The Oxidation of Copper

A REVIEW OF PUBLISHED DATA

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A review of published papers on the oxidation of copper is given with emphasis on work done in the last decade. Experimental techniques and theoretical rate laws are discussed. Oxidation isotherms in the range 18–1020° C show that for data obtained at high temperatures there is good agreement between the various investigators, but that at lower temperatures the agreement is poor. At low temperatures quasi-logarithmic oxidation seems to prevail; over an extended range of intermediate temperatures, oxidation ranges from cubic to parabolic, while at high temperatures the parabolic law is generally obeyed. Single-crystal work on copper is reviewed with respect to oxidation rate and orientation of the oxide layer on different crystal faces. Information on the composition of the oxide layer has been compiled. Studies of the morphology of the oxide reveal whisker growth and nucleation phenomena in the oxidation of copper.

The literature on the oxidation of copper published up to 1949 was exhaustively reviewed by Tylecote.[1] Several partial reviews have been produced since, notably those by Kubaschewski and Hopkins,[2] Tylecote,[3] and Hauffe.[4] The present compilation was made during the preparations for an experimental study on the relation between the morphology of oxide growth and the kinetics of the oxidation of copper. Owing to this special point of view, some aspects have been treated in rather more detail than usual, while others—notably the questions of impurities and alloys—have been deliberately omitted or given less attention. To avoid repetition, complete coverage has been attempted only for the period since Tylecote's review,[1] although older material has been included where necessary.

The subject is important both technically and theoretically. Copper has figured prominently in the development of the theory of oxidation reactions,[5–8] and many of the fundamental concepts about the motion of ions and electrons through the oxide layer have been derived from, or verified by, experiments on oxides of copper.[9–15] Closer study of the literature, however, still reveals some gaps, as well as conflicting evidence with regard to essential aspects such as the type of rate law obeyed in certain temperature/film-thickness ranges, the composition and structure of the oxide layer, and often even the order of magnitude of oxide formation under given conditions. It was felt that a compilation of the data that had been collected might be helpful in assessing the actual position of theory and experiment, and that it might also serve a practical purpose by providing a quick reference source.

Experimental Techniques

Before entering into the discussion of the empirical material, a few comments on experimental techniques may be useful. The following are commonly used in oxidation studies: (micro-) gravimetric, manometric,[16, 17] coulometric (sometimes called electrometric), and interference methods. Except for a few instances,[18, 19] X-ray and electron diffraction have been employed only for qualitative identification or for orientation studies, and not for quantitative kinetic work.

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The gravimetric method seems to be the one most commonly used in recent years. Descriptions of several instruments,[20–27] some equipped for automatic recording,[27–31] and two bibliographies on microbalance techniques[32, 33] have appeared during the last decade. Some of the work on the oxidation of copper has been done with balances equipped for photographic recording.[3, 34, 35]

The coulometric method, originally developed by Evans and Bannister[36] and by Miley,[37, 38] has been used in many instances. It has several attractive features, notably its high sensitivity (with a refined technique, fractional monolayers of oxide can be detected[39]), and the possibility of determining both cuprous and cupric oxide in the same run. The method has undergone considerable refinement[40–44] since its early applications. Recently, Lambert and Trevoy[39] have demonstrated the importance of the complete elimination of dissolved oxygen and also of plateable cations from the electrolyte, which can be achieved by pre-electrolysis.

The most serious source of error in the coulometric method as applied to the oxides of copper was apparently, before its detection by Campbell and Thomas,[40] the rapid and preferential dissolution of CuO in the electrolyte commonly used, NH_4Cl. Potassium chloride, while free from this disadvantage, sometimes fails to give separation of the two oxides.[42, 43, 45] Mills and Evans[44] recently suggested a phosphate buffer of *p*H 6·9 as a suitable electrolyte. Some of the earlier coulometric results now appear definitely erroneous, while in certain cases agreement with other methods may have been fortuitous.[46] With a proper technique, however, the method seems valuable.

Optical methods have been used extensively for thin oxide layers. In the simplest form of the interference method, the thickness of the oxide layer is put equal to that of an air film exhibiting the same interference colour. Elaborate refinements have been developed, but with these the method becomes rather tedious. The subject has been treated exhaustively by Winterbottom,[47] and several reviews are available.[48–50] A recent application to the oxidation of copper is found in the study of the low-temperature oxidation of single crystals by Young, Cathcart, and Gwathmey.[51]

The interference method shares with the manometric and the gravimetric methods the great advantage of being non-destructive and allowing nearly continuous recording. However, recent studies of the morphology of oxide growth during the early stages for which the method is applicable

cast considerable doubt on its basis, i.e. the assumption of a plane parallel, compact oxide layer. The increasing number of observations of non-continuous oxide growth (reviewed later) also suggests great caution as to the concept of "film thickness". In fact, it would appear preferable to avoid this term completely unless its validity is demonstrated by electron-microscopic evidence. The alternative term, amount of oxide formed per unit area of the metal surface (in $\mu g/cm^2$), appears preferable, even if less descriptive. It is also subject to an important source of error—the degree of surface roughness of the metal, which can be considerable for abraded or reduction-cleaned surfaces.

Rate Laws

The theory of oxidation rates has been developed mainly by Wagner,[5] Mott,[7, 56–60] Cabrera,[7, 61] Gulbransen,[94, 95] Hauffe,[4] and their collaborators. Several exhaustive [2, 4, 7] and shorter [52–55] reviews are available. Five basic types of rate laws have been established:

the linear $m = k_1 \cdot t$ . . (1)

the parabolic [5, 7, 57] $m^2 = k_2 \cdot t$ . . (2)

the cubic [56, 7, 63] $m^3 = k_3 \cdot t$ . . (3)

the inverse logarithmic [57, 60, 7] $\frac{1}{m} = k_i \cdot \log\left(\frac{t}{\tau} + 1\right)$ (4)

the direct logarithmic [7, 58, 62] $m = k_l \cdot \log\left(\frac{t}{\tau} + 1\right)$ (5)

Here, m refers to the amount of oxide formed, t to the time of oxidation, while $k_1 \ldots k_l$ and τ are constants with regard to time, but not to temperature or oxygen pressure. Additive constants can appear if the reaction has followed a different law during a preceding period.

With the exception of the linear law, which applies to the case of a non-protective oxide layer, the above expressions are all derived from the assumption that transport of cations (or electrons, case (5)) across the growing film is the rate-determining step. According to this picture, the sequence normally expected would start with the direct logarithmic law for the thinnest films and at low temperatures and continue via the inverse logarithmic and the cubic to the parabolic law for thick films and high temperatures. (The cubic law is predicted [7, 61, 63] for the upper end of the thin-film region by virtue of the p-type conductivity [67–70] of cuprous oxide.) Estimates of the limiting film thickness for the various rate laws have been made by Mott and Gurney [165] and by Hoar [76] and others.

