THE INFLUENCE OF CRYSTALLOGRAPHIC ORIENTATION ON THE OXIDATION OF Cu*

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Abstract—The oxidation of polycrystalline, (001), (011) and (111) surfaces of Cu was studied at 200° and 600°C, with O pressures of 10^{-2} and 1 torr. The relative order of oxidation rates was (001) > polycrystalline > (111) > (011), the differences in rate becoming larger with the increases in temperature and pressure. For all Cu surfaces after oxidation for 3 h at 200°C and 10^{-2} or 1 torr of oxygen Cu_2O was the only oxide formed, at 600°C and 10^{-2} torr Cu_2O was the major oxide with weak reflection of CuO, whereas at 600°C and 1 torr the outer layer was only CuO. Initially, Cu_2O nucleated and grew on the surface and when this became sufficiently thick, CuO nucleated on the Cu_2O surface. The degree of orientation of oxides increased with an increase in temperature and a decrease in pressure, and also with short vacuum annealing. The presence of CuO and of oxide whiskers was dependent on temperature and pressure and on the substrate orientation. The appearance of CuO whiskers was related to the thickness of Cu_2O and not to that of CuO, localized stresses in the Cu_2O layer being responsible for the growth of CuO whiskers. Whisker growth seemed to have no great effect on the kinetics and mechanism of oxidation.

Résumé—L'oxydation de surfaces polycristallines et des faces (001), (011) et (111) du cuivre a été étudié à 200 et à 600°C, sous des pressions d'oxygène de 10^{-2} et de 1 torr. Les vitesses d'oxydation se sont classées dans l'ordre (001) > polycristalline > (111) > (011), les différences de vitesses s'accentuant pour des élévations de température et de pression. Pour toutes les surfaces de cuivre, après 3h d'oxydation à 200°C et sous une pression d'oxygène de 10^{-2} ou de 1 torr, le seul oxyde formé est Cu_2O; à 600°C et 10^{-2} torr, l'oxyde Cu_2O est majoritaire, avec de faibles réflexions de CuO, tandis qu'à 600°C et 1 torr, la couche d'oxyde extérieure est uniquement composée de CuO. Initialement, il se produit une nucléation et une croissance de Cu_2O sur la surface et quand cet oxyde devient suffisamment épais, il se produit une nucléation de CuO sur la surface de Cu_2O. Le degré d'orientation des oxydes croît avec une augmentation de la température, une diminution de la pression, et également avec un court recuit sous vide. La présence de CuO et de "whiskers" dépend de la température et de la pression et aussi de l'orientation du substrat. L'apparition de whiskers de CuO est liée à l'épaisseur de Cu_2O et non à celle de CuO; des tensions locales sont la cause de la croissance des whiskers de CuO. Cette croissance des whiskers ne semble pas avoid un grand effet sur la cinétique et le mécanisme de l'oxydation.

Zusammenfassung—Die Oxydation von polikristallinem Kupfer und von (001)-, (011)- und (111)-Oberflächen von Kupfereinkristallen wurde bei Temperaturen von 200 und 600°C und bei Sauerstoffdrucken von 10^{-2} und 1 torr untersucht. Die Oxydationsgeschwindigkeit nahm in der Reihenfolge (001)-Fläche > polikristallines Kupfer > (111)-Fläche > (011)-Fläche zu. Die Unterschiede nahmen mit ansteigender Temperatur und Gasdruck zu. An sämtlichen Oberflächen wurde innerhalb von 3 Stunden bei 200°C und 10^{-2} bzw. 1 torr nur Cu_2O gebildet, bei 600°C und 10^{-2} torr wurden nur sehr geringe Mengen CuO gebildet, während bei 600°C und 1 torr eine äußere Schicht aus CuO entstand. Auch in diesem Fall entstehen zu Versuchsbeginn Keime von Cu_2O, die zu einer Schicht zusammenwachsen. Erst wenn diese ausreichend dick ist, erfolgt Keimbildung von CuO auf der Cu_2O-Oberfläche. Das Maß der Orientierung der Oxide nahm mit ansteigender Temperatur und abnehmendem Sauerstoffdruck zu. Auch eine kurze Vakuumbehandlung steigerte den Orientierungsgrad. Die Gegenwart von CuO und von Oxidwhiskern hing nicht nur von Temperatur und Druck, sondern auch von der Orientierung der Unterlage ab. Die Bildung von CuO-Whiskern steht im Zusammenhang mit der Dicke der Cu_2O-Schicht, nicht aber mit der des CuO. Örtliche Spannungen in der Cu_2O-Schicht scheinen für das Wachstum der CuO-Whisker verantwortlich zu sein. Das Whiskerwachstum hat offensichtlich keinen großen Einfluß auf die Kinetik und den Mechanismus der Oxydation.

INTRODUCTION

NUMEROUS workers have studied the oxidation of polycrystalline[1-5] and mono-crystalline Cu[6-12] at various temperatures. Investigations of the initial stages[4,13-15] show good agreement on the mechanism of nucleation, the shape of nuclei and the nuclei density on various planes. The initial stages occur by three processes, namely the dissolution of O in the metal, marked by an incubation period, growth of nuclei and the joining of nuclei to form a uniform film. The nucleation process is considered as the rate-determining step for the overall oxidation rate.[15]

The appearance of an outer CuO layer depends on the temperature[1,16,17] and pressure[16,17] of oxidation. A higher O pressure favours the formation of CuO and a rapid increase in oxidation rate. Effects of vacuum cooling are significant in the decomposition of CuO to Cu_2O.[18] The degree of orientation increases with temperature[8] and there is good agreement in the epitaxial relationships between $Cu||Cu_2O$ and $Cu_2O||CuO$.[7,8,10,11,26,27] Whisker growth accompanying these processes on poly-crystalline Cu has also been studied,[1,19-23] but there is still some disagreement about the growth mechanism.[24]

The above studies are extended here by using a wide range of conditions and by placing special emphasis on the influence of O pressure for longer periods of oxidation than previously. A relative study of whisker growth on single crystal substrates is also reported. The basis for studies of whisker growth, oxide stress development and adhesion, substructure and dislocation distribution in copper oxides which will follow this paper, is also provided.

