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## Reaction thermodynamics and kinetics on in situ $\text{Al}_2\text{O}_3/\text{Cu}$ composites<sup>①</sup>

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**Abstract:** The preferred internal oxidation of aluminum in Cu-Al alloy was used to obtain in-situ  $\text{Al}_2\text{O}_3/\text{Cu}$  composites. The reinforcement particles were mainly  $\gamma\text{-Al}_2\text{O}_3$ , some  $\theta\text{-Al}_2\text{O}_3$  and a little  $\alpha\text{-Al}_2\text{O}_3$ . Thermodynamics analyses show that the chemical reactions are  $3\text{Cu}_2\text{O} + 2\text{Al} = 6\text{Cu} + \text{Al}_2\text{O}_3$  or  $3\text{CuO} + 2\text{Al} = 3\text{Cu} + \text{Al}_2\text{O}_3$ . A related equilibrium diagram was drawn. The experiments and investigation show that the formation rate of  $\text{Al}_2\text{O}_3$  was controlled by the diffusion of oxygen in matrix.

**Key words:**  $\text{Al}_2\text{O}_3/\text{Cu}$  composites; internal oxidation; thermodynamics; kinetics **Document code:** A

### 1 INTRODUCTION

Pure copper and its alloys have good electrical and heat conductivity and poor mechanical properties so that they cannot often meet the needs of modern industry. In the condition of keeping high conductivity, how to improve the mechanical properties, especially hot strength and thermostability, is one of the important problems that many researchers are paying close attention to<sup>[1~5]</sup>. Now the related research mainly concentrates on second phase dispersive strengthening<sup>[6,7]</sup>.

Oxide dispersive strengthening (ODS) uses tiny oxide particles as reinforcers. The volume fraction of the oxides is only a few percent. The oxides used have good thermostability, which do not dissolve even heating at a temperature near the metal matrix melting point. Therefore, the dispersive oxides have good dispersive strengthening effect at an elevating temperature<sup>[8~11]</sup>. In this paper in-situ  $\text{Al}_2\text{O}_3/\text{Cu}$  composites are prepared by means of internal oxidation in nitrogen base atmosphere. The microstructure of the composites is analyzed. The thermodynamics

and kinetics on the internal oxidation of aluminum are discussed.

### 2 EXPERIMENTAL METHODS AND RESULTS

Cu-Al alloy powder and oxidizer CuO and  $\text{Cu}_2\text{O}$  powder are heated at 900 °C to take oxidation and reduction reaction so that aluminum is oxidized to get in-situ  $\text{Al}_2\text{O}_3$ . The process flow to fabricate the composites is as follows,

atomization Cu-Al powder	} blending →
+ oxidizer CuO or $\text{Cu}_2\text{O}$ powder	
internal oxidation → reduction →	
press-moulding → sintering	

Fig.1 is the transmission electron microscope image of  $\text{Al}_2\text{O}_3/\text{Cu}$  composites. From Fig. 1(a) it can be seen that  $\text{Al}_2\text{O}_3$  particles uniformly distribute over the copper matrix. The shape of  $\text{Al}_2\text{O}_3$  particles is spherical or elliptical<sup>[12]</sup>. Their size is usually 5 ~ 10 nm, the average distance between the particles is about 30 nm. Fig.1(b) is electron diffraction pattern corresponding to Fig.1(a). Indexed result of the diffraction spots

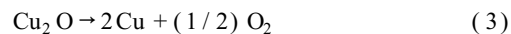
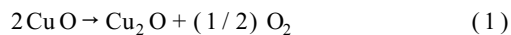
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is shown in Fig.1(c). The analysis results show that the particles in the Fig.1(a) are  $\gamma$ - $\text{Al}_2\text{O}_3$ , their crystal structure is nearly face center cubic. In Fig.1(b), the regular spots represent copper matrix and the round rings stand for the dispersive  $\text{Al}_2\text{O}_3$  particles. The X-ray diffraction pattern of the extraction powder of the composites by thick nitric acid is shown in Fig.2. Investigation shows that the extraction powder mainly consists of  $\gamma$ - $\text{Al}_2\text{O}_3$ , a little  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\theta$ - $\text{Al}_2\text{O}_3$ . The results support the results of the electron diffraction above.

