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INVESTIGATION OF THE OXIDATION KINETICS OF COPPER AND THE INTERNAL IRREGULAR STRUCTURE OF THE SEMICONDUCTING CUPROUS OXIDE PRODUCED

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Abstract. The oxidation kinetics of copper at two different temperatures (949, 1030°C) has been investigated. The role of the internal irregular structure resulting during sample preparation has been discussed and it is concluded that the growth mechanism is controlled by the diffusion of copper cations and vacancies from the interior towards the outside surface under the influence of a concentration gradient. This concentration gradient was found to vary in a complex manner and not to obey a simple relation. Alloying copper with small amounts of metals of higher valency disturbs the concentration gradient in a way permitting the acceleration of the oxidation process.

Zusammenfassung. Die oxidationskenetik des kupfers bei zwei verschiedene Temperaturen wurde untersucht. Die rolle des innerlichen unregelmassigen Struktur, die während der Probevorbereitung entstand, wurde diskutiert, und es wurde beschlossen dass der Wachstummechanismus ist durch die Diffusion von Kupferkationen und fehlstellen von inneren nach aussen controlliert, und zwar unter dem Einfuss eines Konzentrationsgradienten. Dieser Konzentrationsgradient ändert sich auf eine komplzierte Weise und folgt nicht eine einfache Beziehung. Durch dass legieren des Kupfers mit kleinen Mengen von Mettallen höhere Valenzen wird diser Konzentrationsgradient gestört so dass der Oxidationsprozess beschleunight wird.

The understanding of the kinetics of all reacting systems in a solid, especially that concerned with the production of semiconducting materials having controllable defect properties, have been the object of many investigations.

Cuprous oxide is one of the earliest semiconductors whose properties were investigated as being dependant on the conditions of preparation, especially on temperature and oxygen pressure as well as the purity of the initial material used.

Our study was concerned with the kinetics of the oxidation process for both spectroscopically pure and commercial copper in air at two different temperatures (949 and 1030°C), using a new, simple and accurate method. Volume ratios which may be expected to give a rough measurement of the stresses developed in material, have been calculated and the irregular internal structure resulting from the mechanical processes arising during the preparation mechanism was then deduced.

Experimental

Spectroscopic pure copper (Johnson, Matthey Co.) and commercial copper in the form of small sheets $13–15\times7–9\times0.1–1.4$ mm were first freed from oxide layers by emery paper, and polished mechanically using carborundum polishing powder of different grades. The sample was then etched in a 2N HNO_3. Finally the copper plate was degreased with acetone, washed with distilled water and dried. Contacts were made of nickel–chrome wires, which have the least tendency for corrosion, in such a way that the area of contact is very small to limit its reaction with the formed cuprous oxide at high temperatures. The nickel–chrome contacts were fixed to the ends of the sample using pure copper cups.

The oxidation process took place in a furnace having a satisfactory zone of uniform temperature and an automatic temperature control. The temperature could be measured with an accuracy of 0.25°C at 1000°C using a chromel–alumel thermocouple previously calibrated at the National Institute for Standardization, Cairo.

A simple and satisfactory method to measure the resistance was done by a precision Wheatstone bridge and a high sensitive galvanometer. This allowed the measuring of the sample resistance down to 10^{-3} ohms with an error of 0.01%.

Results and Discussion

The kinetics of oxidation were studied with the aid of a family of resistance change versus time curves which were measured during the oxidation process immediately after inserting the copper plates in the

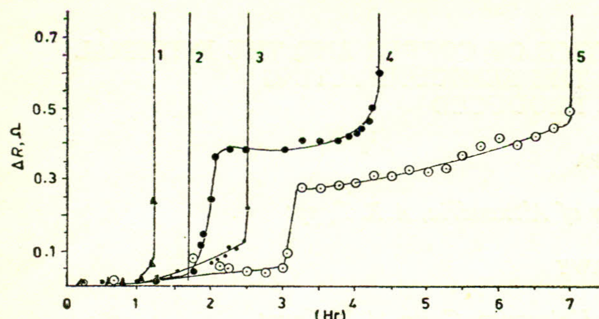

Fig. 1.

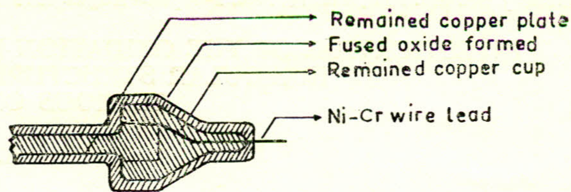

Fig. 2.

