sputtered nickel films, thinner than about $120\text{m}\mu$., are initially non-magnetic, showing neither magneto-optic rotation nor tractive effects in a magnetic field. After heating to 300° or 400° C., however, the films become strongly magnetic and exhibit both effects. Films of considerably greater thickness (and films sputtered with an induction coil) in most cases exhibit magnetism *ab initio*. The interpretation offered by Ingersoll and de Vincy is that amperian currents require orbits wider than those of atomic size in which to circulate. The question as to whether the changes on heating are connected with oxidation effects is disposed of since exactly the same behavior occurs with films given heat treatment in a non-oxidizing atmosphere.

Edwards¹⁵⁸ confirmed Sorensen's work, finding that thin films

of nickel and iron undergo a very large change in magnetic induction at a fairly well-defined critical thickness (which he gives as about 50 m μ . for iron, in good agreement with Sorensen's figure). Edwards also noted another peculiarity of thin films of iron and nickel. Under certain conditions, the hysteresis loops which they give are very broad — in fact, nearly rectangular. The interpretation put forward is that the function which determines hysteresis may be of a type which vanishes either for very large or very small crystals, and hence an imperfect crystalline structure in thin films could be responsible for the abnormality. On the basis of this interpretation, Edwards suggests that magnetism would appear to be a crystalline rather than an atomic phenomenon.

The Electrical Properties of Thin Films. The modern conception of the nature of electricity is closely bound up with the fortunes of the electron as the fundamental unit of negative electricity. Motion of the electrons, the positive ions remaining stationary, constitutes what is defined as an electric current, which flows in a direction opposite to that of the motion of the electrons. Since, in the case of characteristic metallic lattices, modern theory holds that, in addition to the positive fixed ions, there is a "cloud" of free electrons which are not fixed, it is generally believed that it is the motion of these free electrons or "electron gas" which constitutes the electrical current produced by application of an external electromotive force. The resistance of a metal represents its simplest electrical property, namely, the resistance which it offers to the flow or passage of the electric current. According to conventional theory, the conductivity of a metal is inversely proportional to its resistance. By analogy with the kinetic theory of gas molecules, the following classical expression has been derived for the conductivity of a metal:

$$k = \frac{e^2 N L}{2 m v}$$

in which e is the charge on the electron

N is the number of molecules per unit volume

L is the mean free path of an electron

m is the mass of the electron

v is the velocity of the electron

Metallic conduction, distinct from electrolytic conduction in which chemical change and polarization can occur, is closely dependent on temperature conditions. The general function relating the resistance R of a pure metal to the temperature for, temperatures in the ordinary range, is of the type:

$$R = a + bT + cT^2$$

where T is the absolute temperature

a , b , c are constants, and c is very small.

However, when the temperature is reduced to the neighborhood of absolute zero, the electrical resistance of metals decreases virtually to zero and gives rise to so-called superconductivity. Certain metals, however, including copper and platinum, do not become superconducting; their resistance after reaching a minimum rises again.

The generally accepted interpretation of electrical resistance of metals at ordinary temperatures, taking into account this phenomenon of superconductivity at low temperatures, is that "viscous" or "frictional" forces are exerted on the electrons, probably by the positive ions.

In the case of thin films of metals, there is an enormous dependence of the conductivity on the film thickness. Reinders and Hamburger¹⁵⁹ found that conductivity is not observed *ab initio* in all cases and only occurs after a certain critical film thickness is reached. Below this critical thickness, both at low temperatures and even at ordinary temperatures, the resistance was found to be infinite. Richter¹⁶⁰ showed that the specific conductivity makes a jump of the order of 10^9 times its value on passing the critical thickness.

PROPERTIES OF METALLIC FILMS AND SURFACES

The actual critical thickness at which conductivity commences is smaller for metals of higher melting point, for example:

For tungsten it is $0.2\text{m}\mu$.

For iridium it is $0.4\text{m}\mu$.

For platinum it is $1.65\text{m}\mu$.

For silver it is $4.5\text{m}\mu$.

In the case of silver films, both the above workers found that a constant value of the conductivity was reached and Richter puts the film thickness at which constancy is attained as in the region of $40\text{m}\mu$, but even for films of greater thickness than this, the conductivity is smaller than it is for massive metal. Hamburger attributes this to porosity, but Richter relates it to the free path of the electrons. He suggests that if the thickness of the film approaches this magnitude, there is a falling off of the conductivity. In the case of silver, Summerfeld¹⁶¹ has calculated the free path of the electrons as about $52\text{m}\mu$, which is not in acute disagreement with the critical conducting film thickness. Bridgman¹⁶² considered the same theory in connection with his study of the applicability of Ohm's Law, but he pointed out that experimental verification is extremely difficult.

Perhaps more so in the case of electrical conductivity measurements on thin films than in any other branch of investigating their behavior, the interference of unspecified conditions makes itself felt. Whether this may be paraphrased as a statement that the theory of electrical conductance is in a less robust condition than other physical theories may be a controversial issue. Braunsforth¹⁶³ found, for example, that cathodically sputtered films exhibit maximum resistance shortly after their production. Their resistance then falls off to reach an end value. This behavior is accelerated by heating. He also found that the resistance is greatly affected by gas adsorption, in the case of films of resistance over $10,000\Omega$; the resistance is first increased and then falls off. Janitzky¹⁶⁴ put forward a theory to explain this

phenomenon in terms of lattice distortion due to the increased volume from the gases adsorbed, which would account for the initial increase. The subsequent falling off is explained by the dissociation of the adsorbed gas, due to its higher dissociation constant.

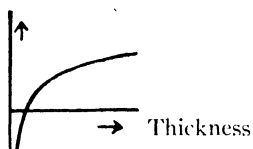
Again, the electrical properties of metallic films are greatly influenced by the temperature of formation and also by the temperature at which measurements are carried out. Perucca¹⁶⁵ showed, in the case of gold films of less than 1,000 Å. thickness that the curve relating the conductivity to the thickness varies with the temperature at which the film is formed. In the case of high-temperature formation, a point of inflection is observed.

