synthesis. Hydrogen does not seem to help the synthesis of dihydropentaborane.

The choice of a circulating or single pass system for making pentaborane depends mostly upon how much diborane is available for the job. If relatively small quantities are on hand, a circulating gas system will utilize the material most efficiently. On the other hand, if diborane is considered expendable, a single pass system is so much easier to build that this method will be preferable.

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[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

Low Temperature Oxidation of Copper. II. Reaction Rate Anisotropy[1]

BY T. N. RHODIN, JR.[2]

The oxidation rate of single crystal copper surfaces exposed to pure oxygen at low temperatures from 78 to 323°K. has been observed to be highest for the least densely packed (100) face and smallest for the most densely packed (111) face. The rate anisotropy is adequately described by the mathematical treatment of Mott and Cabrera although the physical significance of their assumptions is ambiguous. The reaction rate anisotropy was also shown to be consistent with the theoretical requirements of Frank and Van der Merwe for the existence of oriented overgrowths. According to their model, pseudomorphic oxide structures may account for the oxidation rate anisotropy.

Introduction

There are at least two important aspects to the manner in which reaction potentials on a given metal surface are affected by surface structure in the formation of protective oxide films.

First, the chemical activity of the metal surface is dependent on the atomic spacing and geometry of the surface atoms. Second, the mechanical properties of very thin oxide films that form in the initial stages of attack, such as permeability and cohesion, are influenced by the short range forces of the underlying metal.

It is desirable to evaluate the reactive nature of metallic oxide films on the basis of fundamental considerations of this type. Should these fundamental considerations of thin oxide film formation at low temperatures prove valid, they promise to be of importance in understanding oxidation phenomena under more general conditions. There is reason to believe that similar considerations valid at higher temperatures can be evaluated on the basis of the less complicated oxidation effects observed at low temperature. Single crystal copper surfaces in oxygen atmospheres at low temperatures were systematically studied from this viewpoint.

Procedure and Materials

Single crystals of copper suitable for surface studies have been successfully prepared and characterized.[3a,3b] The physical mechanism of formation of very thin oxide films at low temperatures has also been evaluated in some detail on both a theoretical[4a,4b] and experimental basis.[5a,5b] The orientation relationships existing between copper and cuprous oxide have been thoroughly investigated and confirmed.[6] The energetics involved in the formation of oriented over-growths have also been considered in some detail.[7a,7b] Finally the vacuum microbalance has been shown to be a powerful tool in the study of the surface chemistry of small surfaces.[8a,8b]

The samples were electropolished single crystal plates of copper (0.5″ × 0.75″ × 0.005″) sectioned from a large single crystal grown in a standard Bridgman manner. The copper was vacuum cast to a purity of 99.995% with iron and aluminum chief remaining impurities determined by spectrochemical analysis. Considerable efforts were made to define the surface crystallography and roughness on an atomic scale and true surface areas were determined using a specially developed differential adsorption technique. The criteria by which the crystallography and flatness of the surface on a microscale were evaluated are described in detail elsewhere.[8b] It is believed that the surfaces of this study are essentially flat on a molecular scale and that the surface arrangement of the atoms is approximately that of a known undistorted crystal face.

The oxidation kinetics were followed with a sensitive vacuum microbalance previously described[9] with which weight changes as small as 10^{-7} g. were determined with an accuracy of ±20%. The average oxide film thickness was calculated from weight changes in the usual manner assuming the formation of cuprous oxide except that the true surface areas were known in this study and the average true surface areas before and after oxidation were used in order to obtain a more precise value for the average oxide film thickness.

The uptake of oxygen by the surface was measured in the time range from 5 seconds to 1 month for eight temperatures in the range 78 to 323°K. on each of two samples for each of the three major crystal faces (100), (110) and (111). The weight changes reported here correspond only to that fraction of the oxygen uptake which was not outgassable at 500°K. These values were independent of oxygen pressure in the range 10–100 mm. The temperatures were determined with a chromel–alumel thermocouple mounted in a dummy plate identical in shape, size and material to the sample hanging on the balance. The other techniques for maintaining and measuring vacuum conditions were not especially improved over those previously described.[8a,8b] Although the edge area was reduced to a minimum (<0.1% total area) localization of the reaction at the edges is possible to some extent. It is believed, however, that selective edge attack is more likely at high temperatures. This effect at low temperatures is considered to be a minor one because extended oxidation at much higher temperatures (>300°) showed no evidence of non-uniform oxidation.