### 3 THERMODYNAMICS OF ALUMINUM OXIDATION

Up to now using oxide powder as oxidizer is the most common and the best method of internal oxidation<sup>[4,5]</sup>. Generally, after Cu-Al alloy and oxidizer powder are blended, the mixture is sealed into a vacuum container. The oxidizer will

reduce to get off active oxygen to oxidize aluminum into  $\text{Al}_2\text{O}_3$  at heating. Possible chemical reactions are as follows<sup>[13]</sup>,



According to chemical thermodynamics, the free energy change of chemical reaction is

$$\Delta G = \Delta G_0 + RT \ln Q_p$$

where  $Q_p$  is the concentration product of chemical reaction. When a chemical reaction reaches to equilibrium  $\Delta G = 0$ , that is

$$\Delta G_0 = -RT \ln Q_p$$

From Eqn.(1), we can get

$$\Delta G_0 = - (1/2) RT \ln (p_{\text{O}_2} / p_{\text{O}_{20}})$$

Applying of related thermodynamic data and simplifying, above equation can be converted

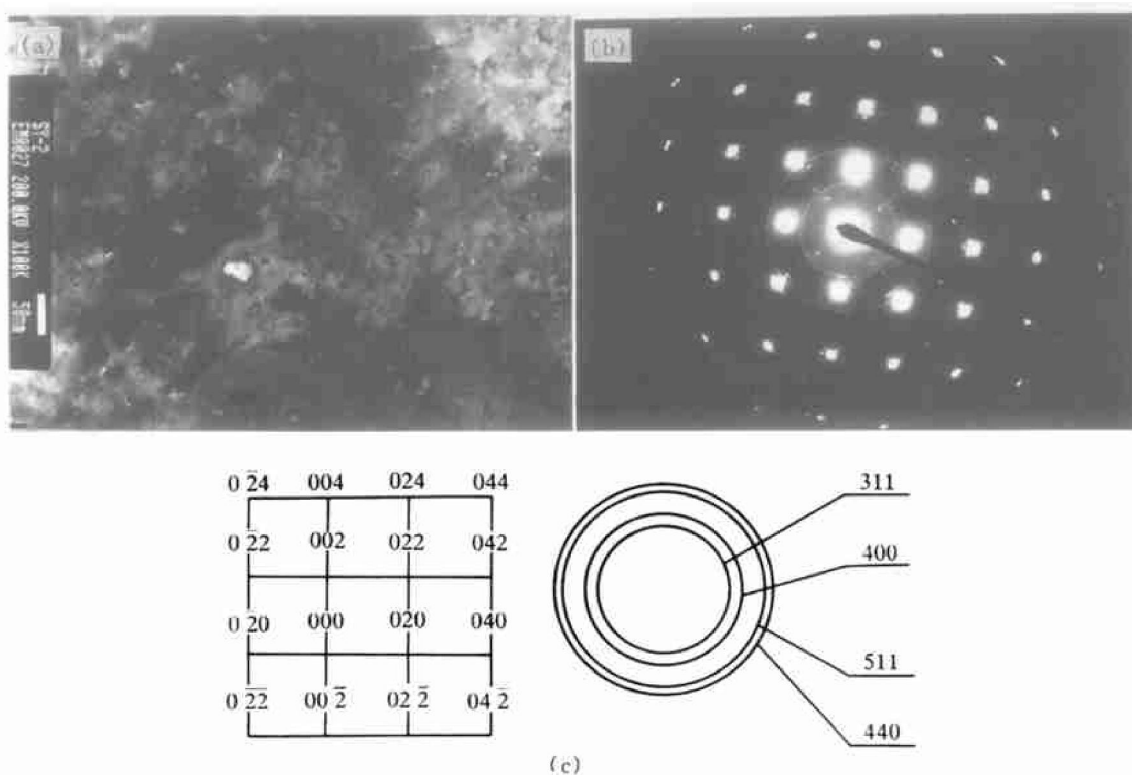


Fig.1 Structure of  $\text{Al}_2\text{O}_3/\text{Cu}$  composites

(a) — TEM image of  $\text{Al}_2\text{O}_3/\text{Cu}$  composites; (b) — Electron diffraction pattern; (c) — Diffraction index

**Fig.2** X-ray diffraction pattern of extraction powder of composites

to:

① for Eqn.(1) ( $\text{CuO} \rightleftharpoons \text{Cu}_2\text{O}$ ),

$$\lg p_{\text{O}_2} = -15254.9545 / T + 16.5372$$

② similarly, for Eqn.(2) ( $\text{CuO} \rightleftharpoons \text{Cu}$ ),

$$\lg p_{\text{O}_2} = -16435.148 / T + 14.7245$$

③ for Eqn.(3) ( $\text{Cu}_2\text{O} \rightleftharpoons \text{Cu}$ ),

$$\lg p_{\text{O}_2} = -17615.33 / T + 16.9118$$

④ for Eqn.(4) ( $\text{Al}_2\text{O}_3 \rightleftharpoons \text{Al}$ ),

$$\lg p_{\text{O}_2} = -58353.4676 / T + 15.9150$$

where the unit of oxygen partial pressure and temperature is Pa and K respectively.

Based on the four equations above an equilibrium diagram is drawn as Fig.3, which shows the equilibrium state at different condition. According to Fig.3, CuO or  $\text{Cu}_2\text{O}$  will reduce to give off active oxygen to oxidize aluminum provided the oxygen partial pressure is controlled in some range at a certain temperature. The higher the heating temperature, the higher the oxygen partial pressure at which oxidizer can reduce to oxidize aluminum. Eqns.(5) and (6) given above are possible based on the thermodynamics.

#### 4 KINETICS ON INTERNAL OXIDATION OF ALUMINUM

##### 4.1 Relation between thickness of $\text{Al}_2\text{O}_3/\text{Cu}$ layer and oxidation time

**Fig.3** Equilibrium diagram of related reaction direction

Because the diffusion coefficient of oxygen in copper is far larger than that of aluminum, the diffusion of Al atoms in copper can be neglected at forming  $\text{Al}_2\text{O}_3$ . The concentration distribution of Al, O in the matrix is shown in Fig.4. The concentration of oxygen on the interface between CuO( $\text{Cu}_2\text{O}$ ) and Cu- $\text{Al}_2\text{O}_3$  is  $C_m$ . The concentration of oxygen on the interface between

Cu-Al matrix and Cu-Al<sub>2</sub>O<sub>3</sub> is  $C_0$ . The concentration difference  $\Delta C = C_0 - C_m$  is a constant at a given temperature. According to Fick's first law, the diffusion flow of oxygen

$$\frac{dm}{dt} = -D_0 \frac{C_0 - C_m}{x} \quad (7)$$

where  $x$  is the thickness of internal oxidation layer,  $t$  is the time of internal oxidation,  $m$  is the mass of oxygen in the Cu-Al<sub>2</sub>O<sub>3</sub> layer,  $dm$  is an increment of  $m$  within  $dt$  time increment.

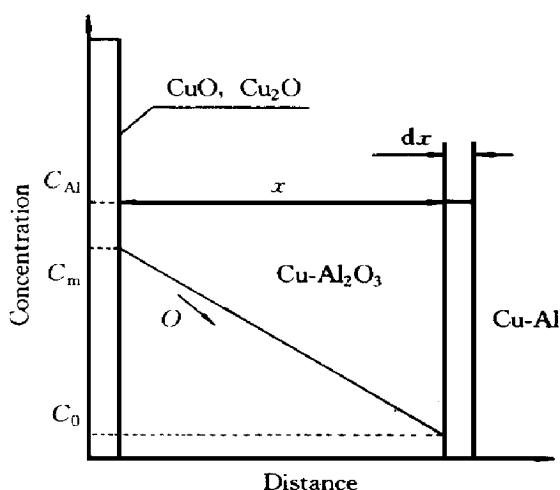


Fig. 4 Model of oxygen diffusion

Because  $dm$  is directly proportional to the increase in the thickness of the internal oxidation layer  $dx$ , that is  $dx = K dm$  ( $K$  is a constant),

$$dx = -KD_0 \frac{\Delta C}{x} dt \quad (8)$$

When Eqn.(8) is solved, we can obtain

$$x^2 = K't \quad (9)$$

where  $K'$  is the parabolic rate coefficient,  $K' = 2KD_0(C_m - C_0)$ . Fig. 5 shows the influence of internal oxidation conditions on the thickness of internal oxidation layer. It is clear that there is a parabolic rule between the time of internal oxidation and the thickness of internal oxidation layer. Therefore, the longer the time, the thicker the internal oxidation layer.

