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REVIEW OF PUBLISHED INFORMATION ON THE OXIDATION AND SCALING OF COPPER AND COPPER-BASE ALLOYS.*†

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS.

Part I of the review describes methods used in experimental work on the oxidation of metals, including weighing, optical and electrolytic methods for measurement of oxidation rates, and X-ray and electron-diffraction methods for the study of oxide-film structures.

The rate of oxidation of copper and the structure of the films formed are considered in Part II. There is a reasonably good agreement on the oxidation rate/temperature characteristic for copper, the logarithm of oxidation rate/reciprocal of absolute temperature curve consisting of two straight lines of different slopes intersecting at about 600° C.

In Part III are reviewed the influence of alloying elements on the oxidation of copper and some effects of variations in the oxidizing atmosphere. A comprehensive table incorporates references to all the work found dealing with the oxidation of copper-base alloys. Selective oxidation and subscale formation are included in this section and modern theories on oxidation phenomena are also discussed.

Part IV deals with the practical aspects of oxidation, with particular reference to the adherence of troublesome scales. Little has been published about the scaling characteristics of copper and copper-base alloys at normal processing temperatures, and slight information is available on the effects of impurities in bright-annealing atmospheres.

INTRODUCTION.

A NUMBER of reviews covering the oxidation and scaling of metals have been published, one of which was issued by the Department of Scientific and Industrial Research [1] in 1935 and one more recently by Lustman [2] in 1946. In 1940 Vernon [3] reviewed recent studies on thin oxidation films, and Mott [4] contributed a paper on the mechanism of oxidation. The theories of Wagner and his co-workers were considered by Price [5] in 1937. Mention must also be made of Dr. U. R. Evans's book [6] in which much information is to be found on this subject. These reviews and many of the original papers have been consulted in preparing the present review of available information.

Part I describes experimental techniques used in the study of oxidation of metals and alloys. Part II is a summary of information

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on the oxidation of copper and includes reference to the mechanism of oxidation, the constitution and structure of the oxide film, and the effects of temperature, time, oxygen concentration, &c., on the rate of growth and type of oxide formed. The effect of alloying elements on the oxidation of copper and the effect of variations in the oxidizing atmosphere are considered in Part III, selective oxidation and internal oxidation and subscale formation being included. Some practical aspects of the oxidation of copper and copper alloys, such as scale thickness, adherence, and the prevention of scaling by the use of neutral or reducing atmospheres, are outlined in Part IV.

I.—Methods of Identification of Oxide Films and Measurement of Film Thickness and Rate of Oxidation.

One of the earliest and probably most commonly used means of determining oxidation rate, and therefore film thickness, is the gravimetric method. By this method, either continuous measurement of the increase in weight may be made with the aid of a special balance or calibrated silica spring [7] or the specimen may be removed from the oxidation furnace (together with any loose scale), and the increase in weight measured. In some cases the loss in weight is recorded on removal of the scale.

Recently improvements have been made in gravimetric technique by Dumez [8] who adapted the normal type of chemical balance to the automatic recording of oxidation curves at constant and varying temperatures. Chevenard [9] has designed a special balance employing a quartz or Invar beam with a fine-wire suspension, also with automatic recording. Both Dumez and Chevenard have placed the furnace above the balance in order to reduce the amount by which the heat from the furnace disturbs the operation of the balance. Continuous measurement reduces errors due to exfoliation of scale on cooling, permits the detection of small changes in oxidation rate due to film cracking, and facilitates repetition.

The above methods are generally used for the thicker films and exfoliating scales, but suffer from inherent inaccuracies when applied to thin films. It is in this sphere that the greatest progress has been made in the last decade. The electron-diffraction camera has been employed by many investigators, and two techniques have been developed: (i) The film may be examined in situ on the metal, whereupon information regarding its structure and composition may be obtained from diffraction data. The electron-diffraction patterns are produced by the surface layers, some 100–300 Å. thick; no information is afforded about the structure of the interior of thicker films, and films of less

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than about 100 Å. may exist without detection. (ii) Alternatively, the film may be stripped by chemical means and examined by transmission. This method can be used for films thinner than about 500 Å., but its value is doubtful owing to the possibility of changes in the structure of the films due to removal from the metal base. No reliable indication of film thickness can be obtained either by electron diffraction or transmission.

Many workers have used one of the optical methods [10, 11, 12, 13] which involve the reflection of polarized light. At least one of the methods available is applicable to films less than 50 Å. in thickness. Lustman and Mehl [11] have recently employed an optical method in their investigation of the oxidation of single crystals of copper. This involves the use of polarized monochromatic light obtained from a mercury-vapour lamp. The refractive index and thickness of the film on copper may be determined by comparing the measured change in ellipticity with the theoretical relationship determined by Leberknight and Lustman.[14] The range of thickness covered in the investigations of Lustman and Mehl [11] was from 0 to 1600 Å., and an accuracy in measurement of 1–5% is claimed. The main disadvantage of this method is that the film constants have to be determined for the oxide (or sulphide) present, and that it gives a reliable result only when the film consists of crystals of a single oxide or sulphide of known structure.

The standard of accuracy in the measurement of film thickness by the optical method described above is far greater than that obtained in the temper-colour method, which consists of a comparison of the interference colours formed by the film with some standard, and which is not applicable to films less than about 400 Å. in thickness.

The electrolytic method [15, 16] requires that the time be observed for the cathodic reduction of each part of the film substance. The film thickness may be determined from the quantity of electricity required for this reduction. Some knowledge of the expected film composition is necessary, but, for example, in the case of copper it is possible to obtain the thickness of each component of the film, whether CuO, Cu_2O, or sulphide. The method can be used for films up to about 2000 Å. thick.

It has been shown [17] that the above method, where reduction takes place in an open cell in contact with the atmosphere, is unreliable for very thin films (less than 100 Å.), and a closed-cell method has been developed which gives good agreement with the best optical methods in this range of thickness. The development of the electrolytic technique provides a satisfactory quantitative method by which the thickness of the separate parts of complex films can be measured. An X-ray method has recently been used for the measurement of the parameters of oxide films on iron.[18] This method could probably be used for thick films on copper (1000–10,000 A.).

A method used by Pilling and Bedworth [19] and others consists in measuring the change in resistance of a wire or thin film of metal due to the reduction of its current-carrying cross-section owing to oxidation. This technique was employed by Pilling and Bedworth for curves at 400° and 500° C., but does not seem to have been used extensively. Measurements of contact resistance provide yet another method by which film thicknesses may be estimated.[20] However, a precise knowledge of the composition of the film and of its electrical properties is necessary for accurate interpretation of the results.

One further method used in oxidation research,[21] consists of measuring the decrease in pressure of the oxidizing atmosphere when the specimen is heated in a closed system. From this measurement the amount of oxygen absorbed by the specimen may be calculated.

The results described in the following sections have been obtained by one or more of the above methods, and in order to avoid lengthy descriptions, the following abbreviations have been used:

G = Gravimetric (whether continuous or interrupted).
ED = Electron diffraction.
O = Optical.
M = Metallographic (chiefly for subscale).
ER = Electrolytic reduction (open or closed cell).
DP = Decrease in pressure in closed system.
R = Increase in electrical resistance.

II.—THE OXIDATION OF PURE COPPER.

1. *Mechanism of Film Growth.*

In the oxidation of metals the rate of reaction in most environments is controlled by the rate at which metal or oxygen can penetrate the oxide layer. In general, as the oxide becomes thicker the rate of reaction becomes slower, provided that the film is continuous and therefore protective. The early gravimetric work of Pilling and Bedworth [19] indicated that the type of oxidation depended upon the ratio of the volume of metal oxide to the volume of metal from which it forms, that is upon the ratio, $Wd : wD$, where W is the molecular weight of the oxide, w the weight of metal contained in W, D the density of the oxide, and d the density of the metal. If this ratio is less than unity the film will be discontinuous and will permit oxygen to reach the metal surface via the discontinuities. If the ratio is greater than

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unity the initially formed thin film will be compact and continuous, but as it thickens discontinuities may appear as a result of thermal stresses or compression stress. The latter would be expected to be highest where the volume ratio greatly exceeds unity.

Metals for which the volume ratio is less than unity include barium, caesium, calcium, lithium, magnesium, potassium, sodium, strontium; for others of common practical interest, including copper, the ratios exceed unity, that for cuprous oxide on copper being about 1·7.

It may be shown that metals which form compact films (which grow by means of a diffusion process due to a concentration gradient) should oxidize according to the parabolic law, where the square of the weight, and hence the thickness, is proportional to the time, i.e. :

$$y^2 = Kt + A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where y = thickness, t = time, and K and A are constants.

In the early work on copper this was found to be true, but departures from this relationship were found later. In the early stages of growth, especially at low oxygen pressures, the oxygen supply is not sufficient to cause oxidation of the metal atoms as fast as they diffuse to the surface, leading to a linear rate of growth :

$$y = Kt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as was observed, e.g. by Wagner and Grünewald [22] using a gravimetric method at 1000° C., with an oxygen pressure of 1 mm. of mercury. The growth was linear up to a film thickness of 10^{-3} cm. after which it became parabolic.

Dighton and Miley [23] have shown by the electrolytic-reduction method that for temperatures between 180° and 288° C. copper first oxidizes according to the parabolic law, and then as the time increases above 1–3 hr. the oxidation rate decreases, following the logarithmic relationship :

$$y = K \log\ a(t + 1/a) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

y, K, and t having the same meaning as in equation (1), and a being a constant.

Campbell and Thomas [24] (*DP*) obtained an approximately cubic relationship of the type :

$$y^3 = Kt + c \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for the oxidation of oxygen-free copper between 100° and 256° C.

According to Cabrera and Mott [25] the parabolic type of thickening can only be expected well outside the range of thickness over which a space charge is effective. This is about 10^4 Å. in the case of copper. Anderson [26] has also derived the cubic law for space-charge conditions, when the mean free path is large compared with oxide thickness. If the mean free path is small a law of the type $y^4 = Kt$ would be expected. Cabrera [27] has explained theoretically the reasons for the cubic type of oxidation, and why a logarithmic law would be expected for film thicknesses obtained on copper below about 100° C. Such a relationship was found by Lustman and Mehl [11] for copper at temperatures between 88° and 155° C.

At low temperatures, in the vicinity of room temperature, Cabrera and Mott [25] suggest that the oxide film on copper should thicken logarithmically up to about 100 Å., and then stop. However, work carried out by Evans and Miley [28] at 80° C. shows that copper achieves a film thickness of approximately 100 Å. in about 5 hr., but that this is not the limiting thickness. At higher temperatures, Cabrera and Mott [25] recognize a type of thickening which is initially logarithmic but which later becomes parabolic.

At medium and high temperatures all evidence shows that copper ultimately follows the parabolic law. However, the rate-determining process may be either the outward diffusion of copper or the inward diffusion of oxygen. Bardeen, Brattain, and Shockley [29] and Castellan and Moore [30] have shown, by using radioactive tracers, that the diffusion of copper ions in cuprous oxide is the rate-determining factor in the oxidation of copper between 800° and 1000° C.