EXPERIMENTAL PROCEDURE

Materials

Single crystals of 99·98 % purity Cu in the (001), (001) and (111) orientations and polycrystalline 99·98 % purity copper, were obtained as 1 mm thick sheet. Duplicate specimens, approximately $1 \times 1 \times 0 \cdot 1$ cm, were spark machined from these samples, annealed in H for 3 h at 650°C and for 1 h in vacuum, before finally electro-polishing in 50 % H_3PO_4 + 50 % H_2O solution followed by washing in distilled water and drying. After this treatment the polycrystalline specimens contained relatively large grains (1 mm average dia.).

Vacuum microbalance and oxidation procedure

An automatic, continuously recording, high vacuum Sartorius microbalance (Type 4102) was used, the system being shown schematically in Fig. 1. The balance was connected through fine leak valves to the gas inlet and all connections were greaseless. A three-stage Pirani gauge was used for the measurement of oxygen pressure and an ionization gauge for the measurement of vacuum in the system ($< 10^{-8}$ torr was attainable). The gases used were spectroscopically pure.

The specimen was placed in the balance using a quartz wire (Fig. 1) and a thin platinum sheet was used as a counterweight. The balance itself was capable of adjusting the difference in weight between the specimen and the counterweight up to 99·99 mg in various ranges.

The system was evacuated and the specimen heated to 500°C using a Kanthal-wound well-insulated furnace. H was then admitted for the reduction of any surface
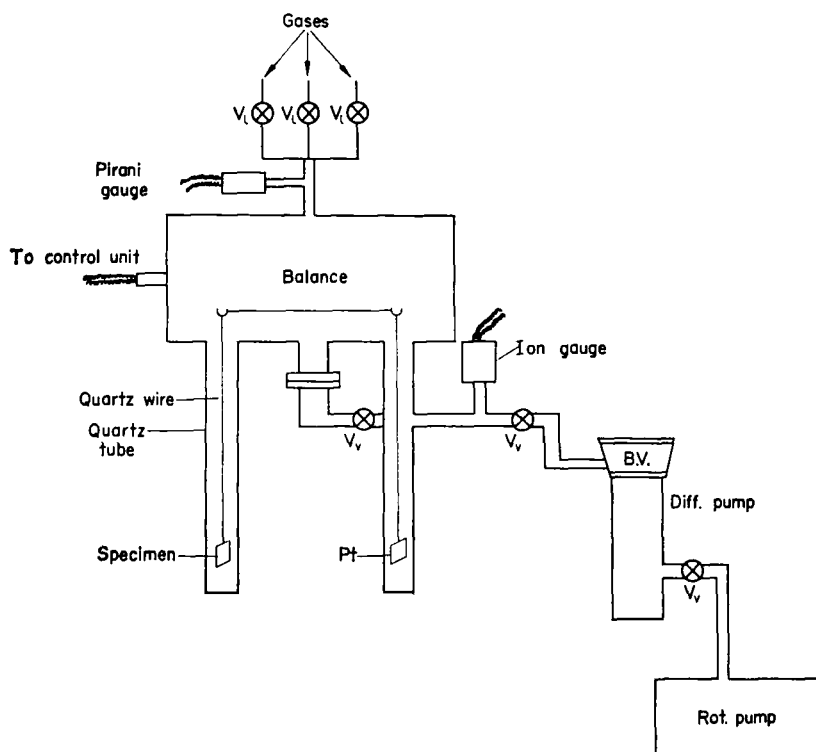
FIG. 1.   Schematic diagram of microbalance system.

oxide and left for 1 h and then pumped out. This procedure was repeated three times. The temperature was then raised to 650°C and the specimen annealed *in vacuo* at 10^{-7} torr for 2 h, the temperature then being adjusted to the required value and the specimen allowed to attain it for 1 h. Pure O gas was then admitted to the required pressure through the leak valve and the weight change continuously recorded. Because of radiometric and buoyancy effects, which are pressure and temperature dependent, it was necessary to correct the observed kinetic data. These corrections involved making the initial and final measurements of the balance deflection while the specimen was at the oxidation temperature in high vacuum. Since the relative proportion of Cu_2O in an oxide film containing both Cu_2O and CuO increases during evacuation[18] at elevated temperatures, at the expense of CuO, it was necessary to use separate specimens of each orientation, one for the kinetic data, and the other for electron microscopy and electron diffraction examination which was cooled rapidly to room temperature before evacuation.

Surfaces of the specimens were observed in an optical microscope, and by electron microscopy using a two stage Pt–C replica technique and an A.E.I. E.M.6 electron microscope. The crystal structure and the oxide orientations were determined by reflection electron diffraction by employing a high resolution electron diffraction manipulator attachment to the electron microscope.

RESULTS

Kinetics

Data for 3 h of oxidation on the various Cu crystal faces for 200°C are shown in Fig. 2 and for 600°C at 10^{-2} and 1 torr in Figs 3(a) and 3(b) respectively. Each curve is the average of two experiments on each surface, the agreement within the sets of data being quite good at 1 torr (within 5 per cent) but poorer at 10^{-2} torr (within 15 per cent). This is probably due to the larger radiometric effect at lower pressure.

The oxidation data at 200°C and 1 torr are plotted in the form $W = A \log t + B$ (W = weight increase and t = time) in Fig. 4 and those at 600°C and 1 torr in a parabolic manner in Fig. 5. The data obtained for 10^{-2} torr at both temperatures did not fit any normal oxidation rate law for the entire recorded oxidation period. All the curves depict oxidation at a declining rate after a rapid initial rate at both pressures and temperatures.

Electron diffraction analysis

The results of electron diffraction studies on all the surfaces after oxidation for 3 h under the various conditions are contained in Table 1.