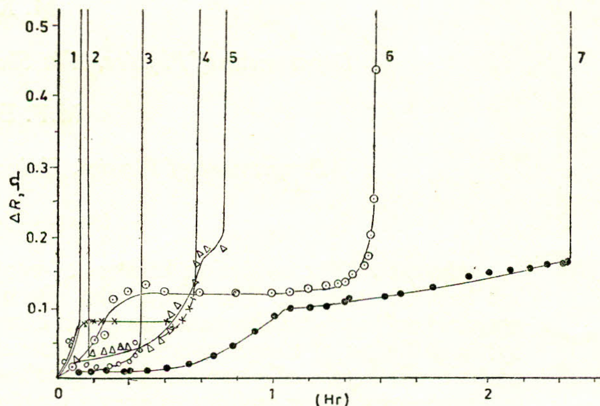

Fig. 3.

furnace. Fig. 1 represents a group of curves showing the increase of resistance with time for both commercial and spec. pure copper plates while being oxidized at 949±4°C. For plates 1–3 the resistance slightly increased denoting a decrease in cross-sectional area of the plates as the thickness of the oxide layer formed by oxidation increased. The measured resistance was equivalent to two parallel connected resistances, one of which was the resistance of the oxide layer formed and the other was that of the remaining non-oxidized copper, which was always in good contact with the nickel–chrome leads by means of the copper cups at the ends of the plates. Finally, as the copper plates approached complete oxidation, the resistance change had a sharp increase towards a value which corresponds to the resistance of the oxide plate formed which in this case became in series connection with the resistance of the nickel–chrome leads.

For plates 4 and 5, however, the first region of slow increase was followed by a rapid increase of resistance. This almost sudden increase seems to correspond to the formation of series resistance which arises from the tarnish oxide layer formed around the contact area and between the flattened nickel–chrome contacts and the metal copper plate. The maximum value of contact resistance depends on the contact area. The characteristic time depended only on the pressure arising from hammering of the copper cups into the copper plates when fixing the leads to the specimen. The time of rise was found to increase with increasing contact pressure at the contacts. At the end of this time the oxide layer on the copper plate and that on the internal walls of the copper cup were fused together, thus forming a protecting layer from further oxidation of the contacts. Fig. 2 shows the copper plate with its sealed leads after the assumed fusion.

Now the increase in the second region is slightly different as the reaction proceeded in a similar way to that in the first region till the copper plate was completely consumed and changed to the oxide giving an optimum resistance in the curve. The time of full oxidation of the used copper plates was obtained from the position of optimum resistance in these curves.

The same measurements were also carried out on another group of commercial and spec. pure copper plates in air but at 1030±4°C. Fig. 3 represents the relation between the change in resistance with time at this temperature. The first region here indicates a consumption of plate thickness from the very beginning, beside the formation of contact oxide layer giving a steadily increasing resistance at a constant rate instead of abrupt increase which takes place at 949°C, i.e. the increase in the oxidation temperature promotes the rate of interdiffusion of the reacting pieces. The second region is almost the same as that obtained at 949°C. The spec. pure copper gave also the principal features of $\triangle R$, T relation as commercial copper and have almost the predicted time of full oxidation. The thickness of the formed oxide layer x' is related to the decrease in thickness of metal plate x as follows

$$x = \frac{1}{\Phi} x'$$

Φ is the ratio of the molecular volume of the oxide formed and atomic volume of metal, and is defined as the volume ratio of the oxide.

According to tables of the atomic and molecular volumes the volume ratio were found to be 1.64 for Cu_2O and 1.72 for CuO.

The volume ratios of the cuprous oxide formed at 949 and at 1030°C have been obtained for plates of different thicknesses at room temperature. The average value of Φ at 949°C was found to be 1.606, whereas of 1.602 at 1030°C indicating that the percentage of cupric oxide in the oxide prepared is larger for plates oxidized at 949°C than that oxidized at 1030°C which is in good agreement with the results obtained by other workers.

Figure 4 shows the relation between the oxide layer (Φx) and its time of formation. The oxidation process was found to be parabolic (Fig. 5), obeying the parabolic rate law oxidation $x'^2 = K'_p t$; where K'_p is the reaction constant expressed in cm²/sec.$^{-1}$ Its value has been calculated and found to be 2.5313×10^{-7} cm²/sec at 949°C and 7.091×10^{-7} cm²/sec at 1030°C.