The temperature coefficient of the conductivity behaves in the case of thin films of metal in much the same anomalous way, as compared with the behavior in the case of massive metal, as the conductivity itself. It is negative for very small thicknesses, and gradually changes to the positive values which obtain for massive metal as the thickness increases. The actual values are smaller than in the case of massive metal, and Braunsforth¹⁶⁶ showed that in the case of aged films which have adsorbed much gas, the temperature coefficient may fall to a very low value. Braunsforth also obtained a negative coefficient in the case of alloy films, while Hamburger and Reinders¹⁶⁷ found a negative coefficient in the case of pure metal films (they used tungsten for experimental purposes) produced at low temperatures. They explained this on the basis of the abnormally large distance between the atoms and assumed that, as the temperature rises, the movement of the atoms is facilitated, which would account for the increase in the value observed.

The curve shown in Diagram 6 is typical. The thickness at which the curve commences to rise steeply is of the order of magnitude of 50 – 200 Å.

Temperature Coefficient

DIAGRAM 6



Typical curve showing relationship between thickness of thin metal film and its temperature coefficient of electrical conductivity

The superconductivity of thin films has been investigated by a few Soviet research workers, and appears also to exhibit some anomalies by comparison with the superconductivity of massive metals. For instance, Alekseevskii¹⁶⁸ showed that pure tin superconducting films have a larger critical field than massive tin, the critical field increasing as the film thickness decreases. Shalnikov¹⁶⁹ showed that superconductivity in thin films is destroyed only by very strong magnetic fields. Both these workers have found that the age of the film affects its superconductivity. Alekseevskii demonstrated that tin films had considerably higher critical fields directly after condensation at the temperature of liquid helium than after they were allowed to heat up to room temperature; and Shalnikov, who worked with lead, thallium and tin films, showed that in recrystallized films lower magnetic fields and higher electric currents are needed to destroy the superconductivity than in non-recrystallized films.

A large amount of work has been done on the investigation of the electrical properties of thin films.

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The Photoelectric Properties of Thin Films

Under certain circumstances, negative electricity, i.e., electrons, are emitted from a metallic surface as a result of the action of light, giving rise to what are known as photoelectric or photoconductive effects. The rate of emission of the electrons is dependent on a number of factors, such as pressure and temperature, in addition to being essentially dependent on the nature of the light, whose wavelength must be less than a certain critical value which is characteristic for each surface. In some instances a so-called inverse photoelectric effect is observed, the charge on the electron being reversed. The photoelectric effect is usually strongly selective for different wavelengths and it is subject to the phenomenon of "fatigue."

Wilson¹⁷⁰ has investigated the photoconductive effect exhibited by thin metallic films exposed to ultraviolet light at liquid air temperatures. He worked with films of copper, platinum, palladium and bismuth, sputtered on glass. On the basis of his results, he suggested three alternative hypotheses, namely, that the effect may be caused only by ultraviolet light, that it may be restricted to thin films and related to their structure or may be due to an external photoelectric current passing between discontinuous patches of the film.

The Chemical Properties of Thin Films and Surfaces

A full discussion of the chemistry of metal surfaces and thin

metallic films is far beyond the scope of this monograph. So far as metal surfaces are concerned, their chemistry embraces the whole subject of corrosion and related phenomena; and in the case of thin films, it would swallow a good part of colloid chemistry.

It may merely be noted that the chemical reactivity of metallic films and surfaces shares the abnormalities of the film and surface atomic structures. Thus, the vapor pressure is much higher than in the case of massive metal. Silver films of 300 Å. thickness, for instance, have been found to evaporate completely in less than an hour at 350°C. and atmospheric pressure. Amorphousness is frequently exhibited, and in some cases, for example, with silver, the transformation to the crystalline state proceeds with explosive violence. Another instance of the remarkable chemical activity of thin films is afforded by the fact that extremely thin films may be rendered visible. Estermann and Stern¹⁷¹ showed that it was possible to make films of silver as thin as $\frac{1}{5}$ Å. visible by deposition from a silver nitrate-hydroquinone solution.

Oligodynamic effects have been noted by several workers in the case of even extremely thin films of active metals such as silver.

The formation of oxide or other coatings on the surface of metal has been very briefly referred to in Chapter II, and it has been indicated that the mechanism of formation is extremely complex. In this connection, it is appropriate to emphasize the significance of the fact which emerges -- a point of great importance in the optical and other applications of metals -- that thin films of metal do not oxidize (or form other surface films) in the same way as massive metal. Sometimes they oxidize, or tarnish, more readily, sometimes less readily than the bulk metal. This fact may be connected with the different types of sorption which take place in the interactions between gases and solids.

It has been suggested, on the basis of photoelectric measurements, that when a clean metallic surface of massive metal is exposed to air, there is an instantaneous adsorption of gas by the

surface. Hunter¹⁷² has shown that the rate at which the adsorption takes place governs the subsequent time interval before true oxidation of the surface commences. This would appear to indicate that, in reality, the process of surface-film formation is a discontinuous one, involving first the surface layer and then the underlying metal. The surface layer would appear to have quite special chemical properties which bring it into line with thin metallic films, whose behavior is also anomalous. All the evidence seems to classify the chemical activity of films and surfaces as primarily a sorption phenomenon. Heterogeneous gas catalysis provides additional evidence of this.

Quantitatively, the chemical activity of films and surfaces is influenced by their physical nature; accordingly, their history plays an important part in determining their chemical behavior.

Chapter VI

THE PROPERTIES OF SURFACES AND THIN FILMS OF ALUMINUM AND ITS ALLOYS

In connection with the characteristic surface properties of aluminum and with the properties of thin aluminum films, the greatest interest has been centered on the optical behavior and a good deal of this chapter is concerned with the optical properties of aluminum and its alloys. What work has been done on the magnetic and electrical properties and also on the chemical behavior, apart from corrosion phenomena, suggests that they hold out great possibilities, both for the study of physical problems and for practical applications of scientific or technological character.

Any account of the properties of aluminum, which, because of its position among the element, is a metal characterized by great reactivity, always tends to savor of the disingenuous by exhausting the superlatives: its optical reflectivity, for example, is outstandingly good; its electrical conductivity is very high; and its chemical affinity for oxygen is so remarkable that the oxide film on aluminum can be exploited to give an extremely versatile range of properties which can serve many and widely varying uses.

In order to place aluminum among other metals, at the end of each of the following sections a tabular summary of the properties of the chief metals of interest is given for comparison.