It was also observed that after 10 h of oxidation for 10^{-2} torr at 600°C, the outer oxide layer on the (001) plane contained a mixture of CuO and Cu_2O and a non-uniform distribution of whiskers. The outer oxide was greyish red in colour.
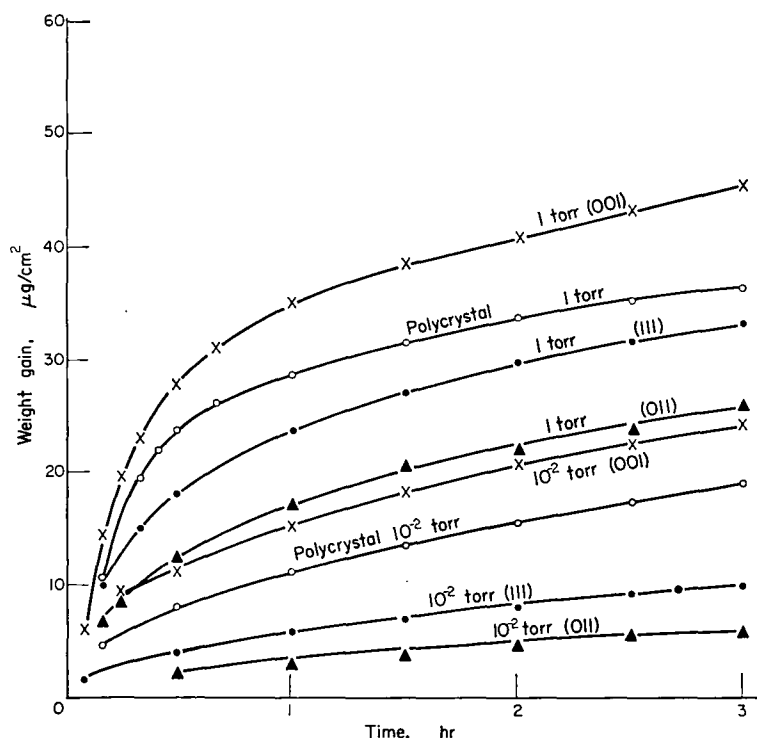

FIG. 2.   Influence of crystallographic orientation and O pressure on the oxidation rate of Cu at 200°C.
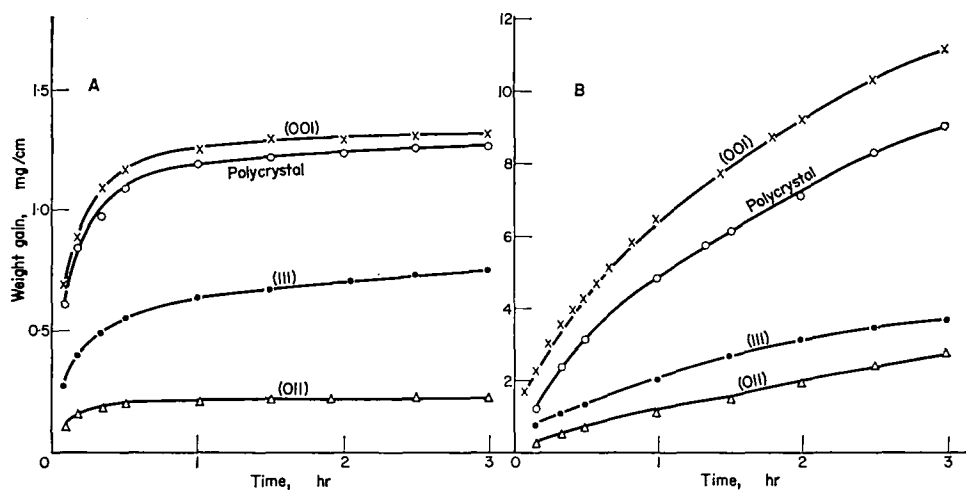
FIG. 3.   Influence of crystallographic orientation on the oxidation of Cu at 600°C
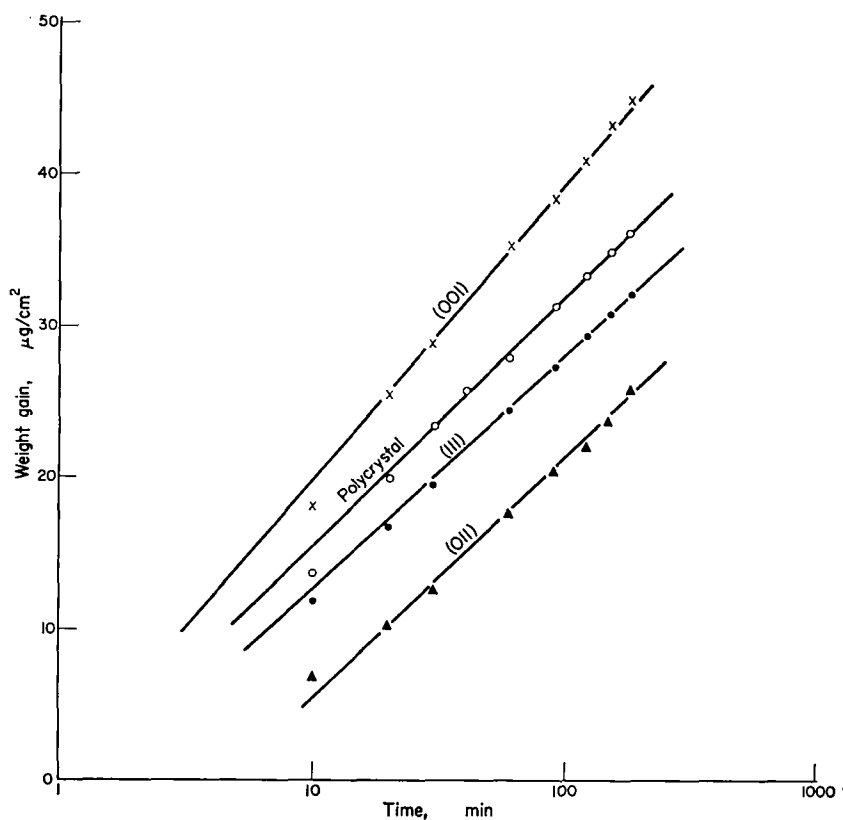(A) 10^{-2} torr; (B) 1 torr.

