Kinetic equation based on non-steady-state diffusion of oxygen in solid copper[①]

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Abstract: The kinetics of internal oxidation of dilute Cu-Al alloys, containing 0. 447 5% - 2. 214% Al (mole fraction) was investigated over the temperature range of 1 023 - 1 273 K and the depth of internal oxidation was measured by microscopy. Based on non-steady-state diffusion, a rate equation is derived to describe the kinetics of internal oxidation of plate: $X = k\sqrt{t}$, where X is the oxidation depth, t is the oxidation time. For the internal oxidation of Cu-Al alloys employed in the synthesis of alumina dispersion strengthened copper, the permeability of oxygen in solid copper is obtained from the internal oxidation measurements. Investigation shows that the depth of the internal oxidation is a parabolic function of time, the typical shape of the front of internal oxidation is of planar morphology, and there is no evidence for preferential diffusion along grain boundaries.

Key words: Cu-Al alloys; non-steady-state diffusion; internal oxidation; rate equation

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1 INTRODUCTION

Internal oxidation provides a method of dispersion hardening. Considerable efforts have been devoted to this method and encouraging results have been obtained in some systems, for example, Cu-Al, Cu-Cr, Cu-Ti, and Co-Ti alloys[1-5]. And now internal oxidation has become the most convenient method for producing oxide dispersion strengthened (ODS) copper on a commercial scale[6-11].

The internal oxidation rate equation based on quasi-steady-state assumption is often referred in the literatures[5, 12-14]. On the other hand, the non-steady-state diffusion rate equation is seldom reported. The diffusion of oxygen in solid copper during internal oxidation is considered in the non-steady-state, and the research on non-steady-state diffusion rate equation will be necessary in order to better describe the kinetics of internal oxidation.

In the present research, the non-steady-state diffusion rate equation for internal oxidation of Cu-Al alloy plate was derived. According to this equation, the permeability of oxygen in solid copper was estimated from the internal oxidation measure-ments in Cu-Al alloys.

2 EXPERIMENTAL

The Cu-Al alloys for internal oxidation were prepared by melting oxygen-free high conductivity copper (≥99. 95%) together with electrolytic aluminum (≥99. 90%) in a vacuum induction furnace. The melts were cast into ingots of 80 mm in diameter and 150 mm in length. The aluminum mole fractions (x_{Al}) of the prepared Cu-Al alloy ingots are 0. 447 5%, 0. 989 2%, 1. 695 7%, and 2. 214 0%, respectively. Then the ingots were scalped and swaged to square bar of 14 mm × 14 mm. The square bars were then annealed for homogenization at 1 173 K in argon for 10 h. The oxidation samples of 120 mm × 10 mm × 1. 5 mm were cut from the as-annealed bars. In order to standardize the surface condition, each sample was cleaned and smoothed on fine metallographic emery paper prior to the oxidizing treatment.

In order to induce internal oxidation without formation of a surface scale, the specimens were packed in a powder mixture of 30% Cu_2O, 20% Cu

and 50% Al_2O_3, and sealed in evacuated copper containers. The Cu and Cu_2O powders were served to establish the oxygen partial pressure at the dissociation pressure of Cu_2O while the Al_2O_3 was served to minimize sintering of the mixture. Each container held one specimen of each alloy. Oxidation temperatures of 1 023, 1 123, 1 223, and 1 273 K were used with at least four oxidation times being employed for each temperature.

The oxidized planar specimens were mounted and sectioned perpendicular to the broad face with at least 2 mm being removed from the length in order to eliminate end effects. After metallographic preparation, the depth of oxidation of each sample was measured at 10 points in the cross section under an optical microscope equipped with a micrometer stage. The OM and SEM micrographs were taken to the samples.

3　RESULTS AND CALCULATION

3.1　Profile of interface

Fig. 1 shows that the typical shape of internal oxidation front is of planar morphology, and there is no evidence for preferential diffusion along grain boundaries. This suggests that in the process of internal oxidation, oxygen permeates mainly in the form of volume diffusion.

