

Brief Review of Oxidation Kinetics of Copper at 350 °C to 1050 °C

YONGFU ZHU, KOUJI MIMURA, JAE-WON LIM, MINORU ISSHIKI, and QING JIANG

Copper's oxidation mechanism and purity effects were elucidated by oxidizing 99.99 pct (4N), 99.9999 pct (6N), and floating zone refined (>99.9999 pct) specimens in 0.1 MPa oxygen at 350 °C to 1050 °C. Throughout the temperature range, the oxidation kinetics for all specimens obeys the parabolic oxidation rate law. The Cu_2O scale grows predominantly, and the rate-determining step is concluded to be outward diffusion of copper atoms in Cu_2O . The activation energy at high temperatures, where the lattice diffusion predominates, is 173 kJ/mol, but it becomes lower at intermediate temperatures and even lower at low temperatures because of the contribution of the grain boundary diffusion. At high temperatures, oxidation kinetics is almost uninfluenced by purity, but the lattice-diffusion temperature range is wider for higher-purity copper. At intermediate temperatures, copper oxidation is enhanced because trace impurities can impede growth of Cu_2O grains to facilitate grain boundary diffusion. At low temperatures, grain boundary diffusion is possibly hindered by impurities segregated at grain boundaries.

I. INTRODUCTION

THE subject of copper oxidation is important both technically and scientifically. Copper has figured prominently in the development of oxidation-reaction theory; experiments on copper oxidation have supported or verified many fundamental concepts about the motion of ions and electrons through the oxide layer.^[1] Elucidating copper oxidation will further the understanding of corrosion.

Copper oxidation in the temperature range of 350 °C to 1050 °C has been studied extensively. Several researchers have reviewed salient results.^[1–5] For oxidation under ambient oxygen pressures at which only Cu_2O is thermodynamically stable, a single Cu_2O layer is formed. At oxygen pressures above the dissociation pressure of CuO , a CuO layer will be formed on the Cu_2O layer. Throughout the entire temperature range, the oxidation kinetics of copper follows the parabolic oxidation rate law.

Typical Arrhenius plots of the parabolic rate constants k_p at 350 °C to 1050 °C reported for double-layer formation ($\text{CuO} + \text{Cu}_2\text{O}$) are depicted in Figure 1.^[6–10] The activation energies (Q_a) for the copper oxidation reported in the literature are shown in Table I.^[6–13] On the basis of their change in slope, the Arrhenius plots in Figure 1 are roughly divisible into three regions: a high temperature region (900 °C to 1050 °C), an intermediate temperature region (600 °C to 850 °C), and a low temperature region (350 °C to 550 °C).

The Cu_2O scale grows predominantly in the high temperature range; the lattice diffusion in Cu_2O is inferred to be the rate-determining step.^[10] In the intermediate temperature range, a decrease in temperature dependence occurs. The Cu_2O scale continues to grow predominantly, and the decrease in the temperature dependence is probably attributable to the contribution of the grain boundary diffusion in addition to the lattice diffusion.^[10] However, it is noteworthy that the temperature range of lattice diffusion in the high temperature range and the corresponding activation energy differ among authors (Figure 1 and Table I). Considerable scatter of the temperature dependence is apparent in the intermediate temperature range. Further, in the case at 300 °C to 550 °C, the oxidation mechanism remains ambiguous. According to Tylecote^[7] and Valensi,^[13] the temperature dependence was lower than those at 600 °C to 900 °C, but that obtained by Park and Natesan^[10] was much higher. Valensi^[13] and Park and Natesan^[10] claimed that the growth of the CuO oxide or whiskers predominates during oxidation and inferred that the rate-determining step is diffusion of Cu and/or O atoms in CuO . However, their studies provided no direct and reliable data to prove the predominant growth of the CuO oxide or whiskers.

Regarding the discrepancy in the temperature dependence for the copper oxidation, Mrowec and Stoklosa^[6] interpreted that it might result from errors made in the determination of parabolic rate constants; in most studies, k_p is calculated without considering the decreased surface area of the metallic substrate during oxidation. On the other hand, studies of oxidation kinetics of other metals have shown that k_p can be influenced by purity—*e.g.*, Ni,^[14] Zn,^[15] Co,^[16] Zr,^[17] and Hf.^[18] Some researchers^[2,6,19] have suggested that different purity might also be responsible for the discrepancy in the activation energies reported for copper oxidation, but this has not been clarified in the literature.

We have studied the copper oxidation mechanism at 350 °C to 1050 °C and the purity effect^[20–23] to address the issues of the copper oxidation described above. Based on those studies, the oxidation mechanism of copper at 350 °C to 1050 °C was examined in this study.