FIG. 4.   Weight gain/log time plots for oxidation of various Cu faces in 1 torr at 200°C.
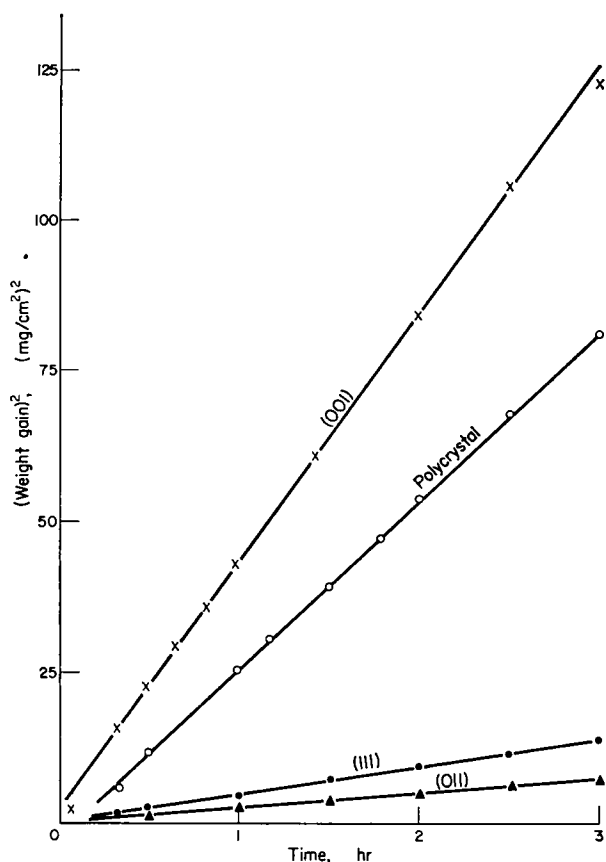
FIG. 5. (Weight gain)²/time plots for oxidation of various Cu faces in 1 torr at 600°C.

Morphology of Cu oxides

The replica electron micrographs of the oxygen–oxide surfaces show that for 10^{-2} torr at 200°C there is a high concentration of secondary nuclei over a thin basal oxide layer (Fig. 6). At this stage, the shape and density of nuclei are difficult to correlate on the various surfaces. However, the structures shown for 1 torr undoubtedly represent a later stage of film development than at 10^{-2} torr for the various surfaces (Fig. 7). At 1 torr these nuclei tend to join with one another and spread out to form a uniform oxide layer, the rate of the process varying with crystal orientation. Figure 8 shows the (001) surface after oxidation for 3 h at 1 torr and 200°C, followed by vacuum annealing for 1 h at 200°C. This treatment seems to leave the oxide in a generally roughened bulk-form, probably due to the continued interaction of the film and the oxygen-containing metal.