The derivation of the direct logarithmic law by Mott [58] and Cabrera [7] explains its validity only for films thin enough to allow electron transport by the tunnel effect. In practice, this rate law has been observed at much higher film thicknesses. Evans has shown that a logarithmic law can be expected when the effective area involved in oxidation is not constant, as in films containing flaws that facilitate the access of oxygen to the metal,[64, 65] or when cavities in thicker films progressively reduce the area available for diffusion.[66] In the latter case, however, $\sqrt{t}$ may take the place of t in an equation of type (5), as has been shown by Evans.[53] Still another derivation of equation (5) has been given by Grimley and Trapnell.[71, 72]

Recently, Uhlig [73, 74] has postulated a basically different mechanism which would explain the persistence of the logarithmic law to film thicknesses of the order of 10^4 Å. He assumes that the rate-controlling step is not diffusion through the oxide film, but the rate at which electrons can cross the metal/oxide interface. (This assumption is supported by the effects on the oxidation rate of allotropic and magnetic transitions of the metal, and by a direct relationship between the activation energy of oxidation and the work function of several metals.)[75, 76] A discussion of the influence of the space-charge layer set up near the oxide/metal interface on the rate of escape of electrons from the metal leads to two stages of oxidation, corresponding to the building up of a zone of uniform charge density next to the metal (where all available electron traps are saturated), and of an outer zone with decreasing space charge, where the charge density falls below that of the trapping sites. The first stage is characterized by a logarithmic equation; the second, depending on the manner of distribution of trapping sites, may either give a logarithmic law (with constants different from those of the first stage), or a cubic one.

It has been shown [7, 53, 76, 80] that the rate laws (2)–(4) can be considered as approximate solutions, in certain limiting cases, of a general rate equation first proposed by Mott: [78]

$$\frac{dy}{dt} = C \cdot \sinh \frac{E}{ykT} \quad . \quad . \quad . \quad . \quad (6)$$

where y, the thickness of the oxide layer, is proportional to m in equations (2)–(4), while E is the energy of activation for the migration of cations in the direction of growth under the influence of concentration and electrical potential gradients. For limited variations of y, or m, this can be approximated by:

$$\frac{dm}{dt} = \text{const.}\ m^{-\nu} \quad . \quad . \quad . \quad . \quad (7)$$

where ν depends on temperature, thickness of oxide film, and oxygen pressure, as discussed in detail by Grimley.[72] It follows that, again over limited ranges of m, t, and T, the rate laws based on the diffusion picture can be approximated by:

$$m^n = K \cdot t \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Generally $n\ (= \nu + 1)$ will gradually decrease with time (film thickness) and temperature. This expression has been used extensively by Tylecote.[3] Young, Cathcart, and Gwathmey [51] have pointed out its near equivalence to the inverse logarithmic relationship.

Mixed laws can occur when two reaction steps have comparable influence on the reaction rate. Such a case was found in the oxidation of copper to Cu_2O at low oxygen pressures and 1000° C, where Wagner and Grünewald [6] concluded that the reaction at the Cu_2O/O_2 interface competed with diffusion through the oxide layer. In this case, the "reaction resistivities" [77] can be considered additive, yielding the following modification of the parabolic law:

$$\frac{m}{k_1} + \frac{m^2}{k_2} = t \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Fig. 1 presents a compilation of the rate laws reported by different investigators, in order of alleged temperature range of validity.

At low temperatures, the direct and inverse logarithmic laws have been observed, but not in their proper sequence according to the Mott–Cabrera theory. Several authors [16, 73, 80, 81, 90] have found the two-stage direct logarithmic oxidation behaviour predicted by Uhlig, but it should be noted that many of the published curves show more than two logarithmic stages. Young, Cathcart, and Gwathmey [51] found an inverse logarithmic law for the crystal faces (100),

(111), (110), and (311) at 70° C and at higher temperatures for the first two faces; while for the (110) and (311) faces, oxidation conformed to a law of the type $m^n = k \cdot t$, with n ranging from 3·0 to 4·8. However, even though the exact type of rate law is not agreed upon, the three laws reported for the low-temperature range are quite similar qualitatively: they all show a steeper initial ascent, followed by a rather sharp bend of the curves of m/t, and a slower increase at long times than is characteristic for the parabolic or the cubic law.

Systematic errors in the determination of the amount of oxide may account for some of the discrepancies. In particular, the observation of a logarithmic law *following* a period of parabolic oxidation [79] might be the result of a partial dissolution of the thicker films formed during prolonged oxidation, in the ammonium chloride electrolyte used for coulometric measurements.

In the intermediate temperature range the direct logarithmic law was observed by Tylecote [82] at film thicknesses where the leak path or the cavity mechanism suggested by Evans might apply. The observation, by de Carli and Collari,[34] of an inverse logarithmic law at 400° C and at rather high film thicknesses cannot be accounted for by Mott's tunnel mechanism.

The theories of Mott, Cabrera, and Hauffe predict a region of transition between the inverse logarithmic and the parabolic law, in which the cubic law should be obeyed. According to Fig. 1, the cubic law does appear in the range 120–750° C, but it does so in a rather sporadic fashion, and apparently only as an exception to the normal case of parabolic oxidation. This is best illustrated by Tylecote's exhaustive investigation.[3] He reports intermittent periods of nearly cubic oxidation in practically the whole range of his study (200–750° C). In particular, cubic periods occurred both preceding and following parabolic ones, a behaviour that is difficult to explain in terms of the Mott–Cabrera–Hauffe theory.

In the high-temperature range, only parabolic behaviour has been reported. In two very accurate studies,[19, 83] the