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II. EXPERIMENTAL METHODS

A floating zone refined (FZR, >99.9999 pct) copper, a 99.9999 pct (6N) copper, and a 99.99 pct (4N) copper^[24] were used to study the oxidation mechanism and the purity effect. Table II shows impurity concentrations of FZR, 6N, and 4N specimens as determined using the glow discharge mass spectrometry (GDMS) method. The specimens were disc-shaped: 0.4 to 0.5 mm thick with a 5-mm diameter. Before oxidation, all specimens were annealed in H₂ atmosphere at 600 °C for 24 hours for recrystallization.

Copper oxidation was carried out in 0.1 MPa oxygen with a gas flow rate of 100 ml/min. The weight gain was measured using thermo-gravimetry (SDT 2960; TA Instruments), with a sensitivity of 0.1 μg. Recording of the weight gain started when the samples were heated in the reaction gas to the

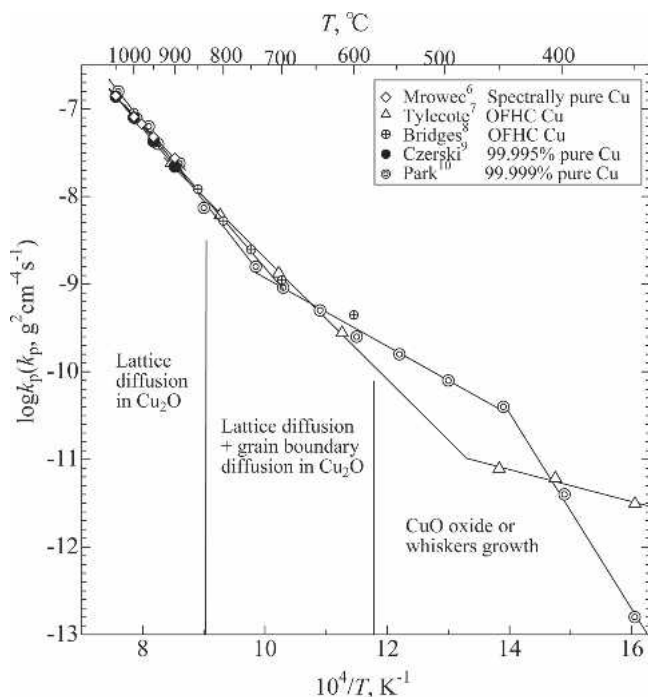


Fig. 1—Typical Arrhenius plots of the parabolic rate constants of copper oxidation for the double-layer formation (Cu₂O + CuO), as reported in the literature.

desired test temperature. Because the copper base surface area decreased during oxidation, the calibrated surface area was therefore used to estimate the time dependence of the weight gain per unit area in the manner reported by Mrowec.^[6]

Cross-sections of specimens were characterized using the metallographic method with a scanning electronic microscope (SEM) and electron probe microanalyzer (EPMA).^[20–23] To observe the microstructure of the oxide scales clearly, a 0.003 N HCl solution was used for etching the Cu₂O layer, where the solvent comprised 67 vol pct water and 33 vol pct ethanol.

III. RESULTS

Figure 2 shows parabolic plots of the mass gain per unit area for FZR, 6N, and 4N copper oxidized at 350 °C to 1050 °C. All parabolic plots show straight lines, indicating that the oxidation kinetics of FZR, 6N, and 4N copper at 350 °C to 1050 °C obeys the parabolic oxidation rate law, consistent with results reported in the literature.^[1–5] At 900 °C to 1050 °C, 4N and 6N copper oxidize as rapidly as FZR copper does. By decreasing the temperature to 600 °C, the oxidation rate increases in the order FZR Cu < 6N Cu < 4N Cu. At temperatures below 600 °C, 6N Cu oxidizes as rapidly as FZR Cu does, whereas 4N Cu oxidizes slightly more slowly than FZR and 6N Cu do.

Arrhenius plots of the parabolic oxidation rate constants k_p , as calculated from mass gain data, are shown in Figure 3. It is interesting that the temperature dependencies in Figure 3 closely resemble the results from the literature shown in Figure 1. As with Figure 1, the Arrhenius plots in Figure 3 are roughly classifiable into three regions: a high temperature region (900 °C to 1050 °C), an intermediate temperature region (600 °C to 850 °C), and a low temperature region (350 °C to 500 °C). In contrast to the case at 900 °C to 1050 °C, the temperature dependence for each copper is lower at 600 °C to 850 °C, and even lower at 350 °C to 500 °C. In detail, the temperature dependence for FZR Cu becomes lower at 800 °C and even lower at 600 °C. Similar behavior is apparent for 6N Cu at 850 °C and then at 600 °C, and for 4N Cu at 900 °C and then at 600 °C. By calculation, the activation energies (Q_a) at high temperatures for FZR copper (800 °C to 1050 °C), 6N copper (850 °C to 1050 °C), and 4N copper (900 °C to 1050 °C) are almost equal: 173 kJ/mol. In the intermediate temperature range, the Q_a value is 93 kJ/mol for FZR copper (600 °C to 800 °C), 111 kJ/mol for 6N

