

Oxidation Mechanism of Copper at 623–1073 K *

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In reviewing the results reported for copper oxidation at intermediate temperatures from 573 to 1173 K, the oxidation mechanism at the lower part of this temperature range and the reason for the change in activation energy with decreasing the temperature remain unclear. To make it clear, copper oxidation is studied at 623–1073 K under 0.1 MPa O₂ using a commercial 99.9999% pure copper. The oxidation kinetics is essentially parabolic, and the activation energy decreases from 111 kJ/mol at 873–1073 K to 40 kJ/mol at 623–773 K. The growth of Cu₂O is predominant and it obeys the parabolic law at 623–773 K, as well as the case at 873–1073 K. In addition to grain boundary diffusion of copper along the fine and thin columnar Cu₂O grains, the non-protective CuO whisker layer, which cannot keep the oxygen potential constant at the Cu₂O/CuO interface, should be responsible for the decrease in the activation energy at 623–773 K.

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1. Introduction

It has been reported that copper oxidation at intermediate temperatures from 573 K to 1173 K essentially obeys the parabolic rate law.^{1,2)} However, the Arrhenius plot of the parabolic rate constants shows a break at around 823 K^{3,4)} or around 723 K,⁵⁾ and the reported activation energy values in two temperature regions are widely scattered, as tabulated in Table 1.

According to the literature results for copper oxidation,^{3–7)} it is generally accepted that the growth of Cu₂O is predominant at 873–1173 K. The rate-determining step in this temperature range is the outward diffusion of copper in Cu₂O, as agrees well with Wagner's scaling theory.⁸⁾ Moreover, simultaneous lattice diffusion and grain boundary diffusion have been found to be responsible for the growth of Cu₂O in this higher temperature range.⁹⁾

On the other hand, the oxidation mechanism at temperature

below 873 K remains unclear. It is still in doubt whether the growth of Cu₂O or that of CuO is predominant for copper oxidation in this lower temperature range.^{3,5,6,10,11)} The explanations for the change in the activation energy are also ambiguous. Valensi³⁾ insisted that the growth of CuO should be responsible for the decrease in the activation energy at 823–1173 K, but Park⁵⁾ ascribed the very high activation energy in his work to the growth of CuO whisker layer at 623–723 K.

Furthermore, Matsunaga and Hamma¹²⁾ found that the grain boundary diffusion could contribute to copper oxidation at 773 K under 6.5 Pa oxygen pressure, where the growth of Cu₂O was predominant. They suggested that the decrease in the activation energy under 0.1 MPa O₂ or air at and below 773 K should be also due to the grain boundary diffusion. So, it is important to examine whether the growth of Cu₂O or that of CuO is predominant for copper oxidation in this lower temperature range.

To obtain the real activation energy values at intermediate temperatures, copper oxidation will be studied at 623–1073 K using a commercial 99.9999% pure copper. The oxidation mechanism at lower part of the temperature range and the reason for the change in activation energy with decreasing the temperature will be clarified.

2. Experimental Procedure

The main impurities in the commercial 99.9999% pure copper were Al (0.4 ppm), Si (0.3 ppm), Se (0.3 ppm) and S (0.06 ppm). The specimens were in shape of discs with 0.4–0.5 mm in thickness and 5 mm in diameter. Prior to oxidation, the specimens were annealed in H₂ atmosphere at 873 K for 24 hours for recrystallization of copper.

Copper oxidation was carried out at 623–1073 K under 0.1 MPa oxygen with a gas flow rate of 0.1 L/min. Ar + 1% O₂ was also used to examine the oxygen pressure dependence. The mass gain was measured with thermogravimetry (SDT 2960 by TA Instruments), the sensitivity of which was 0.1 µg.

Since the surface area of the specimen decreased during the oxidation, the calibrated surface area was used in the manner reported by Mrowec.¹³⁾

Table 1 Activation energies for copper oxidation at intermediate temperatures.

Type of copper	Atmosphere	Temperature range (K)	Activation energy <i>Qa</i> (kJ/mol)	Reference
OFHC	0.1 MPa O ₂	573–823	84	Valensi <i>et al.</i> ³⁾
		823–1173	158	
OFHC	Air	573–773	39	Tylecote <i>et al.</i> ⁴⁾
		873–1173	123	
99.999%	0.1 MPa O ₂ or air	623–723	224	Park <i>et al.</i> ⁵⁾
		723–1073	84	
99.9999%	0.1 MPa O ₂	573–773	40	Present work
		873–1073	111	
	Ar + 1% O ₂	573–773	58	
		873–1073	111	

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The cross-section of the specimens was characterized with SEM and EPMA. To observe the microstructure of the scales, a 2N HCl aqueous solution and a 0.003N HCl solution were used for etching the CuO layer and the Cu₂O layer, respectively. The solvent for the second solution was composed of 67 vol% water and 33 vol% ethanol.

