RECENT PROGRESS IN THE NATURAL PROTECTION OF METALS

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INTRODUCTION

Metals have many "enemies" that work toward their destruction. When not carefully protected, they are continually "eaten" by these assailants and are rapidly transformed into other substances, such as rust on iron and tarnish films on copper and silver. Lacquers, paints and varnishes are some means of providing *artificial protection* for metals, whereas certain solid films (particularly oxide films) provide much *natural protection* for them.

The natural protection afforded by oxide films formed on the surface of stainless steel and some other metals has led to a rapidly increasing amount of interest in the films. The publications listed by the author [1] give references to the studies of these films, carried out in several countries and based on optical measurements, determination of corrosion probability, electron diffraction patterns, and film-stripping, photo-electric, polarimetric, spectrophotometric, chemical, electrochemical, gravimetric, electrical resistance, and electrolytic reduction methods. Space here will not permit a complete discussion of many valuable researches which have contributed to the present knowledge of the structure, composition, thickness, laws of growth, chemical and physical properties, and protective qualities of the surface films. Some contributions influencing the recent advancements in natural protection will be reviewed, with special emphasis given to some of the work with which the author has been associated in Oklahoma. [2,3,4]

A THEORY OF DRY CORROSION

In the oxidation of metals it was formerly considered that oxygen atoms pass through the oxide film to react with the metal. Pfeil [5] has shown that at high temperatures excess iron atoms pass through the oxide layer to react with the oxygen and that both oxygen and metal atoms move in the diffusion process. Wagner [6], in his theory of oxidation and tarnishing, considers that (1) cations from the base metal diffuse outwards across the film, (2) electrons diffuse outwards, and (3) anions diffuse inwards. He believes that the cations move more than the anions in most cases, even at lower temperatures. It is generally agreed that both theories lead to the same parabolic law for the growth of films on common metals.

Hoar and Price [7] have given a simplified electrochemical derivation of Wagner's fundamental tarnishing equations. When the tarnish film has a constant specific electrical conductivity the tarnish equation is

$$dZ/dt = K/y \quad\dots\dots\dots\dots\dots\text{(a)}$$

where
$$K = (n_1 + n_2)\ n_2 sE/F \dots\dots\dots\dots\text{(b)}$$

Z being the amount of tarnish product in equivalents per sq. cm. per second, t the time in seconds, y the thickness of the film in cm., n_1, n_2 and

n, being the transport numbers of the cations, anions and electrons respectively, s the specific electrical conductivity of the film, E the E.M.F. in volts, equivalent to the affinity of the reaction between the cations and anions, and F the faraday. By expressing y in terms of Z and integrating equation (a) a parabolic equation of film thickening is obtained.

When the specific electrical conductivity of the film substance varies with the pressure of the attacking gas the tarnishing equation is naturally more complicated.[7] According to Wagner's classification of film substances, the rate of formation of cuprous oxide should be dependent upon the gas pressure. Cruzan and the author's experiments[3] on the formation of cuprous-cupric oxides showed that the rate of growth of cuprous oxide films was influenced very much by the oxygen pressure.

Price[6] stated that Wagoner has given to the subject of dry corrosion a scientific basis equivalent to that given to wet corrosion by Evans[8] in his papers showing that wet corrosion is electrochemical in nature. The reactions in dry corrosion resulting from attacks of oxygen, hydrogen sulphide, and other gases on metals to form solid surface films are also considered to be electrochemical in nature. The whole tarnish system is regarded as a current-producing cell with the metal and the attacking gas acting as the two electrodes, the film acting as the electrolyte owing to its ionic conductivity and also as the external circuit owing to its electronic conductivity, and with the E.M.F. of the cell supplied by the affinity of the reaction.

PROTECTION THROUGH SELECTIVE OXIDATION AND CATHODIC DEPOSITION

Price and Thomas[9] have greatly extended Wagner's theory of tarnishing, and explained why some oxides have high protective effects against oxidation or tarnishing while others give little protection. The theory thus developed predicts that a protective oxide should have a high electrical resistance, e. g., alumina, beryllia and silica. The alloying constituent added to the metal to be protected should have a sufficient affinity for oxygen. The radii of the cations in the protective oxide film should be smaller than those of the ions of the metal to be protected, and the protective oxide must not be one that is deficient in cations.

Traces of silver oxide in beryllia or alumina films reduce the electrical resistance and hence the tarnish resistance, and highly protective films cannot be formed on silver alloys by heating them in air. Accordingly, Price and Thomas[9] have developed two practical methods of forming pure films of alumina or beryllia on silver:

(1) Selective oxidation of silver alloys, containing 1% aluminum or beryllium, by heating in hydrogen containing 0.1 mm. partial pressure of water vapor.

