JOURNAL OF MATERIALS SCIENCE **34** (1999) 701–706

Microstructural evolution during combustion reaction between CuO and Al induced by high energy ball milling

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The product of the combustion reaction between CuO and Al induced by high energy ball milling has been characterised by using X-ray diffractometry and scanning electron microscopy. It has been observed that the combustion reaction can be ignited very easily by the ball milling. The reaction product consists of polycrystalline Cu in bulk and particle forms and a large number of nanometer sized spherical Al_2O_3 particles attached to the surface of the Cu. It has been demonstrated that this microstructure is evolved through rapid solidification of Cu and Al_2O_3 melts and rapid condensation of Cu vapour. Cu and Al_2O_3 phases are separated in the reaction product. The reason for this is mainly attributed to the large difference in their density and the shaking force of the ball mill. © *1999 Kluwer Academic Publishers*

1. Introduction

Over the last 15 years or so, high energy ball milling has been widely utilised in three major areas: (1) alloying of two or more metals or alloys to form new alloy phases, e.g., [1–4]; (2) destabilisation of the crystal structure of intermetallic compounds or elemental substances, often leading to formation of metastable amorphous phases, e.g., [5–8]; and (3) activation of the chemical reactions between two or more substances (so called mechanochemical processing), e.g., [9–12]. The majority of previously published research utilising high energy ball milling has been focused on mechanical alloying and structural destabilisation. Mechanochemical processing has only recently started to attract many researchers' attention.

Reduction of CuO by using various metals and carbon has been studied quite extensively [9–11, 13, 14]. It has been well established that combustion reactions between CuO and metals such as Ca and Fe which are more active than Cu can be ignited by high energy ball milling of the mixture of their powders. In contrast, reduction between CuO and carbon during high energy ball milling progresses slowly and shows no sign of combustion [13]. The previous studies on mechanically activated combustion reactions were mainly focused on the understanding of the relationship between the reaction kinetics and the ball milling conditions. In contrast, the microstructural evolution during combustion reactions has often been neglected, although some authors paid brief attention to this aspect in passing [12, 15, 16]. This is rather unfortunate, as much of the information needed for understanding the reaction kinetics can be obtained by examining the microstructural evolution during the combustion reaction. The understanding of microstructural evolution is also essential if the mechanically induced combustion reaction is used in processing materials. The present study has been conducted with the aim of shedding some light in this respect.

2. Experimental procedure

The materials used in this experiment were CuO (Aldrich Chemicals, $\geq$99%, particle size $<5\ \mu$m) and Al (CERAC, 99.97%, particle size ranging 10–50 μm) powders. In each run, the total amount of powder mixture used was 12.4 g, and this includes 5% stoichiometric excess of Al. Three stainless steel balls with a diameter of 9.5 mm were used to mill the powder, giving a ball/powder mass ratio of approximately 1 : 1.2. The hardened steel vial containing the steel balls and powder was sealed in a glove box filled with high-purity argon. The ball milling was performed in a SPEX 8000 mixer/mill.

The progress of the ball milling was monitored by analysing the ball milled powders using an X-ray diffractometer after various times of milling. The X-ray diffraction analysis was performed in a Philips X-Pert system diffractometer with CuK_α radiation and a copper single crystal monochromator. The morphology and cross sections of the particles in the powders were examined by using a Hitachi S4000 Scanning Electron Microscope (SEM) operated at a voltage of 5 kV and a JEOL JSM 840F SEM operated at a voltage of 25 kV. Both of the SEMs are equipped with an energy dispersive X-ray analyser (EDX). To examine the cross section, the powders were embedded in epoxy resin

