Die erwähnte Aufspaltung liegt für Kupfer, wie aus zahlreichen, experimentell bestätigten Rechnungen[12] hervorgeht, zwischen der des Aluminiums und des Messings. Daher ist theoretisch auch für Kupfer keine volle Isotropie des Verfestigungszustands und keine volle Gültigkeit der Pragerschen Formeln zu erwarten.

Wir danken der Deutschen Forschungsgemeinschaft für die Unterstützung der Versuche.

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[12] A. Seeger, Phil. Mag. **46**, 1194 [1955].

Study of Cuprous Oxide formed at 410°C at Pressures of Air between 0.5 and 75 mm of Hg

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(Z. Naturforschg. **11 a**, 41—45 [1956]; eingegangen am 24. September 1955)

Oxides of copper formed at a temperature of 410° C and at pressures between 0.5 and 75 mm of Hg have been studied. At these low pressures we get only one oxide namely Cu_2O. The increase of pressure and the time of oxidation appear mainly to produce a change in the orientation of the Cu_2O crystallites. The films when sufficiently thick peal off, but even at this stage of thickness ($1\ \mu$ to $3\ \mu$) they do not show any electrical resistance or rectification.

In a previous paper[1] we have studied the formation of oxides of copper in air at atmospheric pressure. In the present work we have tried to study the formation of oxides of copper at low pressures. The pressure range selected was 0.5 to 75 mm of Hg. (At high temperatures about 1000° C this range of pressures enables us to obtain a film of cuprous oxide, which exhibits assymetrical conduction i. e. rectification.) The temperature chosen was 410° C. Our previous work has shown that this is approximately the temperature at which cupric oxide changes from a three ring pattern to clear visible orientation (110 and 011).

Experimental

All the copper blocks to be oxidised were taken from a copper rod ($\frac{1}{2}''$ in diameter). They were cut to a thickness of about $\frac{1}{4}$ inch. The blocks were kept at a temperature of about 1070° C in vacuum (0.04 mm of Hg) for one hour. Then they were suddenly cooled by dropping them in water. This procedure was repeated for about 20 times. This removed the strains which might have been developed in the process of manufacturing[2] copper rods. In the case of last heating, the copper blocks were cooled suddenly in vacuum by pouring water over the silica tube. These blocks showed on their surfaces microscopic crystallites showing spots on electron reflection rings. The blocks were now polished and their surfaces were etched. They showed usual polycrystalline rings as expected from the face centred structure of copper. The spots on the rings were now absent. These blocks free from strains were used in all our work.

Oxidation

The copper blocks, on which oxides were to be formed, were abraded on emery papers of various grades and finally polished with rouge-spread on a thick cloth padding. The abrading and polishing were carried out under liquid paraffin to prevent the formation of a thin layer[3] of Cu_2O. The polished blocks were cleaned by benzene and alcohol and then transferred to a silica tube two inches in diameter and three feet in length. One side of the silica tube was placed in an oven (one foot long) heated by nichrome wire. The temperature was measured by a thermocouple. The nichrome wire windings were adjusted in such a manner that the central portion of the oven, of about 5 inches in length, gave us a uniform temperature. The polished copper blocks were kept in the silica tube such that they lie in the central uniformly heated part of the oven. The silica tube was evacuated by a rotary pump and the current in the oven windings was switched on when the pressure of about 0.04 mm of Hg was reached. The temperature of 410° C was usually attained within about 15—20 minutes. The temperature of 410° C was maintained constant for about ten minutes. By means of a leak valve dry air was then allowed to flow over the blocks at a predetermined pressure and for a fixed interval of time. After that interval, the leak valve was closed, the current was switched off, and the oven was transferred to the other side of the silica tube. The copper pieces were now cooled suddenly in vacuum by pouring water over the silica tube. This procedure usually enabled us to reach

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[1] K. R. Dixit and V. V. Agashe, Z. Naturforschg. **10 a**, 152 [1955].