Replica electron micrographs of the various oxygen–Cu_2O and oxygen–CuO interfaces for 10^{-2} and 1 torr at 600°C are shown in Figs 9 and 10 respectively. At 10^{-2} torr the structure of the outer oxide varies markedly with the substrate orientation. The polycrystalline surface shows a faceted structure which varies from grain to grain
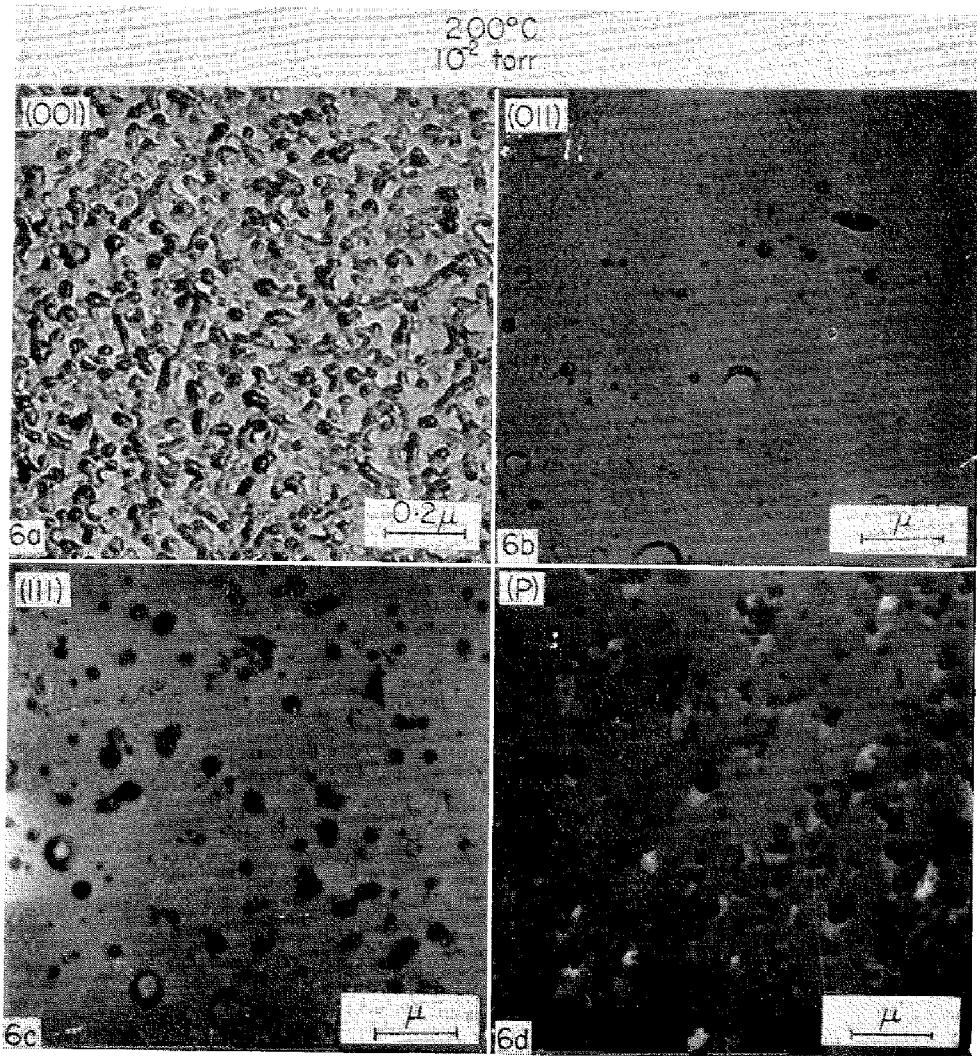
FIG. 6. Replica electron micrographs of the oxide formed on various Cu faces after 3 h in 10^{-2} torr at 200°C (P = polycrystalline).
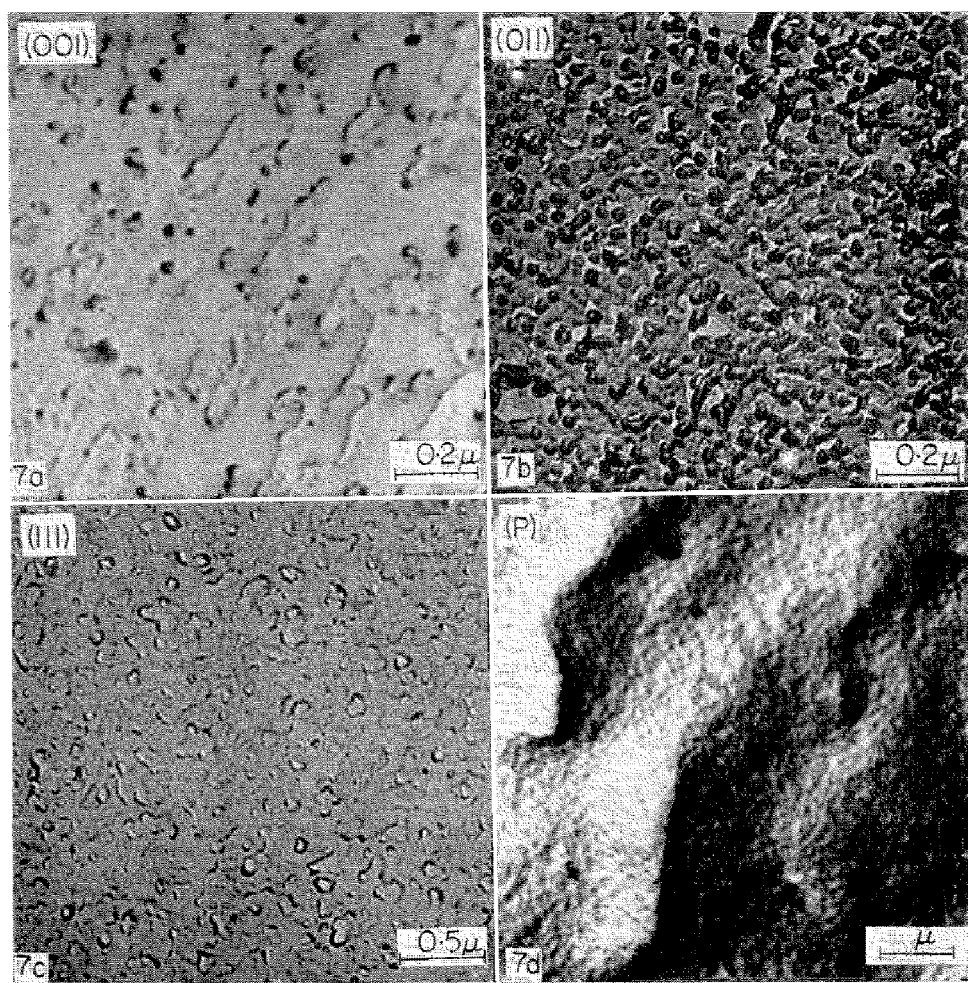
Fig. 7. Replica electron micrographs of the oxide formed on various Cu faces after 3 h in 1 torr at 200°C (P = polycrystalline).
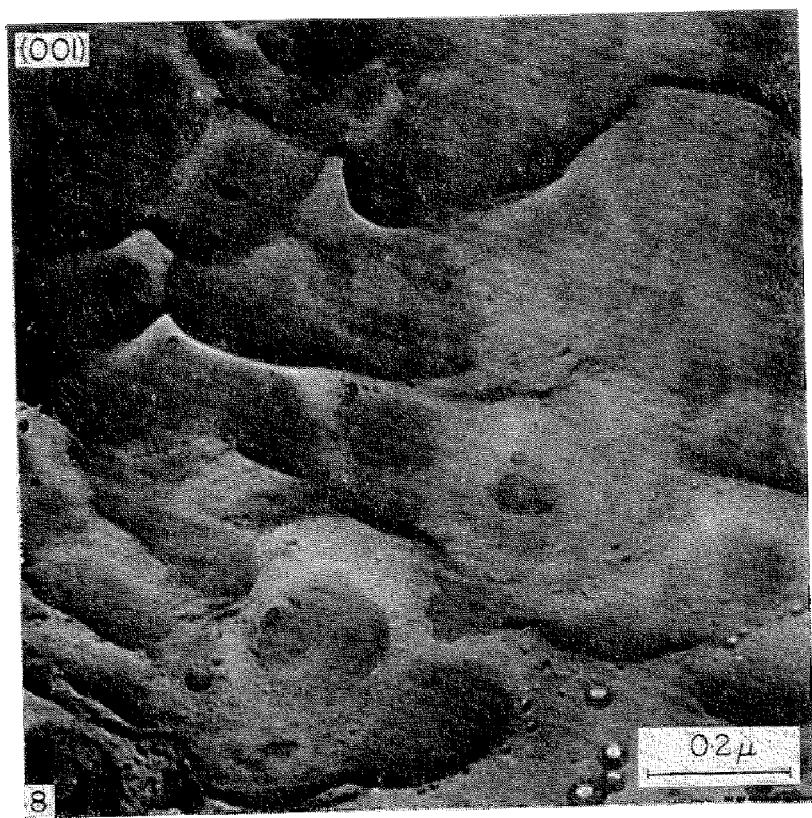
FIG. 8.   Replica electron micrograph of the oxide formed on the (001) face after 3 h in 1 torr at 200°C, followed by annealing for 1 h in vacuum at 200°C.
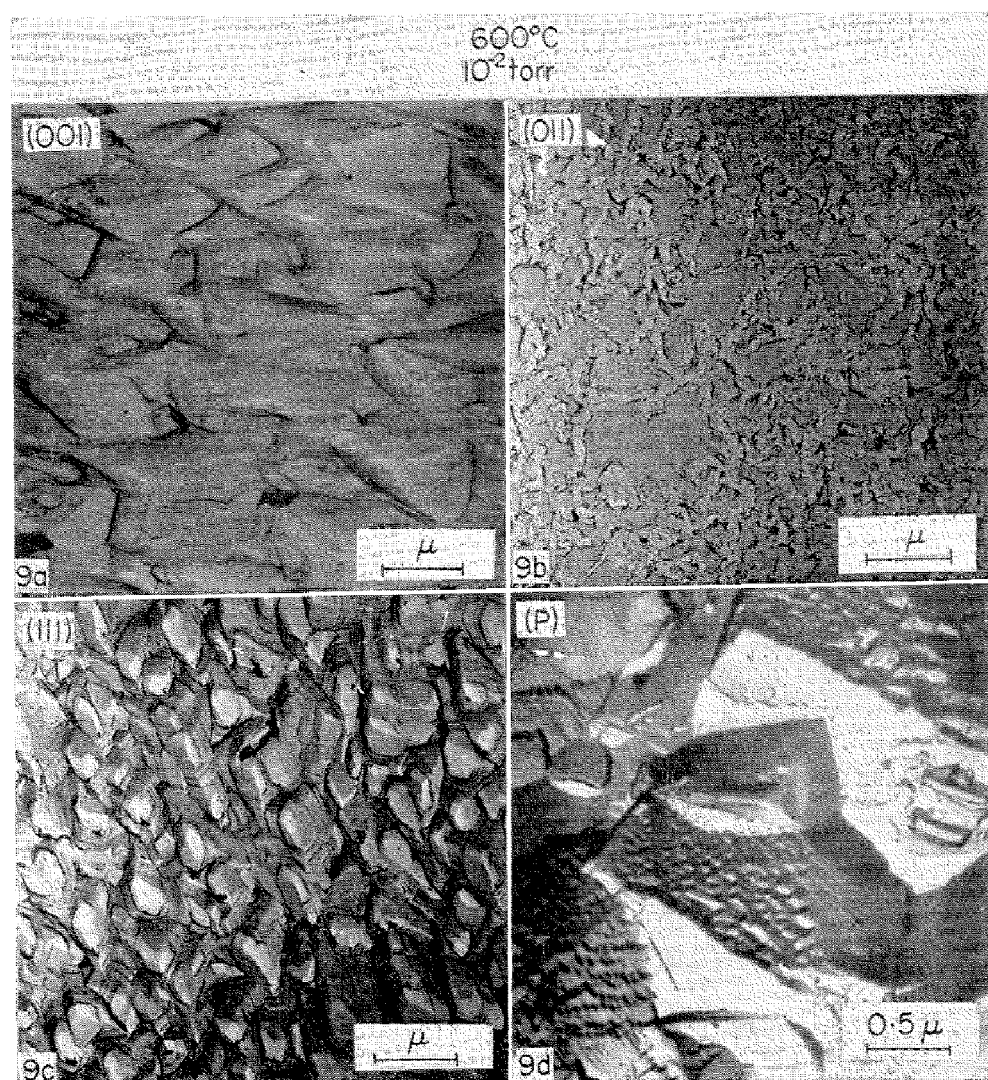
FIG. 9.   Replicas of the oxide formed on various Cu faces after 3 h in 10^{-2} torr at 600°C (P = polycrystalline).
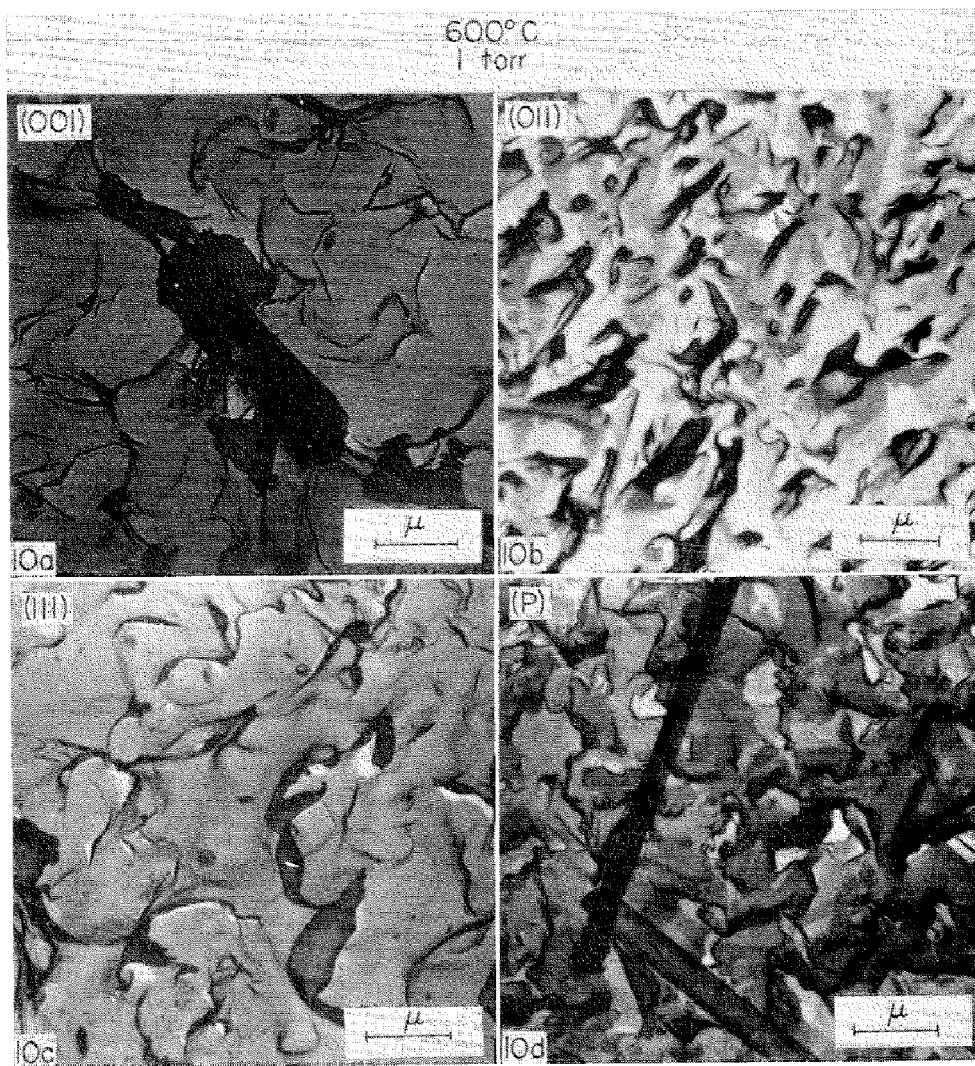
FIG. 10.   Replicas of the oxide formed on various Cu faces after 3 h in 1 torr at 600°C.
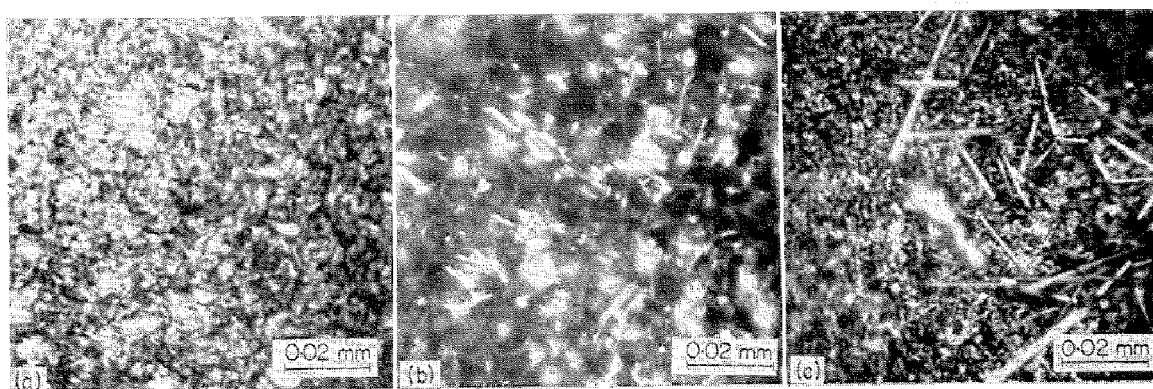