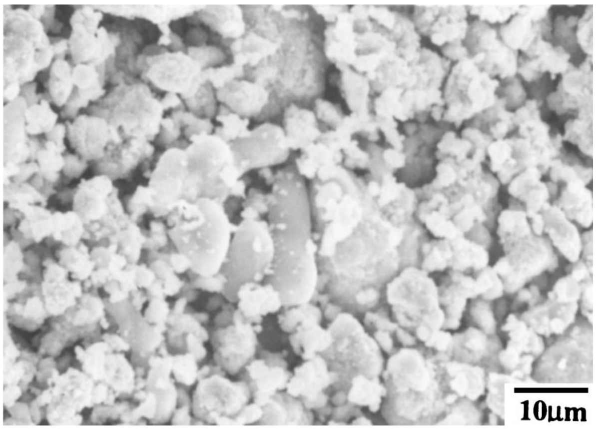

Figure 1 SEM photograph of a mixture of CuO and Al powders which is produced by simple mechanical blending.

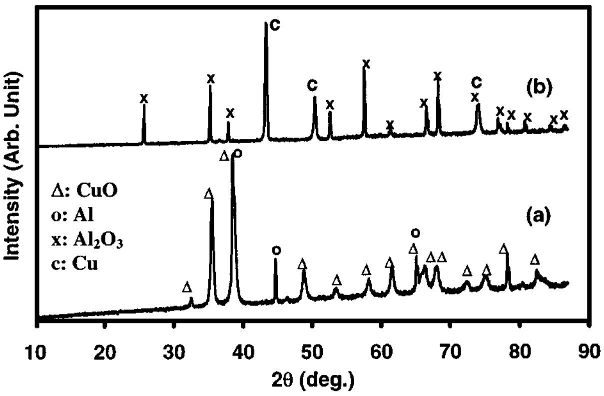

Figure 3 X-ray diffraction patterns of the powders produced after different milling times: (a) 1.5 min and (b) 2 min.

and then mechanically ground using SiC papers with a grit size ranging from 240 to 4000 and polished using 1 μm diamond paste. Some light etching of the polished surface was also performed.

3. Results

Fig. 1 shows a SEM micrograph of a mixture of Al and CuO powders which were blended by slowly rolling the vial containing the powder and balls for about 20 min. Based on the EDX analysis, it was identified that the particles with regular shape and smooth surface are Al particles, while the sponge like particles with irregular shape and rough surface are CuO particles. Fig. 2 shows the typical particle morphology in the powder which was subjected to 1.5 min of milling. As shown in Fig. 2, most of the Al particles still retain their regular shape and smooth surface, while the CuO particles are still sponge like and have a rough surface. This suggests that most of the Al and CuO particles have not experienced any heavy deformation within the 1.5 min of milling. At this initial stage of milling, no sign of the reaction between CuO and Al phases was detected by the X-ray diffraction, as shown in Fig. 3a.

It was observed that the combustion reaction occurred at a time in the range of 1.5–2 min after the milling was started. When the vial was opened after 2 min of milling, both lumpy piece with metallic copper colour and powdered product with grey colour were observed. The X-ray diffraction pattern (Fig. 3b) of the powdered product confirms that the combustion reaction between CuO and Al had occurred. Fig. 4a shows the morphology of the particles in the powdered product. The shape of the particles is either elongated or equiaxed. The surface of the particles is very rough, and shows many white spots when observed in SEM at low magnifications. When observed in SEM at high magnifications, numerous small spherical particles were seen to be attached to the rough surface, as shown in Fig. 4b. The typical EDX spectrum (Fig. 4c) from one of the spherical particles shows only the K_α peak of Al. This proves that the spherical particles are Al_2O_3, since the only major phase that contains Al is Al_2O_3. The majority of the Al_2O_3 particles have a size in the range of 0.1–1 μm in diameter, while a few large Al_2O_3 particles with a size in the range of 1–10 μm in diameter were also observed. Occasionally, nearly spherical Cu particles were also observed, as shown in Fig. 5. Some dimples are visible on the smooth surface of the Cu particles.