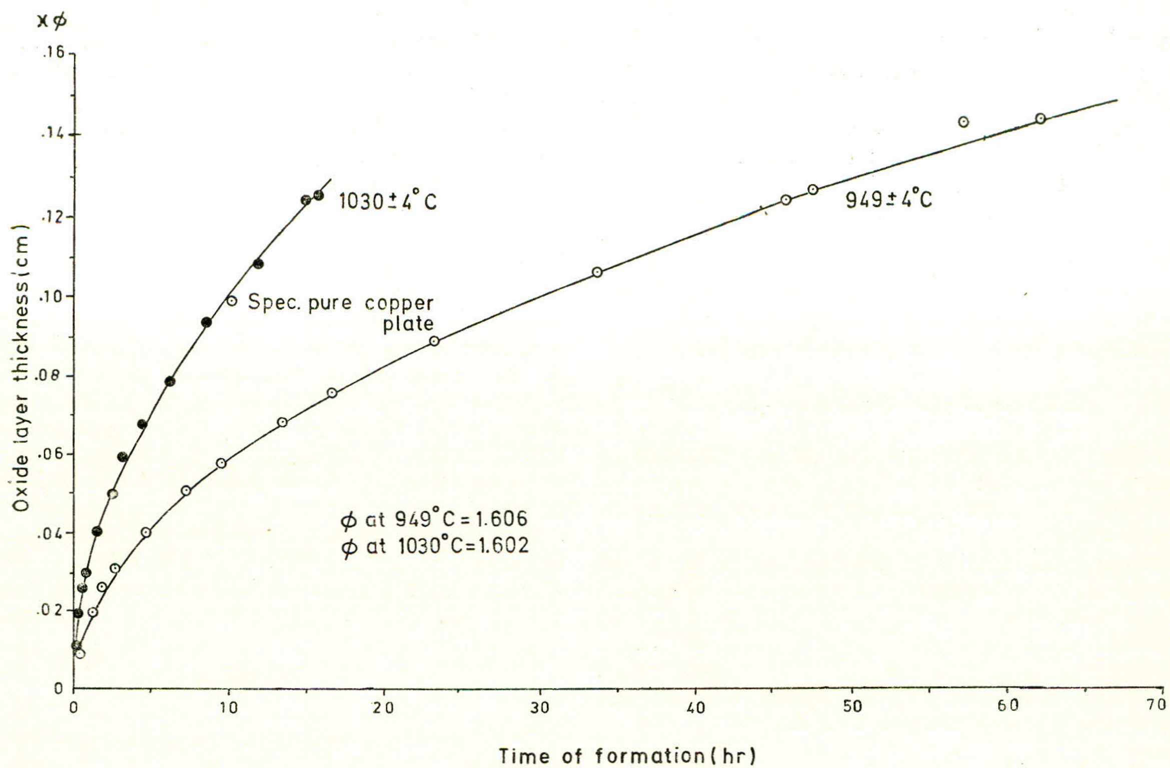

Fig. 4

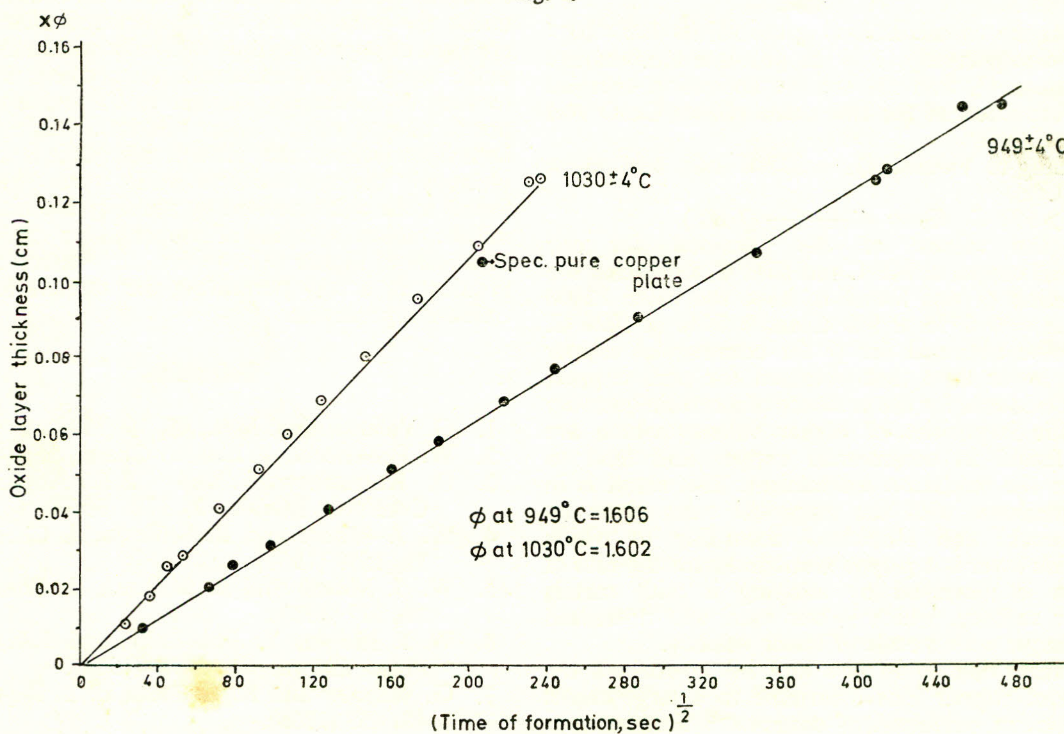

Fig. 5

In case of high volume ratios the formation of non-ideal layers may be expected since the value of the volume ratio may be used as a rough indication of the uniformity of the oxide layers formed. In our case, where the volume ratio is somewhat greater than unity and volatile compounds are absent we have to consider the growth of continuous coherent surface layers. If in these layers a diffusion process is rate determining, then, provided no 'ageing effect' alters the diffusion coefficient and the surface area remaining constant throughout the oxidation process, one may expect a uniform oxide product with the same density