There is now considerable evidence for the view that in cuprous oxide films the metal atoms diffuse outwards by means of vacant sites in the oxide lattice. Wagner [31, 32] postulates that the diffusion of atoms through the oxide layer involves dissociation almost completely into ions and electrons. The cations and electrons move outwards and the anions inwards across the film. According to Hoar and Price's electrochemical interpretation [33] the growing film may be regarded as a current-producing cell with the metal/film and oxygen/film interfaces as the anode and cathode respectively and with the film serving both as electrolyte and external circuit, as it has both electronic and ionic conductivity. Thus it would seem that the resistance to oxidation is closely connected with the electrical resistance of the film.

According to Mott [4] when Cu_2O is heated in oxygen its conductivity increases owing to stoichiometric excess of oxygen. It seems that the excess oxygen is not taken up interstitially, the oxygen atoms being too large to fit in the interstitial positions in the oxide lattice. The lattice accommodates excess oxygen through the absence from their normal lattice points of a few copper atoms. These vacant lattice points are mobile; i.e. an adjacent metal atom can move into them, and then another atom will move into the position which has been left vacant,

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Dünwald and Wagner[31] (*G*) were able to show that Cu_2O films had an excess oxygen content of the order of 0·1%. However, Fröhlich[35] has demonstrated by the chemical analysis of thick films formed on copper at 900° and 1000° C. over a period of 5–21 days, that the films contain excess copper. Whereas the theoretical copper content of Cu_2O is 88·82%, Fröhlich obtained figures ranging from 88·82 to 89·31%. Rother and Bomke[36] have shown that in films on copper oxidized for long times at 1065° C., both the electrical conductivity and copper content vary markedly through the film as shown in Fig. 1. Lustman and Mehl[11] have shown a similar variability in thin films formed at low temperatures. It appears that the part of the oxide film near the metal surface is predominantly metallic and possesses metallic conductivity. If the scale is removed together with the above-mentioned ' layer and chemically analysed, a metal excess may result.

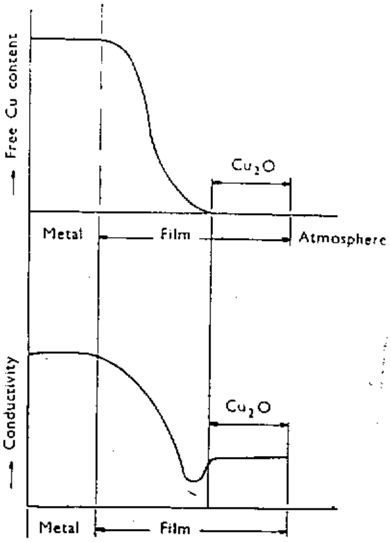

FIG. 1.—Change in Copper Content and Conductivity in Film on Copper (*Rother and Bomke*[36]).

Dravnieks and McDonald[37] suggest that the consumption of metal due to outward diffusion should lead to voids on the oxide/metal interface. Either these will result in the collapse of the oxide film, producing new metal-to-oxide contact, or they must be filled with oxide due to inward diffusion of oxygen. Dravnieks postulates that the spaces are filled with columns of oxide which also act as conduits for the delivery of metal atoms to the bulk of the scale. Such a system suggests that oxidation proceeds both inwards and outwards from the original metal surface, and explains why the result of the complete oxidation of a copper wire is not a hollow " tube " of oxide but a comparatively solid oxide " wire ". Dravnieks and McDonald[37] extend their theory to show how the existence of voids or cavity barriers leads to the slowing down of oxidation and hence to the logarithmic law, as also derived by Evans[38] (see below).

2. *The Effect of Internal Stresses.*

From the later work on copper and from work on other metals it is now clear that the volume ratio is only a rough guide to the oxidation characteristics of metals. Indeed, it has recently been shown by Gulbransen [39] that films on magnesium with a volume ratio 0·84 are protective in certain circumstances. This is apparently due to the fact that these films, with a volume ratio less than unity, can stand considerable tensile stresses before they break down.

The existence of internal stresses in thin films formed on oxides with volume ratios greater than unity has been demonstrated by Evans.[40] The films were isolated by dissolving away the metal substrate, whereupon they assumed a wrinkled appearance. Films with a volume ratio exceeding unity, as they grow thicker, tend to break down in a number of ways owing to these compressive stresses. Evans [38] has recently put forward a theory showing how the manner of breakdown may lead to any one of the first three oxidation equations enumerated above. If adhesion between the metal and film is poor, and the strength of the film substance is high, a blister will be formed as in Fig. 2 (*a*). As the film thickens further, these blisters may lead to a porous film of type (*b*) or (*c*) in Fig. 2. A less common form of breakdown is "flaking" ((*d*) in Fig. 2). This type is most likely to occur by the joining together of a large number of nearly continuous blisters. However, once flaking has started it is likely to spread rapidly. The third method of film breakdown is shown in (*e*) (Fig. 2). This is called "shear-cracking", and is most likely to occur where the adhesion between the metal and the film is good but the inherent strength of the film substance is relatively poor.

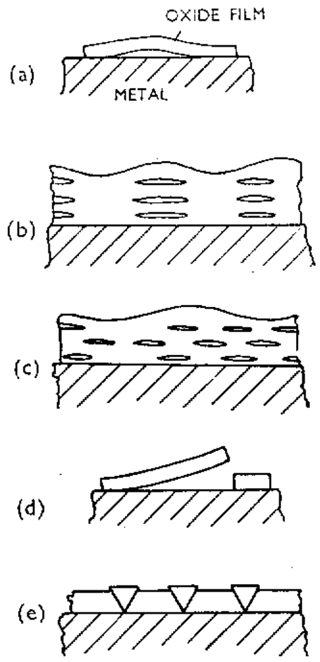

Fig. 2.—Forms of Film Breakdown (*Evans* [38]).
(*a*), (*b*), and (*c*) Blistering; (*d*) Flaking; (*e*) Shear-Cracking.

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One possibility suggested by this theory is that the form of the specimen, i.e. bent wires or flat strip, may have a profound influence on the stresses in the films, and on the manner of breakdown and therefore on the oxidation law.

3. *The Effect of Temperature.*

When oxidation is a simple diffusion process, i.e. when the parabolic law is obeyed, the temperature dependence of the oxidation rate should be in agreement with the Arrhenius equation:

$$K = Ae^{-Q/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where K is the "rate constant" (g.^{2} cm.$^{-4}$ hr.$^{-1}$), A is a constant (g.^{2} cm.$^{-4}$ hr.$^{-1}$), R is the gas constant, T the absolute temperature, and Q the activation energy (cal.).

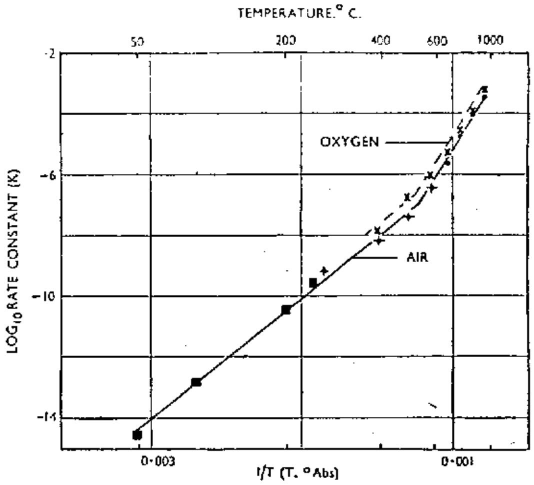

Fig. 3.—Oxidation Rate of Copper in Air and Oxygen.

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× $\left\{\begin{array}{l}\text{Pilling and Bedworth }^{19}\\ \text{Feitknecht }^{41}\end{array}\right\}$ in oxygen.
● Pilling and Bedworth [19] (in air).
+. Hudson *et al.*[42] (in air) (Cu + 0·47% As).
■ Vernon [43] (in air).

When the logarithm of the oxidation rate is plotted against the reciprocal of the absolute temperature, a straight line should result. The rate constants obtained by Pilling and Bedworth [19] and by Feitknecht [41] for copper oxidized in oxygen (Fig. 3), when plotted in this way, appear to fall on two straight lines intersecting at about 580° C. The results of Hudson and his co-workers,[42] and of Vernon [43] for copper oxidized in air, if plotted in the same way, also form two straight lines which are parallel to those of Pilling and Bedworth.[19]

Scales formed on copper between 300° and 900° C. at normal pressure consist of two layers, CuO overlying Cu_2O. The relative thickness of the CuO layer tends to decrease as the oxidation temperature increases, since CuO dissociates at 1025° C. at 150 mm. pressure.

According to Valensi [44] the upper part of the curve (Fig. 3) results from the reaction:

$$Cu + O_2 \longrightarrow Cu_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This reaction can be made to proceed exclusively by the oxidation of copper between 900° and 1000° C. at pressures between 15 and 120 mm., respectively, i.e. below the dissociation pressure of CuO. For this reaction Valensi has obtained by calculation and confirmed by experiment the formula:

$$K = 957e^{-37,700/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

At low temperatures, corresponding to those giving the lower straight line in Fig. 3, Valensi gives the rate-determining reaction as:

$$Cu_2O + O_2 \longrightarrow CuO \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

for which he obtains the formula:

$$K = 0{\cdot}054e^{-20,140/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Formulæ (7) and (9) define approximately the two straight lines shown in Fig. 3. These lines are, according to Valensi, the extreme tangents of a curve, and at intermediate temperatures the points in Fig. 3 represent a combination of reactions (6) and (8).

Table I shows the constant A and the activation energy Q, calculated

TABLE I.—*Comparison of Oxidation Constants Obtained by Various Investigators for Copper* ($K = Ae^{-Q/RT}$).

Type of Copper	Medium	Temperature Range, ° C.	Oxidation Constants		Reference
			Q, cal.	A, g.^{2} cm.$^{-4}$ hr.$^{-1}$	
Tough-pitch .	Air	50– 250	19,300	0·056	Vernon [43]
,, .	,,	700–1000	42,000	6300	Pilling and Bedworth [19]
,, .	Oxygen	500– 900	29,400	50	,,
,, .	,,	750–1020	42,000	6300	Feitnecht [41]
Oxygen-free .	Air	300– 550	20,140	0·054	Valensi [44]
,, .	,,	550– 900	37,700	957	,,
Tough-pitch .	,,	715– 970	29,000	40	Krupkowski [45]
,, .	,,	800–1030	41,000	6000	,,
Arsenical .	,,	300– 500	18,300	5×10^{-3}	Hudson,[42] *et al.*
(Grade not known)	,,	800–1000	39,000	...	Castellan and Moore [30]

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6300	Pilling and Bedworth[19]
50	,,
6300	Feitnecht[41]
0·054	Valensi[44]
957	,,
40	Krupkowski[45]
6000	,,
$\times 10^{-3}$	Hudson,[42] *et al.*
...	Castellan and Moore[30]

from the results obtained by different workers, for various temperature ranges. It is clear from the table that the activation energy corresponding to the high-temperature section of the oxidation range is of the order 29,000 to 42,000 cal., which corresponds fairly well with Valensi's figure of 37,700 cal. In the low-temperature range the data is rather meagre, but the activation energy obtained by Valensi of 20,140 cal. is well corroborated by Vernon[43] on pure copper, and Hudson *et al.*[42] on arsenical copper (Table I).