Table I. Activation Energies Reported in the Literature for Copper Oxidation at 350 °C to 1050 °C

Type of Copper	Atmosphere (1 atm)	Temperature (°C)	Activation Energy (kJ/mol)	Reference
Spectrally pure	Air	900 to 1050	140	Mrowec and Stoklosa ^[6]
OFHC	Air	300 to 500	39	Tylecote ^[7]
		600 to 900	123	
OFHC	O ₂	700 to 1000	132	Bridges <i>et al.</i> ^[8]
99.995 pct	Air	900 to 1050	159	Czerski <i>et al.</i> ^[9]
99.999 pct	O ₂ or air	750 to 1040	172	Park and Netasen ^[10]
		450 to 750	84	
		350 to 450	223	
—	Air	750 to 1000	146	Kofstad ^[11]
99.999 pct	O ₂	660 to 937	179	Sartell and Li ^[12]
OFHC	O ₂	300 to 550	84	Valensi ^[13]
		550 to 900	158	

Table II. Analytical Results of FZR, 6N, and 4N Copper by Glow Discharge Mass Spectrometry

	FZR Copper	6N Copper	4N Copper
Al	N.D.	0.4	1.1
Si	0.004	0.3	1.5
P	N.D.	0.01	4.2
S	0.003	0.06	4.1
Fe	N.D.	N.D.	0.7
Ni	N.D.	0.004	0.4
Se	N.D.	0.3	0.2
As	0.003	0.01	0.4
Sb	N.D.	N.D.	0.9
Ag	N.D.	0.008	5.5
Bi	N.D.	N.D.	0.06
Pb	N.D.	0.04	N.D.

Data are given as mass ppm.
N.D. = not detectable.

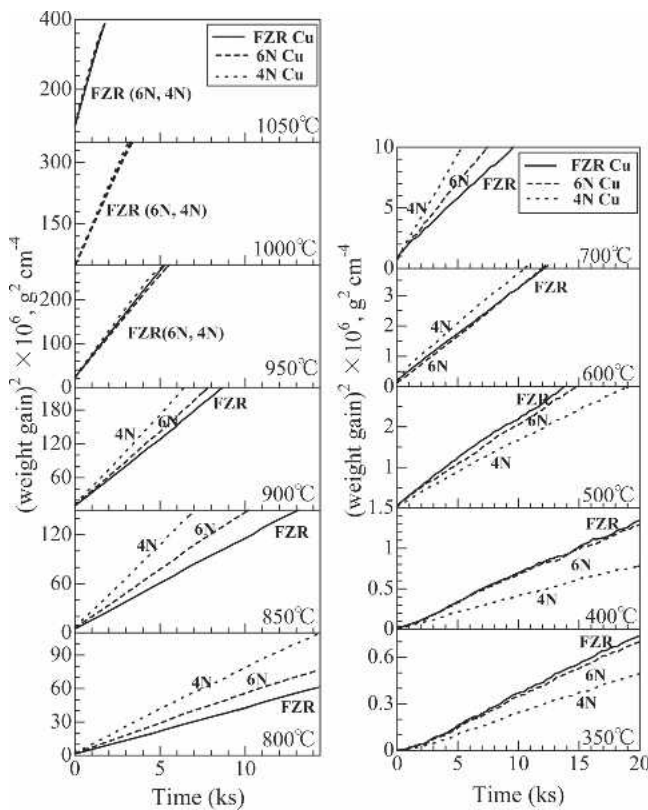


Fig. 2—Parabolic plots of the weight gain for FZR, 6N, and 4N copper oxidized at 350 °C to 1050 °C in a 0.1 MPa oxygen atmosphere.

copper (600 °C to 850 °C), and 95 kJ/mol for 4N copper (600 °C to 900 °C). In the low temperature region (350 °C to 500 °C), the same value of 40 kJ/mol is obtained for FZR and 6N copper, whereas it is higher for 4N copper, 52 kJ/mol.