all over the thickness of the formed oxide. Accordingly $x' = \triangle m\ (M_{ox}/M_{x}\rho)$. Where $\triangle m$ is the weight per unit area of the formed oxide layer x', M_{ox} and ρ are the molecular weight and density of the oxide, while M_x is the weight of the native component per molecule of oxide formed.

This argument can only be applied for thick plates with which an approximate agreement may be expected, as in our case. As the surface layers need not necessarily agree with that of the bulk material, layers may be either porous or in a compressed state.

Substituting for x' in the parabolic rate law

$$(\triangle m)^2 = K'_p(M_x\rho/M_{ox})^2 t = K_p t$$

K_p is also the parabolic rate constant but expressed in $g^2\ cm^{-4}/sec$ and can be evaluated experimentally by measuring the increase in weight with time increment, $K_p = 0.449\ K'_p$.

Assuming the density of prepared oxide to be the same for the two oxidation temperatures, therefore, K_p will have the value $3.1840 \times 10^{-7}\ g^2\ cm^{-4}/sec$ at 1030°C and $1.1366 \times 10^{-7}\ g^2 cm^{-4}/sec$ at 949°C.

According to Valensi and Feitknecht observation, K_p for the oxidation of pure copper with oxygen depends on the temperature as follows:[1,2]

$$K_p = A_1 \exp(-Q_1/RT) + A_2 \exp(-Q_2/RT)$$

A_1 and A_2 are constants having the values 1.5×10^{-5} and 0.266 respectviely. T is the absolute temperature of oxidation, Q_1 and Q_2 are the activation energies for the formation of the two oxide phases Cu_2O and CuO respectively.

According to Valensi $Q_2 = 37700$ cal; and $Q_2 =$ 20140 cal.

For $T > 550°C$ $K_p = A \exp(-Q/RT)$.

From the values of K_p obtained for our commercial copper at 949°C and 1030°C, and using the last equation Q was found to have the value 32800 cal. and $A = 0.0776$ at 949°C and 0.0944 at 1030°C.

The value obtained for Q for commercial copper which is lower than that obtained for pure copper, is a good evidence for the presence of a certain quantity of metallic impurities of higher valency which are usually found in commercial copper and tend to accelerate the oxidation mechanism. This result is in good agreement with the empirical rules given by Kubaschewski and Hopkins,[3] according to which if the oxide layer is a p-type semiconductor the rate of oxidation is increased by alloying it with metals of higher valency, which is our case, and decreased by alloying it with metals of lower valency.

Now according to Moore and his coworkers the diffusion of copper ions determine to a large extent the kinetics of oxidation of copper.[4-6] Wagner considered the diffusion of copper ions to take place under the influence of a linear concentration gradient of copper vacancies in the oxide layer which has a relatively poor agreement with the experimental observations.[7,8]

These results are in agreement with our observation during a number of preliminary measurements of change of resistance with time in which the battery of the used Wheatstone bridge is connected only to the bridge at the instant of taking the reading. In trying to balance the bridge the galvanometer current was observed to decrease, indicating that some internal processes were taking place inside the specimen. It was necessary to keep the current flowing in the bridge untill these procsesses stopped. It is assumed that the carriers (holes) in the oxide layer of copper plate decreased by a certain amount which was necessary to neutralize the positive copper ion vacancies existing in the oxide layer formed during oxidation. The time of this effect was found to increase rapidly as the thickness of the oxide layer increased giving a strong evidence that the formed concentration gradient varies in a non-linear manner within the oxide layers formed.

Conclusion

The growth mechanism of oxide layers is completely controlled by the diffusion of copper cations and electrons from the interior towards the outside surface under the influence of the constructed concentration gradient of copper cations vacancies within the formed oxide layer. Such concentration gradient was found to vary in a complex manner in the oxide layer and not to obey a simple linear relation. This unexpected behaviour affects the growth mechanism and gives ultimately the non-uniform oxide layers, which were found to be characterised by porosity especially at the middle region. Alloying of copper with a small amount of metals of higher valency disturbs the concentration gradient in a way permitting the acceleration of the oxidation processes.

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