The properties other than "surface properties" of massive aluminum are not, of course, referred to in the following tables.

The Optical Properties of Aluminum and Aluminum Alloys

The optical properties of aluminum are of great importance, since they fit the metal and its alloys for a variety of valuable practical applications in industry and science.

It is essential in discussing the behavior of aluminum with regard to optics to take into consideration the special nature of this metal and its remarkable affinity for oxygen. In the case of massive aluminum, there is no doubt that the presence of the natural oxide film affects every result which has been obtained, and while some workers have made allowance for this fact, others have not. Thus, Taylor¹⁷³ demonstrated that the reflecting power of aluminum straight from the rolls changed from 53 to 82% when a thin layer of the surface was removed on a lathe. The age and condition of the surface film are important factors not often estimated in conjunction with optical investigations on an aluminum surface which has undergone no special surface treatment.

The oxide film, when crystalline, is optically dielectric, so that in the case of massive aluminum, the optical nature of the metal is that of an absorbing medium coated with a thin film of dielectric. The problem has to some extent been discussed theoretically, but the optical properties of the natural oxide film do not appear, from the literature on the subject, to have been determined. In the case of thin films of aluminum, more particularly in the case of those films deposited by sputtering or evaporation, however, the conditions are different due to the fact that such thin films do not oxidize in the same way as massive metal, due to the structural properties. Although the oxidation phenomena of these thin films of aluminum have not been fully investigated, the published figures from many sources for the optical constants and also considerations based on the anomalous electrical behavior of the films indicate that the behavior of thin deposited aluminum films is not directly comparable with that of the massive metal.

From the foregoing remarks it will be clear that the properties determined by different workers will not always compare very well. In the tables given below the results are in many cases quite discordant. Apart from the influence of the surface film, the constants determined by different workers are not in all cases identical and the particular constants for which values are derived are not always clearly defined by their authors. This applies particularly to the reflectivity values. In many instances, also, no indication is given of the temperature at which the optical properties are measured and no work appears to have been done in connection with the effect of temperature on the optical properties of the metal. Hamaker¹⁷⁴ was able to show in the case of tungsten that the reflectivity is a direct function of the temperature.

The Reflectivity of Aluminum and Its Alloys. The reflecting power or reflection factor has been defined¹⁷⁵ as the ratio of the light reflected by the body to the incident light.

The light reflected according to the laws of regular reflection, i.e., specular reflection, is known as the directly reflected light and the corresponding reflecting power is called the direct reflecting power. The light which is diffused, i.e., which is sent out in directions other than that of regular reflection, gives the diffuse reflecting power. The total reflecting power is obtained by considering the whole of the light reflected by the body, regular and diffuse.

In some instances, it may be of interest to measure the apparent reflection factor for an element of area and this is defined as the product of the ratio of the light emitted per unit solid angle in the direction considered to the light incident on that element of area multiplied by π . The ratio referred to, in the case of smooth or glossy surfaces viewed in directions close to that of specular reflection, may often be greater than unity.

Tables V to IX show the reflecting power of massive aluminum

and its alloys and of thin films of aluminum and its alloys. Diagram 8 illustrates the reflecting powers of three groups of aluminum alloys: the aluminum-silicon alloys, the aluminum-magnesium alloys and the aluminum-silver alloys. Table VI shows the reflecting power of aluminum subjected to various surface treatments, of which the most important are the so-called reflector processes "Alzak" and "Brytal," which depend in essence on "stabilizing" a first-formed electrolytically etched or "brightened" surface by the formation of an extremely thin, protective, transparent, surface film. Hase¹⁷⁶ has published some diagrams for the diffuse reflectivity of variously surface-treated aluminum, but since they do not contain curves for the more recently developed and much more important reflector surface-treatments, they have not been reproduced here.

In the tables, the wavelength is in all cases given in in Ångstrom units. The spectrum scale is reproduced below for reference.

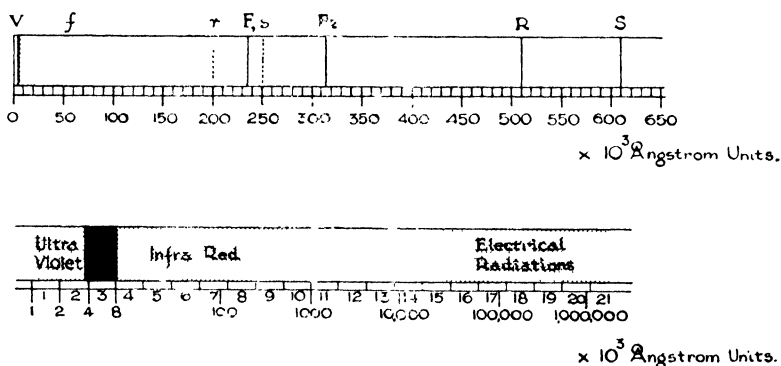


DIAGRAM 7

Spectrum Scale (From Edser)

In A the scale is graduated in Angstrom units, showing the limits of infrared radiations which have been explored up to the present. The narrow black line V to the left represents visible spectrum.

In B the scale is graduated in octaves. The black portion represents the visible spectrum (about one octave from $\lambda = 4,000 \text{ \AA}$. to $\lambda = 8,000 \text{ \AA}$. To the left are the two octaves of ultraviolet waves which have been investigated and to the right about $6\frac{1}{2}$ octaves, between which limits the infrared radiations have been studied.

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It has been noted above that the age and condition of the always-present surface oxide film on aluminum have, *inter alia*, an important influence on the reflectivity values. It should also be remarked that this influence may be selective. For instance, it has recently been pointed out by Taylor and Edwards¹⁷⁷ that, while a test-piece of aluminum foil exposed in the laboratory near a window for three years was found at the end of that time to have lost 15% reflectivity for visible light, its infrared reflection factor had in the same interval of time only fallen off from 97 to 95%, in spite of three years' accumulation of dust and fumes.

In general, it will be seen that the reflectivity values decrease with the wavelength of the reflected light.