(2) Cathodic deposition of a uniform film of alumina or beryllia on the silver to be protected.

Both of these methods have produced films giving marked protection and reproducible results.

Price and Thomas[9] have also applied this selective oxidation principle to the oxidation of copper alloys. By heating copper containing 5% aluminum at 800° C. for 15 minutes in a hydrogen atmosphere with 0.1 mm. partial pressure of water vapor, continuous films of pure alumina were formed on the surface which resulted in greatly increased resistance to further oxidation an in ordinary atmosphere or to tarnishing in moist ammonium sulphide gas in air. They anticipate that this selective oxidation principle, which provides the conditions favorable to the oxidation of only the baser element of the alloy, will be applicable to other

alloys, such as those of iron and nickel, where there is need of improved oxidation resistance. The tarnishing of copper was almost completely prevented by cathodic deposition of a beryllia film on the surface. Price and Thomas predict that the applications of these methods to copper may be of greater importance industrially than that to silver.

TARNISH FILMS ON COPPER

On the basis of these theories of dry corrosion Dyess and the author [2] have discussed the tarnishing of copper by moist hydrogen sulphide gas in air. Thicknesses of tarnish films on copper, consisting of various mixtures of cuprous oxide, cupric oxide and cuprous sulphide, were measured by the electrolytic reduction method [1]. The oxide parts of the films were prepared by heating the specimens in an electric furnace and the sulphide components were obtained by exposing the specimens to moist hydrogen sulphide gas in air under controlled conditions. Such complex films were found to have approximately the same thickness values as oxide films of the same colors and orders.

Copper abraded in air at ordinary temperatures oxidizes rapidly until a protective film is formed after the oxidation by diffusion through the film is very slow. An average thickness value of 80 Å (Angstroms) was measured on coarsely abraded specimens exposed to air for one day.

When oxide-coated copper was exposed to moist hydrogen sulphide in air, cuprous sulphide was formed (1) by combining some sulphur with copper from the base metal, and (2) by replacing some oxygen from the oxides. No evidence was obtained of the replacement of sulphur by oxygen, even when the sulphide-coated specimens were subjected to oxidation treatment in an electric furnace.

Oxide films within the thickness range 125 to 275 Å gave markedly greater protection against severe attacks of moist hydrogen sulphide in air than did thinner films containing pores and thicker ones with cracks. The film affording maximum protection was about 200 Å thick.

CUPROUS-CUPRIC OXIDE FILMS ON COPPER

Since the electrolytic reduction method had been adapted[10] to the measurement of the respective amounts of each oxide in cuprous-cupric oxide films, Cruzan and the author [3] employed it in the study of the influence of film thickness on the formation of cupric oxide in cuprous oxide films on an abraded copper surface. When diffusion through cuprous oxide films becomes sufficiently difficult some cupric oxide is developed in the films, presumably through the oxidation of cuprous oxide. In this way the composition of the oxide films on copper is determined largely by the thickness of the films, those of thickness values below a critical thickness range being of the cuprous oxide composition, and those of values within the range being of either the cuprous or the cuprous-cupric oxide composition while those of values above the critical thickness range are always of the cuprous-cupric oxide composition. The critical thickness range found in the present work was approximately 400 to 800 Å of cuprous oxide. The thickness of a film is a function of the temperature at which it is formed, the oxygen concentration, the period of time during which it is heated, and any factor that may alter the perviousness of the film such as the nature of the material, purity of the atmosphere in which it is developed and treatment of the surface. The presence of any cupric oxide nuclei, due to previous heat treatment in the manufacture of the metal or otherwise, might cause the secondary reaction to start more readily and thus affect the location of the critical thickness range. Ac-

cordingly, the critical thickness range for one material and set of conditions is not expected to duplicate that of another. Hence the critical thickness range for the formation of cupric oxide in cuprous oxide films on a given copper material is determined directly by the thickness of the films and indirectly by all of the factors that affect the thickness.

Murison's electron diffraction observations [11] concerning the conditions favorable to the formation of cupric oxide in the films at a higher temperature were extended to include the proper period of heating and film thickness as well as oxygen concentration. The thicknesses resulting from heating specimens in different atmospheres, for a given time, varied directly with the oxygen concentration. The time required to produce films of a given thickness varied inversely with the oxygen concentration (within the pressure range studied). Dunholter and Kersten's electron diffraction analyses [12] of copper oxide films on mirror-like surfaces were considered to be in satisfactory agreement with the present results.