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[1] This research was supported in part by Army Air Forces Contract AF-33(038)-6534.

[2] Engineering Department, E. I. du Pont de Nemours & Co.

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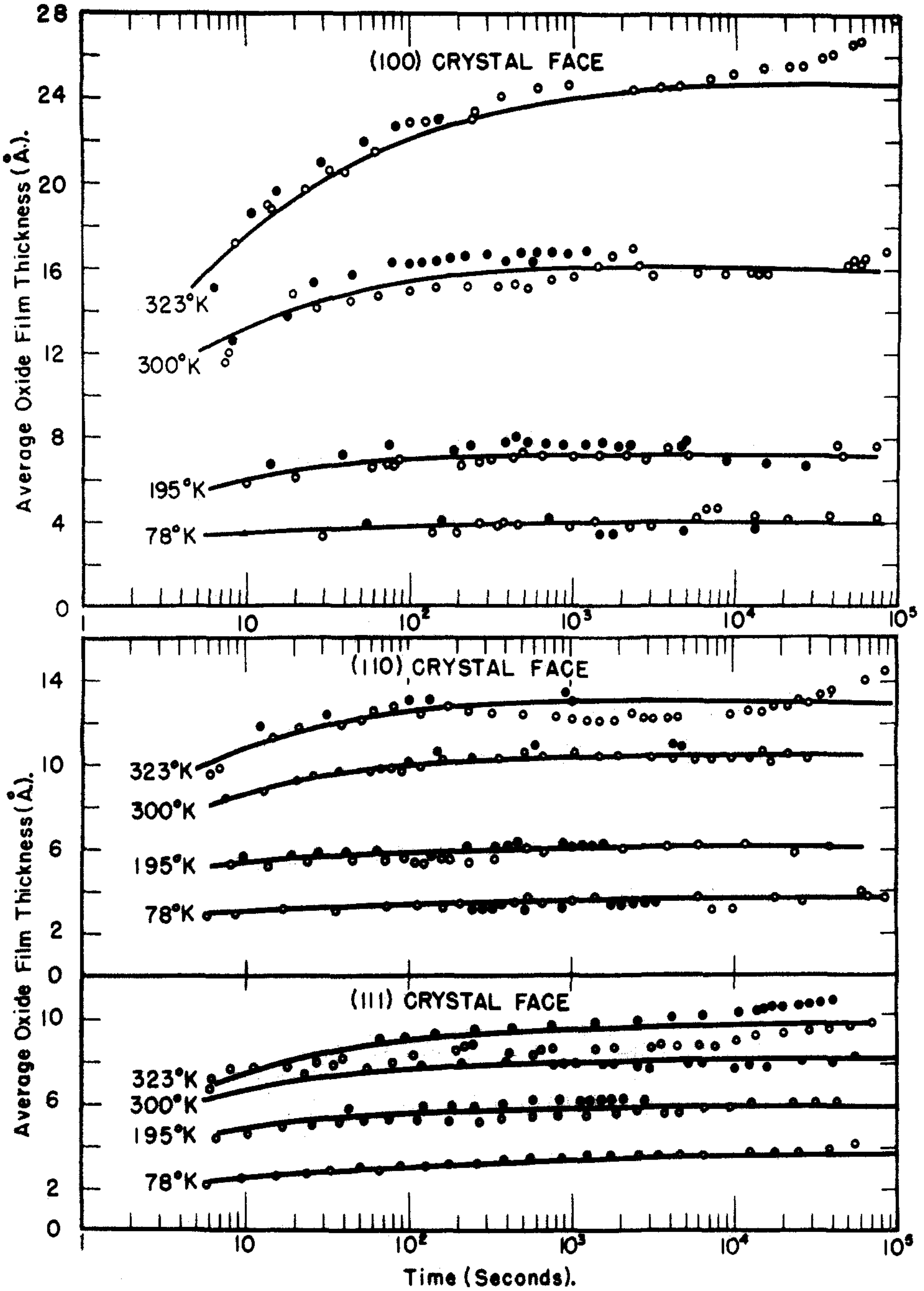

Fig. 1.—Oxidation isotherms of single crystal copper surfaces 78–323°K.: O and ● are samples No. 1 to 30 of crystal faces (100), (110) and (111), respectively. Isotherm curves are calculated.