FIG. 11.   Optical micrographs of the oxide on (001) surfaces at 600°C.
a. 1 hr at 1 torr; b. 3 h at 1 torr; c. 10 h at 10^{-2} torr.
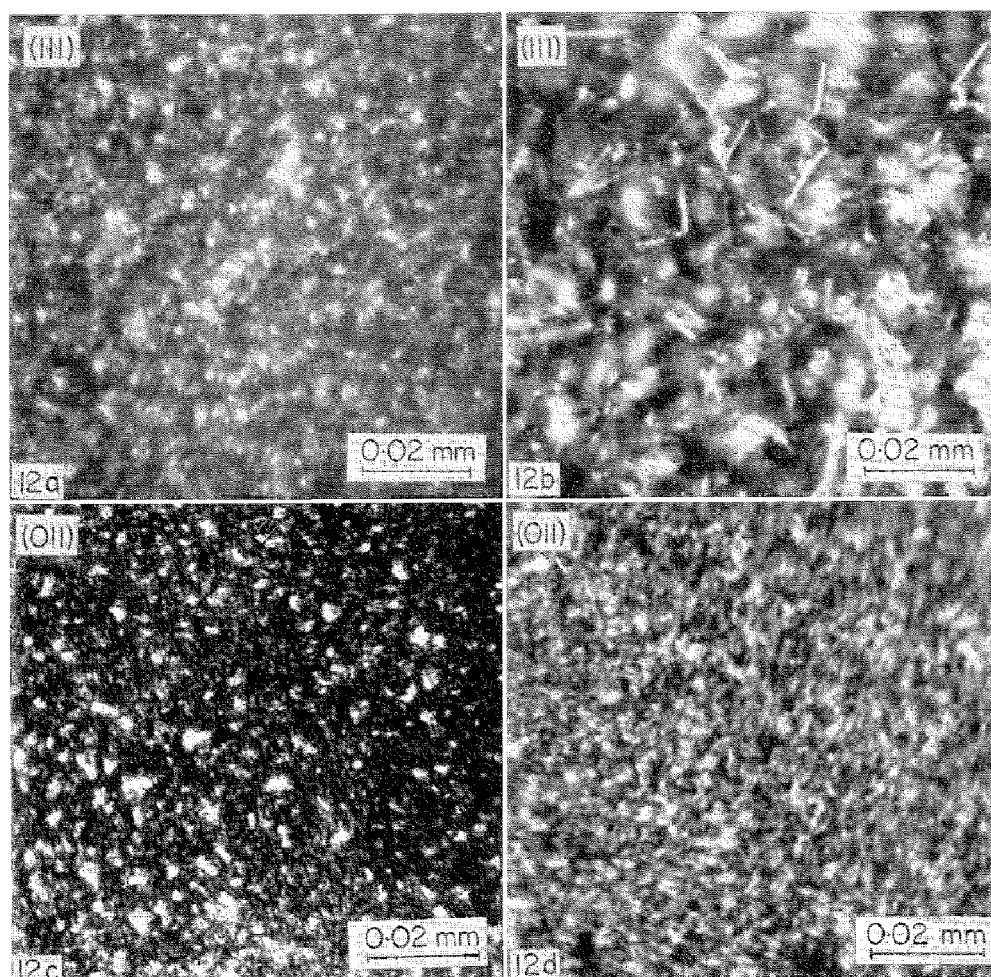
FIG. 12. Optical micrographs of the oxide formed on (111) and 011) Cu faces after 3 h in 1 torr and 10^{-2} torr at 600°C.