IV. DISCUSSION

A. Oxidation Mechanism of Copper in 0.1 MPa Oxygen at 350 °C to 1050 °C

With reference to the literature,^[1–5] the Cu₂O scale grows predominantly in the high temperature range (900 °C to

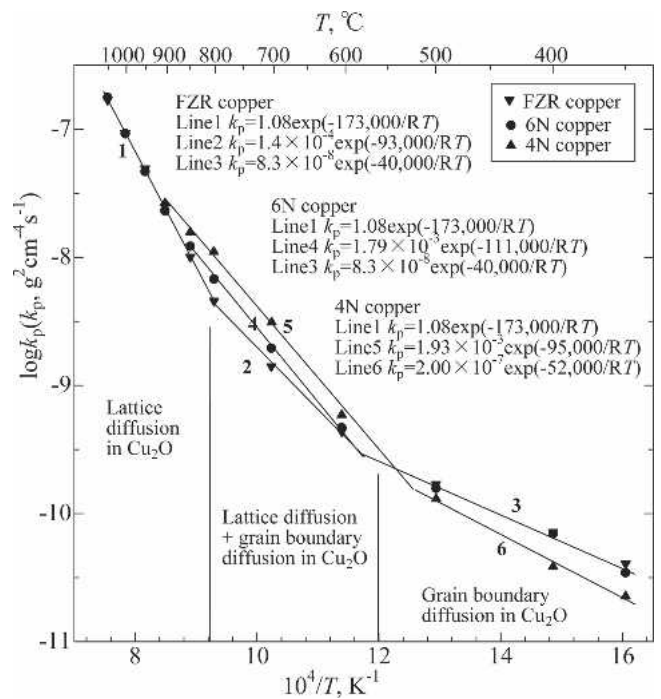


Fig. 3—Temperature dependence of the parabolic rate constants k_p for FZR, 6N, and 4N copper at 350 °C to 1050 °C in a 0.1 MPa oxygen atmosphere. The Arrhenius equation $k_p = Ae^{-Q/RT}$ is also given, where A is a constant ($\text{g}^2 \text{cm}^{-4} \text{s}^{-1}$), R is the gas constant (8.314 J/mol K), and Q is the activation energy (J).

1050 °C), and the lattice diffusion in Cu₂O is inferred to be the rate-determining step attributable to the growth of large Cu₂O grains.^[10] The Cu₂O scale also grows predominantly in the intermediate temperature region (600 °C to 850 °C). A decrease in the temperature dependence likely occurs because of the contribution of grain boundary diffusion.^[10] For that reason, Q_a values of 173 kJ/mol for FZR copper at 800 °C to 1050 °C, for 6N copper at 900 °C to 1050 °C, and for 4N copper at 950 °C to 1050 °C in this work are inferred to represent the activation energy for double-layer formation (Cu₂O + CuO), where the lattice diffusion predominates in Cu₂O. In the intermediate temperature region, the Q_a values of 93 kJ/mol for FZR copper at 600 °C to 800 °C, 111 kJ/mol for 6N copper at 600 °C to 850 °C, and 95 kJ/mol for 4N copper at 600 °C to 900 °C might contribute from the lattice diffusion and grain boundary diffusion.

The oxidation mechanism of copper at 350 °C to 500 °C has remained ambiguous in the literature. Therefore, the copper oxidation at this temperature will be studied as follows. In addition, the oxidation mechanism of copper in the whole range of 350 °C to 1050 °C will be examined further.

1. Growth of the scales of CuO and Cu₂O

To investigate copper's oxidation mechanism, it is necessary to know which of Cu₂O or CuO grows predominantly responsible for parabolic oxidation kinetics. The fractions of CuO reported by different authors were investigated.^[8,13,25,26,27] Figure 4 shows that good consistency exists in the respect that the fraction of CuO is extremely low at 800 °C to 1000 °C. The fraction of CuO remains at a very low level between 600 °C and 800 °C, as reported by Bridges *et al.*^[8] and De Carli and Collari.^[26] However, data scattering below 600 °C is apparent. On decreasing the oxidation

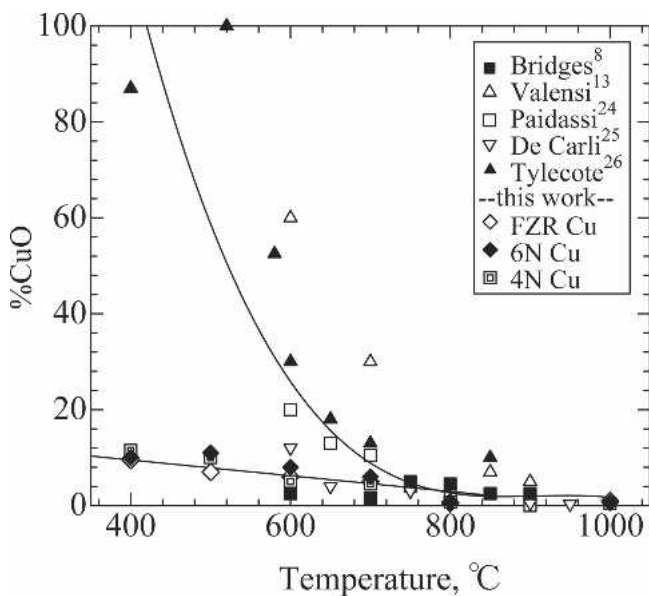


Fig. 4—Fraction of CuO formed at 400 °C to 1000 °C. In this work, the oxidation time is 30 minutes for specimens oxidized at 1000 °C and 800 °C, 240 minutes at 600 °C, and 480 minutes at 400 °C.