TABLE V. *Reflecting Power of Ordinary Polished Aluminum*
(Normal Incidence)

Wavelength in Å	Percentage Reflecting Power	Reference
910,000 — 20,000	99 — 97	Waltersdorff ¹⁷⁸
250,000	100	} Coblentz ¹⁷⁹
120,000 — 10,600	87 — 73.3	
67,500	Small Maximum	
120,300	97.3	} Drude ¹⁸⁰
104,900	96.9	
93,800	97.4	
80,200	96.9	
67,500	98.2	
52,400	93.8	
39,600	91.4	
30,600	88.3	
17,100	30.8	
10,600	73.8	

TABLE V (*Continued*)

Wavelength in Å	Percentage Reflecting Power	Reference
23,000	100	Edison Pettit ¹⁸¹
22,000	96	
18,000	97	
16,000	98	
12,500	96	
10,000	93	
9,500	94	
9,000	88	
8,500	87	
8,000	85	
7,500	88	
7,000	87	
6,500 (red)	59	Hase ¹⁸²
5,400 (green)	57	
4,600 (violet)	45	
6,000	89	Williams & Sabine ¹⁸³
5,000	88	
4,500	87	
4,000	86	
3,500	85	
3,000	83	
2,500	80	
2,250	79	
5,780	78.1	Wulff ¹⁸⁴
5,460	78.0	
4,355	75.9	
4,060	71.2	
3,660	74.0	
3,340	72.2	
3,125	67.9	
2,930	66.2	
2,650	52.3	
2,537	48.2	
2,380	41.3	
5,800 — 5,000 (green)	89	Strong ¹⁸⁵
5,000 — 4,300 (blue)	87	
4,300 — 3,900 (violet)	86	
2,536	80	Luckiesh ¹⁸⁶
5,800 — 2,000	76 — 30	
4,200	68 (Small Maximum)	

THIN FILMS OF ALUMINUM AND ITS ALLOYS

TABLE V (*Continued*)

Wavelength in Å	Percentage Reflecting Power	Reference
5,500—3,000	75.50	Coblentz ¹⁷⁹
5,500	72	Landolt-Börnstein ¹⁸⁷
4,000—2,000	80—65	Nutting ¹⁸⁸
3,663	90—92	} Taylor ¹⁸⁹
2,967	86—87	
2,652	84—86	

Uljanin¹⁹⁰ gives the following figures for angles of incidence varying from 50 to 85°:

TABLE VI. *Reflecting Power of Ordinary Polished Aluminum*
(*Varying Incidence*) (After Uljanin)

Angle of Incidence	Red (7,500—6,500 Å.) g = 4.49 n = 1.48	Yellow (5,800—5,300 Å.) g = 4.00 n = 1.22	Blue (500—4,300 Å.) g = 3.77 n = 1.01
50	1.222	1.232	1.225
75	1.860	1.797	1.677
85	1.524	1.443	1.336

g = extinction coefficient
n = refractive index

TABLE VII. *Reflecting Power of Surface-treated Aluminum*
(*Normal Incidence*)

Surface Treatment	Wavelength in Å.	Percentage Reflecting Power	Reference
Etched with HF	Visible Light	87—82	} Taylor and Edwards ¹⁹¹
Etched with HF	2,967	82—81	
Etched with NaOH	Visible Light	84—82	
Electrolytically brightened	Visible Light	87	} Taylor ¹⁹²
Electrolytically brightened	2,967	84	
Electrolytically brightened	Visible Light	85	
and aluminized	2,967	69	

TABLE VII (Continued)

Wavelength in Å	Percentage Reflecting Power	Reference
"Brytal" ¹⁹¹ (a)	Visible Light	84
"Brytal" ¹⁹⁴ (b)	Visible Light	82
"Brytal" ¹⁹¹ (c)	Visible Light	77

} British
Aluminium¹⁹³

(Incidence 30° from Normal)

"Alzak" ¹⁹⁶ (a)	Corresponding 2360K	87
"Alzak" ¹⁹⁶ (d)	Corresponding 2360K	Up to 80
"Alzak" ¹⁹⁶ (e)	Corresponding 2360K	78

} N.P.L.¹⁹⁵

- (a) Superpurity aluminum, 99.99% grade
 (b) Extruded and sheet aluminum, 99.99% purity
 (c) Commercial grade aluminum, 99.0% purity
 (d) Specially rolled reflector quality aluminum
 (e) Grade "E" aluminum, 99.8%

The visible light referred to is that obtained from a tungsten lamp, color temperature approximately 2,000° K

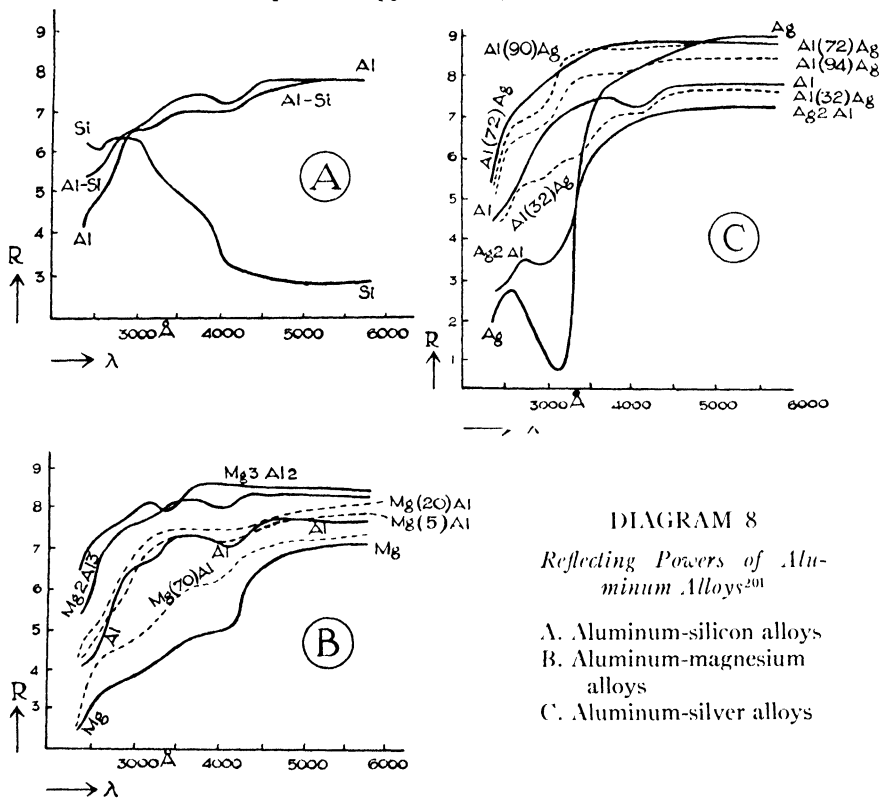


DIAGRAM 8

Reflecting Powers of Aluminum Alloys²⁰¹

- A. Aluminum-silicon alloys
 B. Aluminum-magnesium alloys
 C. Aluminum-silver alloys