4. *Composition of Oxide Films on Pure Copper.*

Cruzan and Miley[15] studied the formation of cuprous and cupric oxide films on copper by the electrolytic-reduction method. Films of different thickness were formed by continuous heating at 240° C. in air for various times. It was found that all films less than 400 Å. thick consisted entirely of Cu_2O, while some of the films of an intermediate thickness (400–800 Å.) contained CuO, and all the films exceeding 800 Å. contained CuO. The thickness of the cupric oxide film never exceeded 150 Å. On the basis of their own results and those of Murison[46] (*ED*), and of Dunholter and Kersten[47] (*ED*), Cruzan and Miley put forward the following theory :

When diffusion through cuprous oxide films becomes sufficiently difficult cupric oxide is developed in the films, presumably from the oxidation of cuprous oxide. In this way the composition of the oxide film on copper is related to its total thickness. The thickness is a function of the temperature at which the film is produced, the period of time during which it is formed, the oxygen concentration in which it is developed, and any factor that might alter the permeability of the film, e.g. state of original surface, thermal stressing due to temperature cycle, &c. The presence of any cupric oxide nuclei due to the previous heat-treatment in the manufacture of the metal or otherwise, might cause a secondary reaction to start more readily and thus affect the relative proportions of cuprous and cupric oxide for such a material.

According to Cruzan and Miley prolonged heating produces thick CuO films which tend to exfoliate and can easily be separated from the underlying Cu_2O film. Murison[46] and later Miyake[48] (see Table II), both using electron-diffraction methods, have reported an oxide (designated CuO′ in Table II) formed within the range 300°–500° C., which had a structure different from those of Cu_2O and CuO. The new pattern varied from that of normal CuO in that an additional diffraction was observed and the relative intensities of the rings were changed. Such differences suggest that the new oxide may in fact be

TABLE II.—*Oxide Films Obtained Using Two Methods of Heating* (Miyake [48]).

Materials Examined	Heating Method †	Surface Products and Temperatures or Times of Oxidation After Which They Were Detected				
		Cu_2O	CuO'	CuO	Other Oxide, if Observed	Formation of Scale
Pure Copper (Cu 100%)	A	About 200° C.	300°–500° C.	(Experiments above 600° C. impossible)	...	Observed
	B	Very short time	Short time (10–20 sec.)	Rather long time (few min.)	...	Observed
7% Tin bronze Copper–7% manganese alloy Copper–7% nickel alloy Copper–7% magnesium alloy	A and B	Almost the same as in the case of pure Cu				
Aluminium bronzes: (97–90% Cu, 3–10% Al)	A	About 200° C.	300°–500° C.	600°–900° C.	...	Not observed
	B	*	*	*	Al_2O_3 after a few min.	Not observed
(98% Cu, 2% Al)	A and B	Almost the same as in the case of pure Cu				
70 : 30 Brass	A	*	*	*	ZnO after a few min. at less than 900° C.	Not observed
	B	Very short time (few sec.)	Short time (10–20 sec.)	Rather long time (few min.)	...	Not observed
Beryllium bronzes (98–85% Cu, 2–15% Be)	A and B	*	*	*	BeO after a few min. at about 800° C.	Not observed
Surface colour		Red (with an interference colour)	Black	Black	Al_2O_3 retains almost original metallic lustre. ZnO yellowish white. BeO retains almost original metallic lustre	

* Indicates that the oxide was not detected.

† A: Heated in electric furnace (200°–950° C.). B: Heated in gas flame (slightly reducing).

	B	Very short time (few sec.)	Short time (10–20 sec.)	Rather long time (few min.)	...	Not observed
Beryllium bronzes (98–85% Cu, 2–15% Be)	A and B	*	*	*	BeO after a few min. at about 800° C.	Not observed
Surface colour		Red (with an interference colour)	Black	Black	Al_2O_3 retains almost original metallic lustre. ZnO yellowish white. BeO retains almost original metallic lustre	

* Indicates that the oxide was not detected. † A : Heated in electric furnace (200°–950° C.). B : Heated in gas flame (slightly reducing).

an intermediate stage in the formation of the CuO, in which the atom sites are not occupied by copper and oxygen atoms in equal numbers.

Hickman [49] (*ED*) shows that there is a change in composition with temperature, from pure CuO at 20°–300° C., to a mixture of Cu_2O and CuO at 350° C., and 100% Cu_2O at temperatures above 450° C. The pressure used was equivalent to 1 mm., and there may have been some dissociation at the higher temperatures.

Valensi [44] (*G*) has shown by theoretical treatment that ideally the composition of the oxide film on copper should vary with temperature from 98% CuO at 300° C. to 90% Cu_2O at 900° C., and gives experimental figures which agree well with the calculated ones as shown below :

Temperature, ° C.	CuO, % Calculated	CuO, % Experimental
900	10·0	5·0
700	20·0	30·0
500	75·0	80·0
300	98·0	95·0

The discrepancy between these results and those of other workers is put down to the effect of the gas content of the copper, which Valensi minimized by vacuum-annealing for 12 hr. at 950° C. He [44] found that the composition at 860° C. was constant irrespective of film thickness. His theory suggests that this should be true at all temperatures.

Palmer [50] first detected the presence of CuO on copper at 165° C. on a highly activated (rough) surface.

5. *Effect of Oxygen Concentration and Pressure.*

The effect of oxygen concentration at 240° C. has been studied by Cruzan and Miley [15] (*ED*). They found that increasing the oxygen concentration increased the proportion of CuO in the film by a small amount, while decreasing the oxygen concentration by the admission of nitrogen into the furnace atmosphere, prohibited the formation of the CuO film entirely.

If the electrical theory of film formation is correct, increase in the oxygen pressure P should increase the electrical conductivity by increasing the number of ions and vacant spaces. Further, Mott has shown [4] that if complete dissociation into ions and electrons takes place, the electrical conductivity should vary as $P^{\frac{1}{8}}$, but if no dissociation takes place as $P^{\frac{1}{4}}$.

Dünwald and Wagner [34] (*G*) heated copper at 800°, 900°, and 1000° C. in oxygen and measured the conductivity of the Cu_2O film formed. They found that it varied linearly as the seventh root of the pressure of oxygen. This indicates that dissociation was very nearly complete. The rate of oxidation was also proportional to the seventh root of the pressure.

Examination of Pilling and Bedworth's results [19] (*G*) shows a similar relationship for pressures in the range 800–0·3 mm. of mercury, at 800° C. However, below 0·3 mm. the oxidation rate falls off far more rapidly than this relationship would indicate (Fig. 4). Wilkins [21, 51] (*DP*) working at temperatures from 150° to 200° C., found a similar change, but the pressure at which it occurred—which he termed the "limiting pressure"—varied according to the state of the copper surface. It appears that at high pressures the diffusion of oxygen through the film is the controlling factor in the rate of oxidation and the film at the surface is fully saturated with oxygen. As the pressure is reduced a point is reached where the rate at which oxygen is adsorbed is the controlling factor, the film surface ceases to be saturated with adsorbed oxygen, and a rapid decrease in oxidation rate results. At low pressures the rate of gas flow past the heated specimen has a profound effect on the oxidation rate, as Pilling and Bedworth [19] (*G*) have shown (Table III).

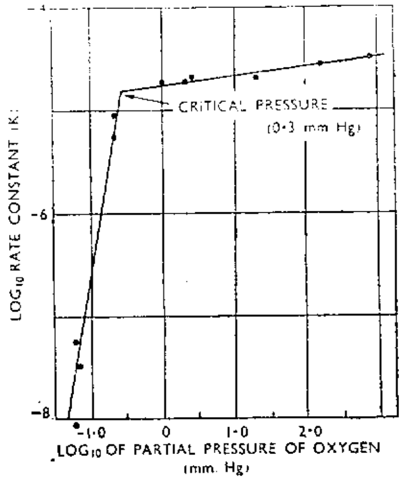

FIG. 4.—Effect of Oxygen Partial Pressure on Oxidation Rate of Copper at 800° C. (*Pilling and Bedworth* [19]).

TABLE III.—*Effect of Rate of Gas Flow on Oxidation of Copper at 800° C.* (Pilling and Bedworth [19]).

Rate of Flow, c.c./min.	Oxidation Rate Constant K, g.^{2} cm.$^{-4}$ hr.$^{-1}$ × 10^{-7}
In oxygen mixture; oxygen partial pressure: 1·7 mm. Hg.	
14	0·046
95	0·77
110	10·00
245	36·0
550	70·0
In air; oxygen partial pressure: 155 mm. Hg.	
Open furnace	270
15	250
145	260

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Rate Constant K, ' hr.$^{-1}$ × 10^{-7}
re : 1·7 mm. Hg.
0·046
0·77
10·00
36·0
70·0
5 mm. Hg.
70
50
60

Palmer [50] (*R*) found that below a pressure of 300 mm. on a highly activated surface, the oxidation-rate constant *K* was directly proportional to the partial pressure. Above this pressure the oxidation rate was substantially independent of pressure.

6. *Orientation and Structure.*

A number of investigators have determined the orientation of the oxide with respect to the metal surface. Preston and Bircumshaw [52] (*ED*) examined electrolytic copper oxidized in air at temperatures up to 400° C. It was found that the cuprous oxide film which was formed had a preferred orientation with the (111) plane parallel to the surface. No indication of possible preferred orientation of the underlying copper is given. The "activation" of the surface by repeated oxidation and reduction gave small crystals of Cu_2O with random orientation.

In contrast to Preston and Bircumshaw's results, Miyake [48] (*ED*) reported that in many cases the crystals of cuprous oxide were orientated so that the (110) planes tended to become parallel to the surface. This agrees with Thompson,[53] who found that the surface layer of his copper specimens was orientated with the (110) plane parallel to the surface and that the Cu_2O film formed had a similar orientation. Mehl, McCandless, and Rhines [54] found that the orientation of the film was identical with that of the underlying copper lattice.

Lustman and Mehl [11] made a comprehensive investigation of the oxidation of single crystals of copper at low temperatures. They found that at temperatures between 105° and 118° C. the rate of oxidation of different crystal faces varied. They thought that this was probably due to the observed difference in orientation between the metal crystal and the oxide crystal that formed on it. However, the relationship was very complex and varied with temperature.

Electron-diffraction studies by Phelps and his co-workers [55] on the oxidation of copper in oxygen at 200° C. showed that the Cu_2O film was relatively coarsely crystalline. The size varied from a mean of 500 Å. at 5 min. to 750 Å. at 30 min. They were of the opinion that films containing small crystals were the most protective and that the coarse nature of the Cu_2O film was one reason for its non-protective character.

Smith [56] (*ED*) showed that thin films formed on copper heated in air, and removed by dissolution in potassium sulphate, had no preferred orientation and consisted wholly of Cu_2O. Unheated films consisted of copper and Cu_2O, but the lattice of the copper was expanded 1·5%, which Smith thought might have been due to dissolved oxygen.

Bénard and Talbot[57, 58] (*G*) found that the oxidation rate of copper at 850°–900° C. increased with amount of cold work, owing to the increasing degree of preferred orientation. The rate of oxidation of single-crystal faces decreased in the following order:

(210)–(221)
(211)–(110)
(111)
(100)
(123)

According to Cabrera and Mott,[25] if the difference between the lattice parameters of the exposed plane of the metal and the oxide is less than 15%, the film will be pseudomorphic; if it is greater than this figure, the film will take up very nearly its own unstrained lattice parameter.