temperature from 600 °C to 350 °C, a sharp increase occurred in the fraction of CuO up to over 90 pct, as reported by Valensi^[13] and Tylecote.^[27] The various data reported by different authors might be related to the measurement methods they adopted.^[21,28,29] For that reason, this study verifies the fraction of CuO at 350 °C to 1050 °C using a direct and reliable metallographic method.

Figure 5 shows typical cross-sections of double-layered scales on FZR copper oxidized at 1000 °C, 800 °C, 600 °C, and 400 °C under 0.1 MPa oxygen pressure. In contrast to the Cu₂O scale, the CuO scale is much too thin for all specimens, even at 400 °C. Moreover, the thickness of CuO and Cu₂O formed at 350 °C to 1050 °C was measured; the fractions of CuO for FZR, 6N, and 4N copper were calculated as shown in Figure 4. The CuO fraction remains very small for all temperatures for all specimens, and only a slight increase in the CuO fraction was observed at 350 °C to 500 °C. This result supports those reported by Bridges *et al.*,^[8] Paidassi,^[25] and De Carli and Collari,^[26] but it differs greatly from those of Valensi^[13] and Tylecote.^[27] Consequently, it is clear that, similarly to the case at 600 °C to 1050 °C, the Cu₂O scale grows predominantly at 350 °C to 500 °C. Moreover, Cu₂O growth obeys the parabolic oxidation rate law.^[21] Taken together, these facts show that the parabolic oxidation kinetics of copper at 350 °C to 1050 °C are attributable to the predominant growth of Cu₂O by outward diffusion of copper atoms.

2. Contribution of grain boundary diffusion to copper oxidation

In a previous paper,^[30] the authors studied oxidation of a less-pure copper (99.5 pct). That study concluded that because of the grain boundary diffusion, the oxidation of copper was enhanced, while the activation energy was decreased. With reference to it, the contribution of grain boundary diffusion should also be investigated to explain the decrease in the activation energy in the intermediate and low temperature range in Figure 3.

In the literature,^[31,32] Smeltzer *et al.* studied grain boundary diffusion in metal oxidation. Assuming that the grain boundary diffusion coefficient D_b is much higher than the lattice diffusion coefficient D_l , the oxidation rate can be described as

$$d(x^2)/dt = 2D_l\Omega\Delta c + 4D_b\Omega\Delta c d/\delta_t, \quad [1]$$

where x = the scale thickness at time t , Ω = the volume of oxide per metal atom, Δc = the concentration difference across the scale, d = the grain boundary width, and δ_t = the average grain diameter at time t .

Eq. [1] might also be written as:

$$d(x^2)/dt = k_p(\text{eff}) = k_p(\text{latt}) + k_p(\text{bound})f, \quad [2]$$

where $f = 2d/\delta_t$ is the fraction of all diffusion sites situated in the grain boundaries, $k_p(\text{eff})$ is the instantaneous rate constant, $k_p(\text{latt}) = 2D_l\Omega\Delta c$ is the parabolic rate constant attributable to lattice diffusion, and $k_p(\text{bound}) = 2D_b\Omega\Delta c$ is the parabolic rate constant attributable to grain boundary diffusion. Thus, the contribution of grain boundary diffusion can be estimated as

$$k_p(\text{bound})f/k_p(\text{latt}) = 2dD_b/(D_l\delta_t). \quad [3]$$

Eq. [3] suggests that the grain boundary density in the scale should be considered to explain the influence of grain boundary diffusion on the oxidation rate. The Cu₂O layer microstructure at 350 °C to 1050 °C was examined to confirm the case in this study.

As illustrated in Figure 5, the columnar Cu₂O grains are large for FZR copper oxidized at 1000 °C and 800 °C for 30 minutes. However, the mean lateral size of the Cu₂O grains becomes much smaller at 600 °C and 400 °C, even though the oxidation time is much longer. Moreover, the respective changes in the mean lateral size of Cu₂O grains for FZR, 6N, and 4N copper at 350 °C to 1050 °C are plotted in Figure 6. In the high temperature range, the mean Cu₂O grain sizes are as large as over 100 μm for FZR copper (800 °C to 1050 °C), 6N copper (850 °C to 1050 °C), and 4N copper (900 °C to 1050 °C). In the intermediate temperature range, however, a quick decrease in the mean Cu₂O grain size is observed for FZR, 6N, and 4N copper. At temperatures less than 600 °C, the size of all Cu₂O grains decreases to a much lower value than 1 μm, with the grains for FZR and 6N copper being slightly larger than those for 4N copper.