TABLE 1. ELECTRON DIFFRACTION DATA

Temperature °C	Pressure torr	Oxide film colour	Orientation and composition of oxide films			
			Polycrystalline	(001)	(011)	(111)
200°C	10^{-3}	Pale brown	Cu_2O	(001) [1$\bar{1}$0] Cu‖ (111) [1$\bar{1}$0] Cu_2O	(011) [1$\bar{1}$0] CM‖ (011) [1$\bar{1}$0] Cu_2O	(111) [1$\bar{1}$0]‖ (111) [1$\bar{1}$0] Cu_2O
	1	Reddish brown	Cu_2O	As above + S.A. polycrystalline Cu_2O	As above + S.A. polycrystalline Cu_2O	As above + S.A. polycrystalline Cu_2O
	10^{-1}	Red	Cu_2O + S.A. CuO	(001) [1$\bar{1}$0] Cu‖ (111) [1$\bar{1}$0] Cu_2O + (001) [1$\bar{1}$0] Cu_2O + CuO (weak reflections)	As above + CuO (weak reflections)	As above + CuO (weak reflections)
600°C	1	Black	CuO	(111) [1$\bar{1}$0] Cu_2O‖ (111) [1$\bar{1}$0] CuO	(011) [1$\bar{1}$0] Cu_2O‖ (011) [1$\bar{1}$0] CuO	(111) [1$\bar{1}$0] Cu_2O‖ (111) [1$\bar{1}$0] CuO

*S.A. = Small amount.

and is probably related to the metal substrate. At 1 torr the structure becomes more complex with the formation of an entire layer of CuO and the appearance of whiskers.

