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Chemical Reaction of CuO-Al System in Preparation of Al_2O_3/Cu Composite*

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Abstract: Chemical reaction in CuO-Al pre-fabricated blocks is controlled at different temperatures. Thermal analysis curves were determined and X-ray diffraction was used to carry out phase analysis of samples after their reactions, whereby the reaction temperature for producing heat explosion and reaction products at different temperatures were obtained. The results indicate that as the medium temperature rises, three different regions of reaction in the CuO-Al system can be classified. When the temperature is less than 1 200 K, there is no chemical reaction; when the temperature is in the range 1 200～1 437 K, a partial chemical reaction takes place whose products are Cu_2O, $CuAlO_2$ and Al_2O_3; when the temperature is over 1 473 K, chemical reaction occurs in the CuO-Al system and the reaction products are Cu and Al_2O_3. It is in this latter region that thermal explosion is occurs readily.

Key words: CuO-Al system; chemical reaction; thermal explosion; thermal analysis curve

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1 Introduction

Al_2O_3/Cu composite is a kind of widely-used foreground materials with high strength and high electric-conductivity. At the same time, owing to the enhancement of the Al_2O_3 particles, this materials is characterized by such better abilities to resist wear and arc erosion[1]. At present, Al_2O_3/Cu composite has been used in microwave tubes as the structural materials and is expected to be used in many applicability including electrode heads of welding equipment, shifting switches, contact heads with silver, horizontal continuous cast crystallizers and IC lead-in wire frameworks. Nowadays the methods adopted to manufacture Al_2O_3/Cu composite are mainly powder metallurgic and internal oxidization. The authors have adopted the direct internal oxidization method in liquid Cu to produce Al_2O_3 particles in Cu matrix via shape core growth, where the shape core is characterized by thermodynamics stability, better combination of boundary faces of composites.

When CuO and Al are added to liquid Cu under certain conditions, CuO and Al can react with each other sharply to emit a huge amount of heat instantly and to make the system temperature soar. As a result, the surrounding gas expands so sharply that thermal explosion occurs[2,3]. Thermal explosions may cause the liquid to splash, leading to failure of the internal oxidation technology and may even cause damage to the equipment. This has become a key link in manufacturing Al_2O_3/Cu composite. In

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order to make the internal oxidation reaction smooth and to avoid or lessen the occurrence of thermal explosions, the process must be carefully controlled. The experimental studies on the occurrence temperature of the thermal explosion reaction as well as the reaction products have been done in the paper, whereby the theoretical bases are provided for technology of the manufacture of Al_2O_3/Cu composites.

2 Experimental Method

Raw materials used for the experiment are: CuO powder, with an average particle size of 71 μm and a purity ≥99.0%; Al powder, with an average particle size of 71 μm and a purity≥99.5%; and Cu powder, with an average particle size of 71 μm and a purity≥99.8%.

CuO, Al and Cu powders were prepared in conformity with the balance equation: $3CuO+2Al=3Cu+Al_2O_3$. The powders were mixed uniformly and then pressed into prefabricated blocks of 14 mm dia. ×25 mm at a pressure of 260～290 MPa in a universal materials testing machine. After drying and degas treatment for 2 h at 573 K, the materials were heated in air at temperatures of 1073 K, 1183 K, 1203 K, 1223 K and 1473 K respectively, and held at each temperature for 30～50 min.

The thermal analysis curves of temperature varying with time were recorded using a XWT-464 balance recording meter coupling with a temperature determining electric dipole. The sample temperature was compared with the medium temperature. If chemical reactions occur, the sample temperature will be obviously higher than the medium temperature. X-ray diffraction device of D/max-3C was used for analyzing the reaction products.