3. Results and Discussion

3.1 Oxidation kinetics of copper

Parabolic plots of the mass gain per unit area measured at 1073 K and 673 K are shown in Fig. 1. The oxidation kinetics follows the parabolic rate law essentially. At 1073 K, the oxidation rate under Ar + 1% O₂ is almost the same as that under 0.1 MPa O₂, but it becomes lower at 673 K.

The Arrhenius plot of the parabolic rate constants k_p at 623–1073 K, inserted in Fig. 1, shows that the points fall close to the same straight line in the temperature range higher than 873 K. However, the points follow two different lines with lower slopes at lower temperatures, depending on the oxygen pressure. As shown in Table 1, the activation energy for copper oxidation at 873–1073 K under 0.1 MPa O₂ is 111 kJ/mol, which is the same as that for copper oxidation under Ar + 1% O₂. On the other hand, the activation energy for copper oxidation under 0.1 MPa O₂ is 40 kJ/mol, which is lower than that of 58 kJ/mol obtained under Ar + 1% O₂.

The tendency, that the activation energy becomes smaller in the lower temperature range under 0.1 MPa O₂ in this work, is in good agreement with the results reported by Valensi *et al.*³⁾ and Tylecote *et al.*⁴⁾ This indicates that the considerably high activation energy in the lower temperature range obtained by Park⁵⁾ in Table 1 seems to be an exception. The activation energies for the oxidation of 99.9999% pure copper in the higher temperature range and that in the lower temperature range in this work are relatively close to those for the oxidation of OFHC copper in Tylecote *et al.*'s work, but are somewhat lower than those obtained by Valensi *et al.*

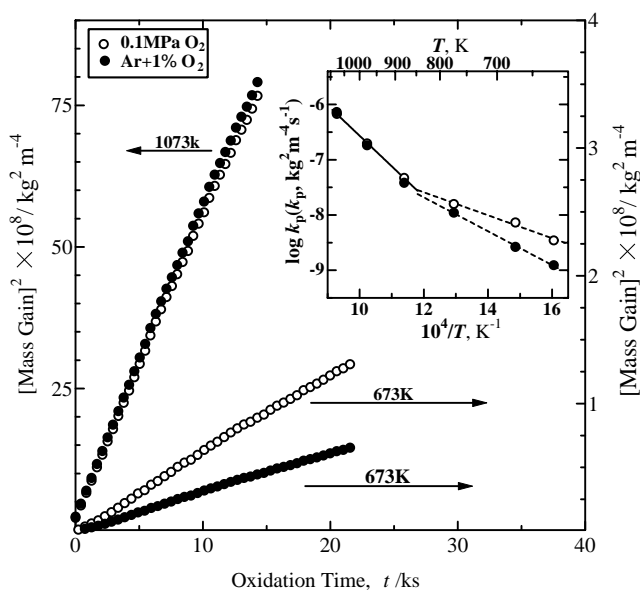


Fig. 1 Oxidation kinetics of copper at 673 K and 1073 K under 0.1 MPa O₂ and Ar + 1% O₂.

In fact, some factors might have an influence on the results, such as purity degree of the copper specimens,^{1,9,14)} sensitivity of thermogravimetry and errors made in the determination of the parabolic rate constants.¹³⁾ It is understandable that, therefore, the somewhat disagreement appears in the activation energy values obtained by different authors. The higher purity (99.9999%), the high sensitivity TGA and calibration of surface area in this work may lead to more reliable results.

3.2 Rate-determining step

To examine whether the growth of Cu₂O or that of CuO should be responsible for the parabolic oxidation rates, change in the thickness of Cu₂O and CuO layers is necessary. In the literature, the fraction of CuO varied considerably among different indirect evaluation methods, such as hydrogen reduction method,³⁾ coulometric analysis,¹⁰⁾ and XRD.⁶⁾ It remains unclear that, among these indirect methods, which one is suitable to determinate the fraction of CuO. As a direct and reliable technique, the metallographic method is used in this work, by which Paidassi *et al.*⁷⁾ obtained a low CuO fraction at 873 K.