3.2　Kinetic equation

Internal oxidation is a process by which oxygen diffuses into an alloy and causes sub-surface precipitation of the oxides of one or more alloying elements.

Considering a planar specimen of Cu-Al alloy in which Al is a dilute solute and forms a very stable oxide (Al_2O_3), as a simplification to internal oxidation kinetics, the following approximations have been made(Fig. 2).

(a) ($D_{Al} = 0$): the diffusion coefficient of solute Al in Cu (D_{Al}) can be neglected, which means that the counter-diffusion of solute Al is assumed to be negligible.

(b) (c_0 = constant): the oxygen is taken up rapidly from the oxidizing atmosphere, so that the surface oxygen concentration is practically equal to the solubility (c_0) of oxygen in Cu.

(c) (Sharp moving boundary): the reaction takes place only and completely at a sharp boundary plane between the internally oxidized and the remaining part of the specimen. This means in front of the advancing sharp boundary, the concentration of freely diffusing oxygen is zero, while behind it all of the solute Al in Cu-Al alloys has been converted to Al_2O_3.

Suppose the oxidation front (moving boundary) at time t is at point of $X = X(t)$.

According to Fick's second law, in the region $0 < x < X$, there is

$$\frac{\partial c}{\partial t} = D_0 \frac{\partial^2 c}{\partial x^2} \text{ (at } 0 < x < X, \text{ for all } t) \qquad (1)$$

where c is the oxygen concentration.

And $c = c_0$ (at $x = 0$ for all t) $\qquad (2)$
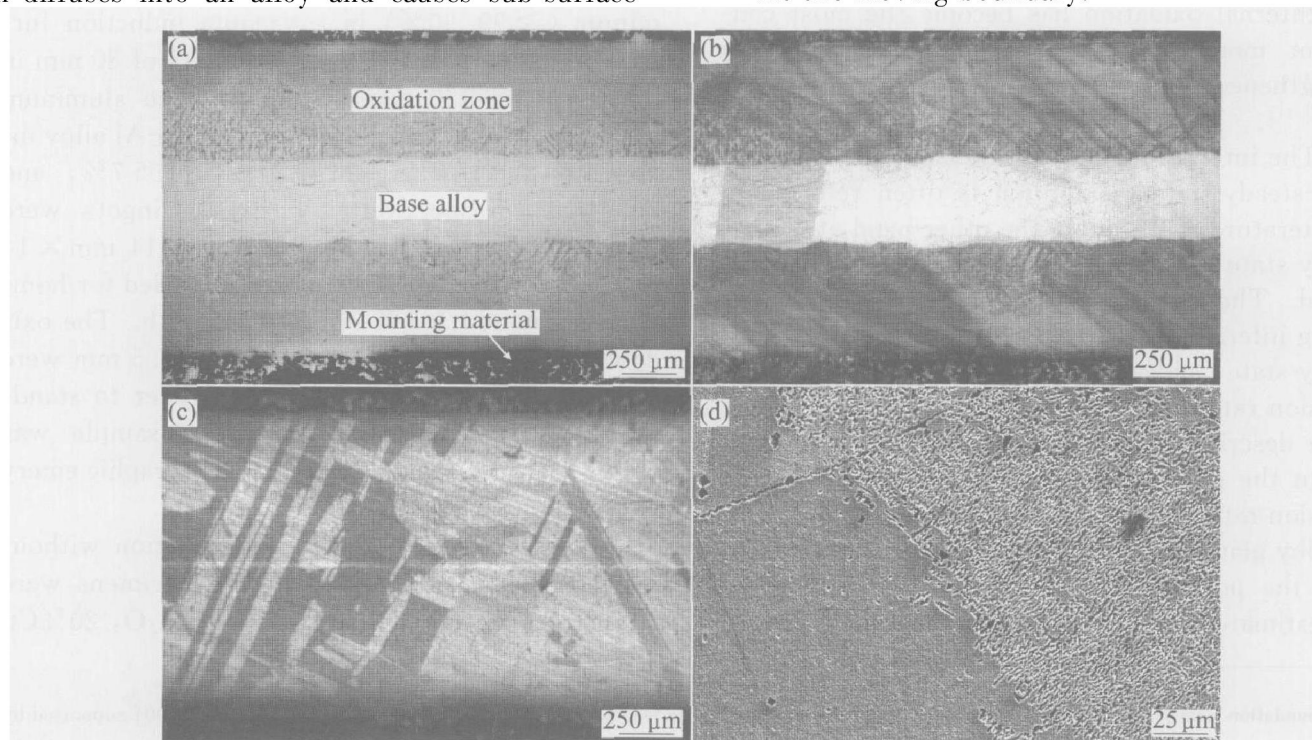
At the moving boundary:

