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THERMOANALYTICAL STUDY ON THE REACTION OF THE $CuO–Al_2O_3(\eta, \gamma$ AND $\alpha)$ SYSTEMS

TAKESHI TSUCHIDA, RYUSABURO FURUICHI, TSUNEYUKI SUKEGAWA, MASAKI FURUDATE and TADAO ISHII

Department of Applied Chemistry, Faculty of Engineering, Hokkaido University, Sapporo, 060 (Japan)

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ABSTRACT

The reaction processes proceeding in the CuO-Al_2O_3(η, γ and α) systems were investigated by means of TG, DTA and high-temperature X-ray diffraction. In the CuO–η-Al_2O_3 and CuO–γ-Al_2O_3 systems, the formation of 80% $CuAl_2O_4$ (reaction 1) occurred on heating to 1000°C. The resulting $CuAl_2O_4$ decomposed to $CuAlO_2$, Al_2O_3 and O_2 (reaction 2) in the temperature range 1130–1230°C. The incongruent melting of $CuAlO_2$ (reaction 3) occurred at about 1250°C. On the other hand, the CuO–α-Al_2O_3 system did not show the formation of $CuAl_2O_4$ on heating to 1000°C, and CuO decomposed to Cu_2O (reaction 4) at 1045°C and then the resulting Cu_2O reacted with α-Al_2O_3 to form $CuAlO_2$ (reaction 5). The difference in reaction process between the CuO–η-Al_2O_3, CuO–γ-Al_2O_3 and CuO–α-Al_2O_3 systems can be attributed to the reactivity of η-, γ- and α-Al_2O_3 in $CuAl_2O_4$ formation.

$$CuO + Al_2O_3 = CuAl_2O_4 \tag{1}$$

$$4\ CuAl_2O_4 = 4\ CuAlO_2 + 2\ Al_2O_3 + O_2 \tag{2}$$

$$2\ CuAlO_2 = Al_2O_3 + \text{liquid} \tag{3}$$

$$4\ CuO = 2\ Cu_2O + O_2 \tag{4}$$

$$Cu_2O + Al_2O_3 = 2\ CuAlO_2 \tag{5}$$

INTRODUCTION

According to the phase diagram of the copper oxide–alumina system [1–3], it is known that two aluminates, i.e., $CuAl_2O_4$ and $CuAlO_2$, form at high temperatures. $CuAl_2O_4$ has a partly inverse spinel structure ($\lambda = 0.20$ [4]), which belongs to the cubic space group (Fd3m, O_h^7 and $a = 8.08$ Å [5]) without tetragonal distortion. The structure of $CuAlO_2$ belongs to the rhombohedral system ($D_{3}^{5}d$-R$\bar{3}$m) with $a = 5.896$ Å and $\alpha = 28.1°$ [6]. Only one communication by Bessonov et al. [7] has reported the formation process of these aluminates. They investigated the reactions in the copper oxide–alumina system by using the high-temperature X-ray diffraction technique. The fundamental study on the kinetics and mechanism of the reactions in the copper oxide–alumina system is important in connection with the practical problem of the corrosion of alumina refractories in copper smelting furnaces.

The purpose of the present study is to investigate the reaction process occurring in the CuO–η-Al_2O_3, CuO–γ-Al_2O_3 and CuO–α-Al_2O_3 systems during heating to 1300°C and to discuss the reactivity of η-, γ- and α-Al_2O_3.

EXPERIMENTAL

η-Al_2O_3 and α-Al_2O_3 were prepared by calcining bayerite (β-$Al_2O_3 \cdot 3 H_2O$) at 700 and 1300°C for 3 h in air, respectively. γ-Al_2O_3 was prepared by calcining boehmite (α-$Al_2O_3 \cdot H_2O$) at 700°C for 3 h in air. The preparation techniques of bayerite and boehmite are described in a previous paper [8]. CuO was obtained by the thermal decomposition of basic cupric carbonate, $CuCO_3 \cdot Cu(OH)_2 \cdot H_2O$, at 700°C for 1 h in air. CuO and Al_2O_3 samples were sieved to obtain -300 mesh fraction and equimolar amounts of them were mixed for 1 h in an agate mortar. Pure $CuAl_2O_4$ was prepared as follows. After heating a mixture of CuO/γ–Al_2O_3 (1.1/1 mole ratio) at 1000°C for 5 h in air, unreacted CuO was removed from the product by extraction with a hot NH_4Cl–NH_4OH solution, the product was washed and dried. X-ray diffraction of the product obtained revealed the presence of well-crystallized $CuAl_2O_4$ alone. All reagents used were of GR grade and were supplied by Kanto Chemical Co.