Microstructure of Cu₂O layer and CuO layer for copper oxidation is shown in Fig. 2. Figure 2(A) and (B) are the microstructure of the Cu₂O layers. All the scales consist of two layers: one inner thicker layer and the other outer thin layer. Characterization of the cross-section with EPMA demonstrates that the inner layer is Cu₂O, and the outer layer is CuO.¹⁴⁾ The inner Cu₂O layer grown at 973 K consists of relatively coarse columnar grains extending through the entire scale. The Cu₂O layer grown at 673 K is also composed

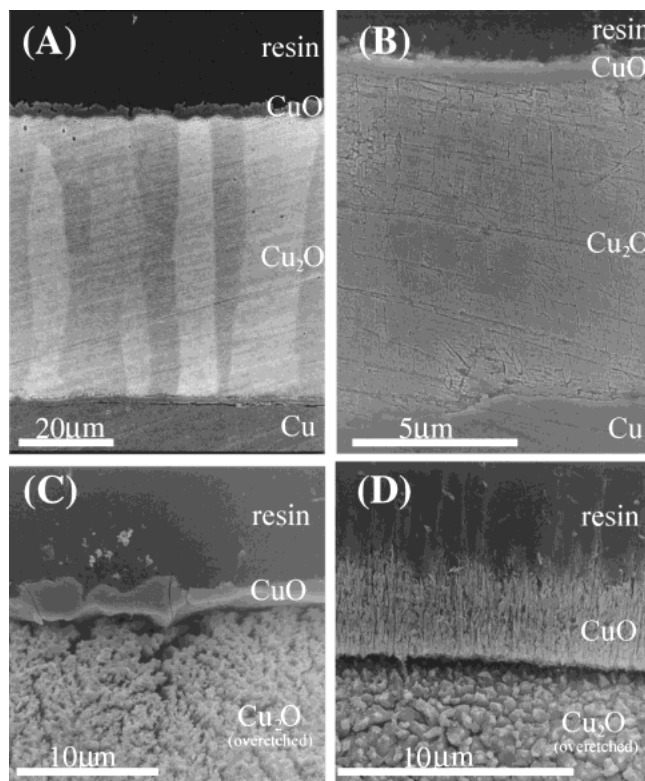


Fig. 2 Microstructure of Cu₂O layer and CuO layer for copper oxidation under 0.1 MPa O₂. (A) Cu₂O layer 973 K, 14.4 ks, (B) Cu₂O layer 673 K, 28.8 ks, (C) CuO layer, 1073 K, 14.4 ks, (D) CuO layer 773 K, 28.8 ks.

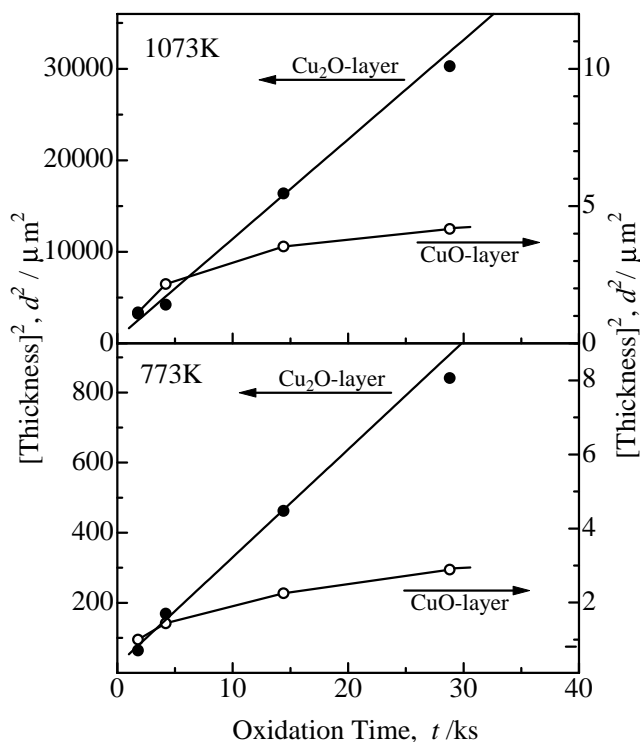


Fig. 3 Growth of Cu_2O and CuO layers under 0.1 MPa O_2 at 1073 K and 773 K.

of columnar grains perpendicular to the copper base, but they are considerably fine and thin. Figures 2(C) and (D) show the microstructure of the CuO layer at 1073 K and 773 K under 0.1 MPa O_2 , where the Cu_2O layer was over-etched. The CuO layer is compact at 1073 K, consisting of single-layered CuO crystals. The CuO layer at 773 K, mainly composed of the whiskers rooted from the Cu_2O layer, can be clearly observed. The CuO whisker layer is very loose, because it is very easy to be wiped off from the surface of the oxides.