Fig. 1　Photomicrographs of Cu-Al alloys after partial internal oxidation for 10 h at 1 273 K
(a) —OM micrograph of Cu-1.695 7% Al alloy (un-etched); (b) —OM micrograph of Cu-1.695 7% Al alloy (etched);
(c) —OM micrograph of Cu-0.989 2% Al alloy (etched); (d) —SEM micrograph Cu-2.214% Al alloy
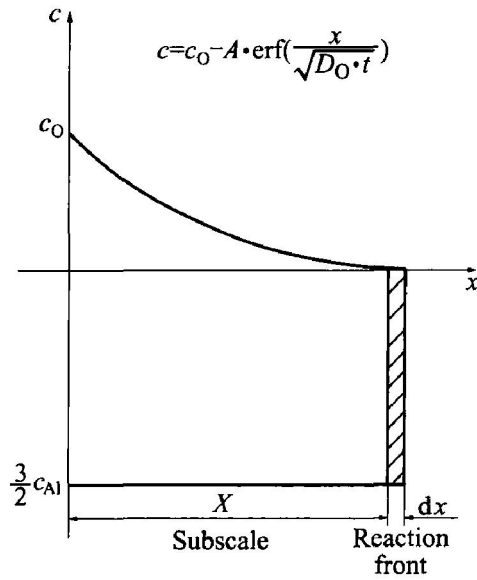
Fig. 2   Schematic concentration profiles of internal oxidation

$$c = 0 \ (x = X \text{ for all } t) \tag{3}$$

In order that the reaction front can advance a distance δX, we need to supply an amount $(3/2) c_{Al} \delta X$ of oxygen. According to Fick's first law, the amount of oxygen arriving at X in a time interval δt is $-D_0 \delta t \partial c / \partial x_{x=X}$, and conservation at boundary requires:

$$-D_0 \cdot \partial c / \partial x_{x=X} = \frac{3}{2} \cdot c_{Al} \cdot dX / dt \tag{4}$$

The solution of equation (1) satisfying equation (2) is

$$c = c_0 - A \cdot erf \left[\frac{x}{2 \sqrt{D_0 \cdot t}} \right] \tag{5}$$

where A is a constant, $erf(\cdot)$ is the error function. $erf(Z) = \frac{2}{\sqrt{\pi}} \cdot \int_0^z \exp(-\eta^2) d\eta$

The constant A is determined by the condition (3), which gives

$$A \cdot erf \left[\frac{x}{2 \sqrt{D_0 \cdot t}} \right] = c_0 \tag{6}$$

Since equation (6) has to be satisfied for all values of t, $X/\sqrt{t}$ must be a constant, that is

$$k = X/\sqrt{t} \text{ or } k^2 = X^2/t \tag{7}$$

Considering boundary condition (4), we find

$$\frac{2}{\sqrt{\pi}} \cdot A \cdot \exp \left[-\frac{X^2}{4D_0 t} \right] = \frac{3}{2} \cdot c_{Al} \cdot \frac{X}{\sqrt{D_0 t}} \tag{8}$$

Substitution of equation (7) into equation (6) and equation (8) yields

$$A \cdot erf \left[\frac{k}{2 \sqrt{D_0}} \right] = c_0 \tag{9}$$

$$\frac{2}{\sqrt{\pi}} \cdot A \cdot \exp \left[-\frac{k^2}{4D_0} \right] = \frac{3}{2} \cdot c_{Al} \cdot \frac{k}{\sqrt{D_0}} \tag{10}$$