#### 4.2 Effect of internal oxidation temperature

The parabolic rate coefficient  $K'$  relate to the concentration difference  $\Delta C$ , the diffusion coefficient of oxygen in Cu-Al<sub>2</sub>O<sub>3</sub> layer and the

Fig. 5 Effect of time on thickness of internal oxidation layer

aluminum concentration  $C_{Al}$  at the interface between the Cu-Al<sub>2</sub>O<sub>3</sub> layer and Cu-Al matrix. Because the diffusion coefficient of oxygen in the matrix is much greater than that of aluminum in the matrix, the diffusion of aluminum in the matrix can be ignored.  $C_{Al}$  can be taken as a constant that equals the aluminum concentration of Cu-Al alloy. The parabolic rate coefficient  $K'$  is mainly affected by  $C_{Al}$  and the temperature which change obviously the concentration difference  $\Delta C$ , oxygen diffusion coefficient  $D_0$ . Because  $C_m \gg C_0$ , so  $C_m - C_0 \approx C_m$ ,  $K' \approx 2KD_0C_m$ .

For Cu-Al<sub>2</sub>O<sub>3</sub> alloy system<sup>[14]</sup>,

$$D_0 = 0.017 \exp(-8052/T)$$

$$C_m = 26 \exp(-15199/T)$$

$$D_0 C_m = 0.442 \exp(-23251/T) \quad (10)$$

where  $C_m$  is an oxygen concentration equilibrated with CuO or Cu<sub>2</sub>O.  $D_0$  is the diffusion coefficient of oxygen in Cu-Al alloy. So  $D_0 C_m$  value directly reflects the internal oxidation rate, cm<sup>2</sup>/s. Take logarithm for Eqn.(10), there is

$$\lg D_0 C_m = -10098/T - 0.335 \quad (11)$$

Eqn.(11) shows that  $\lg D_0 C_m$  has linear relation with  $1/T$ . Elevating the temperature is beneficial to the diffusion of oxygen and forming Al<sub>2</sub>O<sub>3</sub>.

### 4.3 Kinetics model of internal oxidation of Cu-Al alloy

According to experiments and discussion above, internal oxidation is controlled by O atom diffusion in copper matrix. Assume the Cu-Al powder is spherical, as shown in Fig.6. The radius of the sphere is  $R$ ,  $A_1$  and  $A_2$  is a part of inside and outside sphere surface separately,  $x$  is the thickness of internal oxidation layer,  $dx$  is an increment of  $x$ .  $C_m$  and  $C_0$  are the oxygen concentration on  $A_1$  and  $A_2$  respectively. The concentration of aluminum in Cu-Al alloy is  $C_{\text{Al}}$ ,  $D_0$  is the diffusion coefficient of oxygen in Cu-Al alloy. The oxygen entered into volume unit ( $A_2 dx$ ) through diffusion is

$$-D_0 \frac{C_0 - C_m}{x} A_1 dt \approx \frac{C_m D_0}{x} A_1 dt \quad (12)$$

In the volume unit the mass of aluminum is  $C_{\text{Al}} A_2 dx$ , which needs oxygen of  $1.5 C_{\text{Al}} A_2 dx$  to obtain aluminum oxide. Thus

$$\frac{C_m D_0}{x} A_1 dt = 1.5 C_{\text{Al}} A_2 dx \quad (13)$$

The radius of  $A_1$  sphere is  $R$ , that of  $A_2$  is  $R - x$ . Solving Eqn.(12) following result can be obtained

$$x^2 = \frac{8 C_m D_0}{C_{\text{Al}}} t \quad (14)$$

When internal oxidation is finished and  $x = R$

$$R^2 = \frac{8 C_m D_0}{C_{\text{Al}}} t \quad (15)$$

Substitute  $C_m$ ,  $D_0$  and  $C_{\text{Al}}$  with the experimental data, a relationship among the radius  $R$ , time  $t$  and temperature  $T$  is obtained as follows,