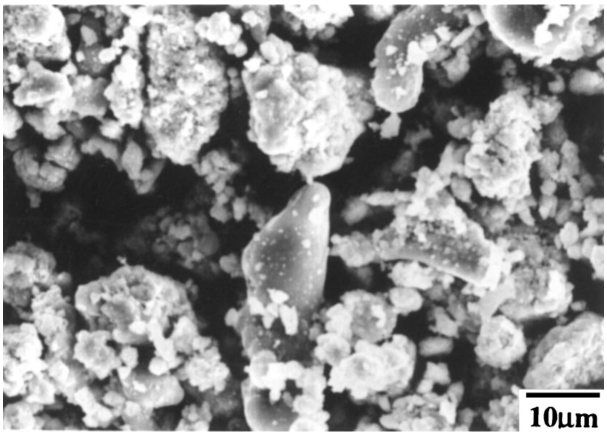

Figure 2 SEM photograph of a mixture of CuO and Al powders after being subjected to milling for 1.5 min.

The size of the lumpy piece is approximately 10–20 mm in diameter and 1–5 mm in thickness. The surface of the lumpy piece is also very rough, and when it was examined by using SEM at a high magnification, it was observed that a large number of spherical Al_2O_3 particles are attached to the surface, as shown in Fig. 6. The size of the alumina particles on the surface of the lumpy piece is in the same range as that of the alumina particles on the surface of the powdered product. To characterise the microstructure of the reaction product, the cross section of the lumpy pieces was examined by using SEM. Fig. 7a shows the typical microstructure of the lumpy pieces. As shown in Fig. 7a, the matrix is polycrystalline metallic Cu with equiaxed grains, as confirmed by EDX analysis (Fig. 7b). The average size of the grains is approximately 15 μm in diameter. A number of nearly spherical second phase particles with a size ranging from 0.2–1 μm in diameter are embedded in the Cu matrix. A typical EDX spectrum (Fig. 7c) from one of the particles show predominately Fe and Cr peaks. This shows that the second phase particles in the microstructure are Fe and Cr rich particles. Many of the second phase particles were analysed by using EDX, they are all Fe and Cr rich particles. This shows that no alumina particles are embedded in the metallic