Comparison of Figure 3 with Figure 6 shows that temperature dependencies for FZR, 6N, and 4N copper correspond well to their respective changes in the lateral mean size of the Cu₂O grains with temperature. This correspondence supports the conclusions reached in the literature: lattice diffusion predominates at high temperatures during copper oxidation because of the large Cu₂O grains; also, the decrease in the activation energy in the intermediate temperature range results from the contribution of the grain boundary diffusion that is attributable to the marked decrease in the Cu₂O grain mean size. In the case of 350 °C to 500 °C, considering that the Cu₂O grains for FZR, 6N, and 4N copper at 350 °C to 500 °C are so small, it is reasonable that grain boundary diffusion would contribute much more to oxidation than to that in the intermediate temperature range according to Eq. [3]. Thus, the considerably low activation energy values at 350 °C to 500 °C for FZR, 6N, and 4N copper can be explained in terms of the grain boundary diffusion.

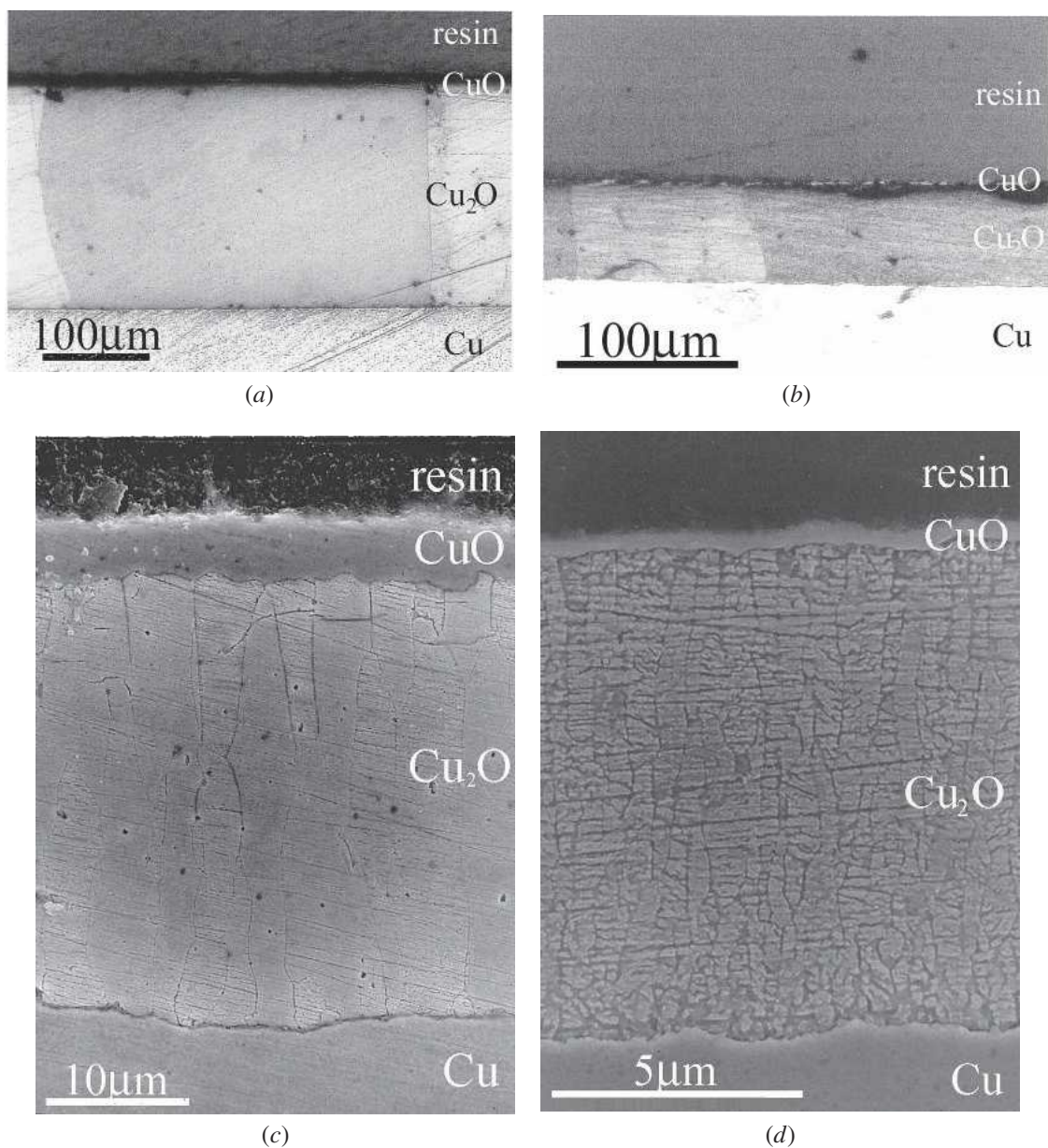


Fig. 5—Cross-sections of the oxide scales ($\text{Cu}_2\text{O} + \text{CuO}$) on FZR copper oxidized in a 0.1 MPa oxygen atmosphere. (a) 1000 °C, 30 minutes; (b) 800 °C, 30 minutes; (c) 600 °C, 240 minutes; (d) 400 °C, 480 minutes.

In summary, the Cu_2O scale grows predominantly over the whole range of 350 °C to 1050 °C, and the rate-determining step is inferred to be outward diffusion of copper atoms in Cu_2O . The lattice diffusion contributes to copper oxidation at high temperatures, just as the grain boundary diffusion does at 350 °C to 500 °C. In the intermediate temperature range, copper oxidation is contributed from lattice diffusion and grain boundary diffusion.

B. Temperature Dependence for Single-Layer Formation in Ar + 1 pct Oxygen

As reviewed previously,^[22] the temperature dependencies (activation energies) for the single-layer formation (Cu_2O) reported in the literature were also in disagreement. For that reason, additional work was done to obtain the activation energy for the single-layer formation by oxidation of FZR