Simultaneous TG–DTA measurements of samples (< 20 mg) were carried out using a Rigaku Denki thermoanalyzer (model 8085) at a heating (or cooling) rate of 10°C min^{-1} in air.

High-temperature X-ray diffraction of the CuO–Al_2O_3 systems was conducted with Ni-filtered Cu K_α radiation (40 kV, 20 mA) and a scanning speed of 2° min^{-1} using a Geigerflex 2013 (Rigaku Denki Co.), to which a furnace for heating the sample (type A-4, 2311) was attached. During the heating of the sample at a rate of 3.4–3.6°C min^{-1} up to 1180°C in air, the intensity of the following X-ray diffraction lines was recorded repeatedly in the range $2\theta = 34$–$40°$: CuO (111), ($\bar{1}$11); η- and γ-Al_2O_3 (311); α-Al_2O_3 (104), (110); $CuAl_2O_4$ (311); $CuAlO_2$ (102), (101); Cu_2O (111).

RESULTS AND DISCUSSION

The information about individual thermal changes of Al_2O_3, CuO and $CuAl_2O_4$ will serve in understanding the reaction process in the CuO–Al_2O_3 system. The DTA curves of η- and γ-Al_2O_3 are shown in a previous communication [9]. An exothermic peak corresponding to the transformation to α-Al_2O_3 appeared at 1277°C for η-Al_2O_3 and at 1235°C for γ-Al_2O_3.

Figure 1 shows TG and DTA curves of the heating and cooling processes for CuO in the range 800–1150°C in air. On heating, two endothermic peaks appear at 1029 and 1115°C. The peak at 1029°C is accompanied by a weight loss of 10.2 wt% in TG, which agrees approximately with that of 10.06 wt% due to the thermal decomposition of CuO

$$4\,CuO = 2\,Cu_2O + O_2 \tag{1}$$

In fact, the X-ray diffraction of the sample, which was heated to 1055°C and then cooled to room temperature, revealed the presence of Cu_2O and CuO. The formation of CuO results from the re-oxidation of Cu_2O during the cooling of the sample in air, i.e., the backward reaction of reaction (1), which will be described in detail later. The peak at 1115°C is presumed to correspond to the melting of Cu_2O, since the sample was observed to be in a molten state when heated to 1150°C. This melting resulted in a weight increase of about 1.8 wt% in TG. The weight increase in TG was also observed by Endoh et al. [10]. From the phase diagram of the RO–R_2O binary system containing a gaseous component [11], it is found that the

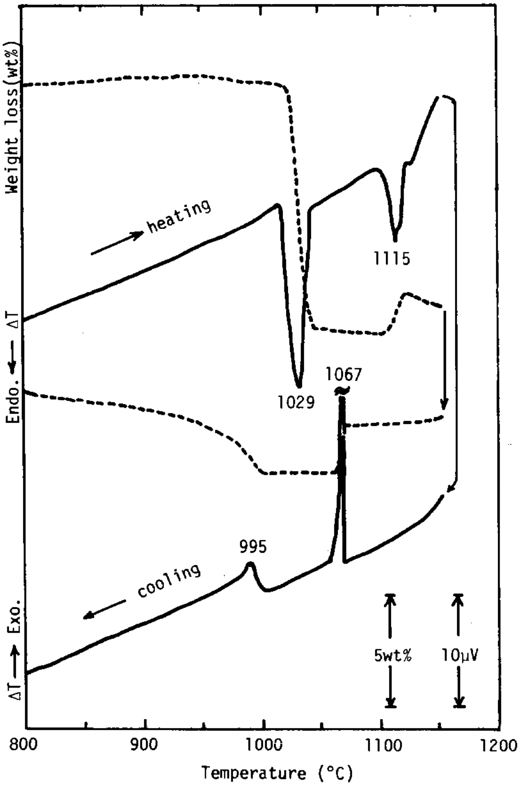

Fig. 1. TG (- - - - -) and DTA (————) heating and cooling curves of CuO.