[3] C. S. Lees, Trans. Faraday Soc. **31**, 1102 [1935].

[2] A. Guinier, X-ray crystallographic Technology, Hilger and Watts Ltd., London 1952, p. 244.

room temperature in about two minutes. As an additional precaution water was run over the tube for about 15 minutes before the blocks were taken out and transferred to the electron diffraction camera.

We have worked at pressures 0.5, 1.0, 2.0, 5.0, 10, 16, 30, 40, 50 and 75 mm of Hg and the time interval for oxidation ranged from about half a minute to about 14 hours. The maximum time for which the oxide was formed at any pressure indicates the limit for which an oxide film can be allowed to grow on the substrate. A film thicker than this limit peals off.

The surface layer of the oxide films thus formed was studied by electron reflection. The camera was the same as used in our previous work and we also worked at about 30 kV. The growth of oxide was also studied by weighing the oxide films formed at four pressures, viz. 0.5, 2.0, 5.0 and 10 mm of Hg. The weights were taken in air on a micro-balance.

Results

Fig. 1 shows the nature of the oxide films formed as a function of the pressure of air and the time of oxidation.

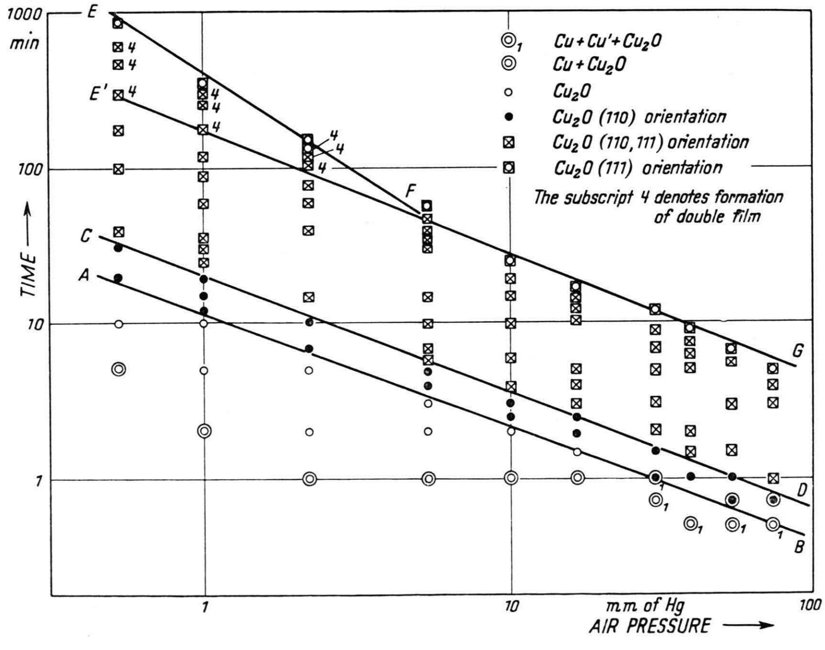

Fig. 1. Shows the manner in which the structure of the film formed changes as a function of the time of oxidation and of the pressure of air at which oxidation takes place.

(1) At very short intervals of time, we get rings corresponding to two face centred configurations, one corresponding to a cell size (3.6 Å) of copper and the other corresponding to a cell size (4.26 Å) of cuprous oxide. The rings corresponding to copper are first strong and then become weak. On the other hand rings corresponding to cuprous oxide are first weak and then they become strong. This indicates as expected an increase in the thickness of the oxide film with an increase in time. This is true at all pressures studied. However, at pressures beyond 30 mm of Hg, we observe double rings. These correspond to spacing of 3.6 Å and 3.65 Å. Such rings have been observed in evaporated copper layers. Pinsker[4] explains them on the assumption that 3.6 Å rings correspond to those of normal copper, where as 3.65 Å rings correspond to those of copper crystallites in which a small amount of oxygen has been dissolved. The amount of oxygen is so small that an oxide is not formed and yet it is appreciable enough to increase the cell size of copper. At these pressures and at these times in addition to the crystallites of copper in which oxygen has dissolved some crystallites of Cu_2O are also present. They show their normal rings (4.26 Å).