Optical micrographs for the oxidation of (001) Cu surface at 600°C under various conditions are shown in Fig. 11, and for (111) and (011) surfaces after 3 h of oxidation at 600° in Fig. 12.

The density of whiskers on polycrystalline surfaces varied from area to area and in some areas there were no optically visible whiskers. Whereas on (001) and (111) Cu surfaces after 3 h in 1 torr at 600°C, the whisker size and density were fairly uniform, on (011) surface long needles did not grow but there were relatively short and uniform needles. On the other hand, after 10 h and 10^{-2} torr at 600°C, long needles grew on (001) Cu, but they were non-uniform in their distribution on the surface.

DISCUSSION

The order of reaction rates with respect to the crystallographic orientation of Cu was (001) > polycrystalline > (111) > (011), the same as observed by Lawless and Gwathmey.[8] The curve for polycrystalline Cu oxidized at all temperatures and pressures lies above the curves for (111) and (011) Cu planes and slightly below the curve for (001) Cu. This suggests that the polycrystalline specimen had a preferred orientation approaching (001), although possibly a contribution from increased oxidation rates due to grain boundaries should not be discounted. The differences in oxidation rates of the (001), (111) and (011) surfaces increased with temperature and pressure, that is with increasing oxidation rate. An increase in O pressure from 0·01 to 1 torr raised the oxidation rate about four times at 200°C and up to 10 times at 600°C. Any acceptable theory must explain why the same trends of rate with crystal face apply over a large variety of oxidation conditions, and with different growth laws applying. The only reasonable explanation for differences in oxidation rates of various Cu planes is given by Lawless and Gwathmey,[8] which states that due to lattice disregistery, misfit dislocations, mosaic structures and incoherent twin boundaries are built into the oxide film to varying degrees depending on orientation. The density of these defects is greater on (001) plane explaining at least partially the enhanced oxidation rate. Present theories of oxidation are inadequate to explain the effect further.

The oxidation data for 1 torr at 200°C agree after an initial deviation with the logarithmic relationship (Fig. 4) and those for 1 torr at 600°C with a parabolic relationship (Fig. 5). The data for 10^{-2} torr at both temperatures did not agree completely with any simple rate law for the entire oxidation period and no attempt was made to force them to any particular relationship. It is not to be expected that simple rate equations will apply when the competing processes of O solubility, film growth and secondary nucleation are considered. The oxidation of a polycrystal is a complex process, involving not only the individual grain orientations but the unknown effect of the grain boundaries and the concentration of other defective regions. It has been shown that the oxide thickness on a polycrystalline specimen varies from grain to grain,[25] so no general explanation for the oxidation of a polycrystal is strictly valid.

The epitaxial relationships of Cu||Cu₂O and Cu₂O||CuO on various planes (Table 1) agree well with earlier work.[7,8,10,11,26,27] It was found that the degree of orientation increased with increasing temperature and decreasing O pressure. Additionally, a short anneal in vacuum completely oriented a small amount of polycrystalline oxide.

There is generally good agreement between the various investigators on the morphology of Cu_2O formations in the early stages of oxidation on the various Cu planes, and the present work fits well into this pattern. In this study at 200°C and 10^{-2} torr (Fig. 6) there is a large scatter of secondary oxide nuclei on a·thin oxide film. This is a transition stage which is dependent on the temperature, pressure and orientation, explaining the different progress of the process from face to face. In the next stage, at 200°C and 1 torr where reaction has been more rapid, the nuclei began to spread out and combine with one another to form a uniform oxide layer (Fig. 7). It is not yet clear whether secondary nucleation process, followed by coalescence to a complete layer, repeats itself several times or whether the layer once formed thickens uniformly, under any given set of conditions. At 600°C the oxide structure differs widely with the pressure and the substrate orientation (Figs 9 and 10). Vacuum annealing has a marked effect on the morphology of the outer oxide (Fig. 8), apparently by interaction of the oxide and the O-containing metal. The effect of annealing on the composition of Cu oxides has been studied previously.[3,18]

The effect of pressure on the oxide composition and structure at 600°C is very distinct. At 600°C and 10^{-2} torr it is possible that the processes of CuO formation and decomposition[18] may be occurring at different sites on the same surface at the same time, so that on cooling the specimen any thin localized region of CuO is decomposed in the transition step. However, at 1 torr the O pressure is high enough to inhibit the decomposition of a relatively thick layer of CuO.

The appearance, density and size of whiskers seems to be related to the ·crystallographic orientation (Figs 11 and 12), Cu_2O thickness and growth rate and the localized stresses. Thus, on a polycrystalline specimen the whisker density and size varied sharply from area to area. On (001) and (111) Cu faces the whisker density and size were fairly uniform at 1 torr, and on the (011) face the density was uniform but the whiskers were very small. In contrast, after 10 h in 10^{-2} torr, long whiskers which were non-uniform in density grew on the (001) face and the outer oxide contained a mixture of Cu_2O and CuO. The latter observation suggests that whisker growth is related to the Cu_2O thickness and the density of whiskers is not strictly uniform even on a given plane. The accumulated localized stress and defective regions are probably responsible for the growth, density and size of whiskers. Probably the Cu_2O on (001) Cu contains a high percentage of localized stress areas and possibly appropriate dislocation arrangements relative to that on (111) and 011) planes, which help in the rapid growth of whiskers.

CONCLUSIONS

1. The relative order of oxidation rates of various Cu surfaces was found to be (001) > polycrystalline > (111) > (011), the differences becoming larger with temperature and pressure.
2. At 200°C, after the formation of a thin Cu_2O layer, secondary nuclei develop before spreading out later to form a uniform oxide layer, the process depending on the pressure and orientation.
3. At 600°C the formation of Cu_2O and CuO is dependent on O pressure.

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4. The degree of orientation increases with increasing temperature and decreasing pressure and also with vacuum annealing.

5. The rate of formation of Cu_2O and localized stresses in it cause the appearance of whiskers. The whisker density and size vary from surface to surface and are not uniform even on a given plane.

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