melting of Cu_2O occurs with a pick-up of oxygen. On cooling, the DTA curve shows two exothermic peaks at 1067 and 995°C, the former is extraordinarily sharp ($\Delta T = 6°C$) and the latter is broad. The peak at 1067°C corresponds to the solidification of Cu_2O melt, since the weight loss of about 2 wt% observed in TG is approximately comparable to the release of oxygen picked up when the melting of Cu_2O occurred at 1115°C on heating. With a further decrease in temperature, a progressive increase in weight starts at 995°C or below, which will be due to the air re-oxidation of Cu_2O to CuO. The X-ray diffraction of the sample cooled to room temperature revealed the presence of Cu_2O and CuO. The intensity of the diffraction line of the sample showed that the fractional formation of CuO was much lower on cooling from 1150°C than from 1055°C where Cu_2O did not melt. Microscopic observation showed that the bulk of the sample cooled from

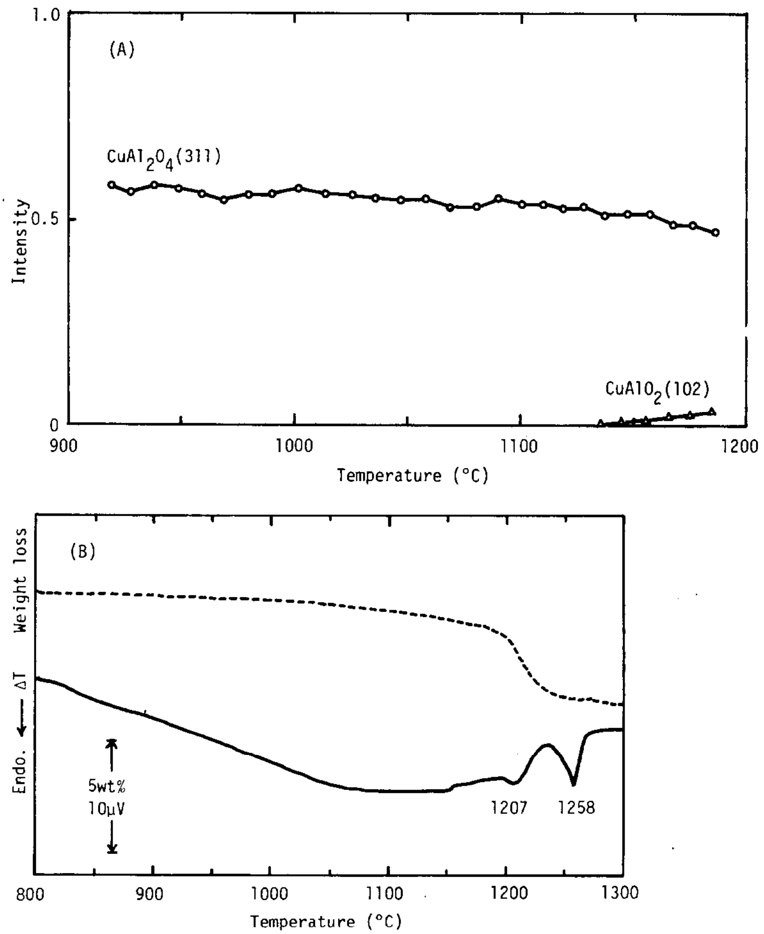

Fig. 2. High-temperature X-ray curve (A), and TG (- - - - - -) and DTA (————) curves (B) of $CuAl_2O_4$.

1150°C to room temperature was a red color, which was covered with a black product layer of CuO. Therefore, it is considered that on cooling the Cu_2O melt from 1150°C, the oxidation of Cu_2O is inhibited by an impermeable layer of CuO formed on the Cu_2O.

Figure 2 shows the high-temperature X-ray curve (A), and TG and DTA curves (B) of $CuAl_2O_4$. As can be seen from Fig. 2A, the intensity of the $CuAl_2O_4$ (311) line begins to decrease gradually at about 1100°C and the $CuAlO_2$ (102) line begins to appear at about 1140 °C, indicating the occurrence of the thermal decomposition of $CuAl_2O_4$

$$4\ CuAl_2O_4 = 4\ CuAlO_2 + 2\ Al_2O_3 + O_2 \qquad (2)$$

In the TG curve (Fig. 2B), the weight decrease occurs gradually at about 1050 °C and predominates at about 1200 °C. The weight decrease in the range 800–1300 °C was observed to be 4.2 wt%, which agrees with the theoretical weight loss of 4.41 wt% in reaction (2). On the DTA curve (Fig. 2B) two endothermic peaks appear at 1207 and 1258°C. The former will correspond to reaction (2) because of the agreement with the temperature of predominant weight loss in TG. The latter, on the contrary, shows a slight increase in weight. The temperature of 1258°C agrees approximately with 1260 [1] or 1238°C [2] which is reported for the incongruent melting of $CuAlO_2$ with a pick-up of oxygen,