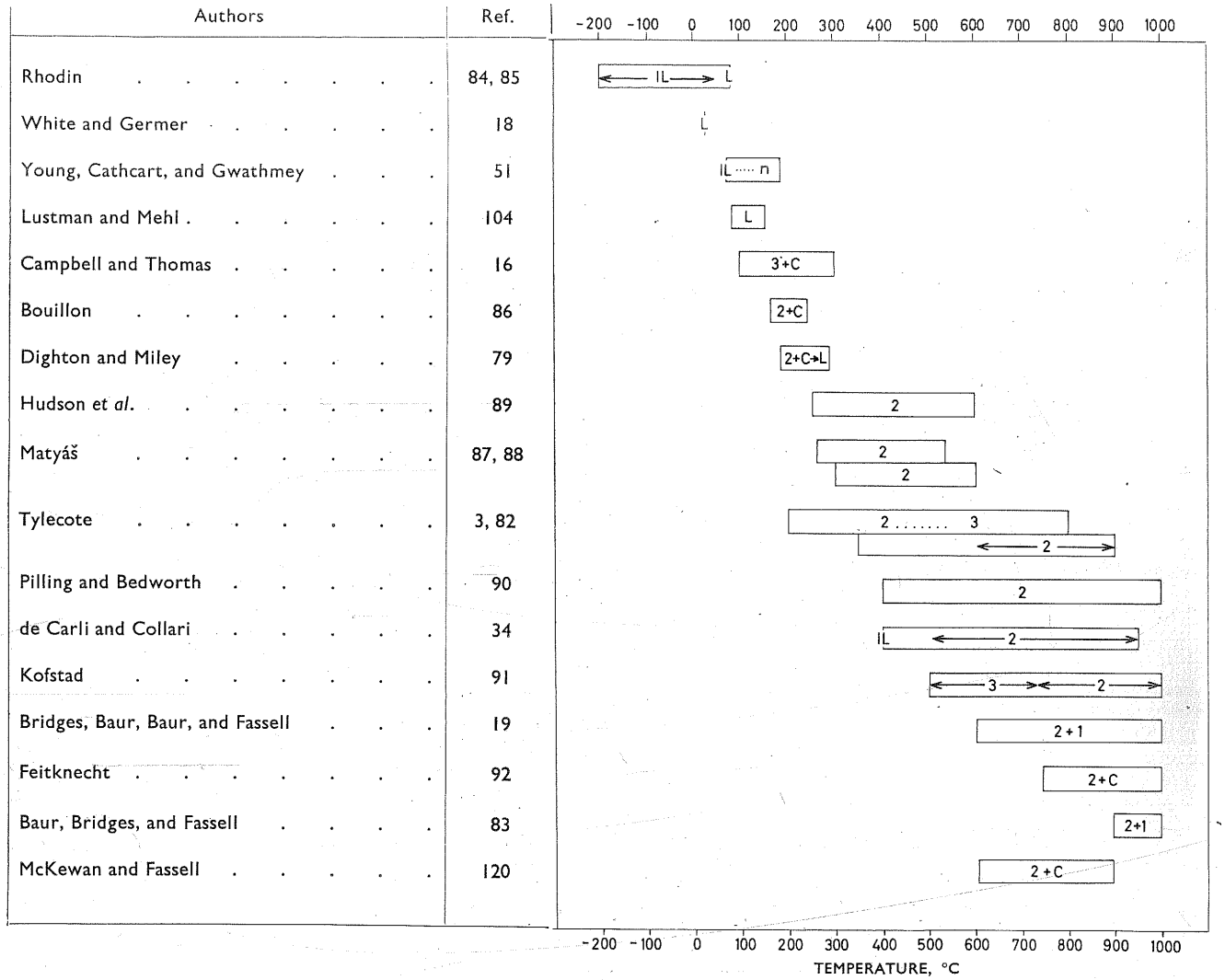

Fig. 1 Rate laws reported for the oxidation of copper.

1 = linear
2 = cubic
3 = parabolic

L = logarithmic
IL = inverse logarithmic

C = an additive constant
$n = m^n \sim t$; $(2 \neq n \neq 3)$

introduction of a linear term corresponding to equation (9) was found necessary.

Oxidation Isotherms

The collection of oxidation curves presented in Fig. 2 was undertaken mainly to provide a basis for estimating the amount of oxide to be expected under given conditions of oxidation. It has also been used to test some of the theoretical expressions against a somewhat wider experimental background than is usually available.

The limitations of such a compilation must be kept in mind. In the first place, the use of data published in graphical form implies considerable inaccuracy, especially at short times. The conversion of values from Ångström units of Cu_2O to $\mu g/cm^2$ of oxygen (1 $\mu g/cm^2 \approx 145{\cdot}9$ Å) rests on the assumptions that the film is compact and plane and consists of Cu_2O only—all of which are more or less questionable, as will be shown later. The pretreatment of samples, their purity, and other experimental conditions have a great—though still incompletely understood—influence on oxidation results. As far as they are stated in the original papers, the