(2) When the time interval is increased rings corresponding to Cu_2O only are visible at all pressures. The patterns show besides the rings of a F. C.

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[4] Z. G. Pinsker, Electron Diffraction, Butterworth's Scientific Publications, London 1953, p. 210.

configuration ($\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$, $\sqrt{11}$, $\sqrt{12}$ etc.) the rings of a B. C. configuration ($\sqrt{2}$, $\sqrt{6}$ etc.). The intensity of $\sqrt{2}$ ring is 0.2 times that of $\sqrt{3}$ ring and the intensity of $\sqrt{6}$ ring is 0.1 times that of $\sqrt{3}$ ring. In Cu_2O, the copper atoms lie on a F. C. configuration and the oxygen atoms lie on a B. C. configuration. The diffracting power of light oxygen atoms is much less than that of heavy copper atoms, and therefore the $\sqrt{2}$ ring would be very very faint. Its presence and intensity in this case can be explained only by assuming a preferred orientation (110).

(3) With a further increase in the time of oxidation, the Cu_2O rings begin to show more marked signs of 110 orientation. This stage of orientation is indicated by the line AB in Fig. 1.

(4) If we increase the time of oxidation still further the crystallites of Cu_2O show a double orientation (110 and 111). This stage where the 111 orientation begins to appear is shown by the line CD in Fig. 1.

(5) It can be seen from Fig. 1 that up to this stage the behaviour at all pressures is nearly the same. But now with an increase in the time of oxidation, there is a marked difference depending on the pressure, in the behaviour of the oxide film formed. At pressures greater than 5 mm Hg, the crystallites in the oxide film become more and more oriented such that (111) faces are parallel to the substrate till finally there is no trace of 110 orientation. Simultaneous to this change over of the double orientation (110 and 111) (Figs. 2* and 3) to single orientation (111) (Fig. 4), the oxide film formed becomes so unstable that it can be removed from the substrate even by a slight rubbing with a finger. Below this pealed off film we see a copper surface. The double oriented film is always compact and adheres firmly to the base.

At low pressures (<5 mm of Hg), with an increase in the time of oxidation we get a similar change over from a double oriented film to a single oriented film. However, the film which peals off at this stage is much thinner and below the thin film we do not observe a copper surface but we observe an oxide surface of a peculiar type. This oxide shows four, rather broad, almost equally spaced rings which approximately correspond to 111, 222, 333, and 444 rings of Cu_2O. After this if we still persist and increase the time of oxidation a very thick film now including the peculiar oxide film, peals off, showing below it a copper surface. Thus the pealing off in this case may be regarded as taking place in two different ways. Either we get a very thin film pealing off leaving a peculiar oxide layer below, or we have a very thick film pealing off, leaving below a copper surface. The thickness of the films pealing off at pressures greater than 5 mm of Hg is about 1 μ, whereas at pressures less than 5 mm of Hg the film pealed off is either 0.1 μ or 3 μ. The line E F G in Fig. 1 indicates that the films peal off completely leaving below a copper surface. The line E′ F which is really G F produced indicates the pealing off of the thin film leaving below the peculiar oxide and not the copper surface.

Time in min	Pressure in mm of Hg			
	0.5	2	5	10
1	—	—	—	0.025
2	—	0.008	—	0.058
3	—	—	0.035	0.076
4	—	—	0.051	0.143
5	0.032	0.051	0.080	—
6	—	—	0.122	0.243
7	—	0.079	0.175	—
10	0.071	0.20	0.274	0.39
15	—	0.232	—	0.45
20	0.160	—	0.345	0.517
25	—	—	—	0.608
30	0.206	—	0.414	—
40	0.258	0.312	0.478	—
50	—	—	0.536	—
60	—	0.4	0.606	—
80	—	0.474	—	—
100	0.312	—	—	—
110	—	0.64	—	—
120	—	0.804	—	—
135	—	1.04	—	—
150	—	1.58	—	—
180	0.432	—	—	—
300	0.580	—	—	—
420	0.797	—	—	—
600	1.12	—	—	—
840	1.58	—	—	—

Tab. 1. Weight of oxide films formed in mg/cm^2.