7. *Effect of Surface State.*

Films formed on smooth and mirror-like surfaces are less permeable than films formed on abraded surfaces containing corrugations, shattered metal, &c., resulting from abrasion treatment, according to Evans and Stockdale.[59] As the stage of growth at which CuO begins to form depends on the permeability of the film, it might be expected that CuO would form sooner on smooth surfaces than on rough ones. That this is so is shown by comparison between the electron-diffraction results obtained by Dunholter and Kersten[47] and by Miyake,[48] respectively. Dunholter and Kersten first detected CuO films at temperatures of from 120° to 180° C. (depending on oxidation time) on surfaces prepared by condensing copper on to glass. On emeried (0000) surfaces prepared by Miyake,[48] CuO was not detected below 300° C.

Lustman and Mehl,[11] using the optical method, found that for low temperatures (105°–155° C.) smooth surfaces oxidized more slowly than rough surfaces. Bénard[58] (*G*) found that the rate of oxidation of copper at high temperatures fell as the surface roughness was decreased. This presumably was due to a decrease in the true surface area. Gulbransen[60] and Valensi[44] have pointed out that the effect of a rough surface will be to show initially an apparent reduction in oxidation rate, since the true surface area will lessen as oxidation smooths out inequalities.

8. *Effect of Other Atmospheres.*

Dyess and Miley[61] (*ER*) determined the thickness of films on copper which were mixtures of cupric oxide, cuprous oxide, and cuprous sulphide. When oxide-coated copper was exposed to moist hydrogen

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sulphide in air at room temperature, copper sulphide was formed, owing partly to combination of some sulphur with copper from the metal and partly to the replacement of some of the oxygen in the oxides by sulphur. No evidence was obtained of the replacement of sulphur by oxygen at 220°–270° C. when sulphide films were heated in air in an electric furnace. Thin oxide films containing pores, and thick ones with cracks, give poor protection against H_2S. It was observed that sulphide films gave more protection against attack by moist H_2S than oxide films of similar thickness. Dyess and Miley suggest that the specific conductivity of the sulphide may be less than that of the oxide.

To some extent this work contradicts the results of Vernon,[62] who found that impure oxide films containing sulphide exposed to air at room temperature had lower oxidation-resistance than pure oxide films. Pure sulphide films not only caused a greater attack on the underlying metal than pure oxide or oxysulphide when exposed to ordinary air (containing some sulphur), but also selectively absorbed sulphur from the atmosphere. On the other hand, sulphur is virtually unable to penetrate pure oxide films.

The effect of atmospheres containing steam and water vapour has been studied by Preston and Bircumshaw [52] (*ED*) and by Hallowes and Voce [63] (*G*). Treatment for 1 hr. in steam at 100° C. gave Cu_2O, and a second phase which was thought to be CuO.[52] The introduction of 10% water vapour made little difference to the rate of oxidation in air at 400° C.[63] At 400° C. the effect of additions of SO_2 and Cl to the atmosphere [63] was to increase the oxidation rate, particularly in the presence of moisture.

Vernon [64] found that up to 10% of SO_2 in dry air had no effect on the oxidation rate of copper at room temperature. However, there was a big increase in the oxidation rate when the relative humidity exceeded about 63%. The effect of additions of CO_2 to atmospheres containing SO_2 and water vapour was negligible. The effect of 0·01% HCl, with and without SO_2 and water vapour, was to produce a marked increase in oxidation rate.

There is considerable evidence that pure steam and pure water vapour have little effect on the oxidation of copper up to 800° C. at atmospheric pressure.[19, 84] However, in the case of steam the impurities present in the water from which it is formed may exert a considerable effect, as has been shown by Hallowes and Voce [65] for an aluminium bronze. In the case of reducing atmospheres, the presence of CO_2, H_2O, and H_2S may markedly affect the scaling properties.

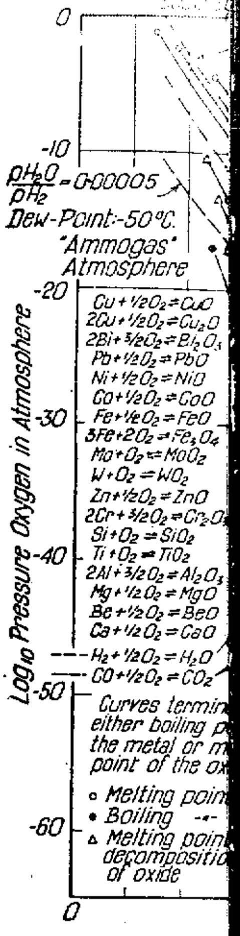
III.—Effect of Impurities and Alloying Elements on Oxide Films on Copper.

1. *Surface Scale.*

Metal oxides differ considerably with regard to their stability. Whereas silver oxide is relatively unstable and can be decomposed when heated to a moderate temperature, oxides of aluminium, magnesium, and beryllium are extremely stable, and can be reduced only with great difficulty. The stability of an oxide is measured by its standard free energy of formation ($-G^{\circ}$), the more refractory oxides (aluminium, magnesium, beryllium) having high free energies, and the less refractory oxides, of silver, copper, &c., having low free energies. A considerable amount of information on this subject has been collected recently by Ellingham,[66] and by Richardson and Jeffes.[67] To the industrial metallurgist and others interested in oxidation problems the dissociation pressure of an oxide is more valuable than the standard free energy of formation. The dissociation pressures of many oxides have been calculated by Lustman,[2] and are given in Fig. 5.

In regard to oxidation, copper alloys form two main groups: (1) alloys with noble metals, which form substantially pure Cu_2O scales, and (2) alloys with baser metals, where the alloying element appears as an oxide in the scale, often in greater concentration than in the alloy itself and sometimes to the exclusion of Cu_2O. The oxides of the noble metals have higher dissociation pressures than Cu_2O, and hence their oxides are not present in films on copper-base alloys. However, the majority of copper-base alloys fall into the second class. Under mildly oxidizing conditions, i.e. with low partial pressures of oxygen, it is possible for the oxide of the baser metal, e.g. alloying elements such as aluminium, beryllium, or silicon, to form exclusively and in preference to Cu_2O. During the early stages of the oxidation of a binary alloy of copper and a baser metal, both oxides will form. Whether or not the oxidation rate of the alloy is less than that of copper will depend on the concentration of the alloying element and the relative diffusion velocities of metal atoms (or ions) in the oxide layers.

Contributions on the theory of the oxidation of binary alloys have recently been made by Smirnov and Orlov[68, 69] Smirnov[68] concludes that the formation of a protective oxide film may be expected when the diffusion velocity of one of the metals becomes small compared with the other as the film thickens. If the diffusion constants of the two metals in the nearly pure oxide of the alloying elements are sufficiently small, the growth of the film will be greatly retarded, and it will have good oxidation-resistant properties. Orlov and Smirnov[69] extend this



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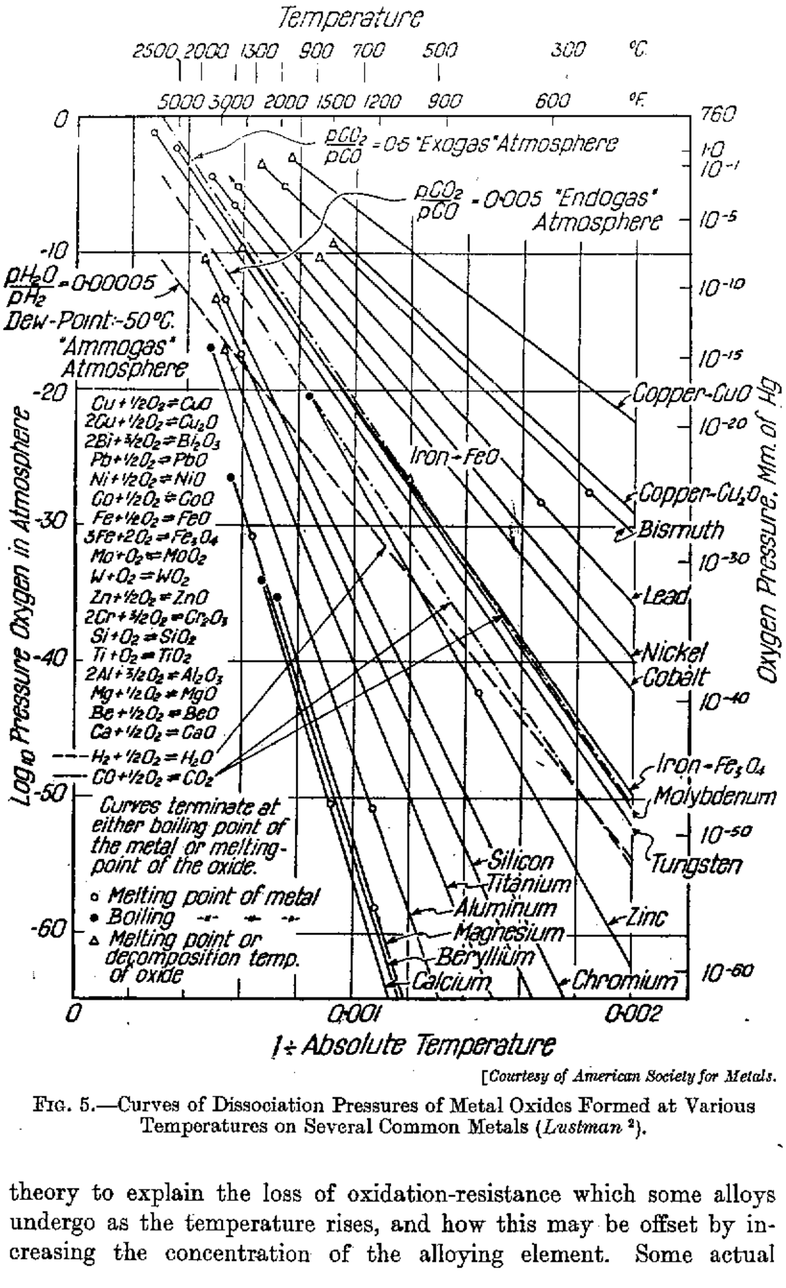

[Courtesy of American Society for Metals.

FIG. 5.—Curves of Dissociation Pressures of Metal Oxides Formed at Various Temperatures on Several Common Metals (*Lustman* [2]).

theory to explain the loss of oxidation-resistance which some alloys undergo as the temperature rises, and how this may be offset by increasing the concentration of the alloying element. Some actual examples are taken from the experimental results of other workers to show how these agree with theoretical predictions.

On the experimental side, some investigators have examined the effects of the addition of a large number of elements on the oxidation-resistance of copper. Many others, however, have examined the effect of one element over a restricted, or sometimes a considerable, range of compositions. It is proposed therefore first to discuss the experimental results of those workers who have dealt with a wide range of different binary and ternary alloys and compared their oxidation-resistances. The results of the other workers in the oxidation field will be collectively discussed under the various alloys investigated. The range of information available is summarized in Table IV.

Miyake[48] investigated a range of copper-base alloys by electron diffraction. Two methods of heating were used, one described as method *A* in which the specimens were brought to temperatures between 200° and 950° C. over a period of 10 min. in free air, and the other (*B*), where the specimens were placed directly in a slightly oxidizing flame and brought up to 800° C. in a very short time.