Eliminating A from equations (9) and (10), we obtain

$$\left[\frac{k}{2 \sqrt{D_0}} \right] \cdot erf \left[\frac{k}{2 \sqrt{D_0}} \right] \cdot \exp \left[\frac{k^2}{4D_0} \right] = \frac{2}{3} \cdot \frac{1}{\sqrt{\pi}} \cdot \frac{c_0}{c_{Al}} \tag{11}$$

Here the rate equation to describe the kinetics of internal oxidation is $X/\sqrt{t} = k$. The value of the constant k is determined by equation (11).

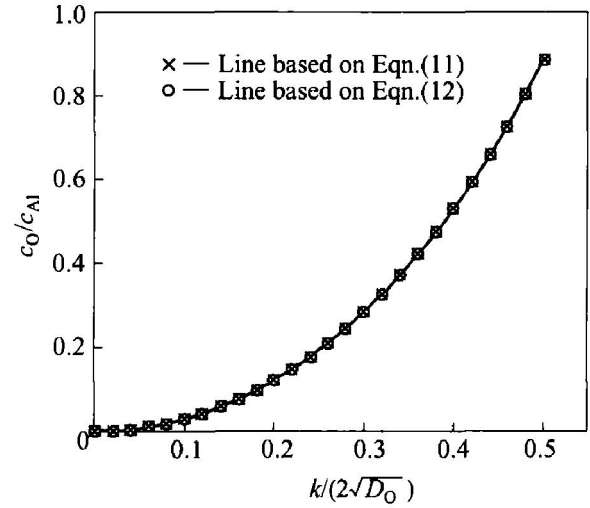The relation between the ratio c_0/c_{Al} and $k/(2 \sqrt{D_0})$ is represented in Fig. 3.

Fig. 3   Relation between c_0/c_{Al} and $k/(2 \sqrt{D_0})$

For the internal oxidation of Cu-Al alloys employed in the synthesis of alumina dispersion strengthened copper, the value of ratio c_0/c_{Al} is small (for example, at 1 323 K, $c_0 = 2.66 \times 10^{-4}$ according to Pastorek[15], when aluminum content is 0.1% (mass fraction), $c_{Al} = 2.3553 \times 10^{-3}$, then the value of ratio c_0/c_{Al} is only 0.113 161).

Considering the condition of $k/(2 \sqrt{D_0}) \leqslant 0.5$ ($c_0/c_{Al} \leqslant 0.9$), the equation (11) describing the relation between the ratio c_0/c_{Al} and $k/(2 \sqrt{D_0})$ can be substituted by (as shown in Fig. 3)

$$k^2 = \frac{4c_0 D_0}{0.629c_0 + 3c_{Al}} \tag{12}$$

By substituting equation (12) into equation (7), we obtain

$$X^2 = \frac{3c_0 D_0}{0.629c_0 + 3c_{Al}} \cdot t \tag{13}$$

3.3   Check and calculation

The measured data of internal oxidation depth are summarized in Fig. 4. It shows that the relation between oxidation depth (X) and time (t) is in good agreement with the result from equation (7). The k^2 values calculated according to equation (7) are given in Fig. 4 as a plot of square of thickness, X^2 vs time, cm^2/s.