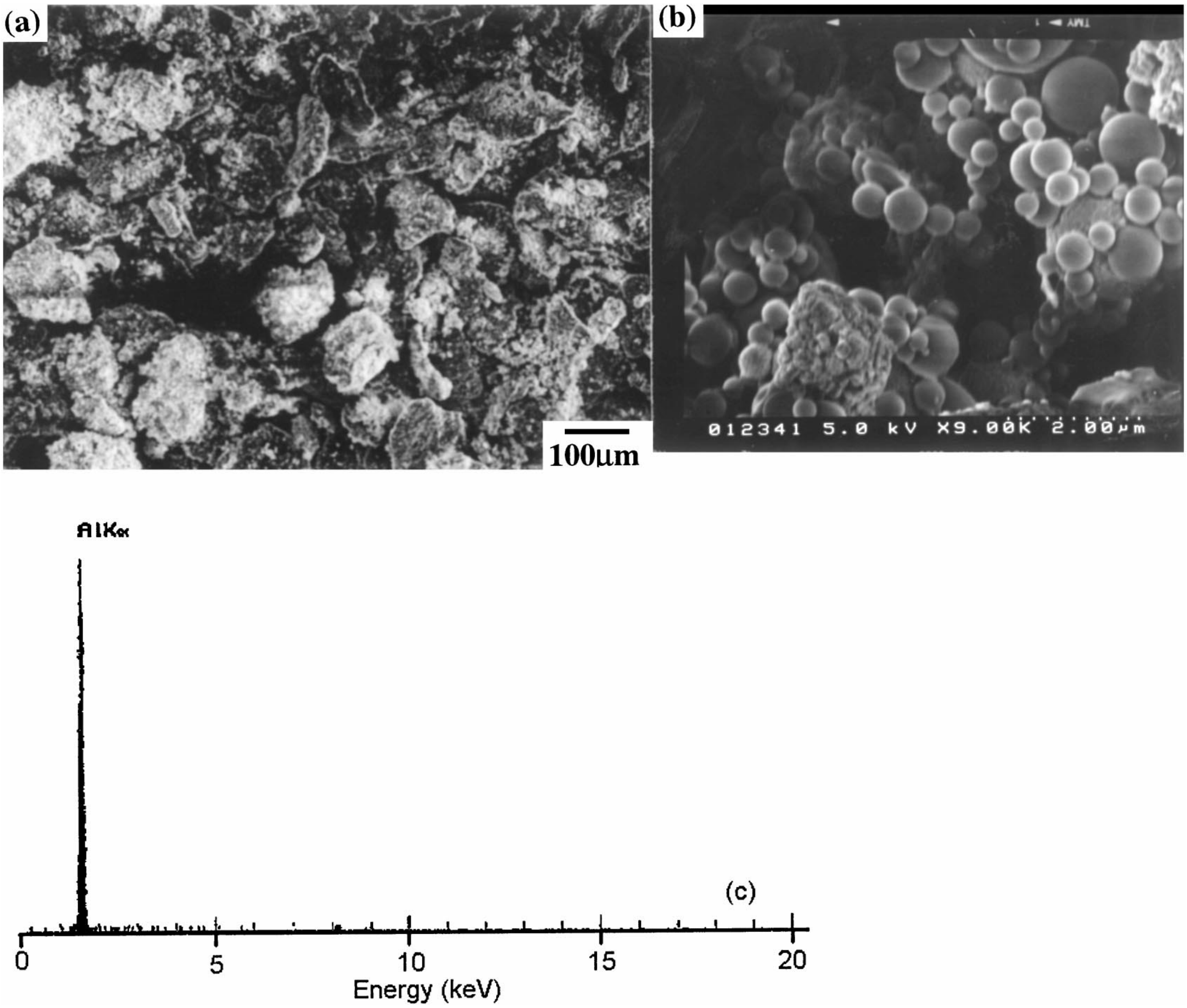

Figure 4 (a) Low magnification SEM photograph of the powdered product after the combustion reaction between CuO and Al in the ball mill; (b) high magnification SEM photograph of the powdered product; and (c) a typical EDX spectrum from one of the spherical particles as shown in (b).

Cu matrix in the lumpy piece. Chemical analysis of the lumpy piece and powdered product by using the X-ray Fluorescence technique shows that they contain approximately 1.4 wt % Fe and 0.25 wt % Cr. There is no doubt that the Fe and Cr elements come from the ball and vial materials.

4. Discussion

The present results show that the combustion reaction between CuO and Al can be very easily ignited by high energy ball milling. This is characterised by both the extremely short milling time required to activate the reaction and the fairly low ball to powder mass ratio

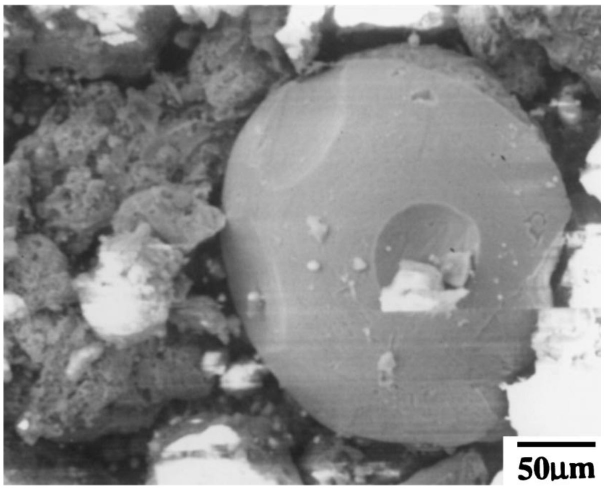

Figure 5 SEM photograph of the powdered product from the combustion reaction, showing a nearly spherical Cu particle.