The results of Miyake's experiments are summarized in Table II. The differences in behaviour of aluminium bronze under the conditions of methods *A* and *B* are ascribed to the insufficiency of oxygen in the gas flame, which probably prevented the formation of CuO. Miyake deduced that the affinity of aluminium for oxygen led to its selective oxidation. It is probable that with the *A* method of heating, an Al_2O_3 scale is formed beneath CuO and Cu_2O. On aluminium bronzes containing more than 3% aluminium, γ-alumina formed underneath the superficial Cu_2O film after prolonged heating in a gas flame. There was no change in surface colour. The surface film on 70 : 30 brass heated in air corresponded to pure ZnO and was yellowish-white in colour. BeO was formed on the surface of beryllium bronze at high temperatures with both heating methods.

Fröhlich[35] (*G*) investigated the oxidation in air of a wide range of copper-base alloys at 800° C. with times up to 24 hr. A summary of his results is given in Table V. Of the alloys investigated the most resistant were those containing aluminium, beryllium, or magnesium. The next most resistant were alloys containing large amounts of tin or zinc. The effect of large additions of arsenic, cerium, and chromium was to increase the oxidation rate.

Fröhlich also made a study of the oxidation of nickel silver (nickel 18, zinc 21%), where he found that preferential oxidation of the zinc had occurred, as shown in Table VI.

Campbell and Thomas[24] (*DP*) determined the oxidation rates in

TABLE I

Alloying Elements	[illegible]
Ag	[illegible] [illegible] [illegible] [illegible] [illegible]
Ag–Au Ag–Pd	[illegible] Ag 40–91, Pd
Al	[illegible] [illegible] [illegible] [illegible] [illegible] [illegible]
Al–As Al–Be Al–Cr Al–Fe	Al 8·0, [illegible] Al 0·049, [illegible] Al 8·0, [illegible] Al 10·0, Fe Al 8, 10, Fe
Al–Fe–Ni	Al 10·0, Fe
Al–Mn	Al 8, 10, Mn Al 7·0, Mn
Al–Ni Al–Si Al–Ti	Al 8, 10, Ni Al 4, 6, Si Al 8, 10, Ti
As	0·46 0–1·0 0·03–0·1 9·5 0·47
Au	90, 95 0–100
Au–Pd	Au 33·3, Pd
B	0·005
Ba	0·10
Be	0·018–0· 0·005–0· 0·38–2· 2·0–15 0·49–9· 1·5–3·
Be–Ni	Be 2·0–2·5, Ni
Bi	0·03
Ca	trace 1·0 0·01
Cb	0·04
Cd	0·25–0· 1·0
Ce	0·01 5·0

* G = gravimetr

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TABLE IV.—*Summary of Information Available on Oxidation of Copper-Base Alloys.*

Alloying Element(s)	Composition Range, %	Temperature Range, °C.	Atmosphere	Method *	Ref.	Notes
Ag	1·0	400	Various	G	63	
	1·0	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	4·0	700	Air	G	35	
	0–100	600–750	Air and oxygen	G	70	
	0–100	750	Oxygen	G	71	
Ag–Au	Ag 0–62, Au 10–59					
Ag–Pd	Ag 40–94, Pd 0–40					
Al	0·01–0·91	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	0·03–0·72	600–1000		M	74	
	1·0–3·0	800	Air	G	35	
	2·0–12·0	400	Various	G	63	
	2·0–10·0	200–950	Air and gas	ED	48	
	0–10	700	Air	G	75	
Al–As	Al 8·0, 10·0, As 0–1·0	700	,,	G	75	
Al–Be	Al 0·049, Be 0·003	600–1000	Air, Cu_2O + Cu	M	74, 73	
Al–Cr	Al 8·0, 10·0, Cr 0–1·0	700	Air	G	75	
Al–Fe	Al 10·0, Fe 2·8	400	Various	G	63	
	Al 8, 10, Fe 0–4·0	700	Air	G	75	
Al–Fe–Ni	Al 10·0, Fe 5, Ni 5	400	Steam + SO_2 + chlorine	G	65	
Al–Mn	Al 8, 10, Mn 0–4	700	Air	G	75	
	Al 7·0, Mn 4·0	180–400	Oxygen	ED	52	
Al–Ni	Al 8, 10, Ni 0–4·0	700	Air	G	75	
Al–Si	Al 4, 6, Si 0–5·0					
Al–Ti	Al 8, 10, Ti 0–4·0					
As	0·46	400	Various	G	63	
	0–1·0	700	Air	G	75	
	0·03–0·12	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	9·5	800	Air	G	35	
	0·47	300–600	Air, chlorine, &c.	G	42	
Au	90, 95	300–950	Air	G	72	
	0–100	750	Oxygen	G	71	
Au–Pd	Au 33·3, Pd 0–61·7	750	,,	G	71	
B	0·005	600–1000	Air, Cu_2O + Cu	M	74, 73	
Ba	0·10	600–1000	Air, Cu_2O + Cu	M	74, 73	
Be	0·018–0·10	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	0·005–0·10	600–1000	,,	M	74	
	0·38–2·4	800	Air	G	35	
	2·0–15·0	200–950	Air and gas	ED	48	
	0·49–9·96	610–910	Air	G	76	
	1·5–3·0	400	,,	G	77	
Be–Ni	Be 2·0–2·5, Ni 0·25 max.	100–300	Oxygen	DP	24	
Bi	0·03	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Ca	trace	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	1·0	800	Air	G	35	
	0·01	600–1000	Air, Cu_2O + Cu	M	74	
Cb	0·04	600–1000	Air, Cu_2O + Cu	M	74, 73	
Cd	0·25–0·28	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	1·0	400	Various	G	63	
Ce	0·01	600–1000	Air, Cu_2O + Cu	M	74, 73	
	5·0	800	Air	G	35	

* G = gravimetric. M = metallographic. ED = electron diffraction. DP = decrease in pressure in closed system.

TABLE IV.—(*continued*).

Alloying Element(s)	Composition Range, %	Temperature Range, ° C.	Atmosphere	Method*	Ref.	Notes
Co	0·14	600–1000	Air, Cu_2O + Cu	M	74, 73	
	8·0	800	Air	G	35	
Co–Si	Co 2·7, Si 0·4	800–1050	,,	G	79	
Cr	0·08–0·10	600–1000	Air, Cu_2O − Cu	M	73	Subscale
	0·08	600–1000	,,	M	74	
	2·0	800	Air	G	35	
Fe	0·1	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	0·037–2·65	600–1000	,,	M	74	
	7·75	800	Air	G	35	
Fe–Ni–Co	Fe 18, Ni 18, Co 10	100–300	Oxygen	DP	24	
Ga	0·03	600–1000	Air, Cu_2O + Cu	M	74, 73	
Ge	0·2	600–1000	Air, Cu_2O + Cu	M	73	Subscale
In	0·25	600-1000	Air, Cu_2O + Cu	M	73	Subscale
Li	0·02	600–1000	Air, Cu_2O + Cu	M	74	
	0·67	800	Air	G	35	
Mg	0·7–2·76	800	Air	G	35	
	0·10	600–1000	Air, Cu_2O + Cu	M	74, 73	
	7·0	200–950	Air and gas	ED	48	
Mn	0·03–1·55	600–1000	Air, Cu_2O + Cu	M	74, 73	
	4·0	400	Various	G	63	
	5·0	800	Air	G	35	
	7·0	200–950	Air and gas	ED	48	
	0–20	700	Air	G	75	
Na	0·1	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Ni	1·0, 20	800	Air	G	35	
	3·0	400	Various	G	63	
	7·0–70	300–900	Air and gas	ED	80	
	0·1–5·0	600–1000	Air, Cu_2O + Cu	M	74, 73	
	7·0	200–950	Air and gas	ED	48	
	0–70	700	Air	G	75	
	44·0	20–400	,,	ED	78	
	0–100	750–1000	Oxygen	G	81	
	0–100	300–800	,, (1 mm.)	ED	82	
Ni–B	Ni 5·2, B 0·38	800	Air	G	35	
	Ni 7·0, B 0·5					
Ni–Be–Si	Ni 45, Be 1·0, Si 1·0–2·0	600–1000	,,	W	83	
P	0·05, 0·54	800	Air	G	35	Subscale
	0·03–0·24	600–800	Air, Cu_2O + Cu	M	74	
	0·03–2·05	600–800	,,	M	73	
	0·25	400	Various	G	63	
Pb	0·03	600–1000	Air, Cu_2O + Cu	M	74, 73	
Pd	0·20	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	0–100	750	Oxygen	G	71	
Pt	0·10	600–1000	Air, Cu_2O + Cu	M	73	Subscale
	90, 95	300–1550	Air	G	72	
S	0·02	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Sb	2·4	800	Air	G	35	
Se	0·1	600–1000	Air, Cu_2O + Cu	M	73	Subscale

* G = gravimetric. M = metallographic. ED = electron diffraction.
W = electric heating of wire (life test). DP = decrease in pressure in closed system.

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Method*	Ref.	Notes
M G G	74, 73 35 79	
M M G	73 74 35	Subscale
M M G DP	73 74 35 24	Subscale
M	74, 73	
M	73	Subscale
M	73	Subscale
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G M ED	35 74, 73 48	
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M	73	Subscale
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M	74, 73	
M G	73 71	Subscale
M G	73 72	Subscale
M	73	Subscale
G	35	
M	73	Subscale

= electron diffraction.
n pressure in closed system.

TABLE IV (*continued*).

Alloying Element(s)	Composition Range, %	Temperature Range, °C.	Atmosphere	Method*	Ref.	Notes
Si	0·045–1·9	600–1000	Air, Cu_2O + Cu	M	74, 73	
	0·5–3·0	800	Air	G	35	
	1·0	400	Various	G	63	
	0–8·0	700, 800	Air	G	75	
Si–Fe	Si 0·9–4·5, Fe 0·06–0·28	725, 827	Air – oxygen	G	84	
Si–Mn	Si 3·0, Mn 1·0	400	Various	G	63	
Si–Mn–Fe	Si 3·0, Mn 1·0, Fe 0·09	100–300	Oxygen	DP	24	
Si–Ni	Si 0·5, Ni 0·75	400	Various	G	63	
Sn	0·31	600–1000	Air, Cu_2O + Cu	M	74, 73	
	2·0	400	Various	G	63	
	2·8–20·0	800	Air	G	35	
	7·0	200–950	Air and gas	ED	48	
	0–16·0	700	Air	G	75	
Sn–Al	Sn 5·4, Al 0·06	600–1000	Air, Cu_2O + Cu	M	74, 73	
Sn–Be	Sn 0·3–5·0, Be 0·006–0·02	600–1000	,,	M	73	Subscale
Sn–P	Sn 6·1, P 0·54	800	Air	G	35	
	Sn 1·9–5·0, P 0·007–0·11	400	Various	G	63	
	Sn 7·5–8·5, P 0·03–0·2	100–300	Oxygen	DP	24	
Sn–Si	Sn 5·02, Si 0·085	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Sr	0·10	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Ta	0·05	600–1000	Air, Cu_2O + Cu	M	74, 73	
Te	0·10	600–1000	Air, Cu_2O + Cu	M	73	Subscale
Ti	0·05	600–1000	Air, Cu_2O + Cu	M	74, 73	
	4·0	800	Air	G	35	
	20	300–800	Oxygen (1 mm.)	ED	49, 85	
Tl	0·03–0·49	600–1000	Air, Cu_2O + Cu	M	73	Subscale
V	0·09	600–1000	Air, Cu_2O + Cu	M	73, 74	
W	0·10	600–1000	Air, Cu_2O + Cu	M	73	
Zn	0·16–0·21	600–1000	Air, Cu_2O + Cu	M	73, 74	
	3·22	400	Various	G	63	
	5·0–40	800	Air	G	35	
	0–40	580–880	Air + oxygen	G	84, 86	
	0–100	300–900	Air, Cu_2O + Cu	M	87	
	30	200–950	Air and gas	ED	48	
	30	100–400	Air	ED	52	
	0–35	700	,,	G	75	
	30, 38	20–300	,,	ED	78	
	40	200–425	,,	G	43	
	26·5–35·5	100–300	Oxygen	DP	24	
Zn–Al	Zn 26–29, Al 2	100–300	,,	DP	24	
	Zn 30, Al 0–2·0	775	,,	G	84, 88	
	Zn 22, Al 2·0	100–400	Air	ED	52	
	Zn 9·29, Al 0·13	600–1000	Air, Cu_2O + Cu	M	73, 74	
Zn–Be	Zn 9·52, Be 0·03	600–1000	,,	M	73	Subscale
Zn–Ni	Zn 21, Ni 18	800–950	Air	G	35	
	Zn 18, Ni 20	20–300	,,	ED	78	
	Zn 25–29, Ni 16–20	100–300	Oxygen	DP	24	
Zn–Si	Zn 9·81, Si 0·085	600–1000	Air, Cu_2O + Cu	M	73	
Zr	0·16	600–1000	Air, Cu_2O + Cu	M	73, 74	
	60	300–800	Oxygen (1 mm.)	ED	49, 85	