Fig. 5 shows the variation of k^2 values (obtained from Fig. 4) with c_{Al} at different tempera-
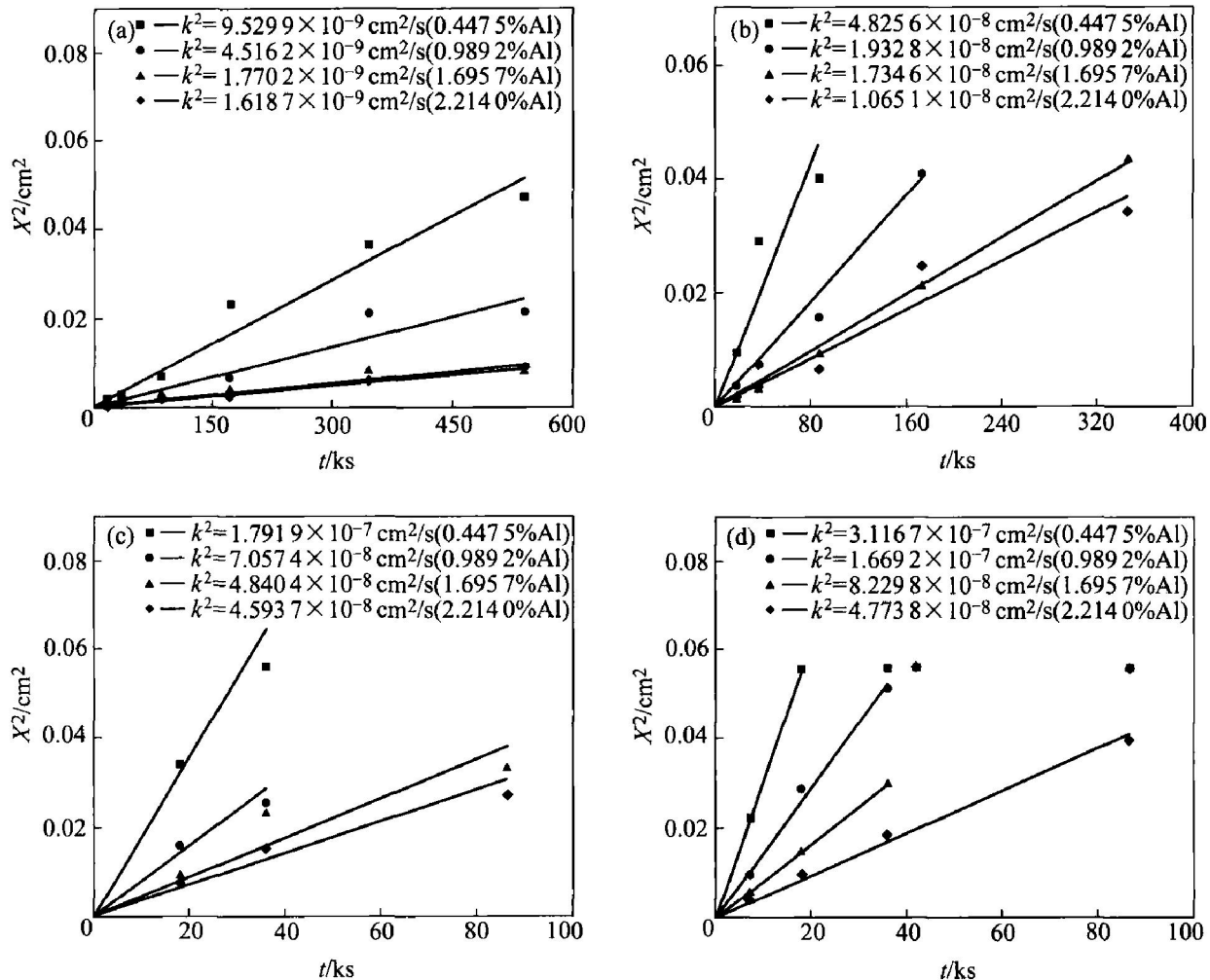
Fig. 4　Variations of oxidation depth with time at different temperatures
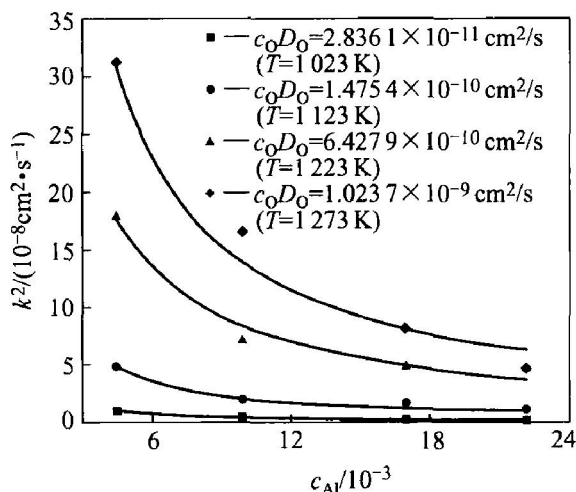(a) −1 023 K; (b) −1 123 K; (c) −1 223 K; (d) −1 273 K