$$2\ CuAlO_2 = Al_2O_3 + \text{liquid} \qquad (3)$$

Figure 3 shows the high-temperature X-ray curve (A), and TG and DTA curves (B) of the CuO–η-Al_2O_3 system. The curves below 700°C in Fig. 3A and 800°C in Fig. 3B are not shown, because no change was observed. In Fig. 3A the intensity of the CuO (111) and $(\bar{1}11)$ lines begins to decrease at about 850°C and the $CuAl_2O_4$ (311) line begins to appear. Since $CuAl_2O_4$ and η-Al_2O_3 have a spinel structure and their (311) lines overlap, it was impossible to determine precisely the initial temperature of $CuAl_2O_4$ formation. With a further rise in temperature, the intensity of the $CuAl_2O_4$ (311) line increases and reaches a maximum at 1130°C, while that of the CuO (111) and $(\bar{1}11)$ lines decreases and disappears at 1120°C. Therefore, it is found that the formation of $CuAl_2O_4$ spinel proceeds in the range 800–1130°C

$$CuO + Al_2O_3 = CuAl_2O_4 \qquad (4)$$

The further rise in temperature leads to a decrease in the intensity of the $CuAl_2O_4$ (311) line and an appearance of the $CuAlO_2$ (102) line. This behavior, as well as that in Fig. 2A, shows that the thermal decomposition of $CuAl_2O_4$ (reaction 2) occurs above 1130°C.

On the other hand, the DTA curve in Fig. 3B shows four endothermic peaks at 1040, 1108, 1221 and 1242°C. The endothermic reaction at 1040°C occurs with a weight decrease. By comparison with Fig. 1, this reaction can

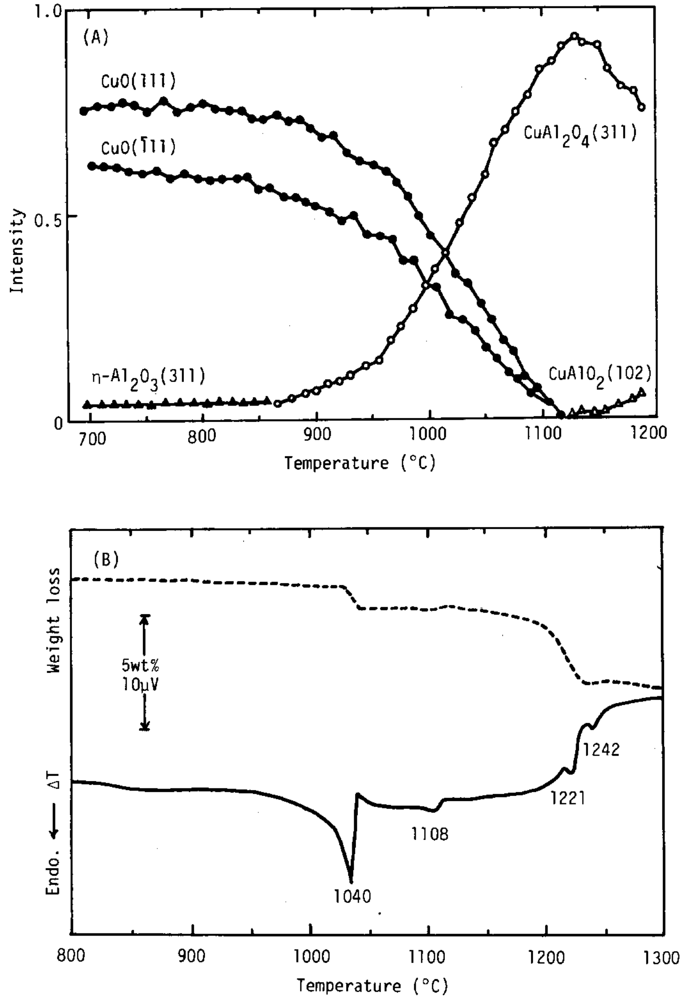

Fig. 3. High-temperature X-ray curve (A), and TG (- - - - - -) and DTA (————) curves (B) of the CuO–η-Al$_2$O$_3$ system.