Results

A. Oxidation Kinetics.—Two typical runs for each orientation at each of four temperatures are plotted in Fig. 1. The average oxide film thickness plotted as ordinate is calculated by the method and with the assumptions previously discussed.[5b] The scatter is also typical and all the extreme points are included. The apparent trends are non-significant except for the enhanced rate at 323°K. where an apparent change in the oxidation kinetics occurs.[5b] The results may be summarized: (1) The rate was initially extremely rapid and then decreased sharply with time. Extension of the isotherms to months indicate that the leveling off is a real effect. (2) The oxidation rate and the limiting oxide film thickness was greatest for the cubic face and smallest for the octahedral face with intermediate values for the rhombohedral face. (3) The limiting oxide film thickness values reported here are in fair agreement but somewhat lower than those previously reported.[5a,10] This difference is attributed to the marked uniformity of the surfaces in this study and to the fairly precise correction for surface roughness that was possible.[8a] (4) The trend of rate with orientation is in agreement with that found by others where it appeared

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(10) "Corrosion Handbook," J. Wiley & Sons, Inc., New York, N. Y., 1948, p. 33.

that the (100) face tended to suffer maximum oxidation and the (111) face minimum oxidation at low temperatures.[11] The trend was observed to shift in a complicated manner at higher temperatures (above 323°K.) as previously reported by others.[12] One should note that precise definition of surface crystallography and structure on a microscale is often very difficult[13] and may be the basis for the lack of better agreement in the literature on metal surface oxidation anisotropy. (5) The temperature coefficient of the reaction rate follows a relationship in which the reciprocal of the effective limiting average oxide film thickness varies inversely in a linear manner with the absolute temperature. The data for the (100) face previously reported[5b] has been augmented and corresponding data for the (110) and the (111) faces has been added to Fig. 2. The values at absolute zero correspond to approximately a monolayer for all orientations.

B. Surface Structure.—Sufficient preliminary studies of the structure relationships between the crystallography of the metal substrate and the oxide overgrowth were initiated to indicate together with studies of others the following conclusions: (1) surface reflection electron diffraction indicated that the (111) face of the oxide grows on the cubic face of the metal with the close-packed direction in the oxide parallel to the [100] direction in the metal. (2) The oxide crystals forming on the octahedral and rhombohedral faces of the metal tended to duplicate the fiber axis orientation and edge orientation of the metal substrate to a considerable degree. (3) Similar examination of the oxidized surfaces indicates that they are composed of very small crystallites of oxide with a highly preferred orientation approaching that of a pseudo-single crystal in some cases. (4) The structure relationships indicate that the face-centered cubic lattice of copper ions (a_0 = 3.60 Å.) expands during oxidation by the insertion of an interpenetrating body centered cubic lattice of oxygen ions to form an expanded face centered cubic lattice (a_0 = 4.26 Å.) of cuprous oxide. (5) The oxide is predisposed to follow the orientation of the metal substrate from which it forms insofar as surface binding forces balance lattice strain. Powerful restraining forces in very thin oxide films which oppose the equilibrium structure may be induced.