copper at 900 °C to 1050 °C in Ar + 1 pct O_2 .^[22] According to it, the activation energy for the single-layer formation governed by the lattice diffusion was 98 kJ/mol.

In this work, the activation energy for the double-layer formation, where the lattice diffusion predominates in Cu_2O , is 173 kJ/mol. However, the value for the single-layer formation, where the lattice diffusion predominates, is decreased to 98 kJ/mol. The difference of 75 kJ/mol between them supports a $(P_{\text{O}_2})^{1/4}$ -dependent parabolic rate constant associated with diffusion of copper atoms via neutral copper vacancies in Cu_2O .^[22]

C. Purity Effect on Oxidation Kinetics of Copper in 0.1 MPa Oxygen at 350 °C to 1050 °C

Figures 1 and 3 show that the oxidation rates and the activation energies for FZR, 6N, and 4N copper are almost

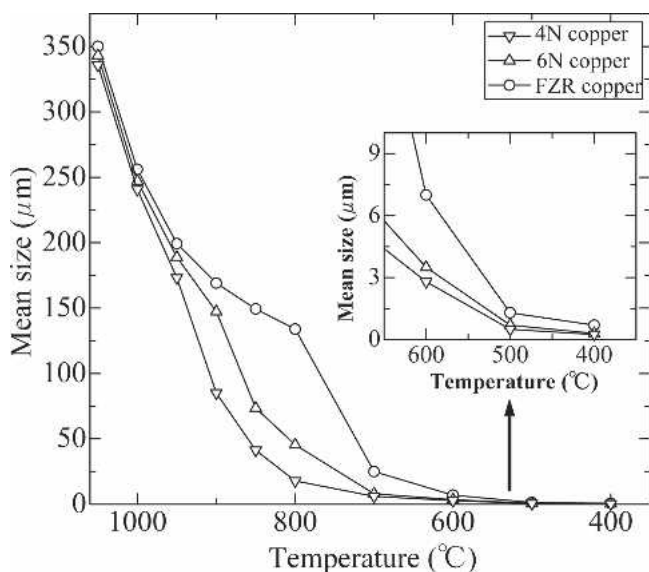


Fig. 6—Mean lateral size of the columnar Cu_2O grains for FZR, 6N, and 4N copper oxidized at 400 to 1050 °C in a 0.1 MPa oxygen atmosphere. The insert shows enlargement of the part at 400 °C to 600 °C. The oxidation time is 30 minutes for specimens oxidized at 800 °C to 1050 °C, 240 minutes at 600 °C and 700 °C, and 480 minutes at 400 °C and 500 °C.

equal in the high temperature range. That fact indicates that trace impurities have almost no influence on the oxidation kinetics of 6N and 4N copper in the high temperature range, where the lattice diffusion predominates. However, the lattice-diffusion temperature range seen in Figure 3 is wider for higher-purity copper: 800 °C to 1050 °C for FZR copper, 850 °C to 1050 °C for 6N copper, and 900 °C to 1050 °C for 4N copper. In the intermediate temperature range, the oxidation rate increases in the order FZR Cu < 6N Cu < 4N Cu. In the low temperature range, in contrast to FZR and 6N copper, the oxidation rate for 4N copper becomes lower, with a higher activation energy value. This difference suggests that the copper's purity influences the contribution of the grain boundary diffusion to oxidation, as clarified next.