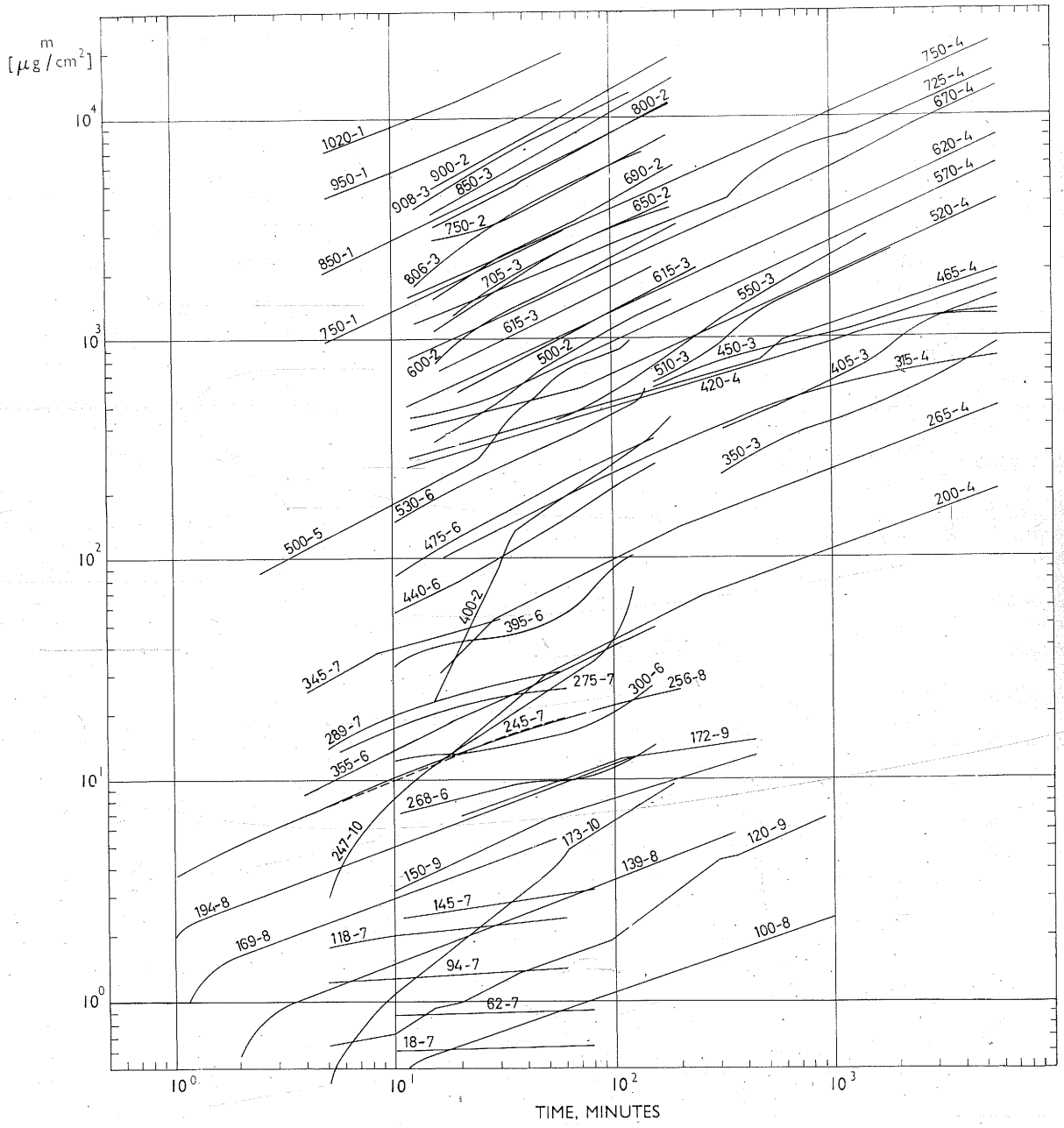

Fig. 2 Collection of oxidation isotherms. The first number on an isotherm refers to the oxidation temperature and the second number to one of the references listed below.

1. Feitnecht (92)
2. de Carli and Collari (34)
3. Tylcote (82)
4. ,, (3)
5. Pilling and Bedworth (90)
6. Matyáš (87)
7. Miley (93)
8. Campbell and Thomas (16)
9. Mills and Evans (44)
10. Bouillon (86)

experimental conditions pertaining to the data presented in Fig. 2 are listed in Table I.

Fig. 2 shows that, in general, agreement between different investigators is good for data at high temperatures, but becomes poorer at lower temperatures. The fact that most results could be represented by straight lines in the log coulometric reduction of the oxide in NH_4Cl, so that too much reliance should not be placed on these. Dissolution of oxide in the electrolyte would clearly favour a high value of n. Unfortunately, part of the available data for low temperatures—especially the microgravimetric results of Rhodin [84, 85]—could not be included in Fig. 2 because they

TABLE I

Experimental Conditions in Studies of the Oxidation of Copper

Authors	Ref.	Material	Oxidation Atmosphere	Surface Treatment	Experimental Method
Pilling and Bedworth (1923)	90	Electrolytic copper, 99·96%	Tank oxygen, tank nitrogen $p_{O_2} + p_{N_2} = 1$ atm.	...	Gravimetric (analytical balance)
Feitknecht (1929)	92	No data given	Before oxidation CO_2-atmosphere Tank oxygen, tank nitrogen $p_{O_2} + p_{N_2} = 1$ atm.	Mechanically polished	Gravimetric (analytical balance)
Miley (1937)	93	99·95% copper, 0·04% oxygen	...	Mechanically polished	Coulometric (electrolyte NH_4Cl)
Campbell and Thomas (1947)	16	O.F.H.C. copper	Dry oxygen, cleaned by vacuum distillation $p_{O_2} = 150$ mm Hg	Mechanically polished	Manometric. Some values gravimetric and coulometric
Rhodin (1950) (1951)	84 85	99·995% copper single crystals Main impurities Al, Fe	Tank oxygen cleaned over P_2O_5 $p_{O_2} = 10^{-3}$–10^{2} mm Hg	Single crystals made by Bridgman method. Surface mechanically and electrolytically polished, reduced in H_2	Gravimetric (vacuum micro-balance)
Tylecote (1950) (1953)	82 3	NPV, NTB, NTC, NTE } copper	Before oxidation N_2-atmosphere Tank air cleaned over KOH, $MgClO_4$, and P_2O_5 $p = 1$ atm.	Chemically polished	Gravimetric (analytical balance) (1953: photographic recording)
Bouillon (1951)	86	Electrolytic copper	Dry tank oxygen $p = 1$ atm.	Electrolytically polished	Coulometric (electrolyte NH_4Cl)
de Carli and Collari (1951)	34	Electrolytic copper, 99·98% (Ni, Fe, Sb, Ag, S: 0·015%)	...	...	Gravimetric (photographic recording)
de Carli and Spinedi (1953)	35	Electrolytic copper, 99·98%	...	...	Gravimetric (photographic recording)
Matyáš (1954)	87	Electrolytic copper	$p = 1$ atm.	Mechanically polished. Etched in H_2PO_4	Gravimetric
Mills and Evans (1956)	44	99·93% copper, 0·04% oxygen	Oxygen cleaned over $CaCl_2$, ascarite, and liquid-oxygen trap $p_{O_2} = 200$ and 500 mm Hg	Electrolytically polished. Reduced in H_2, 400° C	Coulometric (electrolyte $NaH_2PO_4 + Na_2HPO_4$)
Baur, Bridges, and Fassell (1956)	83	O.F.H.C. copper (0·002% B, 0·0015% Si)	Oxygen $p_{O_2} = 10$–95 mm Hg	Etched in ammonium persulphate solution. Washed in distilled water and acetone	Gravimetric (helical quartz spring balance)

t vs. log m co-ordinates of Fig. 2 indicates that equation (8) gives, for practical purposes, an adequate description of the oxidation process.

The exponent of the rate law, n, can be read directly from the slope of the curves in Fig. 2. (An additive constant will affect the rectilinearity and the slope of the log t vs. log m curves, but for constants of reasonable magnitude the effect is slight.) The figure illustrates, more clearly than Fig. 1, the conflict as to the type of rate law obeyed at low temperatures. It should be noted, however, that the group of curves with the smallest slope (highest value of n) was obtained by were obtained with single-crystal material. Further references to measurements on single crystals will be found later in this paper. Many curves show initial downward deflections which might indicate a direct or inverse logarithmic stage. The very steep initial branches of a few curves are clearly exceptional and will be disregarded.

A gradual increase of slope with temperature and film thickness is apparent, which is in agreement with the theoretically predicted sequence of rate laws. There is, however, considerable scatter. Fig. 3 gives the inverse of the exponent n as a function of temperature. At intermediate tempera-

tures, nearly cubic oxidation seems to occur somewhat more frequently than was suggested by Fig. 1, but again the cubic law appears alternately with the parabolic one. Neither is there any range of film thickness in which the cubic law is

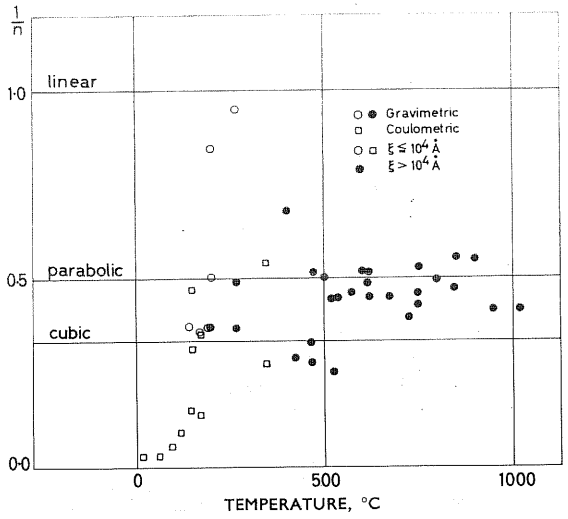

Fig. 3 Inverse of exponent of rate law (equation 8) as a function of temperature. ξ = calculated thickness of oxide layer.

exclusively obeyed (this was checked by plotting n as a function of m for appropriate temperatures). To sum up, it might be said that at low temperatures quasi-logarithmic oxidation (high values of n) prevails; over an extended range of intermediate temperatures, oxidation ranges from cubic to parabolic, while at high temperatures the parabolic law is obeyed.