* G = gravimetric. M = metallographic.
ED = electron diffraction. DP = decrease in pressure in closed system.

Table V.—*Effect of Alloying Elements on Oxidation-Resistance of Copper* (Fröhlich [35]).

Group	Alloying Element and Content, %			Oxidation-Resistance
1	Be (2·4)	Al (2·5, 3·0)	Mg (2·76)	Very high
2	Zn (20–40)	Sn (8·6, 20·0)	Be (1·0)	High
3	Ni + B (5·2–7·0 Ni, 0·38–0·5 B)		Si (3·0)	Fair
4	Ag (4·0) Li (0·67) Ca (1·0) Mn (5·0) Ni (1·0, 20·0)	Co (8·0) P (0·05, 0·54) Sb (2·4) Fe (7·75) Ti (4·0)	Mg (0·7) Sn (2·8) Zn (5·0) Be (0·38) Si (0·5–1·8)	About the same as copper
5	As (9·5)	Cr (2·0)	Ce (5·0)	Inferior to copper

Table VI.—*Change in Composition of Nickel Silver Due to Oxidation at 950° C.* (Fröhlich [35]).

Element	Time, hr.		
	0	15	36
Cu, %	60·7	62·6	67·0
Ni, %	17·7	18·5	18·7
Zn, %	21·6	18·9	14·0

the temperature range 100°–300° C. of a number of binary and ternary copper-base alloys. These included 2% beryllium copper, Everdur, phosphor bronze (8% tin), 70 : 30 and 67 : 33 brasses, nickel silver, aluminium brass, and a copper–iron–nickel–cobalt alloy.

The oxidation of the phosphor bronze, copper–nickel–iron–cobalt alloy, and 70 : 30 brass was of the same type as that of copper, with somewhat lower oxidation rates. The oxidation rate of the other materials, however, decreased to a very low value, the oxygen absorbed in 1 hr. at 200° C., being of the order of $\frac{1}{20}$th that of copper.

Nishimura [75] (*G*) determined the oxidation properties of a number of α-solid solutions of copper at 700° C. in air. He found that the aluminium bronzes were the most resistant, 8% aluminium being required for maximum resistance. The next best were nickel and tin alloys, up to 40% and 16% (the maximum investigated), respectively, being required for maximum resistance. The optimum silicon content was 4%; increasing the silicon content to 8% resulted in a decreasing oxidation-resistance. The effect of zinc was determined up to 35%, about 20% being sufficient to give maximum resistance. Additions of

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(*a*) Alloys contain
2·8% iron).

(*b*) Binary alloys
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(*c*) Three industria
1% manganese, (2) 0·5
phosphorus.

The atmospheres
dry air + 0·1–5% SO

Their conclusions
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Copper–Zinc.

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	Oxidation-Resistance
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up to 20% manganese caused a continuous increase in oxidation-resistance. The effect of up to 1% arsenic was negligible.

Under conditions of intermittent oxidation, which are more representative of practical oxidation conditions, the least resistant materials tend to produce exfoliating scales, while the more resistant materials form adherent scales. Hallowes and Voce [63] (*G*) investigated five varieties of commercial copper and eighteen copper-base alloys for resistance to intermittent oxidation at 400° C. in five atmospheres. The alloys studied may be divided into three groups:

(*a*) Alloys containing 2–12% aluminium (one with 10% aluminium + 2·8% iron).

(*b*) Binary alloys containing small amounts of silver, cadmium, chromium, manganese, nickel, phosphorus, silicon, tin, zinc.

(*c*) Three industrial alloys, containing respectively: (1) 3% silicon + 1% manganese, (2) 0·5% silicon + 0·75% nickel, and (3) 5% tin + 0·1% phosphorus.

The atmospheres other than dry air included: air + 10% H_2O, dry air + 0·1–5% SO_2, and moist air + 0·1% HCl.

Their conclusions were that with the exception of silver all elements effected an improvement to a greater or lesser extent in the oxidation-resistance of copper to dry air, silicon and aluminium being the most effective. The introduction of 10% of water vapour into the atmosphere made little difference except to tin bronzes, the oxidation of which was approximately doubled. 0·1% SO_2 in dry air generally increased attack, and moist air + HCl was exceedingly detrimental. The most resistant materials were the high-aluminium bronzes, with or without iron, and the 3% silicon + 1% manganese alloy.

Copper–Zinc.

Dunn [84] (*G*) observed the oxidation of copper–zinc alloys, containing from 60 to 100% copper, in air at temperatures from 580° to 880° C. In alloys containing from 28 to 40% zinc the scale consisted almost entirely of ZnO, while in alloys containing 0–12% zinc the scale contained copper in the same proportions as in the alloy. In these two groups the rate of oxidation at constant temperature conformed with the parabolic law, but for the intermediate range of alloys (12–28% zinc) the oxidation rate was much less than that corresponding to the parabolic law, and the departure was ascribed to an increase in the grain-size of the film. With one exception the logarithm of oxidation rate was proportional to the reciprocal of the absolute temperature. The addition of water vapour, CO_2, or dry SO_2 to dry oxygen was found to have no accelerating effect on the rate of oxidation, although wet SO_2 produced a considerable increase and HCl was most damaging.

Rhines and Nelson [87] (*M*) have investigated the microstructure of copper–zinc alloys (0–100%) after heating between 300° and 900° C. Two methods of heating were used: heating with free access to air in an electric muffle, and heating in an iron vessel packed with a mixture of Cu_2O and copper metal powder or foil.

Cu_2O was present in the external scale on alloys containing up to 20% zinc heated in air, over the whole temperature range. At low zinc concentrations the Cu_2O is the matrix of the scale and contains embedded particles of ZnO in greatest concentration near the metal surface. As the zinc content of the alloy increases, the ZnO adjoining the metal surface becomes a continuous film, and with even higher zinc contents Cu_2O occurs only as occasional particles in the ZnO film. No Cu_2O forms on samples heated in the Cu_2O–Cu mixture, the scale consisting entirely of ZnO.

Continuous films of ZnO are formed on alloys containing more than 20% zinc oxidized in air. This film is relatively thin and tends to spall on cooling. No continuous film of ZnO is found on the surfaces of samples heated in the Cu–Cu_2O pack, but isolated patches do appear on or just below the surface.

Copper–Zinc–Aluminium.

The effects of additions of aluminium to 70 : 30 brass were investigated by Dunn [84] (*G*) and 1·9% aluminium was found to reduce the oxygen absorbed in 3 hr. at 775° C. in oxygen from 1·0 to less than 0·02 mg./cm.². Preston and Bircumshaw [52] (*ED*) also investigated the behaviour of 70 : 30 brass with up to 2% aluminium at 100°, 183°, and 400° C. in air. It was found that the effect of aluminium was to inhibit formation of a Cu_2O film on the surface at 100° C. Cu_2O was present at 183° C., and at 400° C. ZnO was also present.

Copper–Silver.

Leroux and Raub [70] (*G*) studied the oxidation of the whole range of copper–silver alloys, at 600° and 750° C. in air and oxygen.

More recent work by Raub and Engel [71] (*G*) was carried out at 750° C. in oxygen for times up to 70 hr. Oxidation of alloys containing from 10 to 80% silver was approximately parabolic. In the case of alloys containing 90 and 94% silver, the rate was more rapid at first but tended to negative values later. Minima occurred in each of the curves of oxygen absorbed against silver content of the alloy, at about 70 and 100% silver. The maximum oxidation rates occurred at 100% copper and 85% silver.

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Copper–Gold.

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Gold–10% copper

Copper–Platinum.

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Copper–Palladium.

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Raub and Engel [71] found that alloys rich in copper (e.g. 50% copper) form a homogeneous scale of Cu_2O overlying a subscale of Cu_2O and silver. In the case of alloys containing more than 72% silver oxidation proceeds solely by the formation of a subscale of ever-increasing thickness. At reduced oxygen pressures, i.e. in air, there is a tendency for CuO to form instead of Cu_2O.

Copper–Gold.

Raub and Engel [71] also investigated the oxidation of copper–gold alloys from 0 to 95% gold, at 750° C. The amount of oxygen absorbed per gramme of copper decreases slightly with increase of gold content up to 58%; after that there is a rapid decrease to zero at 100% gold. The 5% copper alloy has a thin film of CuO after 30 hr. at 750° C. due to the low diffusion rate of oxygen in gold. Increasing copper content results in the formation of an outer layer of Cu_2O and an inner scale layer of Cu_2O and gold.

Kubaschewski [72] (*G*) showed that copper-gold alloys containing 5–10% copper follow the parabolic law. He points out that the volume ratio of Cu_2O to that of the alloy is much smaller than that of Cu_2O to copper (= 1·65), and on this basis explains the good adherence of Cu_2O scales on gold–copper and platinum–copper alloys. Kubaschewski gives the following constants for the Arrhenius equation :

Alloy	Temperature Range, ° C.	A (g.^{2} cm.$^{-4}$ hr.$^{-1}$)	Q (cal.)
Gold–5% copper	500–900	675	11,200
Gold–10% copper	400–870	11×10^4	11,500

Copper–Platinum.

According to Kubaschewski [72] (*G*) platinum alloys containing 5% and 10% copper also follow the parabolic law. The activation energy for the 10% copper alloys was 11,800 cal. and A was 42 (g.^{2} cm.$^{-4}$ hr.$^{-1}$). In the region of 900° C. the oxide dissociated, until at about 1200° C. there was a loss in weight, probably due to volatilization of copper. However, there seems to be some evidence for the existence of a gaseous platinum oxide at 1100°–1400° C.

Copper–Palladium.