Table 1 gives the weights of oxide films formed at 0.5, 2.0, 5.0 and 10 mm of Hg. These observations have been also plotted in Fig. 5 a. It can be seen that at higher pressures (>5 mm of Hg) the film when it peals off is about 1 μ thick, while at lower pressure the peculiar oxide begins to form when the film is about 1μ thick.

(6) All these films of Cu_2O (no CuO is formed at these pressures) did not show any appreciable electrical resistance or rectification.

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* Figs. 2, 3, 4 see p. 36 b.

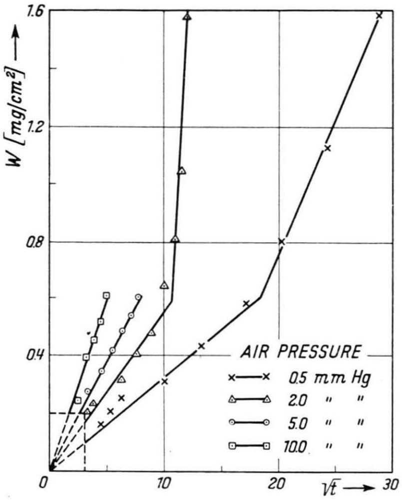

Fig. 5 a. The weight of the oxide film formed at four pressures 0.5, 2.0, 5.0 and 10.0 mm of Hg is shown as a function of t, the time of formation of the film.

Discussion

It is generally known (compare Mott and Cabrera[5]) that the oxide growth follows a parabolic law of the type

$$W^2 = A\,t, \tag{1}$$

where W is the weight of the oxide formed, t is the time of oxidation and A is a constant. We have therefore plotted in Fig. 5 b, the weight of the oxide film formed against the square root of time. It can be seen that at pressures 5 and 10 mm of Hg this law is obeyed for t greater than 8 and 5.5 minutes respectively. While at pressures 2 mm and 0.5 mm this law is obeyed for t greater than 8 and 16 minutes respectively. It should be noted that at these pressures and times the surface structure as shown by electron reflection changes, but the change is quite different for the pressures studied. At comparatively low pressure namely 0.5 and 2 mm of Hg the surface shows that the crystallites of Cu_2O now begin to arrange themselves with the 110 face parallel to the substrate, while at high pressures 5 and 10 mm of Hg this stage of orientation is already complete and now after 8 and 5.5 minutes the crystallites of Cu_2O appear to turn so as to make the 111 face parallel to the substrate in addition.

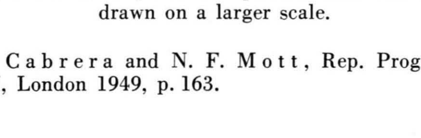

Fig. 5 b. Same as 5a, but the portion near the origin is drawn on a larger scale.

For smaller intervals of time i. e. when the film is thin, this law is not obeyed. This is to be expected as the law (1) cannot be expected to apply to thinner films. At low pressures viz. 2 and 0.5 mm of Hg, this law appears to be obeyed in the range 0.2 to 0.9 μ. The failure to obey the parabolic law for thin films is to be expected. But its failure in the case of thick film ($>0.9\,\mu$) is rather unexpected. But the parabolic law really applies to homogeneous single structure films. In our present case the film is not homogeneous but consists of a double layer, and if the parabolic law is to be applied, it should be applied separately to the two portions and we should get two straigth lines in W, $\sqrt{t}$ curve. This is seen to be the case in Fig. 5 a.

According to Wagner[6] the formation of a metallic oxide is governed by three factors:

(1) The diffusion of oxygen ions, across a film to occupy the vacancies created by the migration of metal ions.