In comparing the data of Fig. 2 with theory, it must be borne in mind that a great part of the experimental work was done from a technological point of view. Few studies have been made under conditions so rigidly restricted as those assumed in the theoretical treatments. As regards purity of the material, there has been a tendency to use O.F.H.C. copper, but no work has been done, to our knowledge, on spectroscopically pure material. Experiments on single-crystal material are available, though not for the complete temperature range under discussion; they will be reviewed in more detail in the next section.

Only a few studies have been made under conditions guaranteeing the occurrence of only one oxide, although the temperature/pressure region for the formation of single-oxide films is at least approximately known (see Fig. 6). Thus, most of the data collected concern " global " attack rather than growth of a single oxide layer, and the influence of CuO formation on the rate of oxidation is still incompletely understood.[96, 97]

The oxidation of copper to Cu_2O, at oxygen pressures excluding formation of CuO, has been studied by Bridges, Baur, Baur, and Fassell.[19] Strict adherence to the modified parabolic law of equation (9) was found over the temperature range 600–1000° C. Hauffe and Kofstad [98] studied the second partial system involved, Cu_2O/CuO (in the absence of metallic copper), and report a strictly cubic rate law. In general, however, formation of CuO is not expected to become rate-determining, since it proceeds more quickly than the diffusion of copper ions through the Cu_2O layer.

There are several " secondary " factors that may cause deviations from theoretical rate laws. Tylecote [3] has pointed out that cracking of blisters at a sufficiently frequent rate may give continuous deviations from the actual rate law. The resultant speed-up of oxidation might be responsible for the occurrence of parabolic portions in what is believed to be the range of validity of the cubic law, though it is difficult to imagine that the balance between cracking and regular (cubic) oxidation would always give parabolic behaviour. Tylecote [3] also points out that the change of preferred orientation from (110) to (100) which occurs when cold-rolled material recrystallizes during oxidation, will affect the slope of oxidation curves, making them concave downward. From Uhlig's theory of space-charge build-up at the metal/oxide interface,[73, 74] another cause of irregularities appears conceivable: the impurity concentration at the metal surface and the rate of heating up to the final oxidation temperature will determine the distribution of trapping sites in the space-charge zone, and thus determine the type of rate law and the extent of its validity. Primary oxide films (which seldom were removed in the earlier work) may have a substantial effect.[3] The shape of the oxidation curves is also affected by the presence of dissolved gas in the metal,[16] by the temperature of annealing, and even by the rate of subsequent cooling of the samples before oxidation.[104] Campbell and Thomas [16] have shown that the presence of moisture in the oxidizing atmosphere substantially reduces the slope of oxidation curves between 100 and 169° C. (Adsorbed moisture will change the charge distribution in the oxide film.[99–101]) Experiments in which these " secondary " variables are not excluded, or at least controlled, cannot serve as evidence for or against the theories suggested. Obviously, more ex-

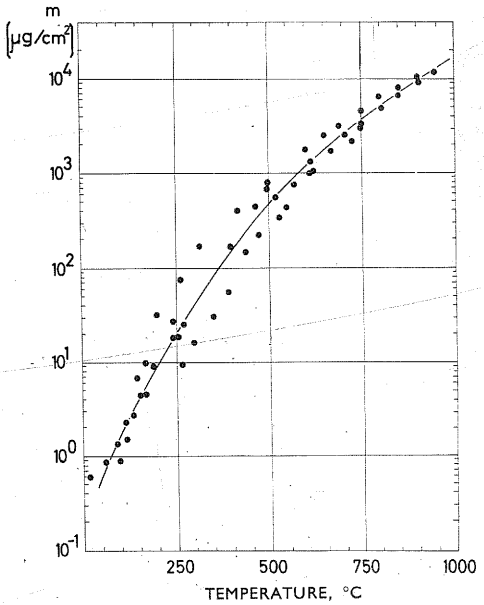

Fig. 4 Isochronal oxidation curve (1 h).

perimental work with special attention to these variables is required to chart the ranges of validity of the various rate laws.

For practical purposes, the available material gives a fairly adequate picture. Fig. 4 shows the amount of oxide formed after one hour at various temperatures. For extrapolations to longer or shorter times the value of n would

have to be known. Its great scatter (cf. Fig. 3) will, however, make such extrapolation rather uncertain.

Oxidation of Single Crystals

The first indication of anisotropic oxidation of copper single crystals was obtained by Tammann,[102] who noted that the individual grains of a polycrystalline sample showed different interference colours after oxidation. Since then much work has been done on the determination of oxidation rates,[51, 85, 103–108] as well as on the orientation of the oxide layer on different crystal faces of the base metal.[85, 103, 109–119] In Table II results of determinations of the relative order of the oxidation rates are chronologically arranged.

between the oxide and the base metal), it can be seen that four equivalent orientations of the oxide face (111) can form on the (100) face of copper. Lawless and Gwathmey infer that when the oxide grains have different orientation possibilities the number of imperfections and grain boundaries will rise, favouring a high rate of oxidation on the (100) face.

The differences in published data on the reactivity of the faces (110) and (111), mentioned above, cannot be explained by the different experimental methods used by Rhodin [85] and Young *et al.*,[51] because the results of Lustman and Mehl,[104] who used the optical method as did Young, agree with those of Rhodin. Gorny [116] suggested that the variation might be due to the small difference in contact potential between the two faces at low temperatures. In that

TABLE II
Oxidation-Rate Studies of Single Crystals of Copper

Authors	Ref.	Faces Studied, in Order of Decreasing Oxidation Rate	Experimental Method	Temperature Range, °C	Atmosphere
Lustman and Mehl (1941)	104	(100) (110) (111)	Optical	80–155	Dry air, 1 atm.
Gwathmey and Benton (1942)	105	(100) (210) (111) (110) (311)	Optical	200	Air, 1 atm.
		(100) (210) * (311) *		500	
Bénard and Talbot (1948)	106	(210) (221) (211)/(110) (111) (100) (123)		900	
Rhodin (1951)	85	(100) (110) (111)	Micrograv-imetric	−195 to 50	p_{O_2} = 10–100 mm Hg
Young, Cathcart, and Gwathmey (1956)	51	(100) (111) (110) (311)	Optical	70–175	Purified dry oxygen, 1 atm.
Harris, Ball, and Gwathmey (1957)	108	(100) (111) (311)	Optical	150	

* Some change in the order of relative rates.