Discussion

A. Physics of Film Growth.—It is regrettable that so little is known of a quantitative nature about the interface energies between metal surfaces and the coherent oxide films that form upon them. It is such considerations that will eventually permit a precise evaluation of chemical attack in terms of surface structure. At present interpretations of reaction rate anisotropy are limited. The film growth is often complicated by nucleation and growth processes in recrystallized regions of the oxide as well as other structural and compositional transitions occurring during film growth. Many efforts have been made to understand the formation of protective films. The recent treatment of Mott and Cabrera[2a] of an idealized system attempts to incorporate these effects into a generalized theory. The rate-determining step in the formation of very thin films is assumed to be the transfer of metal ions through a strong electric field to the reaction zone according to the expression

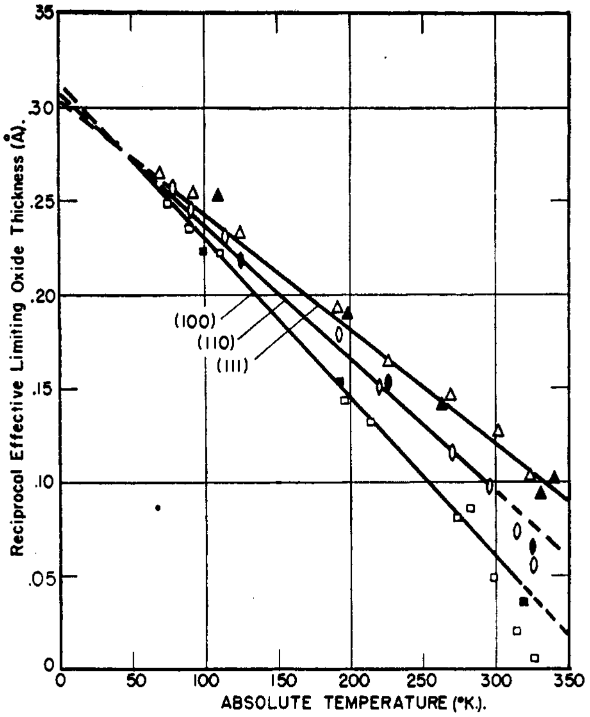

Fig. 2.—Dependence of reciprocal average limiting cuprous oxide film thicknesses with temperature: □, ■, samples No. 1 and No. 2 of (100) orientation; ○, ●, samples No. 3 and No. 4 of (110) orientation and △, ▲, samples No. 5 and No. 6 of (111) orientation.

$$dx/dt = A \exp (V/xkT - W/kT) \qquad (1)$$

where x is film thickness at time t; W is an energy related to the energies of solution and diffusion of the cations into and through the oxide, respectively; V, the contact potential difference between the metal–oxide interface and the oxygen adsorbed at the oxygen–oxide interface; T, the absolute temperature, and A, a proportionality constant that can be calculated from fundamental constants of the oxide film. Equation (1) was found to apply reasonably well by the author in a previous study of the low temperature oxidation of single crystal copper surface,[5b] in which some limitations of the theory are also mentioned. Substituting known physical constants of the metal and the oxide and a value of one monolayer per day for the limiting oxidation rate, in Eq. (1) yields Eq. (2)

$$x_L = aV/(W - 0.0031T) \qquad (2)$$

where a is the distance in Å. a metal ion moves in its transfer from the interface into the oxide and x_L is the film thickness in Å. when the oxidation rate is one monolayer per day, heretofore referred

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[11] B. Lustman and R. F. Mehl, *Trans. A. I. M. E.*, **143**, 1 (1941).

[12] A. T. Gwathmey and A. F. Benton, *J. Phys. Chem.*, **46**, 969 (1942); J. Benard and J. Talbot, *Compt. rend.*, **226**, 411 (1948); A. T. Gwathmey and A. F. Benton, *J. Chem. Phys.*, **8**, 431 (1940).

[13] C. Herring and M. H. Nichols, *Rev. Mod. Phys.*, **21**, 257 (1949).

to as the effective limiting oxide film thickness. The value of a is equal to the lattice parameter of the oxide to a first approximation. The effective average limiting oxide film thickness at low temperature can be calculated from this simple expression for any metal for which the parameters, W and V, are known. As semi-empirical parameters they may be evaluated from the type of temperature dependence illustrated in Fig. 2 and as fundamental constants can be evaluated at least in principle from the semi-conductor properties of the metal–oxide–gas system. A test comparison may be made successfully for the low temperature oxidation of aluminum and copper for which these parameters are known. The inversion temperature above which Eq. (1) does not apply is, however, much lower in the former case, being about 323°K. for copper and 623°K. for aluminum. Using Eq. 2 it can be shown that the values of x_L increase faster with temperature for copper than for aluminum in the temperature range where Eq. (1) is valid.