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TABLE VIII. *Reflecting Power of Aluminum Alloys (Normal Incidence)*

	In Å.	Percentage Reflecting Power				Reference		
		Al (98) Si	Al (94) Si	Al (88) Si	Al (80) Si			
(i) Aluminum Silicon Alloys	5,780	77.9	77.8	73.4	64.4	Wulff ¹⁹⁷		
	5,460	78.0	78.0	73.0	60.2			
	4,355	76.7	73.8	72.0	59.0			
	4,060	72.4	70.3	70.1	60.5			
	3,660	72.3	70.2	68.2	60.1			
	3,340	72.7	69.3	64.7	62.3			
	3,125	70.0	66.0	64.5	59.6			
	2,930	66.5	66.2	64.3	58.7			
	2,650	58.6	59.8	60.0	58.9			
	2,537	52.4	56.0	56.1	58.4			
2,350	48.2	54.1	56.2	56.8				
(ii) Aluminum- Magnesium Alloys		Mg(70)Al	Mg ₃ Al ₂	Mg ₂ Al ₃	Mg(20)Al	Ng(5)Al	Wulff ¹⁹⁷	
	5,780	76.6	85.1	84.5	82.5	78.9		
	5,460	74.0	85.1	84.4	82.7	78.8		
	4,355	69.9	85.0	84.3	77.6	75.4		
	3,660	63.5	86.6	81.0	74.0	72.5		
	3,340	55.3	80.5	81.8	74.3	72.7		
	3,125	52.5	82.6	78.1	72.7	68.9		
	2,970	48.0	80.4	76.7	68.6	66.8		
	2,650	44.4	74.0	72.4	54.7	53.2		
	2,537	41.3	72.3	64.6	52.1	49.7		
	2,350	28.6	64.2	52.0	43.3	42.0		
		Mg (54) Al	Mg (31) Al		Mg (15) Al		Walten- berg and Coblentz ¹⁹⁸	
	7,000	92	86		73			
	5,000	81	87		74			
		Magnalium — Al (69) Mg (31)						Johnson ¹⁹⁹
	3,285	77						
	3,065	69						
	2,816	67						
	2,628	65						
	2,367	61						
	2,263	60						
	2,144	59						
	1,990	56						
	1,936	54						
	1,863	53						

TABLE VIII. (*continued*)

		Percentage Reflecting Power					Reference
		In Å	Al (94) Ag	Al (90) Ag	Al (72) Ag	Al (32) Ag	Ag ₂ Al
(iii) Aluminum-Silver Alloys	5,780	83.8	87.5	88.0	76.0	71.9	} Wulff ¹⁹⁷
	5,460	84.0	88.0	88.2	75.9	72.0	
	4,355	84.2	87.3	88.0	74.0	71.1	
	4,060	82.3	87.0	87.8	70.2	69.2	
	3,660	80.1	87.1	86.9	68.0	64.8	
	3,340	79.2	76.0	85.0	60.1	50.1	
	3,125	72.8	80.3	82.1	57.8	36.2	
	2,970	68.1	72.0	78.6	54.9	32.7	
	2,650	65.0	68.3	71.9	52.1	33.8	
	2,537	62.7	65.4	68.2	48.2	30.1	
	2,350	49.2	49.8	53.0	41.8	25.9	
(iv) Aluminum-Zinc Alloys		Zn (78) Al					} Walten- berg and Coblentz ¹⁹⁸
	7,000	70					
	5,000	74					
(v) “Political”		(Si 1.1, Mg 0.75, Mn 0.42, Ni 0.14)					} Hase ²⁰⁰
	6,500	70					
	5,400	68					
	4,600	66					

The Reflectivity of Thin Aluminum Films for X-rays (0.06 to 20 Å.). The reflectivity of aluminum mirrors for X-rays has been investigated by several workers.²⁰⁵ Valouch²⁰⁶ showed that the reflectivity rapidly decreases as the angle of incidence of the X-rays increases.

The Reflectivity of Thin Aluminum Films in the Ultraviolet. Banning²⁰⁷ compared reflectivities of thin, evaporated films of aluminum and copper between 1,000 and 2,000 Å. and showed the great influence of the atmosphere in which the films were examined. When a few millimetres of hydrogen or carbon monoxide were admitted into the vacuum chamber, there was a marked increase of the direct reflectivity in the ultraviolet, measured by

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a spectrometric method, as compared with that of films exposed to air. The thickness of the films did not appear to affect the reflectivity appreciably unless the films were very transparent.

TABLE IX. *Reflecting Power of Cathodically Sputtered Aluminum Films (Normal Incidence)*

Wavelength in Å.	Percentage Reflecting Power	Source
3,900 — 1,900	70 — 20	} Hulbert ²⁰² } Gleason ²⁰³
1,850 — 1,400	14 — 5	
1,400 — 485	5	
3,610	84	} Johnson ²⁰⁴
3,404	83	
3,216	91	
2,981	90	
2,749	90	
2,573	89	
2,313	91	
2,265	86	
2,196	86	
2,144	84	
1,990	87	
1,936	87	
1,863	70	

TABLE X. *Reflecting Power of Cathodically Sputtered Film of Magnesium-Aluminum Alloy (Mg Content Unknown)*

Wavelength in Å.	Percentage Reflecting Power	Source
Visible Light	95	} Taylor ²⁰⁸
2,967	87	

The Refractive Index of Aluminum. The refractive index, which is the ratio of the velocity of light in the medium under consideration compared with its velocity in air under the same conditions, is measured by the ratio of the sine of the incident angle to the sine of the angle of refraction.

The following values are published in the literature for the refractive index of massive aluminum:

TABLE XI. *Refractive Index of Massive Aluminum for Various Wavelengths*

Wavelength in Å.	Refractive Index	Reference
5,500	1.2	Landholt-Börnstein ²⁰⁹
4,310	0.78	} Quincke ²¹⁰
4,860	0.93	
5,270	1.10	
5,890	1.28	
6,570	1.48	
5,890	1.44	Littleton ²¹¹

The Absorption Index of Aluminum. By definition,²¹² the absorption index, or absorption factor, of a body is the ratio of the light absorbed by it to the incident light.