From a comparison of the results given by Lustman and Mehl [104] and Rhodin [85] with those of Young, Cathcart and Gwathmey,[51] it appears that in the first case the (110) face is more reactive than the (111), and in the other case their order is reversed. But with this exception, and remembering that Bénard and Talbot's measurements [106] were made at much higher temperatures than the rest, there seems to be good agreement between the different authors.

Gorny [116] drew attention to the unexpectedly high reactivity of the (100) face, which contradicts the general opinion that a crystal face in which the superficial atoms are more densely packed should have a greater work function than a face with a less dense concentration of the surface atoms. (Compare Uhlig's theory mentioned above.) In a copper single crystal the faces with greatest density are, in decreasing order: (111), (100), (110), (311), (331), and (210).

On the basis of a suggestion by Cabrera,[121] Vermilyea [122] points out that for high temperatures the oxidation-rate anisotropy is to be expected, because of differences in the equilibrium concentration of metal ions in the oxide at the oxide/metal interface on different crystal faces. For intermediate temperatures Vermilyea predicted that oxidation-rate anisotropy will be more complicated because of the crystallization and recrystallization of the oxide film.

From measurements by Lawless and Gwathmey,[117] presented in Table III (giving the mutual orientation relationships

case the impurities and imperfections in the crystals examined will have a more distinct effect on the oxidation rate. According to Lustman and Mehl,[104] the face of highest oxidation rate is intermediate between (110), (100), and (111); and its exact orientation is strongly temperature-dependent.

The difference in the order of oxidation rates at 200 and 500° C in the work of Gwathmey and Benton [105] may have its explanation in errors in measurement of the optical film thickness, since 500° C is within the range of strong whisker growth. On the other hand, it may be evidence of a temperature-dependence of oxidation rate anisotropy, as in the case mentioned above.

The orientation of the oxide film has been examined in great detail by Lawless and Gwathmey.[117] They found that the degree of orientation varies with pressure, temperature, and film thickness, but the orientation relationships between the oxide and the base metal are always the same. From Table III it can be seen that there is very good agreement between the different authors. The divergences that appear are difficult to comment on without exact knowledge of the experimental conditions. In all cases studied by Lawless and Gwathmey the [110] directions of copper and Cu_2O were parallel; this direction is also the closest-packed one for both copper and Cu_2O. In that orientation relationship the misfit is 18%. For low-index planes a good fit between the closely packed rows proved to be more important than

the requirement of parallelism of the densely packed planes. In the case $(100)_{Cu_2O}$ // $(113)_{Cu}$ the misfit is 0·5%. For high-index planes they found that the orientation is determined by the low-index steps of which the face is composed. Bauer [123] has given a thermodynamical discussion of the orientation relationships and the conditions under which the crystal nucleation on a surface may be described by a formula for the probability of nucleation. The orientation of copper on a partly reduced oxide film has been studied by Jellinek,[124] who also tabulated the degree of misfit between the metal and the oxide for various orientations.

Harris, Ball, and Gwathmey [108] and Grønlund [107] decided in their studies of nuclear and surface growth velocity that CuO did not appear until the laterally growing nuclei had covered the whole surface. Lawless and Gwathmey [117] pointed out that, in general, CuO, when present, was polycrystalline and completely disoriented.

TABLE III

Orientation Relations between Copper and Its Oxide

Authors	Ref.	Faces Studied	Conditions of Oxidation	Film Thickness, Å	Method *	Results
Thiessen and Schütza (1937)	103	(100) (111) (110)	325° C (150 mm air pressure)	3600 2500 900	XRD XRD ED	$(111)_{Cu_2O} \parallel (100)_{Cu}$ $(111)_{Cu_2O} \parallel (111)_{Cu}$ $(110)_{Cu_2O} \parallel (110)_{Cu}$
Yamaguti (1938)	112		1000–1060° C in air, 1–2 h		ED	$(111)_{Cu_2O} \parallel (100)_{Cu}$ $[110]_{Cu_2O} \parallel [100]_{Cu}$ (Stated in terms of angles between sets of planes)
Moore (1938)	113	(100) (110) (111)	Room temp.	300	ED	$(111)_{Cu_2O} \parallel (100)_{Cu}$ $[110]_{Cu_2O} \parallel [100]_{Cu}$ $(110)_{Cu_2O} \parallel (110)_{Cu}$ $[100]_{Cu_2O} \parallel [100]_{Cu}$
Gwathmey (Lawless) (1953)	114	(100) (111) (110) (210) (311) (211)	250–450° C	80–700	XRD	$(111)_{Cu_2O} \parallel (100)_{Cu}$ $(111)_{Cu_2O} \parallel (111)_{Cu}$ $(110)_{Cu_2O} \parallel (110)_{Cu}$ $[110]_{Cu_2O} \parallel [110]_{Cu}$ $(210)_{Cu_2O} \parallel (210)_{Cu}$ For $(110)_{Cu}$ also $[110]_{Cu_2O}$ parallel to $[100]_{Cu}$. $(310)_{Cu_2O} \parallel (311)_{Cu}$ $(110)_{Cu_2O} \parallel (211)_{Cu}$
Goswami and Trehan (1956)	115	(110)	125–300° C	380–1260	ED	$(110)_{Cu_2O} \parallel (110)_{Cu}$
Gorny (1956)	116	(111) (001) (011)	Room temp. 350° C 450° C		ED	$(111)_{Cu_2O} \parallel (111)_{Cu}$ Oxide lattice rotated 30° about $[111]_{Cu}$ $(111)_{Cu_2O} \parallel (001)_{Cu}$ Oxide lattice rotated 15° about $[001]_{Cu}$ $(011)_{Cu_2O} \parallel (011)_{Cu}$ Oxide lattice rotated 35° about $[011]_{Cu}$
Lawless and Gwathmey (1956)	117	(001) (111) (011) (012) (113) (112) (122) (133)	170–450° C 0·8 mm Hg (1 atm.)	200–5000	XRD	$(111)_{Cu_2O} \parallel (001)_{Cu}$, $(001)_{Cu_2O} \parallel (001)_{Cu}$ (infrequent) $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(111)_{Cu_2O} \parallel (111)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ or $[\bar{1}10]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(011)_{Cu_2O} \parallel (011)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(012)_{Cu_2O} \parallel (012)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ or $[110]_{Cu_2O} \parallel [011]_{Cu}$ $(110)_{Cu_2O} \parallel (113)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(44\bar{1})_{Cu_2O} \parallel (112)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(474)_{Cu_2O} \parallel (122)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $(112)_{Cu_2O} \parallel (133)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$
Pigott (1957)	143	(111)	160, 200° C	200	ED	$(111)_{Cu_2O} \parallel (111)_{Cu}$ $[1\bar{1}0]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$ $[112]_{Cu_2O} \parallel [1\bar{1}0]_{Cu}$

* XRD = X-ray diffraction. ED = electron diffraction.