be considered to correspond to the thermal decomposition (reaction 1) of unreacted CuO in reaction (4). The fractional formation of CuAl$_2$O$_4$(α) was calculated to be ca. 80% on the basis of the weight loss due to unreacted CuO in TG. The resulting Cu$_2$O melted with a small endothermic peak at 1108°C in DTA and with a small weight increase by a pick-up of oxygen in TG. This Cu$_2$O formation, however, was not detected by X-ray diffraction and CuO existed up to 1120°C (Fig. 3A). Such a discrepancy in the results obtained by TG, DTA and X-ray diffraction may be attributable to differences in measuring conditions and sensitivity of these experimental techniques. With a further rise in temperature, the weight decrease begins at about 1130°C and predominates at 1200°C. In DTA two small endothermic peaks appear at 1221 and 1242°C. This behavior in TG and DTA is similar to that of $CuAl_2O_4$ in Fig. 2B, though there are some differences in peak temperature and size. As described above, the high-temperature X-ray curve above 1130°C in Fig. 3A is also similar to that in Fig. 2A. Therefore, it is assumed from the above results that the endothermic reactions at 1221 and 1242°C correspond to reactions (2) and (3), respectively. The weight loss of 4.4 wt% was observed in the range 800–1300°C, which agreed well with that of 4.41 wt% calculated on the basis of reactions (1) or (2) in the CuO–η-Al_2O_3 system.

Figure 4 shows the high-temperature X-ray curve (A), and TG and DTA curves (B) of the CuO-γ-Al_2O_3 system. The change in intensity of each

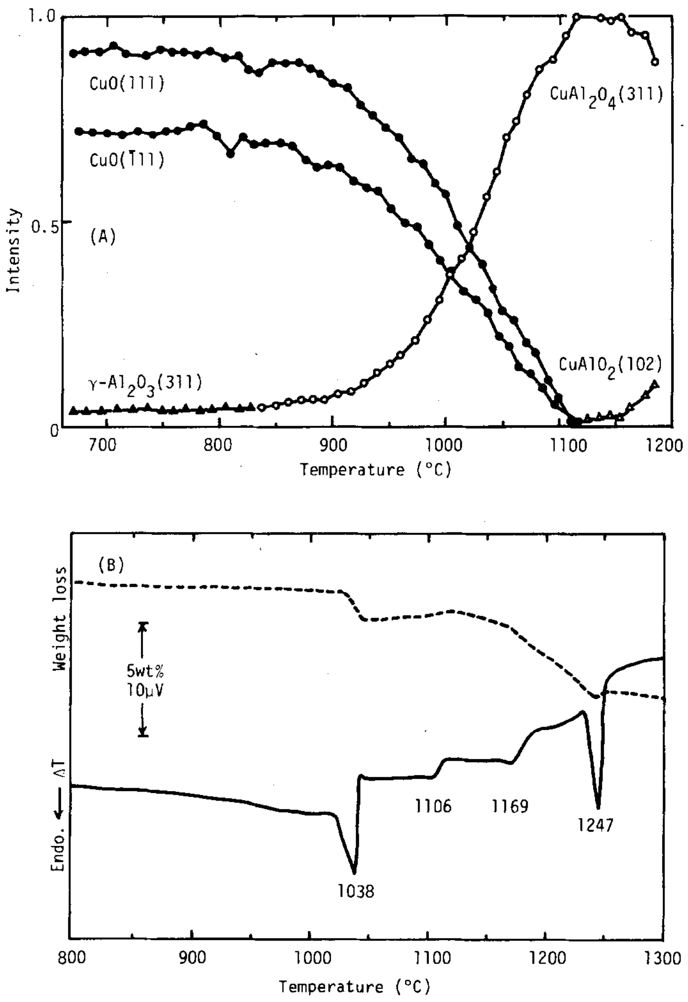

Fig. 4. High-temperature X-ray curve (A), and TG (- - - - - -) and DTA (————) curves (B) of the CuO-γ-Al_2O_3 system.

compound in Fig. 4A is very similar to that in the CuO–η-Al_2O_3 system shown in Fig. 3A. The TG and DTA curves in Fig. 4B are also similar to those in Fig. 3B, though there are differences in temperature and size of the two endothermic peaks at higher temperatures which correspond to reactions (2) and (3). Because of the similarity of the high-temperature X-ray, TG and DTA curves between Figs. 3 and 4, it can be concluded that the reaction behavior in the CuO–γ-Al_2O_3 system is similar to that in the CuO–η-Al_2O_3 system.