If the rate of copper oxidation is determined by the outward diffusion of copper through the Cu_2O , the parabolic plot of the Cu_2O layer thickness should also yield a straight line. However, no similar works have been carried out for copper oxidation at temperatures lower than 873 K.

Changes in the thickness of the Cu_2O layer and the CuO layer grown at 1073 K and 773 K as a function of the oxidation time are shown in Fig. 3. As expected, the parabolic plot for 1073 K yields a straight line for the growth of Cu_2O , but CuO grows extremely slowly. It is worth noticing that the growth of Cu_2O at 773 K also obeys the parabolic law. According to Wagner's scaling theory,⁸⁾ the rate-determining step for the parabolic oxidation of copper in the lower temperature range in Fig. 1 should be also the growth of Cu_2O by outward diffusion of copper.

According to the previous work,⁹⁾ simultaneous lattice diffusion and grain boundary diffusion should be responsible for the growth of Cu_2O at 873–1073 K. In Fig. 2, the columnar Cu_2O grains grown at 673 K are much thinner and finer than those at 1073 K. It is reasonable that, therefore, the grain boundary diffusion would contribute more to copper oxidation in the lower temperature range than to that at higher temperatures. Moreover, the lower activation energy in the lower temperature range should also be somewhat due to the grain

boundary diffusion. In addition, similar results have also been observed for nickel oxidation.^{15,16)} Namely, nickel oxidation through grain boundary diffusion is essentially parabolic, and it leads to a decrease in the activation energy.

3.3 Oxygen pressure dependence of activation energy at intermediate temperatures

Some studies^{5,17,18)} showed that the thin CuO film for copper oxidation at and above 873 K is impervious to oxygen, and the oxygen potential at the $\text{Cu}_2\text{O}/\text{CuO}$ interface is determined by the dissociation pressure of CuO , which is constant at a given temperature. However, few works have been done to investigate the case at lower temperatures. For this reason, examination of the ambient oxygen pressure dependence of the oxidation kinetics at lower temperatures is very necessary.

The typical kinetics for copper oxidation under $\text{Ar} + 1\% \text{O}_2$ can be seen in Fig. 1. As expected, the oxidation rates at 873–1073 K for $\text{Ar} + 1\% \text{O}_2$ are almost the same as those for 0.1 MPa O_2 . However, the rates for $\text{Ar} + 1\% \text{O}_2$ become smaller at 623–773 K, and the corresponding activation energy is also higher. This result means that the oxidation kinetics of copper is dependent on the ambient oxygen pressure in this lower temperature range.

The microstructure of the CuO layer was observed, as can be seen in Fig. 2(C) and (D). In contrast to the compact CuO layer at 1073 K, the whisker CuO layer at 773 K is very loose. This suggests that the faster oxidation rate of copper in the lower temperature range under 0.1 MPa in Fig. 1 should be related to the formation of the loose CuO whisker layer. It is most probable that the loose whisker layer is not impervious to oxygen, and then the oxygen potential at the $\text{Cu}_2\text{O}/\text{CuO}$ interface cannot be kept constant at a given temperature. So, in addition to the grain boundary diffusion of copper, the formation of whisker CuO layer should also be responsible for the decrease in the activation energy at 623–773 K.

4. Conclusions

Copper oxidation at 623–1073 K under 0.1 MPa O_2 and $\text{Ar} + 1\% \text{O}_2$ was carried out by using 99.9999% pure specimen. The following results are obtained.

- (1) The oxidation kinetics at 623–1073 K is essentially parabolic. The activation energy obtained under 0.1 MPa oxygen pressure decreases from 111 kJ/mol at 873–1073 K to 40 kJ/mol at 623–773 K.
- (2) The growth of Cu_2O is predominant, and it obeys the parabolic law even at 623–773 K, as well as the case at higher temperatures.
- (3) The oxidation rate at 623–773 K is found to be dependent on the ambient oxygen pressure, but that at 873–1073 K is independent of the ambient oxygen pressure.
- (4) In addition to the grain boundary diffusion of copper along the thin and fine columnar Cu_2O grains, the non-protective CuO whisker layer should also be responsible for the lower activation energy at 623–773 K.

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