The values of V and W for the three major crystal faces of copper have been evaluated from the slopes and intercepts of the straight line portions of the plots in Fig. 2 and are listed in Table I.

TABLE I

VARIATION OF REACTION RATE PARAMETERS WITH CRYSTAL FACE FOR COPPER

Crystal face	Miller indices	W(e.v.)	V(v.)
Cubic	(100)	1.20	0.89
Rhombohedral	(110)	1.40	1.06
Octahedral	(111)	1.61	1.23

Substitution of these values in Eq. (1) adequately describes the experimental isotherms (Fig. 1) for all three crystal faces in the temperature range up to 323°K. Boundary conditions assumed in the derivation of Eq. (1) predict the deviations observed at 323°K. These deviations increase very rapidly for higher temperatures but there exists evidence suggesting that a modified version of the low temperature mechanism is required allowing for the considerable decrease in the strength of the field accelerating cation transfer.[4a] The physical interpretation of the parameters W and V will remain on a somewhat speculative basis until the characteristics of low temperature oxidation of metals are more generally and precisely understood.

B. Energetics Associated with Oriented Overgrowths. The oxidation rate anisotropy should also be considered in terms of the mechanical properties of the oxide film insofar as they affect the continuity of the film and its tendency to adhere to the underlying metal. Although no quantitative evaluation of metal oxide overgrowths are available, the theoretical considerations of Frank and Van der Merwe[14] of interfaces involving misfitting monolayers and oriented overgrowths may be helpful in a qualitative evaluation. Rather than stressing the geometrical aspects for the formation of oriented crystalline overgrowths, which has been the custom heretofore, they treated the energetics of film formation. In terms of their model the degree of misfit may be defined in terms of surface dislocations. When the misfit exceeds a critical value the strains developed during the thickening of the oxide are no longer balanced by the attractive forces of the substrate and the density of dislocations increases to a point where the film breaks away spontaneously from the substrate. The critical theoretical misfit at low temperatures has been calculated to be approximately 14% whereas the actual corresponding misfit for the copper–cuprous oxide interface is approximately 18%. The view is favored that the condition for critical misfit may be satisfied for the copper–cuprous oxide system and pseudomorphic oxide growth would be expected. There exists a fair amount of experimental evidence that this tendency does actually exist for cuprous oxide overgrowths.[5a] However, although pseudomorphic oxide films may form in the immediate vicinity of the single crystal copper surface, the large strain permissible in very thin oxide films cannot persist into thicker films; hence, as the film thickens a transition occurs from a pseudomorphic structure to an oxide structure which, although it may be highly oriented, will have the equilibrium lattice parameter of the bulk oxide. Flaws and perhaps reaction paths are generated in the oxide film in the region where this transition occurs. It may be that the closer this region is to the underlying metal the less effective the oxide film is as a barrier to the transfer of cations to the reaction zone. The critical mismatch and the density of surface dislocations will vary in a manner dependent on the structural relationships between the oxides and the metal for different crystal faces. For example, consideration of the relative mismatches for the oxide on the (111) and the (100) faces of copper based on a simplified linear Frank and Van de Merwe model suggests that approximately half as many surface dislocations per unit length occur in the former case. It is not unlikely that the tendency to form oxide pseudomorphic after the underlying metal is more favored for the octahedral than for the cubic face. If one considers that the tendency to form oxide films pseudomorphic after the underlying surface, even though such films are very thin, favors the protective nature of the oxide film, this type of consideration may provide a starting point for interpreting the low temperature oxidation rate anisotropy observed in this study. This approach is compatible with the hypothesis of Cabrera and Mott since the values of their parameters W and V must be intimately influenced by the existence of regions of structural transition in the oxide near the metal interface.

A detailed treatment of the speculations discussed, particularly the manner in which the two mechanisms may coöperate, is postponed for a later communication.

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