Raub and Engel [71] (*G*) investigated a range of copper–palladium alloys containing from 0 to 95% palladium. They found a minimum in the oxygen absorbed per gramme of copper at 30–40% copper. The curves had much the same parabolic form as those of the gold–copper alloys, but the oxidation rate of the 95% palladium alloy was only half that of the 95% gold alloy.

Cu–Au–Ag, Cu–Au–Pd, and Cu–Pd–Ag.

Raub and Engel [71] also examined ternary alloys containing 10–58·5% gold, 0–85% silver, remainder copper; 33·3% gold, 0–61·7% palladium, remainder copper; and 6–20% copper, 0–54% palladium, 40–94% silver.

Copper–Nickel.

Dunn [84] (*G*) states that the addition of up to 1% nickel has no effect upon the oxidation rate of pure copper.

Miyake [80] carried out electron-diffraction experiments on copper–nickel alloys containing 7% nickel, 40% nickel, and 70% nickel + 1·4% iron + 1·0% manganese (Monel). He found that the outer layers of the film formed in air at 300°–900° C. on alloys containing 7% nickel consisted solely of copper oxides. When these oxides were removed (the method is not stated) from an alloy containing 7% nickel, a brown film appeared which had a lattice constant corresponding to NiO.

Hickman and Gulbransen [82] (*ED*) examined a range of copper–nickel alloys containing 12–90% nickel, in the temperature range 300°–800° C. NiO was observed in the outer layers of the film at increasing temperatures varying from 500° to 800° C., as the nickel content of the alloy was reduced from 90 to 12%. The authors thought that the reason for the reduction of the oxidation rate with increasing amounts of nickel was the effect of nickel on the diffusion rate of copper through the film. It also appears that copper ions form and diffuse faster through the film than nickel at low temperatures, but that the position is reversed at higher temperatures.

Hessenbruch [83] reports that additions of 1% beryllium, 2% silicon, and 1% beryllium + 1% silicon increase the permissible working temperature of Constantan (45% nickel–55% copper) from 600° to 800° C. With the 1% beryllium + 1% silicon addition, the life of a 0·016 in. dia. wire was extended from 36 to 314 hr., using a heating cycle consisting of 2 min. on and 2 min. off (temperature not stated).

Copper–Titanium and Copper–Zirconium.

Hickman and Gulbransen [85] (*ED*) found that on 80 : 20 and 72 : 28 copper–titanium alloys, TiO_2 only appeared on the surface of the oxide film at temperatures above 500° C. In the case of a 40 : 60 copper–zirconium alloy, they found that zirconia was completely absent from the surface up to the maximum temperature investigated of 700° C.

Copper–Silicon.

Dunn [84] (*G*) investigated a number of copper–silicon alloys containing from 0·9 to 4·6% silicon and from 0·06 to 0·28% iron, at 725° and

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Copper–Aluminium

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827° C. 4·58% Silicon reduced the rate of oxidation at 725° C. to one-quarter of that of pure copper. Smaller amounts had a correspondingly smaller effect. A tightly adherent scale was produced which, when removed in HCl, left a dull transparent film which was thought to be silica. The ratio of copper : silicon in the scale and film together was substantially the same as in the metal.

While at 827° C. an alloy containing 0·9% silicon oxidizes at approximately the same rate as copper, alloys containing 3·25 and 4·58% silicon oxidize initially at about one-third the rate for copper. After a short time, however, the rate increases to approximately that of copper. The scale from alloys oxidized at this temperature was found to contain practically no silicon, and it is therefore not surprising that the final oxidation rate approximated to that of copper.

The explanation put forward by Dunn [84] to account for this result is that the initial film formed on the alloys of high silica content contains some silica in solid solution which renders the film less permeable, but that at a later stage the silica is reduced by copper, assuming that the solubility of silica in Cu_2O is appreciable and that of silicon negligible so that the reaction $SiO_2 + 4\,Cu \rightleftarrows 2Cu_2O + Si$, which normally proceeds to the left, is reversed and proceeds to the right, the silicon freed entering into solid solution in the metal.

Nishimura [75] (*G*) studied the oxidation in air at 700° and 800° C. of a range of copper–silicon alloys containing up to 8% silicon. Increasing the amount of silicon to 4% caused a gradual increase in the oxidation-resistance, while further additions up to 8% silicon decreased it. At 800° C. no sudden increase in the oxidation rate as found by Dunn at 827° C. was noted, although the maximum time investigated by Nishimura was 24 hr. and that of Dunn only 3 hr.

Copper–Aluminium.

Preston and Bircumshaw [52] (*ED*) heated an aluminium bronze (7% aluminium + 4% manganese) in oxygen at 183° C. and obtained a diffraction pattern corresponding to Cu_2O. At 400° C. the outer layer of the surface film was thought to be MnO_2. No evidence of crystalline Al_2O_3 was found.

According to Nishimura [75] (*G*) the addition of more than 2·0% manganese to a 10% aluminium bronze considerably decreases the oxidation-resistance in air at 700° C., although the same addition to a bronze containing 8% aluminium has very little effect.

Nishimura [75] (*G*) has also investigated the effect of nickel, iron, titanium, chromium, and arsenic on the oxidation of 8 and 10% aluminium bronzes at 700° C. in air. The effect of up to 1% arsenic, 1% chromium, 4% nickel, and 6% iron is negligible. Up to 6% titanium decreases the oxidation-resistance slightly. On a bronze containing 4% aluminium, the effect of more than 4% silicon was to decrease the oxidation-resistance considerably, although the effect of silicon on a bronze containing 6% aluminium was slight.

2. *Wagner's Theory of Oxidation and Selective Oxidation of Alloys.*

If Wagner's theory is correct, the electrical conductivity of the oxide film will influence the rate of oxidation to a very great degree, and oxides with low conductivities should produce films with high oxidation-resistance. Examination of Fröhlich's results (Table V) shows that the alloying elements giving the maximum oxidation-resistance are beryllium, aluminium, and magnesium. Price and Thomas [89] have quoted values for the electrical conductivities of the oxides formed by these elements and those giving lower oxidation-resistance, and it will be seen that the three elements giving the best oxidation-resistance also have oxides with the lowest conductivity (Table VII).

TABLE VII.—*Conductivity of Oxides of Elements in Table V at 1000° C.* (Price and Thomas [89]).

Group	Oxide	Conductivity, mhos/cm.	Remarks
1	BeO Al_2O_3 MgO	10^{-9} 10^{-7} 10^{-5}	... ...
2	SnO_2 * ZnO *	10^{-2} 1	} Excess-cation type
3	SiO_2	10^{-6}	...
4	TiO_2 † CoO NiO CaO † FeO Fe_2O_3	10^{-4} 10 10^{-2} 10^{-7} 10^{-2} 10^{-1}	... ... Smaller volume than metal ... ...
5	CeO_2 † Cr_2O_3	10^{-2} 10^{-1}	... ...
Cu (for comparison)	Cu_2O CuO	10 10	... Probably dissociates
Ag	Ag_2O	...	Dissociates

* High oxidation-resistance probably due to oxide being of excess-cation type.

† Element in question insoluble or only slightly soluble in Cu, and 2-phase alloy cannot be expected to have high oxidation-resistance.

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Wagner[31] has shown that where the electrical conductivity of the oxide film formed on a metal is independent of the oxygen pressure, and the controlling factor is a diffusion process, the constant K of the equation of oxide growth:

$$\frac{d\eta}{dt} = \frac{K}{y}$$

should be given by:

$$K = (n_1 + n_2)n_3cE_0/F.$$

where η = number of equivalents of oxide produced per cm.^{2} per sec.
t = time in seconds
y = thickness of film in cm.
F = Faraday's number
E_0 = affinity of the metal for oxygen in volts
n_1, n_2, and n_3 = the transport numbers of cations, anions, and electrons, respectively, in the film,
and c = the specific conductivity of the oxide.

The value of $(n_1 + n_2)n_3c$ is shown by Wagner to be approximately 2×10^{-3} mhos/cm. for cuprous oxide at 1000° C. The value of $(n_1 + n_2)n_3$ for the passage of copper ions through alumina is not available, but the value can in no circumstances be greater than 0·25 (since $n_1 + n_2 + n_3 = 1$), while the value of c for alumina is about 10^{-7} mhos/cm. at 1000° C. The ratio of $(n_1 + n_2)n_3c$ for cuprous oxide and alumina must therefore be greater than:

$$\frac{2 \times 10^{-3}}{0{\cdot}25 \times 10^{-7}}$$

i.e. greater than 80,000.

In other words, if sufficient aluminium is present in copper to cause the formation of an alumina film, the oxidation rate will be reduced by a factor of more than 80,000. Fröhlich, however, found that the addition of 2·5% aluminium to copper only decreased the oxidation rate by a factor of about 36. Price and Thomas[89] suggest that the reason for this discrepancy is that under natural conditions the alumina film that is formed contains veins or bridges of copper or Cu_2O which reduce its electrical resistance.

Price and Thomas therefore made experiments on a copper–5% aluminium alloy. Normal oxidation of this alloy for 4 hr. at 800° C. in dry oxygen produces a tenacious black oxide film. They considered that by carrying out the initial oxidation under conditions so slightly oxidizing that only alumina was formed, a much greater oxidation-resistance could be obtained from this alloy. By heating first in moist hydrogen (0·1 mm. water-vapour pressure) for 15 min. at 800° C., and then exposing to full oxidizing conditions as mentioned above, they decreased the oxidation velocity by a factor of $\left[\frac{1358}{2\cdot78}\right]^2 = 240{,}000$, a figure of the order predicted by Wagner's theory.

Hallowes and Voce [63] found that the selective oxidation of a copper–5% aluminium alloy by Price and Thomas's method protected it from atmospheric oxidation up to 800° C., provided that the film was not scratched or otherwise damaged. It did not confer protection against atmospheres containing SO_2 or HCl.

Price and Thomas [89] extended this technique to a copper–2·5% beryllium alloy, and considerable resistance to tarnishing was obtained by selective oxidation-treatment. Similarly, by electrolytic deposition of a film of BeO the tarnishing of copper at room temperature was almost prevented.[90]

3. *Internal Oxidation and Subscale Formation.*

Copper-base alloys in which oxygen is relatively soluble may develop a subscale or zone of internal oxidation. Underneath the scale proper is a layer consisting of copper with oxygen in solution and containing small particles of the oxide of the alloying element (see Fig. 6). This effect is due to the diffusion of oxygen into the alloy, resulting in preferential oxidation of the alloying element and its precipitation as an insoluble oxide.

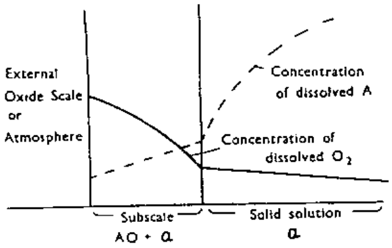

Fig. 6.—Concentration of Oxygen and Solute in α Solid Solution (*Rhines* [73]).