The following values are found in the literature for the absorption index of aluminum:

TABLE XII. *Absorption Index of Massive Aluminum for Various Wavelengths*

Wavelength in Å	Absorption Index	Reference
5,500	3.5	Landholt-Börnstein ²⁰⁹
4,310	2.85	} Quincke ²¹⁰
4,860	3.15	
5,270	3.39	
5,890	3.66	
6,570	3.92	
5,890	3.64	Littleton ²¹¹

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TABLE XIII. *Absorption Index of Thin Films of Aluminum*

Wavelength in Å.	Molar Absorption Index	Reference
1,860--7,000	7.5--4.5	Smakula ²¹³

The Transmission Factor of Aluminum. The following values have been given by Hartzler²¹⁴ for the transmission factor of thin films of aluminum:

TABLE XIV. *Transmission Factors of Thin Films of Aluminum*

Wavelength in Å.	Film Thickness in Å.					
	190	210	280	370	460	940
4,300	31	26	15	18	1.3	0.3
3,100	37	21	14	11	1.1	0.2
2,000	42	24	19	8.2	1.2	—
1,608	35	15	12	2.6	—	—

The Emissivity of Aluminum. The emissivity of aluminum is largely dependent on its surface condition; in general, non-metallic substances exhibit high emissivity properties and aluminum oxide is no exception. The natural oxide film is too thin to have an appreciable effect upon emissivity, but thick oxide coatings produced, for example, electrolytically substantially increase the emissivity. Taylor and Edwards²¹⁵ have examined the relationship between the emissivity and the thickness of the oxide film produced by anodic oxidation in sulfuric acid and have shown that the emissivity increases linearly with thickness up to a critical thickness of the order of 8×10^{-5} in. At the same time, they state that surface roughening does not necessarily produce a surface of high emissivity and that a bright-polished surface is not an inherent requisite for low emissivity. Samples of alumi-

num foil used for thermal insulation under varying service conditions were found to have an average emissivity of 5.4% after five years, as compared with 4.5% for new foil. The figure for commercial foil is given by these authors as in the region of 3%.

Moeller and Miething²¹⁶ measured the emissivity of a freshly molten aluminum surface exposed to air and found it to lie between 0.12 and 0.17 for wavelength of $0.65\ \mu$., at temperatures between 700 and 1,000°. Hase²¹⁷ examined the emissivity in relationship to the surface condition, temperature (range 300 to 600°), wavelength (between 1 and $9\ \mu$.) and angle of emission. He found that polished pure aluminum showed emissivity about the wavelength 3μ . practically independent of temperature.

Hagen and Rubens²¹⁸ compared the observed value of the emissivity for long wavelengths ($\lambda = 25.5\mu$., in the heat ray part of the spectrum), which they found to be 1.97 at 170°, with that derived by calculation from the electrical conductivity, which was calculated as 1.60.

The Electrical Properties of Thin Films of Aluminum. The electrical properties of thin films of aluminum have been investigated by a few workers²²³.

Woltersdorff²²⁴ gives the following values for the specific electric resistance of aluminum films of varying thickness.

The Photoelectric Properties of Aluminum. The threshold value for the photoelectric behavior of aluminum varies enormously with the surface condition of the metal, depending essentially upon its gas content and previous history. The photoelectric effect is strongly selective, according to different workers. Compton²²⁷ found a maximum at $220\ m\mu$., while Pohl²²⁸ puts it at $260\ m\mu$., and Wright^{228a} at $2166\ \text{\AA}$. Reboul²²⁹ showed that if the ultraviolet light was filtered first through a thin film of silver^{228a}, the photoeffect on aluminum was diminished to about one twenty-second of its original value.

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TABLE XV. *Optical Reflectivity of Various Metals for Normal Incidence Percentage Reflection Factors*

Massive Metal	Thin Film of Metal	Wave Length						$\lambda =$ 2967	Reference
		0.5 μ .	1.0 μ .	4.0 μ .	9.0 μ .	10.0 μ .	Visi- ble		
Antimony	---	---	55	68	72	---	---	---	Coblentz ²¹⁹
Cadmium	---	---	72	96	---	98	---	---	Coblentz ²¹⁹
Cadmium (sprayed)	---	---	---	---	---	---	52	25	Taylor ²²⁰
Chromium Steel (satin)	---	---	---	---	---	---	56	---	Taylor ²²⁰
Chromium Steel (satin) (polished)	---	---	---	---	---	---	62	---	Taylor ²²⁰
Chromium (plate)	---	---	---	---	---	---	62-66	43-58	Taylor ²²⁰
Cobalt	---	---	67	81	---	97	---	---	Coblentz ²¹⁹
Copper	---	44	90	97	98.4	---	---	---	Coblentz ²¹⁹
Gold (plate)	---	47	---	97	98	---	---	---	Coblentz ²¹⁹
Iridium	---	---	78	94	---	96	---	---	Coblentz ²¹⁹
Iron	---	55	65	89	94	---	---	---	Coblentz ²¹⁹
Magnesium	---	72	74	83	93	---	---	---	Coblentz ²¹⁹
Molybdenum	---	46	58	90	---	94	---	---	Coblentz ²¹⁹
Molybdenum	---	55	---	---	---	---	---	---	Summers ^{†221}
Molybdenum	Sputtered in air	31	---	---	---	---	---	---	Summers ^{†221}
Molybdenum	Sputtered in H ₂	20	---	---	---	---	---	---	Summers ^{†221}
Nickel (plate)	---	61	72	91	96	---	---	---	Coblentz ²¹⁹
Nickel (plate)	---	---	---	---	---	---	60-63	29-34	Taylor ²²⁰
Palladium	---	---	72	88	---	97	---	---	Coblentz ²¹⁹
Platinum (plate)	---	58	73	92	95	---	---	---	Coblentz ²¹⁹
Rhodium	---	---	---	---	---	---	70-78	45	Taylor ²²⁰
Rhodium	---	76	84	92	---	95	---	---	Coblentz ²¹⁹
Silicon	---	34	28	28	---	28	---	---	Coblentz ²¹⁹
Silver	(Chemical Re-duction)	91	97	98.5	98.7	---	---	---	Coblentz ²¹⁹
Silver (plate)	---	---	---	---	---	---	90	13	Taylor ²²⁰
Stainless Steel	---	---	---	---	---	---	65	30	Taylor ²²⁰
Tantalum	---	38	78	93	---	---	---	---	Coblentz ²¹⁹
Tellurium	---	---	50	57	---	---	---	---	Coblentz ²¹⁹
Tin††	---	---	54	72	---	84	---	---	Coblentz ²¹⁹
Tungsten	---	49	50	90	---	95	---	---	Coblentz ²¹⁹
Vanadium	---	57	61	79	---	---	---	---	Coblentz ²¹⁹
Zinc	---	---	80	97	---	98	---	---	Coblentz ²¹⁹