Composition of Oxide Films

It has long been accepted that thick scales are, as a rule, composed of an inner layer of Cu_2O and an outer one of CuO. This is in agreement with the theory of composite oxide layers developed by Jost,[125] Wagner,[126] and Valensi.[127] The relative thickness of the two layers is a function of the ratio of the rate constants governing the two partial reactions. Since the activation energies for these reactions are usually different, the thickness ratio will vary with temperature, but it should be independent of time and film thickness provided that the same type of rate law holds for both partial reactions. For the case of copper, Hauffe and Kofstad [98] and, later, Meijering and Verheijke [128] have shown that this is not true: the formation of CuO from Cu_2O follows a cubic rate law, while the lower oxide is generally assumed to grow according to a parabolic one, at least at high temperatures.

The empirical situation is illustrated by Fig. 5, where the $CuO : Cu_2O$ ratios reported by several authors have been collected. Valensi's theoretical curve [127] is also included. Naturally, no CuO is found above the dissociation temperature of this oxide (~1030° C at 160 mm oxygen pressure). Below this temperature, the CuO content of the scales increases with decreasing temperature, and reaches substantial values at intermediate temperatures—a trend observed by all

authors and reported even for dilute copper alloys [129] (the maxima in the alloy curves have been attributed to the presence of the alloying elements).

Below 400° C, published information is conflicting and no clear picture can as yet be derived. Evidence from electron-diffraction and coulometric work shows conclusively that

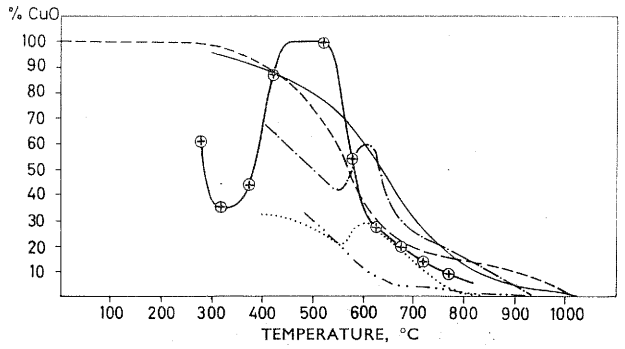

Fig. 5 Percentage of CuO in scales formed at various temperatures.

Valensi (127) (exp.)
" " (calc.)
Tylecote (97)
Dennison and Preece (129) (Cu–1% Mg)
" " " (Cu–2% Cr)
de Carli and Collari (34)

below ~250° C, Cu_2O is the only oxide formed during the earlier stages of the reaction, and that even when CuO does eventually appear, it does not become predominant. Contrary to Valensi's predictions, one would therefore expect a low CuO content at both high and low temperatures, with a maximum at intermediate ones. Such a maximum is apparent in Tylecote's work.[97] The discrepancy between his and Valensi's experimental results can be explained qualitatively—as far as the range 500–700° C is concerned—by the different methods of assessment. Valensi analysed the scales after removal, whereas Tylecote reduced them with hydrogen *in situ* at the temperature of oxidation; Tylecote has also shown that films formed above 520° C become enriched in CuO on cooling. Below 400° C, cooling has the opposite effect, and it appears difficult to find an explanation for the great discrepancies observed in this range.

Electron-diffraction [87, 88, 130, 131] and coulometric [86, 132–134] work indicates clearly that the composition of the oxide layer is a function of time during the earlier stages of the reaction, although it appears to become constant with prolonged oxidation.[127, 19] Tylecote [97] has shown that constancy is reached after a weight gain of roughly 1 mg/cm². Cruzan and Miley,[134] as well as Bouillon,[86] found that no CuO was formed below a critical film thickness. At higher thicknesses the CuO content increased approximately linearly with thickness. The values reported for this critical thickness are in poor agreement (600 Å at 240° C,[134] and 2600 Å at 247° C [86])—possibly because of different systematic errors in the coulometric determinations, in which NH_4Cl was used as electrolyte. On the other hand the discrepancy might be due to differences in preferred orientation of the metal; Lawless and Gwathmey [117] found that the critical film thickness for appearance of CuO is 3000 Å on the (001) face, 1100 Å on (011), but only 800 Å on (113).

Dravnieks [96] observed a spontaneous change in the rate constant at a certain film thickness during oxidation at reduced oxygen pressures at 500° C, which was accompanied by the sudden appearance of CuO on the surface of the oxide layer. From the variation of the critical film thickness with oxygen pressure, he concluded that CuO is nucleated first when the ratio of copper ion to oxygen supply at the outer film surface falls below a certain value.

Tylecote [97] found that the CuO content of his films increased with time at 270° C, in agreement with the electron-diffraction and coulometric results quoted, but at higher temperatures he observed the opposite trend. To explain this reversal, Tylecote assumed that oxidation starts with the formation of Cu_2O nuclei, which are oxidized to CuO before they can form a coherent film. This leads to an increase of CuO content as the nuclei grow, until they touch and a coherent film is formed. The access of oxygen is then limited and the CuO is reduced to Cu_2O by the metal ions diffusing out. At low temperatures where diffusion is slow, this stage is never reached, and only an increase in CuO is observed. At high temperatures, only the second stage is observed.

Although growth of isolated Cu_2O nuclei has been reported in microscopic studies (see next section), the observations do not bear out the assumption that they are immediately oxidized further. In fact, both at 150° and at 500° C [108, 107] no CuO was observed until a coherent film had been formed. In this connection, it should be valuable to examine quantitatively the relationship between CuO content and the appearance of whisker growth on the surface of the oxide layer (cf. next section). Diffraction studies on the whiskers indicate that they consist of cupric oxide, and the temperature domain of their principal occurrence coincides with the range of maximum CuO content as given in Tylecote's work.[97]

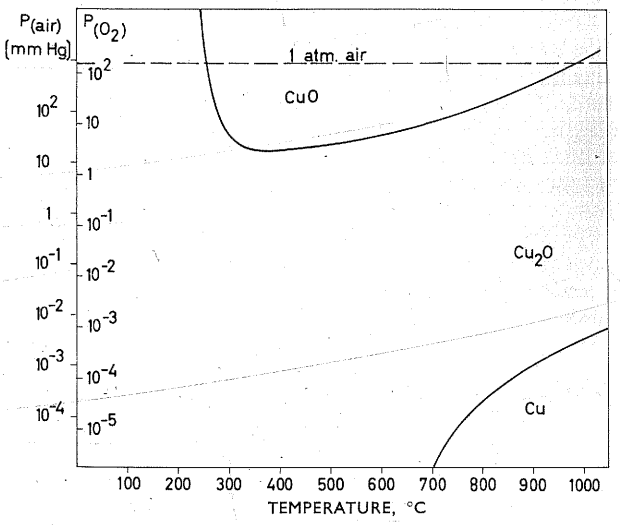

Fig. 6 Temperature/pressure regions of formation of Cu_2O and CuO. (Honjo [135]).