(2) The diffusion of oxygen ions across the boundaries of a crystallite.

(3) The size of the crystallite across which the oxygen ions diffuse (Keimbildung).

The first process which is indicated by equation (1) is applicable to fairly thick films. The diffusion across the boundary is important for films of intermediate thickness; whereas in the case of very thin films the size of the nucleus (size of Cu_2O crystallites in our case) plays a dominent role. At this stage the relation between W and t is given by Wagner as

$$W^2/K_1 + W/K_2 = t\,. \tag{2}$$

If therefore, we plot W against t/W we should get a curve consisting of two portions intersecting at

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[5] N. Cabrera and N. F. Mott, Rep. Progr. Phys., Vol. XII, London 1949, p. 163.

[6] C. Wagner, Z. Phys. Chem. B **37**, 155 [1937]; B **40**, 455 [1938].

a point showing a sharp change of curvature for the two branches. We did this for our films formed at pressures 0.5, 2.0, 5.0 and 10 mm of Hg (Fig. 6).

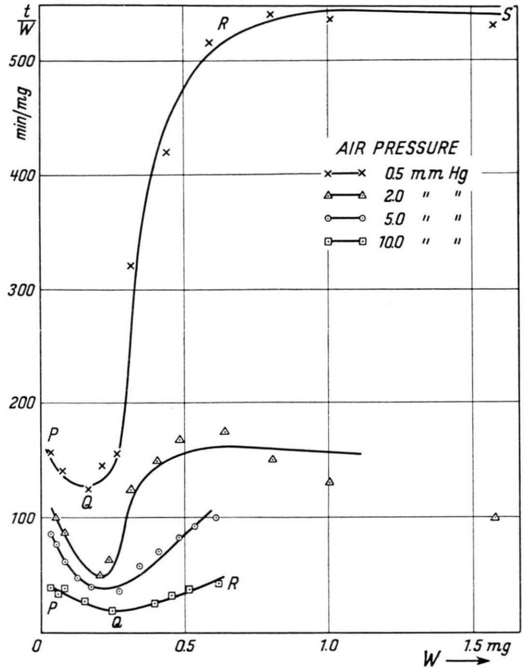

Fig. 6. Shows the variation of the weight of the oxide film formed as a function of t/W, the reciprocal of its rate of growth.

It will be seen that at pressures of 5.0 and 10 mm of Hg the curve consists of two portions and the film ultimately peals off. The film in this case before it peals off is about $1\ \mu$ thick. At pressures of 0.5 and 2 mm of Hg the curve however appears to be made up of three branches. In this case the film can become thicker and is of the order of $3\ \mu$ when it peals off. Thus curiously the films formed at lower pressures are thicker than the films formed at higher pressures. And for these thick films, the curve of W, t/W as drawn by us appears to be made of three parts and not of two parts as in the case of films formed at higher pressure. This third portion appearing in this case is perhaps characteristic and indicates that at this stage the diffusion across the boundaries of crystallites has begun to play a significant role.

Now looking at the curves the portion PQ for all curves correspond only to crystals of Cu_2O which do not show any appreciable orientation. The electron reflection rings are also rather diffuse indicating a small crystal size. The rings become sharper as we approach the point Q. The portion QR indicates the presence of oriented crystals of Cu_2O. The rings are now fairly sharp. The portion RS is observed only for thick films formed at low pressures which also peal off later. This third portion RS is nearly parallel to the W axis and indicates that an increase in W is proportional to an increase in time. This is the stage[6] at which "the action at the boundary of the crystallites alone governs the rate of reaction".

In conclusion we should like to say that in the low pressure region investigated, we see two different behaviours of the oxide films; the behaviour of films formed at pressures up to 5 mm of Hg is different from those formed in the range 5 to 75 mm of Hg.

One of the autors (V. V. A.) is thankful to the National Institute of Sciences for the award of a fellowship during the tenure of which this work was done.