3 Experimental Results and Analysis

3.1 Determination of Thermal Analysis Curves

Fig. 1 shows thermal analysis curves in the case of heat preservation at medium temperatures of 1 073 K, 1 183 K, 1 203 K, and 1 223 K. It can be seen that curves A and B are flat and straight without convex peak. The sample temperature is finally in agreement with the temperature of heat preservation, indicating that within the temperature range of 1 073 K～1 183 K, chemical reaction in the CuO-Al system does not occur. In curve C, when the sample temperature reaches 1 200 K (near the temperature of heat preservation), and the sample is heated for 15 min, the sample temperature rises sharply, reaching 1 356 K. The small platform corresponds to the melting point of Cu. Later the sample temperature continually rises and reaches the highest point of 1 467 K. It takes 5 min for the sample temperature to rise from 1 200 K to 1 467 K. Then the sample temperature drops gradually to 1 203 K, closing and keeping in consistency with the temperature of heat preservation. The appearance of convex peak indicates that under the 1 203 K for heat preservation, the CuO-Al system has the heat to give off, whose thermal resources can only be chemical reaction itself. When the heating temperature is 1 223 K, the thermal analysis curve D is basically similar to curve C, but the

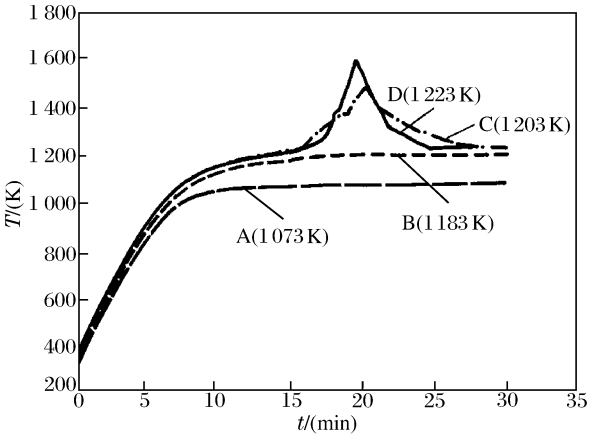


Fig. 1 Thermal analysis curves obtained at temperatures of 1 073 K, 1 183 K, 1 203 K and 1 223 K for samples internal oxidation

highest temperature reached (1 600 K) is above the highest temperature of C curve, which the time for the sample to rise from its heat preservation temperature to the highest temperature is only 4 min, less than the time of curve C. In the experimental process, a slight reaction sound can be heard, indicating that with the rising of heat preservation temperature of media, the reaction rate is accelerated so as to give off concentrated heat and the reaction is going on sharply. It has also found that when samples are put into the oven in air at 1 473 K for heat preservation, the chemical reaction takes place soon in CuO-Al system, gives off a bulk of heat within a short time and makes sample temperature rise and melt rapidly so that most of liquid sprays over the oven top and the explosion can be heard. Accordingly, the appearance of a thermal explosion will lead to failure to test the thermal analysis curves.

3.2 X-ray Diffraction Analysis

Fig. 2 shows the X-ray diffraction analysis results for the samples obtained by the internal oxidization treatment at the heat preservation temperatures of 1 073 K, 1 223 K and 1 473 K. It can be seen that under the heat preservation temperature of 1 073 K, the component phases are CuO, Al and Cu_2O, indicating that there was no chemical reaction in the CuO-Al system. The appearance of Cu_2O is due to the fact that Cu powders are oxidized into Cu_2O in air at the heat preservation temperature. Under the heat preservation temperature of 1 223 K, the component phases are Cu_2O, $CuAlO_2$ and Al_2O_3, indicating that there is chemical reaction occurred in the CuO-Al system, but the chemical reaction did not go to completion. Under the heat preservation temperature of 1 473 K, the reaction occurs rapidly with a thermal explosion. After the reaction, the sample component phases are Cu and Al_2O_3 so that the chemical reaction is complete.

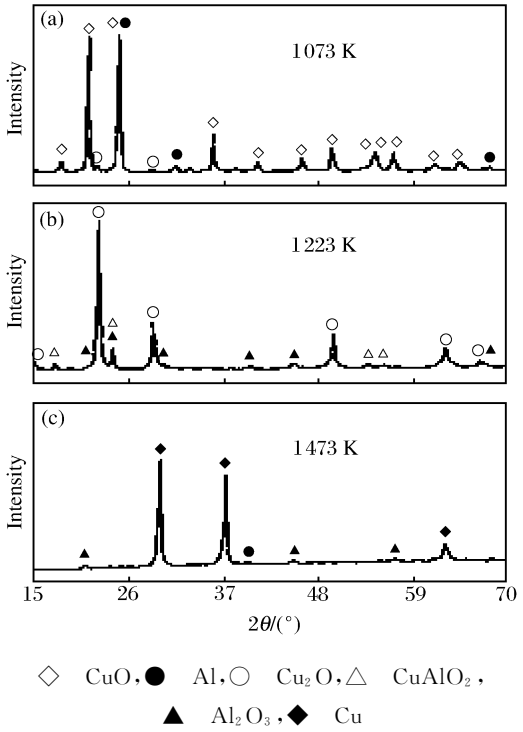


Fig. 2　XRD patterns obtained at temperatures of 1 073 K, 1 223 K and 1 473 K

To summarize, the chemical functions of the CuO-Al system can be divided into three different temperature zones: a stable zone, an incomplete reaction zone and a complete reaction zone.