Fig. 5　Variation of k^2 with c_{Al} at different temperatures

tures. By fitting the data of k^2 with equation (12), the values of $c_O D_O$ and c_O can be calculated. However, the calculated data of c_O are ineffective, and this is because the values of c_O are so sensitive to k^2 that the mini error of k^2 (or X^2 obtained from the measurements of internal oxidation) will lead to the large error of c_O. So here we can only get the effective data of $c_O D_O$, as shown in Fig. 5.

From the calculated data of $c_O D_O$ against $1/T$ shown in Fig. 6, we can get the permeability of oxygen in solid copper:

$$c_O D_O = 1.95 \times 10^{-2} \exp(-41\ 711/RT) \qquad (14)$$
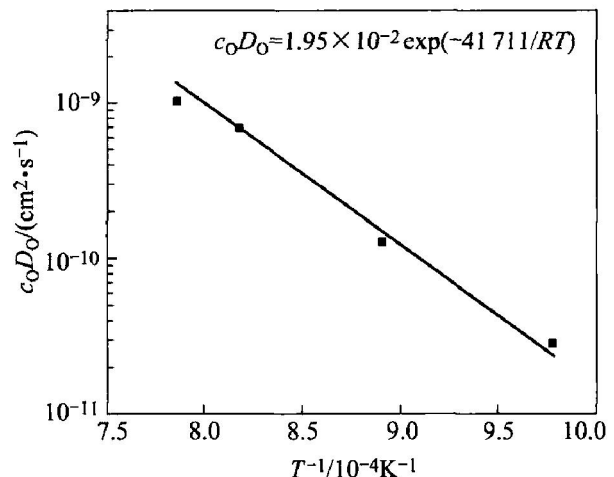
The energy Q associated with temperature de-

Fig. 6　Permeability $c_O D_O (cm^2/s)$ of oxygen in solid copper

pendence of c_0D_0 is 175. 14 kJ according to equation (14).

4 DISCUSSION

From the above study, we can see: (a) the relation between internal oxidation depth (X) and time (t) is in good agreement with the result from the derived equation (7); (b) the energy Q associated with temperature dependence of c_0D_0 calculated from the measured data and the derived equation (12) is 175. 14 kJ, which is in agreement with the value of 165. 90 kJ obtained by Meijering[16] and somewhat lower than the value of 190. 04 kJ obtained by Pastorek[15] from electrochemical measurements. This means that the derived equation based on non-steady-state diffusion of oxygen in solid copper can better describe the kinetics of internal oxidation of Cu-Al alloy plates.

With the development of synthesis technology of alumina dispersion strengthened copper, the researches on internal oxidation kinetics based on no-steady-state diffusion will be important: (a) the process of internal oxidation is diffusion controlled, and the diffusion of oxygen in solid copper is in non-steady-state; (b) these studies can provide basic knowledge for optimizing internal oxidation parameters during the synthesis of alumina dispersion strengthened copper plates, and for obtaining fine oxide particles which play a decisive role in the high temperature properties of alumina dispersion strengthened copper.

5 CONCLUSIONS

1) The kinetic equation of internal oxidation of Cu-Al alloy plate based on non-steady-sate diffusion can be described as $X/\sqrt{t}= k$. And the value of constant k is determined by

$$\frac{k}{2\sqrt{D_0}} \cdot \text{erf}\left[\frac{k}{2\sqrt{D_0}}\right] \cdot \exp\left[\frac{k^2}{4D_0}\right] = \frac{2}{3} \cdot \frac{1}{\sqrt{\pi}} \cdot \frac{c_0}{c_{Al}}$$

For the internal oxidation of Cu-Al alloys employed in the synthesis of alumina dispersion strengthened copper, the rate equation can be simplified as

$$X^2 = 4c_0D_0t/(0.629c_0 + 3c_{Al})$$

2) The permeability of oxygen in solid copper is $c_0D_0 = 1.95 \times 10^{-2}\exp(-41711/RT)$

3) The typical shape of internal oxidation front is of planar morphology, and there is no evidence for preferential diffusion along grain boundaries.