As the solute is exhausted by precipitation, the oxygen supplied to the surface diffuses farther into the alloy and thus produces a subscale of ever-increasing thickness. Rhines [74, 73] (*M*) and his co-workers have investigated subscale formation in a series of α solid solutions. Their work was mainly carried out at 600° and 1000° C., but alloys containing silicon, manganese, phosphorus, and aluminium were also investigated at 871° and 750° C. The duration of test was 2 hr. at 1000° C. and 192 hr. at 600° C. Alloys which formed subscales contained aluminium, arsenic, beryllium, cadmium, chromium, cobalt, iron, lead, manganese, nickel, phosphorus, silicon, selenium, tin, magnesium, and zinc, and also many other elements of less industrial

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importance. Alloys containing silver, platinum, and palladium showed no internal oxidation. When a liquid phase was present, subscale formation was very much more rapid. Rhines found that the rate of growth of the subscale decreased with time, with increasing concentration of alloying element, and with reduction in the oxygen pressure.

Rhines and Nelson [87] (*M*) have undertaken a comprehensive investigation on the structure of the subscale in the copper–zinc alloys oxidized at elevated temperatures. Subscale formation has also been noted by Smith [91] in copper–silicon alloys, by Hensel, Larsen, and Holt [79] in copper–cobalt–silicon alloys, by Blazey [82] in copper containing bismuth and arsenic, and by Fröhlich.[35]

Darken [93] has discussed the mechanism of subscale formation and shown how the rate of growth and composition of subscale may be predicted from a knowledge of diffusion constants, phase relations, and boundary conditions.

The work of Rhines and his collaborators was summarized in 1947.[94] Rhines mentions in the course of his review, that the surface hardening of alloys due to the presence of finely distributed oxide does not seem to be possible. However, work carried out by Meijering and Druyvesteyn,[95, 96] at about that time showed that such hardening is possible. Whereas the hardness of pure copper annealed in air at 950° C. is 50 V.P.N., the hardness of copper containing small amounts of either beryllium, magnesium, titanium, aluminium, or zirconium, was increased to the range 100–170 V.P.N. The maximum hardening effect (170 V.P.N.) was obtained with an addition of 0·2–0·35% beryllium. Amounts of aluminium exceeding 2·0% had no surface-hardening effect, while the addition of small amounts of either manganese, zinc, silicon, tin, or antimony had very little effect. In order to avoid loss by external oxidation, after a thin film of Cu_2O had been formed, diffusion was carried out in nitrogen or carbon dioxide.

The hardening mechanism appears to be similar to that of age-hardening, and the oxide particle-size must be sub-microscopic.

IV.—PRACTICAL ASPECTS OF OXIDATION OF COPPER AND COPPER ALLOYS.

The oxidation of copper and copper alloys is of considerable practical importance both in respect of the behaviour of materials in manufacture and in service, either at ordinary temperatures or at elevated temperatures.

From the published literature reviewed in the preceding section Table VIII has been compiled with a view to showing the extent of present knowledge of the types of scales formed on various copper-base materials heated in air or oxygen at temperatures within or near the usual industrial range of annealing temperatures.

It is unfortunate that little information is available on the thickness of films formed within the normal annealing range, viz.: 400°–600° C. The majority of investigators have carried out work at temperatures of 700°–1000° C. Most of the information given for 400° C. was obtained by alternate oxidation and scale removal.

TABLE VIII.—*Summary of Data for Oxide-Growth Constant* (K) *for Copper and Copper Alloys Heated in Dry Air or Oxygen at Atmospheric Pressure.*

Material	Temperature, °C.	K, g.^{2} cm.$^{-4}$ hr.$^{-1}$	Nature of Film	Ref. No.
Tough-pitch copper	400	$5{\cdot}8 \times 10^{-8}$	Exfoliative	63
Tough-pitch arsenical copper	400	$1{\cdot}8 \times 10^{-8}$		
Phosphorus-deoxidized copper	400	$2{\cdot}9 \times 10^{-8}$		
Phosphorus-deoxidized arsenical copper	400	$1{\cdot}3 \times 10^{-8}$		
Tough-pitch copper + 1% Ag	400	$5{\cdot}8 \times 10^{-8}$	Exfoliative	63
,, + 1% Cd	400	$0{\cdot}35 \times 10^{-8}$		
Brass (70 : 30)	580	$8{\cdot}8 \times 10^{-9}$	Partly adherent	84
,, (60 : 40)	580	$5{\cdot}5 \times 10^{-9}$	Adherent	84
,, (60 : 40)	425	$2{\cdot}2 \times 10^{-10}$		43
Al brass (70 : 30 : 2)	775	$1{\cdot}3 \times 10^{-10}$	Adherent	84
Bronze (2·8% Sn)	800	$2{\cdot}1 \times 10^{-5}$	...	35
,, (8·6% Sn)	800	$1{\cdot}5 \times 10^{-6}$	...	
,, (6·1% Sn, 0·54% P)	800	$2{\cdot}1 \times 10^{-5}$	...	
,, (5·0% Sn, 0·11% P)	400	$2{\cdot}3 \times 10^{-8}$	Slightly adherent	63
Al bronze (7% Al)	400	$<1 \times 10^{-11}$	Adherent	63
,, (10% Al, 5·0% Fe, 5·0% Ni)	400	$<1 \times 10^{-11}$	,,	63
Si bronze (3% Si, 1·0% Mn)	400	$8{\cdot}0 \times 10^{-9}$	Fairly adherent	63
,, (3% Si)	800	$6{\cdot}0 \times 10^{-6}$	...	35
Cupro-nickel (30% Ni)	800	$7{\cdot}5 \times 10^{-5}$	...	81
Cu–Ni–Si (0·75% Ni, 0·5% Si)	400	$6{\cdot}0 \times 10^{-9}$	Exfoliative	63

By means of the rate constant (K) for any particular alloy and temperature, an estimate of the thickness of the oxide film * formed in air may be obtained from the following formula:

$$\text{Thickness of scale formed in 1 hr.} = 1{\cdot}5\sqrt{K}\ \text{cm.}$$

where K = rate constant (g.^{2} cm.$^{-4}$ hr.$^{-1}$).

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* It is assumed that the oxide is Cu_2O or CuO. These will form the bulk of the scale on most copper-base alloys heated in atmospheres rich in oxygen.

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Exfoliative	63

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As has already been mentioned, when the logarithms of the rate constants are plotted against the reciprocals of the absolute temperatures, a straight line, or in the case of copper two straight lines, will result. It is perhaps unfortunate that these two lines formed in the case of copper (and copper containing small amounts of some other elements), intersect within the annealing range, i.e. at about 580° C., but sufficient information is available for this material to be able to calculate the film thickness at any temperature (see Fig. 3).

The only alloy for which there is sufficient data to be able to obtain a complete plot of log K against $1/T$ over the whole range of temperature is a 60 : 40 brass (Fig. 7). In this case the intersection of the two straight lines occurs outside the normal annealing range, i.e. at about 300° C.

However, while the above procedure can give an idea of the thickness of scale produced by an annealing treatment in air, further data is required to calculate the thickness of films formed in bright-annealing atmospheres. For copper for a given time the film thickness will be proportional to the partial pressure of the oxygen present up to a certain critical pressure, after which it varies only slightly with the oxygen pressure (according to the results obtained by Pilling and Bedworth [19] (Fig. 4) and Wagner and Grünewald.[22] The pressure above which the oxidation rate varies only slightly with pressure, depends on the surface finish, but with rolled surfaces is likely to be less than 0·3 mm. (Hg).

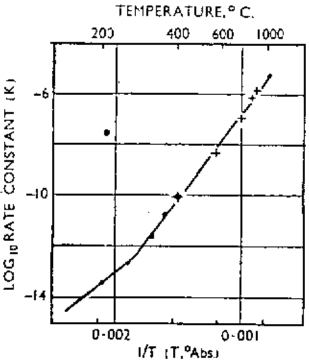

Fig. 7.—Oxidation Rate of 60 : 40 Brass in Air and Oxygen.

KEY.

+ Dunn [84] (in oxygen).
● Vernon [43] (in air).

The oxygen partial pressure of the atmospheres used, other than for cracked ammonia which is reducing, will probably be less that this value, and therefore the oxidizing properties will vary considerably with gas composition, as the relevant part of the curve in Fig. 4 will be the very steep portion. The exact composition of the atmosphere, i.e. whether impurities are present such as HCl, H_2S, or H_2O, &c., will have a marked effect on the scaling behaviour in these atmospheres. The presence of all these impurities can, of course, be avoided, but in industrial annealing practice this is rarely economic, and large fluctuations are to be expected.

Pawlek [97] has investigated the effect of bright-annealing atmospheres on copper and copper-base alloys. The atmospheres covered include partially burnt cracked ammonia, burnt town's gas, and burnt propane, with various ratios of air : gas, and also a vacuum. The effect of annealing copper and the following alloys is shown by means of colour photographs: 5–6% aluminium bronzes, brasses (10–40% zinc), cupro-nickel (78% copper–22% nickel), and aluminium brasses. The effect of the sulphur present in the propane is of particular importance.

Probably the most important property of a scale to the manufacturer of copper-base alloys is its adherence. This property has so far had very little attention according to the literature. Generally a thick scale tends to exfoliate while a thin scale is normally adherent, but there is no doubt that small amounts of alloying elements may exert a marked effect on the property of adherence without affecting the thickness of the film. For example, the presence of 0·47% arsenic makes little or no difference to the rate of oxidation of copper in dry air,[42] but this element helps to give an adherent scale in a firebox atmosphere at low temperatures.

Bamford [98] noted that tough-pitch non-arsenical copper had a very adherent scale which did not flake off on air-cooling from 750° C., and penetrated into the metal (i.e. formed a thick subscale). The addition of 0·45% arsenic was found to obviate this, and the scale was more easily removed. It will be noted that this appears to conflict to some extent with Hudson's results [42] quoted above.

The effect of heat-treatment and cooling rates on the adherence of scales on different types of copper has been investigated by Webster,[99, 100] and his co-workers. The first part of the work [99] was carried out by slowly heating pieces of $1\frac{3}{4}$-in.-dia. tube in two grades of copper: phosphorus-deoxidized (0·009% phosphorus (P.D.O.)) and tough-pitch (Lake) (T.P.). Pieces of each grade were withdrawn at intervals of 100°, from 450° C. upwards, and quenched. At 450° C., after quenching, both coppers had a mottled appearance. Between 550° and 750° C. the scales were completely removed from both coppers. At 850° C. that on P.D.O. was completely removed, while only 5% of that on the T.P. copper was removed. After quenching, the specimens of T.P. were all red, while those of P.D.O. were red to pink. The heating time varied from 17 min. at 450° C. to 88 min. at 850° C.

The second part of the work [100] consisted of annealing the coppers for $\frac{1}{2}$ hr. at temperatures between 500° and 900° C., and either removing the scale by pickling or quenching. An O.F.H.C. copper was added to the series for comparison. The results of quenching were very much the same as those obtained in the previous experiment. In the case of the T.P. and O.F.H.C. coppers, the scale was partially adherent at 800° C.,

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These results show that the effect of adding phosphorus to the copper influences the adherence between the scale and the metal, which the presence of oxygen in the metal does not do.

Sharavsky[101] investigated the effect of small amounts of impurities on the adherence of cuprous oxide films formed on copper at 1000° C. The specimens were taken out of the furnace at 1000° C., and placed in another at 600° C. and furnace-cooled to room temperature. It was found that the elements aluminium, beryllium, silicon, nickel, arsenic, tin, and antimony produced non-adherent scales if the concentration was high enough. The presence of small amounts of silver, phosphorus, manganese, iron, cobalt, zinc, cadmium, gold, thallium, and lead did not have this effect.

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