The temperature range of the stable zone is roughly less than 1 200 K. There is no chemical reaction of CuO-Al system in the air media of 1 073～1 183 K. There is little possibility of using Al liquid to reduce CuO directly; this is mainly due to:

(1) In the temperature range of 1 073～1 173 K, a compacted oxidation membrane can be formed by Al liquid in the air[4], which can block the direct contact between Al liquid and CuO. The poor wettability of liquid Al and CuO isolates them from each other. Thus there is no way for the chemical reaction to proceed.

(2) There exists a decomposition reaction for CuO in the temperature range of 1 073～1 183 K[5]

$$4CuO = 2Cu_2O + O_2 \qquad (1)$$

$$\Delta G_o(1) = 272\,400 - 198.5T \quad (J \cdot mol^{-1})$$

Whether chemical reaction occurs depends on the variation of reaction free energy with temperature.

The standard free energy variation of the chemical equation (1) at 1 073 K is $\Delta G_o = 59.4$ kJ · mol^{-1} and at 1 183 K is $\Delta G_o = 37.6$ kJ · mol^{-1}. In terms of Dodge's method, when $\Delta G_o > 40$ kJ · mol^{-1}, chemical reaction will not occur spontaneously. When $\Delta G_o < -40$ kJ · mol^{-1}, chemical reaction will occur spontaneously. Thus, in the temperature range of 1 073～1 183 K, CuO can not be decomposed spontaneously so that it is in a relatively stable state. This is in agreement with the A and B thermal analysis curves in Fig. 1 as well as the results of the X-ray diffraction analysis in Fig. 2(a).

The temperature range of the incomplete reaction zone is approximately 1 200～1 437 K. It is known from the experimental results that when the system temperature is between 1 203 K and 1 223 K, chemical reaction can occur in the CuO-Al system, whose chemical reaction equation as follows[6,7]

$$12CuO + 4Al = 5Cu_2O + 2CuAlO_2 + Al_2O_3 \tag{2}$$

The chemical reaction Eq. (2) consists of the following steps

$$4CuO = 2Cu_2O + O_2$$

$$2Al + (3/2)O_2 = Al_2O_3 \tag{3}$$

$$\Delta G_{o(3)} = -1\,616\,100 + 278.1T \quad (J \cdot mol^{-1})$$

$$Cu_2O + Al_2O_3 = 2CuAlO_2 \tag{4}$$

$$\Delta G_o(4) = 22\,940 + 8.62T \quad (J \cdot mol^{-1})$$

In the entire process of chemical reaction indicated Eq. (2), whether chemical reaction indicated Eq. (3) can be carried out is great importance, and it can affect the progress degree of chemical reaction indicated Eq. (2). Whether chemical reaction Eq. (3) can be carried out depends upon the free energy variation with temperature and the formation of an oxidation membrane on the Al surface. Since $\Delta G_{o(3)}(1\,203\ K) = -1\,281.5$ kJ · mol^{-1}, the reaction can occur spontaneously with a high driving force. The literatures[8,9] point out that when the temperature surpasses 1 173 K, the solubility of the surface oxidation membrane in liquid Al increases and the oxidation membrane will be damaged, and even dissolved. Accordingly, at 1 203 K, liquid Al may fully contact CuO, giving rise to the reaction Eq. (3). Due to the high rate of the reaction Eq. (3), the decomposition rate of the chemical reaction given by Eq. (1) is accelerated. As a result of the chemical reactions Eq. (1) and (3), it is easy for the chemical reaction Eq. (4) to occur.