A NEW METHOD OF DEVELOPING CUPROUS OXIDE FILMS ON COPPER

The general practice has been to form the oxide films on copper by heating the specimens in air or oxygen. Although a considerable measure of protection against tarnishing and other forms of corrosion is afforded by relatively thin cuprous oxide films, *three* serious difficulties have been encountered in attempts to develop thick homogeneous and continuous cuprous oxide films by this method of direct union of oxygen with the base metal. (1) When bare copper metal is exposed to air at elevated temperatures the oxidation reaction proceeds rapidly at first but continues to decrease as the film thickens, leading normally to a parabolic relationship between film thickness and time. After an appreciable time the film thickens very slowly, unless the temperature is continually raised and this may introduce further difficulties due to differences in the thermal expansions of the oxide and the metal base. (2) It has not been possible by the former method to prepare relatively thick films of cuprous oxide free from cupric oxide, as was discussed above. Hence it has been impossible to determine the properties of thick cuprous oxide films on copper. (3) The density of cuprous oxide is so much less than that of copper that the volume of the oxide is about 1.7 times the volume of the metal used in its formation. This demand for extra space, when the oxygen and metal reactants meet beneath or within the film, results in great stresses that crack the film after a limiting thickness is reached. These cracks in the films destroy much of the protective quality of the thicker films. The new method of developing cuprous oxide films on copper should avoid these difficulties, since there is (1) no diffusion through the film, (2) no cupric oxide formed, and (3) no cracking of the film resulting from lack of space.

It is well known that Fehling's solution is extensively used in the quantitative analysis for dextrose and other reducing sugars. When this solution is boiled with dextrose, cuprous oxide is precipitated. With this information in mind, Reed and the author [4] started the present work with the idea that it might be possible to limit the reducing reactions to the layer of the liquid adjacent to the metal-liquid interface and provide the conditions favorable to the deposition of cuprous oxide onto the copper rather than in the body of the solution. It was considered that the possibility of getting the deposition process to start would be increased by the presence of the invisible air-formed cuprous oxide already on the copper surfaces. Some reducing solution was placed on horizontal specimens and heat applied from beneath the specimens, thus heating the solution in immediate contact with the upper surfaces of the specimens

enough to provide the conditions required for the building of homogeneous films of cuprous oxide. Films conferring five orders of beautiful interference colors have been obtained, over limited areas, by this method. There seems to be no reason to set an upper limit to the thickness that might be attained, since the copper specimens serve merely as supports for the cuprous oxide films formed by deposition of the oxide from the external chemical reactions. For the extension of this localized heating principle to immersed specimens a high frequency induction furnace might serve well unless the low electrical resistivity of copper should introduce difficulties.

For industrial applications these films should be produced over large areas. A catalyst is being sought that will make the reduction reactions proceed at a temperature well below that at which cuprous oxide is precipitated appreciably in the body of the liquid. An encouraging measure of success has been attained. Beautifully colored films are being prepared on immersed specimens at room temperature, but still better conditions for control and reproducibility are desired. Full details of this work will be reported later.

FURTHER MEASUREMENTS AND STUDIES OF OXIDE FILMS

Evans [13] has developed a new method for the transfer of protective oxide films from heat-tinted iron and nickel to celluloid or fabric. The outside surface of the film is cemented to the support and the metal base is separated from the film by anodic dissolution. An optical investigation of oxide films on metals has been made by Leberknight and Lustman [14]. Campbell and Thomas [15] have adapted the electrolytic reduction method [10] to the accurate measurement of cuprous oxide films of atomic dimensions. An ever increasing amount of valuable work on surface films is being done by Vernon [16] and some of his associates. Their extensive studies of the oxidation of iron and zinc have contributed much to the existing knowledge of surface reactions and films.

CONCLUDING REMARKS

Although some differences are yet to be explained, it is gratifying to note that all of the major discrepancies that existed in earlier work have been eliminated. There are many factors that affect the corrosion of metals. The atmospheric impurities, as well as the nature of the protective coating, greatly influence the amount of corrosion of a given material. Steel works placed in the Italian Alps during the World War, that are well preserved in that relatively pure atmosphere, became corroded quickly when removed to the moist and corrosive-laden atmosphere of London. A few years ago, [17] it was estimated that the loss to the world each year through the corrosion of ferrous metals alone was about three and a half billion dollars, nearly as much as was being spent for armaments at that time. Although much progress has been made in the protection of metals by both the artificial and natural processes the loss through corrosion may have increased due to the enormous increase in the uses of metals. Much more research should be directed toward this ever increasing field of importance, the extent of which may be judged from Evans' book [18] that summarizes and evaluates the work of more than seventeen hundred authors.

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