Figure 5 shows the high-temperature X-ray curve (A), and TG and DTA curves (B) of the CuO–α-Al_2O_3 system. The intensity of the CuO (111) and ($\bar{1}$11) lines begins to decrease steeply at 1030°C and then disappears at 1120°C, which indicates the thermal decomposition of CuO. The intensity of the α-Al_2O_3 (104) line decreases slowly above 1040 °C. On the other hand, corresponding to the decrease in intensity of CuO and α-Al_2O_3, the lines of Cu_2O (111) and $CuAlO_2$ (101), (102) begin to appear and increase in intensity. The line of Cu_2O (111) was observed to overlap with that of $CuAlO_2$ (101). The intensity of this overlapped line decreases after a maximum at 1120°C, which results from the melting of Cu_2O. Since the lines of α-Al_2O_3 (110) and $CuAlO_2$ (102) also overlap with each other, it was impossible to determine a precise beginning temperature of $CuAlO_2$ formation. From the above results, it can be considered that after reaction (1), reaction (5) occurs successively above 1000°C in the CuO–α-Al_2O_3 system,

$$Cu_2O + Al_2O_3 = 2\ CuAlO_2 \tag{5}$$

Furthermore, an unknown line was observed at 1070°C or above. X-ray diffraction of the sample cooled to room temperature after runs revealed the presence of some unknown lines at $2\theta = 37.2$, 39.7, 55.0 and 66.1°. These lines were also observed in the systems CuO–η-Al_2O_3 and CuO–γ-Al_2O_3 when heated to 1250 or 1300 °C and then cooled to room temperature.

Some experiments in the CuO–α-Al_2O_3 system were performed under the conditions of a more rapid heating rate (i.e., ca. 9°C min^{-1}) and air flow (100 ml min^{-1}). In the former case, the change in the intensity of each compound occurred at a temperature 20–30°C higher. In the latter case, the result obtained was quite similar to that in static air shown in Fig. 5A. It was found that the reaction temperatures in the CuO–α-Al_2O_3 system (Fig. 5A) disagreed with those reported by Bessonov et al. [7]; for example, they reported that CuO decomposed to Cu_2O at 800°C and $CuAlO_2$ formed at 930°C. According to the isothermal experiments in vacuum or in He flow (30 ml min^{-1}) in the CuO–η-Al_2O_3 and CuO–γ-Al_2O_3 systems (not shown in the figure), it was observed that not only $CuAl_2O_4$ but also Cu_2O and $CuAlO_2$ formed even when heated at 800°C. Therefore, it is considered that a disagreement between the present results and those of Bessonov et al. arises from the difference in the partial pressure of oxygen in a reaction atmosphere.