Research results[6,10] indicate that in the Cu-O-Al system, there exist two kinds of stable ternary oxides: $CuAl_2O_4$ (spinel) and $CuAlO_2$ (hexahedron). When the temperature is lower than 1 173 K, reaction between Cu_2O and Al_2O_3 produces $CuAl_2O_4$. Thus, when the temperature is higher than 1 173 K but lower than 1 473 K, $CuAlO_2$ can be produced. Fig. 3 is the iso-thermal cross-section in the Cu-Al-O ternary phase diagram at 1 273 K. It can be seen that at 1 273 K, Cu_2O, Al_2O_3 and $CuAlO_2$ co-exist, which is in agreement with the XRD results shown in Fig. 2.

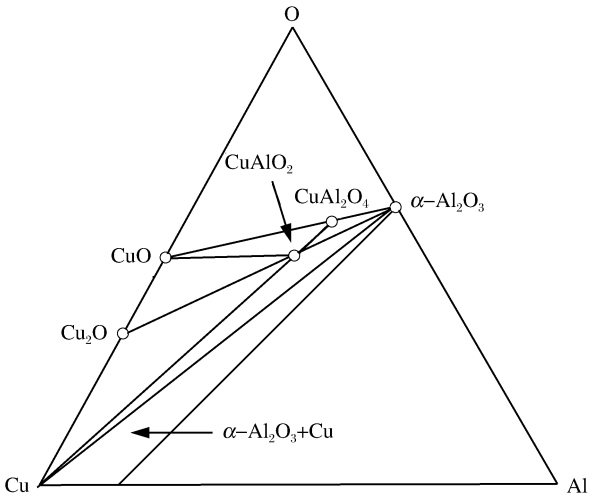


Fig. 3 Ternary Cu-O-Al phase diagram at 1 273 K

The temperature range of the complete reaction zone is roughly higher than 1 473 K. When the temperature in the system reaches 1 473 K, the oxi-

dation-reduction reaction can be carryed out normally in CuO-Al system, whose chemical reaction equation is as follows

$$3CuO + 2Al = Cu + Al_2O_3 \tag{5}$$

$$\Delta G_o(5) = -1\,230\,300 + 71.06T \quad (J \cdot mol^{-1})$$

The degree of progress of the reaction can be assessed using the dimension of the reaction balance constant K. When reaction reaching the balance, the larger the K is, the larger the percentage of reaction products will be, and the more thorough the reaction will be carried out. The balance constant K can be obtained from the following equation

$$K = \exp[-\Delta G_o/(RT)] \tag{6}$$

Where, R is the molar gas constant, $J \cdot mol^{-1} \cdot K^{-1}$.

When $T = 1\,473$ K, $K = 8.27 \times 10^{39}$ can be obtained, the value of the balance constant is rather large, whereby indicating that chemical reaction indicated Eq. (5) can be thoroughly carried out.

4 Conclusions

(1) When the medium temperature is lower than about 1 200 K, there is no chemical reaction in the CuO-Al system; which belongs to the stable zone.

(2) When the medium temperature is about between 1 200 K and 1 473 K, the reaction: $12CuO + 4Al = 5Cu_2O + Al_2O_3 + 2CuAlO_2$ takes place in the CuO-Al system. The reaction can give off the part of heat, but there is no thermal explosion; this is the incomplete chemical reaction zone.

(3) When the medium temperature is higher than about 1 473 K, the chemical reaction equation in the CuO-Al system is: $3CuO + 2Al = 3Cu + Al_2O_3$. The reaction gives out a bulk of concentrated heat with thermal explosion, this is the complete chemical reaction zone.

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制备 Al_2O_3/Cu 复合材料中 CuO-Al 体系的化学反应

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摘要: 对CuO-Al粉末预制块经不同温度下反应, 测试其温度随时间的变化曲线, 利用X射线衍射仪对其反应后的试样进行物相分析, 得出产生热爆的反应温度及不同温度下的反应产物。结果表明, CuO-Al体系反应随介质温度升高, 可分为3个不同阶段, 温度小于1200 K, 不发生化学反应; 温度为1200～1473 K时CuO-Al体系发生部分化学反应, 其产物为Cu_2O、$CuAlO_2$及Al_2O_3; 温度高于1473 K, CuO-Al体系发生化学反应, 其产物为Cu和Al_2O_3, 此阶段易出现热爆现象。

关键词: CuO-Al体系; 化学反应; 热爆; 热分析曲线
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