$$t = 0.003959 R^2 \exp(23239/T) \quad (16)$$

Eqn.(16) is the result of an ideal spherical

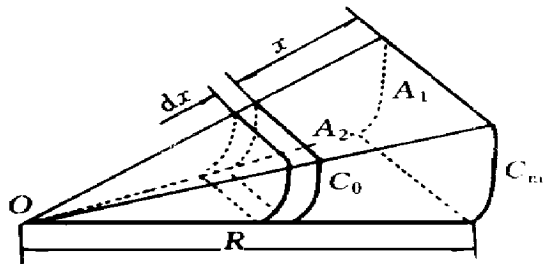


Fig.6 Kinetic model of internal oxidation

diffusion. In this case Cu-Al particles would be surrounded by the oxidizer powder, as shown in Fig.7. But it is not the case because the oxidizer powder is not small and much enough to surround Cu-Al particles. In fact, O atoms that oxidizer get off cannot be wholly absorbed by Al. Therefore, Eqn.(14) can be written as follows

$$x^2 = \frac{a C_m D_0}{C_{\text{Al}}} t \quad (17)$$

where  $a$  is a factor that is less than 8. When the internal oxidation goes to the end, the diffusion distance is  $R$ , thus

$$R^2 = \frac{a C_m D_0}{C_{\text{Al}}} t \quad (18)$$

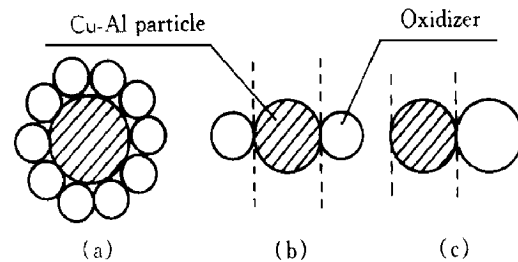


Fig.7 Cu-Al particle surrounding by oxidizer powder

Substitute  $C_m$ ,  $D_0$  and  $C_{\text{Al}}$  with the experimental data, a relationship among the radius  $R$ , time  $t$  and temperature  $T$  is obtained as following equation,

$$t_1 = b R^2 \exp(23251/T) \quad (19)$$

where  $b$  is a constant. For Cu-0.6%Al (mass fraction, %) alloy,  $C_{\text{Al}} = 0.013998$ , assuming  $R = 0.0123 \text{ cm}$  (-60 mesh). According to Eqns.(16), and (19) (taking  $b = 0.06$ ), the relation curves between internal oxidation temperature and needed time can be drawn as shown in Fig.8. Comparing these curves it is clear that sphere diffusion needs shorter time or lower temperature. The electrical resistance is measured after different oxidation time. The property will be near steady after a period of time, which shows that the internal oxidation process has been close to complete. The experimental result is also marked in the Fig.8. The predicting result has same tendency as the experimental result.

**Fig.8** Relationship between temperature and time at certain oxidation layer depth

## 5 CONCLUSIONS

(1) The reinforcement particles that internal oxidation obtains mainly  $\gamma$ - $\text{Al}_2\text{O}_3$ , a little  $\theta$ - $\text{Al}_2\text{O}_3$  and  $\alpha$ - $\text{Al}_2\text{O}_3$ . The  $\text{Al}_2\text{O}_3$  particles uniformly distribute in the copper matrix. The shape of  $\text{Al}_2\text{O}_3$  particles is spherical or elliptical. The size of them is 5 ~ 10 nm, the average distance of the particles is about 30 nm.

(2)  $\text{CuO}$  or  $\text{Cu}_2\text{O}$  will reduce to give off active oxygen to oxidize aluminum provided the oxygen partial pressure is lower than their decomposition pressure. Using  $\text{CuO}$  as oxidizer, the chemical reaction is  $3\text{CuO} + 2\text{Al} = 3\text{Cu} + \text{Al}_2\text{O}_3$ . If  $\text{Cu}_2\text{O}$  is used as oxidizer the chemical reaction is  $3\text{Cu}_2\text{O} + 2\text{Al} = 6\text{Cu} + \text{Al}_2\text{O}_3$ . According to thermodynamics,  $\text{CuO}$  is an ideal oxidizer.

(3) The formation rate of  $\text{Al}_2\text{O}_3$  is controlled by the diffusion of oxygen in  $\text{Cu-Al}_2\text{O}_3$  layer. There is a parabolic relation between the thickness of the internal oxidation layer and internal oxidation time. Elevating the temperature and prolonging the time of internal oxidation are helpful to oxygen diffusion and the formation of  $\text{Al}_2\text{O}_3$ . The theoretical predicting values with the mechanism coincide well with the experimental results.

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