†Incident light between 45° and 70°. ††Woltersdorff²²² gives 95-99% between 2 and 20 μ .

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TABLE XVI. *Specific Electrical Resistance of Aluminum Films*

Thickness in Å.	Specific Electrical Resistance in ohms/cm. $\times 10^{-4}$
40	0.2 — 1.0
50	0.2 — 0.6
60	0.2
70	0.1 — 1.5
80	0.2 — 0.4
90	0.08
100	0.08 — 0.7
Compact Aluminum	0.027

TABLE XVII. *Electrical Properties of Thin Films of Various Metals*

PLATINUM ^{225*}		
Time Minutes	Resistance Ohms	Film Thickness* 1.10^{-8} cm.
20	2.35	1440
5	8.9	360
3	24.5	216
2	50.0	144
1.5	70.0	108
1.0	130.0	72
0.75	226	54
0.5	381	36
0.25	650000	18
IRIDIUM ²²⁵		
Time Minutes	Resistance Ohms	Film Thickness* 1.10^{-8} cm.
3	40	39.8
2	60	26.8
1.5	79	19.9
1.0	130	13.2
0.75	185	9.95
0.5	449	6.6
0.33	1996	4.36

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TABLE XVII (*continued*)

RHODIUM ²²⁵		
Time Minutes	Resistance Ohms	Film Thickness* 1.10 ⁻⁸ cm.
10	5	468
5	32	234
3	84	141
2	130	94
1.5	260	70
1.0	335	46.8
0.75	540	35.2
0.5	2500	23.4
0.33	1000	15.6
NICKEL ²²⁶		
Time Minutes	Specific Surface Resistance Ohm ⁻¹	Thickness mμ.
20	0.155	31.4
6.5	0.030	10.3
2	0.00022	3.2
1	10 ⁻¹⁰	1.6

* Calculated

A number of different research workers²³⁰ have investigated the effect of photoelectric "fatigue" which occurs with aluminum surfaces, due to adsorption of oxygen.

Reboul²²⁹ showed that submicroscopic particles of aluminum exposed to ultraviolet rays in a hydrogen or nitrogen atmosphere are partly positively and partly negatively charged, giving rise to normal or inverse photoeffects. In nitrogen, the inverse effect predominated.

Chapter VII

SOME APPLICATIONS OF THE PROPERTIES OF ALUMINUM FILMS AND SURFACES

Applications of the Optical Properties of Aluminum Films

Aluminum-surfaced Astronomical Mirrors. As will be seen in the section on the optical properties of aluminum, this metal has valuable properties for astronomical mirrors.²³¹ For visible light, its reflectivity is almost as high as that of silver, while for ultra-violet light its reflectivity is higher. Silver rapidly loses its high reflectivity due to tarnishing, while aluminized mirrors do not tarnish; neither do they scratch easily, which makes it possible to simplify their preservation in good condition, since they may be readily cleaned of dust, oil, fingerprints, etc., by simply washing with soap and water.

Another advantage of aluminized mirrors, as compared with silvered mirrors for telescopic observation, is that aluminum films do not scatter light, so that fainter objects may be photographed than with silvered mirrors. Photographically, there is a gain in speed and sensitiveness for practically all spectral classes, and the visual loss is very small. In comparing results observed by means of aluminum mirrors with those obtained from silvered mirrors, a color index correction must be applied, since stars appear bluer through a telescope provided with an aluminized mirror than in an ordinary silvered mirror telescope.

The ideal mirror is required to possess, in addition to high reflecting power and freedom from tarnishing, a low coefficient of

expansion, high conductivity for heat, absence of warping or distortion with age, great rigidity and comparative lightness. Spencer-Jones²³² has pointed out that if an alloy of aluminum with high rigidity, low coefficient of expansion and permanence of form could be developed, it would be of the greatest importance to astronomy.

Not much work has yet been done in investigating the effect of such factors as the thickness, purity and age of the reflecting film on aluminum mirrors. Most of the research in this connection has been carried out on silver. The thickness of the mirror film is, of course, a matter of technical control and is considered in the section on the production methods. The film should not be too thin, in order to avoid scattering of light. Rama Swamy²³³ showed that extremely thin films of aluminum do not exhibit metallic reflection at all, their depolarizing effect being quite anomalous.

The degree of polish of the completed mirror is the same as that of the underlying glass surface.

The purity of the film is very largely dependent on the production method. Impurities in the form of minute quantities of gases, adsorbed by or in some other way loosely bound with the deposited metal, may seriously diminish the reflectivity. Lausch²³⁴ showed in the case of silver mirrors that the reflectivity fell off by more than 40% if the mirror was produced in air instead of in hydrogen. Similarly, impurities may change the absorption index. In the case of silvered mirrors, chemical treatment with nitric or hydrochloric acids, oxygen or hydrogen peroxide has been found by Ritsch²³⁵ to improve the reflectivity, presumably because of increasing the purity of the surface.

No information is available regarding the effect of etching or other surface treatment on aluminum-surfaced mirrors, but experience with such mirrors seems to point to the fact, already referred to, that the thin films of aluminum deposited for mirrors

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do not oxidize normally and are of remarkable chemical purity and stability. Concentrated nitric acid does not attack the aluminum mirror film, but it is dissolved by dilute hydrochloric acid in the presence of copper impurity. Caustics dissolve the aluminum rapidly, Canada balsam dissolves it slowly, so that half-reflecting films should not be cemented with this material. The age of an aluminum mirror is, therefore, of less importance than is the case with silver from the point of view of chemical stability. The effects of grain growth, which produces qualitative degradation in some mirrors, have not been investigated in the case of aluminum mirrors.