To explain the variance of the lattice-diffusion temperature range with purity, the change in the mean lateral size of Cu_2O grains for FZR, 6N, and 4N copper at 350 °C to 1050 °C is again examined (Figure 6). The mean lateral Cu_2O grain sizes for FZR, 6N, and 4N copper are large at high temperatures. However, a rapid decrease in the mean Cu_2O grain size occurs at 800 °C for FZR copper, at 850 °C for 6N copper, and at 900 °C for 4N copper. Those different temperatures indicate that the growth of the Cu_2O grains tends to be hindered by trace impurities at lower temperatures, resulting in higher temperature values where a quick decrease in the mean size of Cu_2O grains occurs for one less-pure specimen. Furthermore, grain boundary diffusion begins at this temperature point correspondingly, thereby explaining the result that the lattice-diffusion temperature range is wider for one higher-purity copper. Namely, the variance of the temperature range of the lattice diffusion can be interpreted in terms of the occurrence of grain boundary diffusion depending on purity.

In the intermediate temperature range, the oxidation rate increases in the order FZR Cu < 6N Cu < 4N Cu. One reason might be the greater contribution of the grain boundary diffusion for one less-pure copper because the mean size of

the Cu_2O grains decreases in the order FZR Cu > 6N Cu > 4N Cu.

Furthermore, the possible impeding role of impurities should be considered to explain the lower oxidation rates of 4N copper with higher activation energy at 350 °C to 500 °C. In Figure 6, because the Cu_2O grains for 4N copper are smaller in contrast to FZR and 6N copper, 4N copper probably oxidizes somewhat faster than FZR or 6N copper does. However, the result is contrary to this fact, suggesting that outward diffusion of copper atoms through grain boundaries is slowed, perhaps because impurities segregated at grain boundaries might play a role of hindering the grain boundary diffusion. Similar results have arisen in the literature^[33] describing outward diffusion in iron by Shima *et al.* Reportedly, the grain boundary diffusion coefficient is much higher than the lattice-diffusion coefficient, but grain boundary diffusion is suppressed by impurities that are segregated at the grain boundaries. Moreover, this effect becomes important at lowered temperatures. In that regard, the lower oxidation rates and higher activation energy for 4N copper at 350 °C to 500 °C might be related to the impediment role of impurities that are segregated at grain boundaries.

In addition, it is noted that the scatter of the temperature dependence at 300 °C to 1050 °C shown in Figure 1 is to a large extent similar to that observed in Figure 3. With reference to the above discussion, the scatter in Figure 1 is also attributable to the different degrees of purity of the copper specimens.

In summary, trace impurities have almost no influence on oxidation kinetics of 6N and 4N copper at high temperatures where the lattice diffusion predominates. However, the enhanced copper oxidation and the decreased activation energy in the intermediate temperature range, which are attributable to the growth of Cu_2O grains, are impeded by trace impurities to facilitate the grain boundary diffusion depending on the purity of copper. At 350 °C to 500 °C, grain boundary diffusion might be hindered by impurities segregated at grain boundaries. The purity effect is inferred to explain the scatter of the temperature dependencies at 350 °C to 1050 °C among different authors.

V. CONCLUSIONS

The oxidation mechanism of copper at 350 °C to 1050 °C and the purity effect were examined by oxidizing FZR, 6N, and 4N copper. The following results were obtained:

1. For copper oxidation at 350 °C to 1050 °C, the Cu_2O scale grows predominantly, and the rate-determining step is inferred to be outward diffusion of copper atoms in Cu_2O .
2. Lattice diffusion contributes to copper oxidation at high temperatures, and the grain boundary diffusion does so at 350 °C to 500 °C. At intermediate temperatures, copper oxidation is contributed from the lattice diffusion and grain boundary diffusion.
3. Activation energy values for the double-layer formation and the single-layer formation where lattice-diffusion predominates in Cu_2O are 173 and 98 kJ/mol, respectively. This relation supports a $(P_{\text{O}_2})^{1/4}$ -dependent parabolic rate constant associated with diffusion of copper atoms via neutral copper vacancies in Cu_2O .

4. The lattice-diffusion temperature range is wider for high-purity copper in the high temperature range. Copper oxidation in the intermediate temperature range is enhanced because trace impurities impede the lateral growth of Cu₂O grains to facilitate grain boundary diffusion. Grain boundary diffusion is impeded at 350 °C to 500 °C by impurities that are segregated at grain boundaries.
5. The purity effect is responsible for the remarkable scatter of temperature dependence data reported by different authors at 350 °C to 1050 °C.

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