REFERENCES

[1] SONG Ke-xing, XING Jian-dong, DONG Qi-ming, et al. Internal oxidation of dilute Cu-Al alloy powders with oxidant of Cu$_2$O[J]. Materials Science and Engineering, 2004, A380: 117 − 122.

[2] Groza J R, Gibeling J C. Principle of particle section for dispersion-strengthened copper[J]. Materials Science and Engineering, 1993, A171: 115 − 125.

[3] ZHOU Guo-hong, LI Hua-lun, HU Rui. On better understanding of dispersion-separation mechanism in internal oxidation of aluminum in Cu-Al alloy[J]. Journal of Northwestern Polytechnical University, 2002, 20(2): 176 − 179. (in Chinese)

[4] LIANG Shu-hua, FANG Liang, FAN Zhi-kang. Internal oxidation of Cr in Cu-Cr/Cu$_2$O composite powder prepared by mechanical activation[J]. Materials Science and Engineering, 2004, A374: 27 − 33.

[5] Nadkarni A V. Dispersion strengthened copper properties and applications [A]. Ling E, Taubenblat P W. High Conductivity Copper and Aluminum Alloys[C]. Warrendale: Metall Soc AIME, 1984. 77 − 101.

[6] WU Jian-jun, ZHANG Yun, SHEN Yu-tian, et al. Internal oxidation of Cu-Al alloy[J]. J Mater Sci Technol, 1999, 15(5): 444 − 448.

[7] SHI Zi-yuan, YAN Mao-fang. The preparation of Al$_2$O$_3$-Cu composite by internal oxidation[J]. Applied Surface Science, 1998, 134: 103 − 106.

[8] Srivatsan T S, Narendra N, Troxell J D. Tensile deformation and fracture behavior of an oxide dispersion strengthened copper alloy[J]. Materials and Design, 2000, 21: 191 − 198.

[9] CHENG Jian-yi, WANG Ming-pu, LI Zhou, et al. Fabrication and properties of low oxygen grade Al$_2$O$_3$ dispersion strengthened copper alloy[J]. Trans Nonferrous Met Soc China, 2004, 14(1): 121 − 126.

[10] CHENG Jian-yi, WANG Min-pu, ZHONG Wei-jia, et al. Properties and microstructures of Cu-Al$_2$O$_3$ alloy produced by internal oxidation[J]. Transactions of Materials and Heat Treatment, 2003, 24(1): 23 − 27. (in Chinese)

[11] SONG Ke-xing, XING Jian-dong, TIAN Bao-hong, et al. Influence of annealing treatment on the properties and microstructures of alumina dispersion strengthened copper alloy[J]. Trans Nonferrous Met Soc China, 2005, 15(1): 1 − 6.

[12] Rhines F N, Johnson W A, Anderson W A. Rates of high-temperature oxidation of dilute copper alloys[J]. Transactions of the Metallurgical Society of AIME, 1942, 147: 205 − 221.

[13] Birks N, Meier G H. Oxidation of Metals and Alloys [M]. London: Edward Arnold Ltd, 1983. 235 − 267.

[14] Tian S G, Zhang L T, Shao H M, et al. Internal oxidation kinetics & diffusion mechanism of oxygen in Cu-Al sintered alloy[J]. Acta Metallurgica Sinica, 1996, 9(5): 387 − 390.

[15] Pastorek R L, Rapp R A. The solubility and diffusivity of oxygen in solid copper from electrochemical measurements[J]. Transactions of the Metallurgical Society of AIME, 1969, 245: 1711 − 1720.

[16] Meijering J L. Internal oxidation in alloys [A]. Herman H. Advances in Materials Research[C]. New York: Wilkey-Interscience, 1971. 1 − 81.

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