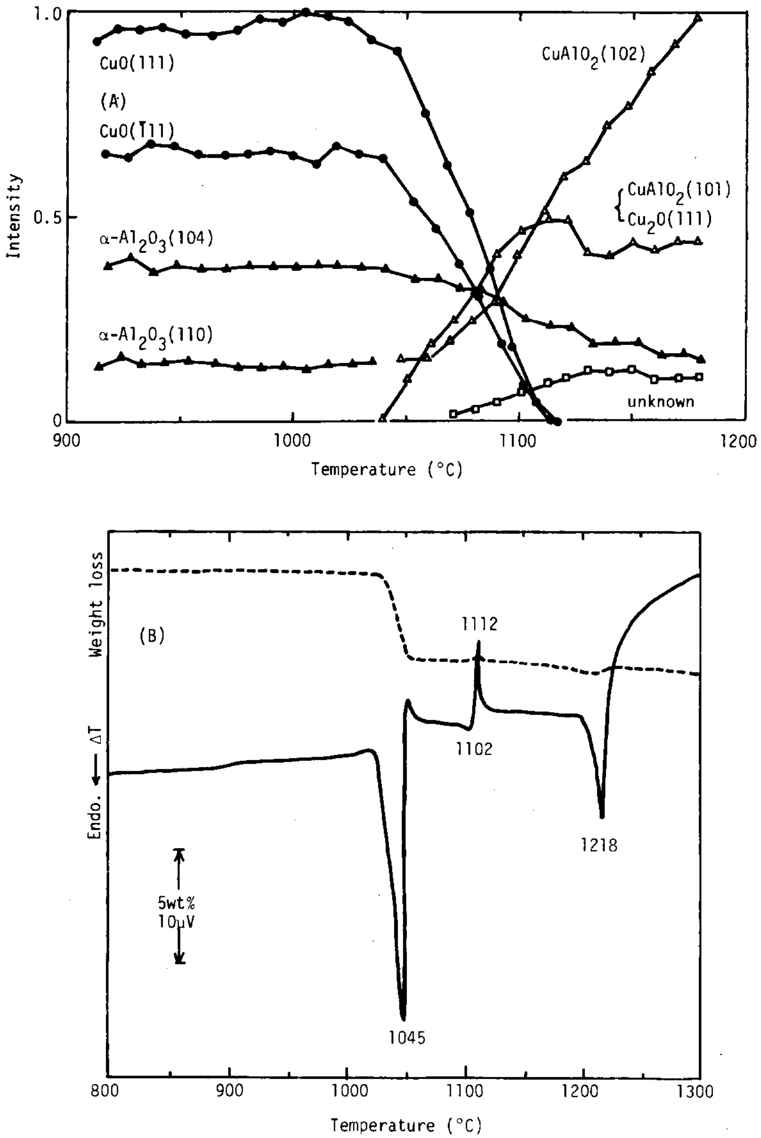

Fig. 5. High-temperature X-ray curve (A), and TG (- - - - - -) and DTA (————) curves (B) of the CuO–α-Al_2O_3 system.

In the TG and DTA curves (Fig. 5B), an endothermic peak appears at 1045°C with a weight loss, which corresponds to the decomposition of CuO to Cu_2O. A part of the resulting Cu_2O reacts immediately with α-Al_2O_3 to form $CuAlO_2$ (Fig. 5A), and the remainder melts at 1102°C with a pick-up of oxygen. Overlapping with the endothermic peak at 1102°C, a sharp exothermic peak appears at 1112°C. This exothermic peak might be attributable to some reaction in the presence of α-Al_2O_3, because it was not observed in the systems CuO–η-Al_2O_3 and CuO–γ-Al_2O_3. However, when the CuO–α-Al_2O_3 system was heated at 5°C min^{-1} this exothermic peak did not appear and only a small endothermic peak appeared at 1103°C. With a further rise in temperature, an endothermic peak appears at 1218°C, which corresponds to reaction (3), i.e., the incongruent melting of $CuAlO_2$. As can be seen from Figs. 3B–5B, η-, γ- and α-Al_2O_3 systems produce the difference in the temperature and size of an endothermic peak corresponding to the incongruent melting of $CuAlO_2$. It may depend on the reactivity of $CuAlO_2$ formed in each system or on the phase and crystallinity of Al_2O_3 present in each system which can act as nuclei when new Al_2O_3 precipitates from the melt.

From the above results, it has been found that the high-temperature X-ray curve, and TG and DTA curves differ remarkably in the CuO–η-Al_2O_3, CuO–γ-Al_2O_3 and CuO–α-Al_2O_3 systems. This difference can be explained by the fact that during heating of the CuO–η-Al_2O_3 and CuO–γ-Al_2O_3 systems to 1000°C, $CuAl_2O_4$ formed, but it did not form in the CuO–α-Al_2O_3 system. Therefore, the formation of $CuAl_2O_4$ is dependent on the difference in the reactivity of η-, γ- and α-Al_2O_3. In the case of α-Al_2O_3, during $CuAl_2O_4$ formation, the packing mode of the oxygen ions has to change from h.c.p. to f.c.c. due to its corundum structure, while this is not the case for η- and γ-Al_2O_3 because they have a spinel structure. Furthermore, it was observed in the CuO–Al_2O_3 systems that on heating the melting of Cu_2O occurred and on cooling the backward reactions of reactions (1) and (3) proceeded. Therefore, the X-ray diffraction of samples which were cooled to room temperature from the various temperatures in TG and DTA experiments did not necessarily reveal the phases that existed at high temperatures. Because the high-temperature X-ray diffraction apparatus can measure continuously the phases existing at high temperatures in situ, it is a very useful apparatus for the analysis of reaction behaviors. When combined with the results of TG and DTA experiments, more precise information about the reaction process is obtained.

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