The dependence of film composition on oxygen pressure has been studied systematically by Honjo,[135] whose results are reproduced in Fig. 6. The oxygen pressure/temperature curves given there delineate the regions in which electron diffraction revealed either CuO or Cu_2O as the outermost oxide in the film. The study was conducted with a fixed oxidation time of " a few minutes ". Incidental observations of other authors [18, 86, 107, 130, 136, 164] are in reasonable agreement with Honjo's results.

Tylecote [97] found only small differences in CuO content for scales produced in air and in oyygen at various temperatures.

He ascribed them to the influence of nitrogen on blistering. At elevated temperatures and oxygen pressures, Bridges, Baur, Baur and Fassell [19] found a slight increase of CuO content with p_{O_2}.

Structure and Morphology of the Oxide

The morphology of the oxide is of great interest mainly because the theory of nearly all rate laws is based on the assumption of plane parallel film growth. In this section, evidence of non-parallel growth will be reviewed, such as nucleation phenomena and whisker growth. A general review on whisker growth in both metals and oxides has recently been given by Nabarro and Jackson.[137]

In his electron-diffraction work, Murison [138] noticed some anomalies in the diffraction pattern of CuO grown at certain temperatures. He assigned this " three-ring pattern " to an unknown oxide CuO'. Honjo [139] suggested that it might be due to a preferred orientation of crystallites of normal CuO. Gulbransen and McMillan [130] explained the anomalies by the presence of oxides of impurity metals. More recently Cowley [140] has shown, by an accurate analysis of the diffraction intensities of single-crystal and powder patterns, that the anomalous intensities in the " three-ring pattern " were due to single-crystal whiskers of ordinary CuO, which grew along the [110] direction and contained an axial screw dislocation. Heidenreich and Storks [141] are of a different opinion. They consider that " the origin of the anomalies must reside either in the structure itself or in the interaction of diffracted beams in the crystal (dynamical effect) ". This, however, has been refuted by Cowley.[142]

Needle crystals of oxide on metals had been observed earlier. Tylecote [144] noticed " hairs of oxide " on electropolished specimens oxidized under certain conditions. They appeared to consist of CuO. Richardson [145] at the same time made a similar discovery in the oxidation of iron. Hardy [146] suggested, on the basis of Frank's theory of crystal growth,[147] that dislocations ending in the metal surface served as nucleation points. The dislocation would be continued into the oxide layer, where it would form a preferred diffusion path, and an oxide whisker could grow.

Pfefferkorn [148–154] made electron-microscopic studies of the growth of oxide whiskers. On copper he found needles and, in a few cases, even plates of oxide. By observing the same whisker after different times of oxidation, he was able to show that the oxide needles grew from the tip and not from the base. By short treatment in a reducing atmosphere, the tips could be deactivated for further growth or changes in growth form could be induced. If one crystal bent and touched another, they would stick together and rapid growth would occur around the point of contact. These properties of growing needles led Pfefferkorn to assume that the whiskers grew by surface diffusion.

Harris, Ball, and Gwathmey [108] have made a transmission electron-microscopic study of oxide films removed by electrolysis from single-crystal surfaces. Three crystal faces were studied: (311), (111), and (100). The oxidation experiments were performed at atmospheric pressure and at 150° C, for times ranging from 20 to 5000 sec. The film thickness was >250 Å. Films of >80 Å were made up of: (*a*) small dense circular particles (nuclei), (*b*) dense masses often rectangular (polyhedra), and (*c*) a crystalline continuum of cuprous oxide (base film). The number of nuclei per unit area of film varied with time, while the number of polyhedra was independent of time. The base film appeared to develop by a process of lateral spreading of oxide crystals from the stable nuclei.

Jaenicke and Albert [157] have made a statistical study of the length distribution of CuO needles at different temperatures. They conclude that whisker growth occurs by surface diffusion with a parabolic rate law, and that it is inhibited randomly by impurities carried along from the metal. The rate of nucleation of the whiskers was proportional to the rate of formation of (stress-induced) dislocations in the underlying oxide. (Stresses in the oxide film can reach appreciable values, as has been shown by Dankov and Churaev [158] and, more recently, in an exhaustive study by Jaenicke and Leistikow.[159])

Earlier, light-microscopic studies of the discontinuous growth of oxide films had been made by Menzel, Stössel, and Menzel-Kopp [155, 163] and by Grønlund,[107] with similar results. Grønlund studied the oxidation of copper single crystals at a pressure of <1 mm Hg and in the range 300–900° C. The temperature most favourable for studying the growth of oxide nuclei was 500° C. The oxide film was examined by light microscopy and electron diffraction. At pressures of $>10^{-2}$ mm Hg, Grønlund found that for oxidation times >20 sec nuclei of Cu_2O formed. They grew laterally and after about 5 min covered the whole surface. At this point CuO appeared. The number of nuclei was independent of oxidation time, but a function of the orientation of the base metal. A more detailed discussion of the growth mechanism of Cu_2O nuclei is given in a paper by Bénard *et al.*[156]

Halliday and Hirst [160] have published reflection electron micrographs of copper surfaces oxidized to the same degree at room temperature and at 300° C, revealing the presence of pronounced mounds on the oxide surfaces formed at the higher temperatures, while the room-temperature film appeared perfectly smooth.

Pfefferkorn [153] pointed out that the surface magnification caused by whiskers must be taken into consideration when a study of the kinetics of the oxidation reaction is made. Concerning the theoretical assumption of uniform film thickness, Markali [161] emphasizes the importance of keeping the observed non-uniform film growth in mind in drawing conclusions on the rate laws of oxidation and its mechanisms. Hauffe,[162] on the other hand, considers that needle growth can be neglected on the assumption that needles grow only on relatively thick layers, so that the rate-determining step is still diffusion through the underlying oxide layer. This appears plausible for CuO needles growing on films of Cu_2O, but not necessarily for the other cases of discontinuous oxide growth reviewed above.

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