Aluminum mirrors do not require frequent burnishing, although they may be reburnished after a year's use if necessary.

Aluminum-Coated Speculum Gratings. Aluminization improves the reflectivity of speculum metal gratings by about 50% for visible light and much more in the ultraviolet. No definition is lost in the finer details of the spectrum. When the films are thin (less than 4,000 Å.), and if the grooves are shallow, the spectrum formed by an aluminized grating, when viewed without a lens, appears to be crossed by light and dark bands. These do not appear in ordinary gratings and only appear in high orders with shallow rulings for films of thickness greater than 4,000 Å.

A further advantage is that the aluminum coating on the speculum grating can be removed by a suitable solvent (KOH) without attacking the speculum: so that the usefulness of the bare speculum grating is not sacrificed.

Reflectors. Aluminum is at the present time one of the most important reflector metals and has extensive use as such for the reflectors of gas and electric heating appliances, for infrared driers, for scientific apparatus, and for all the range of optical reflectors from searchlight down to flash light. A full discussion of this application leads into the field of surface treatment of aluminum

and cannot be entered into here. However, it is noted that the high reflectivity of aluminum is in the first place rendered maximum by some form of electrolytic "brightening" or etching and then given permanency by coating the brightened surface with an extremely thin transparent film of oxide.

Applications of the Electrical Properties of Aluminum Films

Apart from the use of aluminum for rectifiers, which depends on the valve action of the oxide film on aluminum (usually artificially reinforced), the main application of thin films of aluminum in respect of their electrical properties is for obtaining contact or for electrostatic shielding. It is not unusual to deposit a very thin film of aluminum on a glass surface in order to make contact to vacuum condensed substances obtained in high vacuum or to control the electric field configuration, etc.²³⁶

Barium-aluminum alloys have been found valuable for the activation of cathodes in discharge tubes.²³⁷

An interesting suggestion has been made in connection with the construction of heating screens.²³⁸ A continuous thin strand of aluminum is deposited on heat-resisting glass in any phantasy design (usually by means of a spray-pistol) and an electric current is passed through.

Applications of the Chemical Properties of Thin Films and Surfaces of Aluminum and its Alloys

The chemical properties of thin aluminum films and aluminum surfaces depend on the catalytic activity of aluminum.

An important application lies in the use of aluminum-barium and aluminum-strontium alloys which are deposited as thin films on the walls of getters and of amplifier tubes, etc., to remove any residual gases.

Aluminum is used as a catalyst in a number of chemical syntheses and reactions. British Celanese²³⁹ has patented its use as

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a catalyst in the esterification of the hydroxyl groups of acetic acid esters and of polyhydric alcohols with resin acids, for example. An aluminum alloy containing a small addition of nickel has been found extremely effective as a catalyst for the hydrogenation of oils, according to some Soviet research workers.²⁴⁰ Its special merit is that it appears to be practically insensitive to the action of "poisons" such as hydrogen sulfide which upset certain catalysts.

The use of extremely thin films of aluminum for the prevention of tarnish on silver and silver-plated ware has been referred to in the opening chapter of this monograph, and attention has also been drawn to the possibility of substituting sputtered films of aluminum or its alloys for nickel or zinc electrodeposits.²⁴¹

Non-tarnishing films of aluminum may predominate in the gilding and silvering of fabrics and organic materials.

APPENDIX

*Evaporation to a Plane Surface — Distribution of the Film Thickness*²⁴²

(a) Single Point Source:

In the case of evaporation to the inside surface of a sphere of radius ρ from a point source of vapor at its center, a uniform film of thickness τ_0 is obtained where:

$$\tau_0 = \frac{m}{4\pi\delta\rho^2}$$

in which m = mass of metal evaporated and δ = density of metal evaporated.

The film thickness on a plane surface at the normal distance from a point source at P is:

$$\tau_P = \frac{m}{4\pi\delta r^2} \cos \theta = \tau_0 \left(\frac{\rho}{r} \right)^3$$

Here τ_0 is the thickness at distance ρ , r is the distance from the source to P and θ is the inclination of the surface at P to the molecular rays emitted by the source.

(b) Multiple Point Sources:

The film thickness produced on a plane surface by a circular array of vapor sources was studied. If there are N coils spaced uniformly around a circle at a distance r from the surface to be coated, the film thickness at P, which is at a distance a from the intersection of the axis of the circle with the face of the mirror, is given by the expression:

$$\tau_P = \frac{M\rho}{4\pi\delta N} \sum_{i=1}^N \frac{1}{r^3}$$

where M = total mass of metal evaporated and r = distance from ρ to the respective i th coil.

(c) **Continuous Circular Source:**

Dr. E. M. Thorndike has made the same calculation assuming a continuous circular source. The thickness is given in this case by: \

$$\pi_{\rho} = \frac{M \rho}{8\pi^2 \hat{o}} \int_0^{2\pi} \frac{d\theta}{r^3}$$

This involves the integration of the expression:

$$\begin{aligned} \int_0^{2\pi} \frac{d\theta}{r^3} &= \int_0^{2\pi} \frac{d\theta}{(1 + a^2 + \rho^2 - 2a \cos \theta)^{\frac{3}{2}}} \\ &= \frac{4}{[(a-1)^2 + \rho^2] \sqrt{(a+1)^2 + \rho^2}} E \frac{2\sqrt{a}}{\sqrt{(a+1)^2 + \rho^2}} \end{aligned}$$

θ defines the position of the element $d\theta$ of the circular source involved in the integration. Some values of this integral, calculated by Thorndike, are given in the following table:

a	$\rho = 0.5$	$\rho = 1.0$	$\rho = 1.1$	$\rho = 1.2$	$\rho = 2.0$	$\rho = 4.0$
0.00	4.500	2.220	1.910	1.650	0.560	0.090
0.50	3.960	2.290	1.930	1.630	0.540	0.088
1.00	8.280	2.110	1.740	1.450	0.480	0.082
2.00	1.200	0.740	0.760	0.610	0.285	0.068
3.00	0.280	0.240	0.230	0.220	0.145	0.050

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