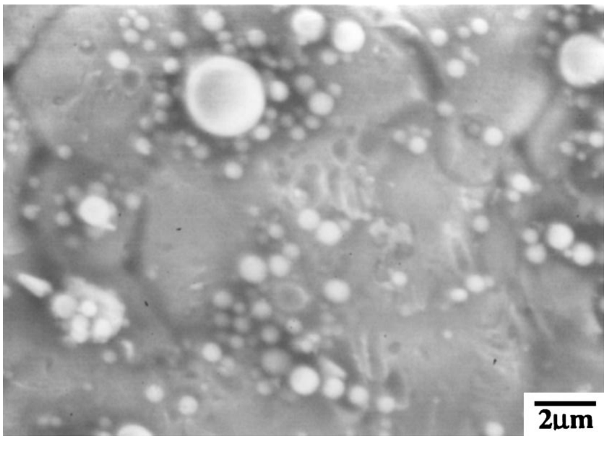

Figure 6 SEM photograph of the surface of the lumpy piece produced after the combustion reaction, showing numerous Al_2O_3 particles attached to the surface.

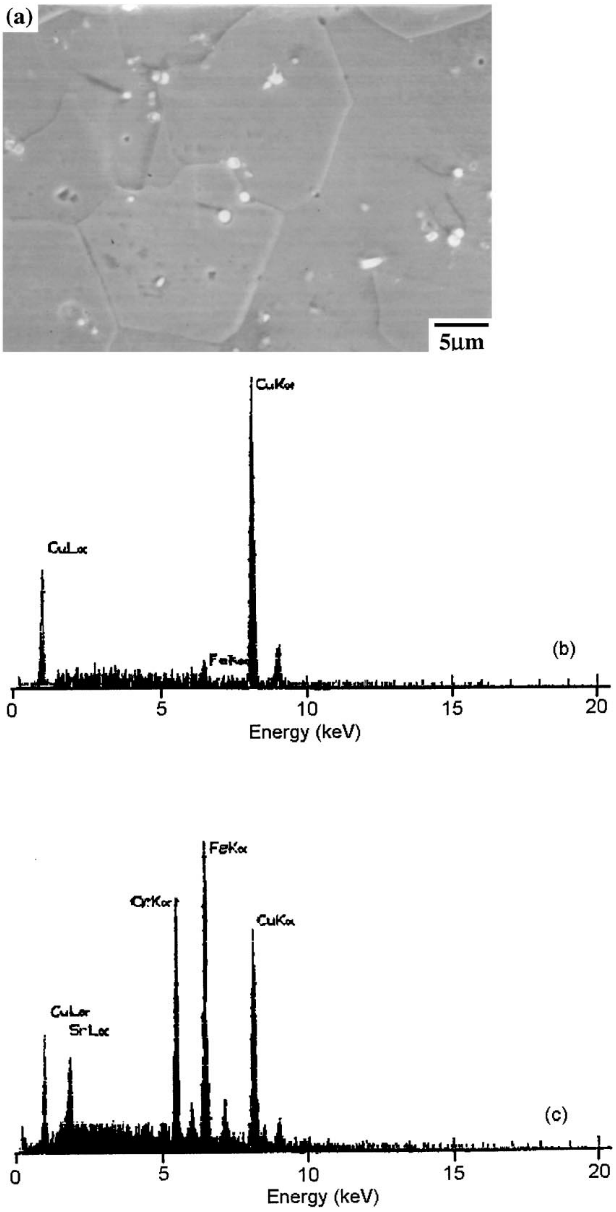

Figure 7 (a) SEM photograph of the cross section of the lumpy piece produced after the combustion reaction, showing a polycrystalline and equiaxed microstructure and second phase particles; (b) a typical EDX spectrum from the Cu matrix; and (c) a typical EDX spectrum from one of the second phase particles.

used. This observation is in clear contrast to the ignition of the combustion reaction between CuO and Fe which requires a much longer time (a few hours) of milling [11, 14]. The clear difference in the required milling time might be due to the difference in the amount of heat release from the reactions.

It is generally agreed that the ignition of the combustion reaction during ball milling is facilitated by the local temperature increase at the collision points between the balls and between the balls and the wall of the vial. Due to the temperature increase, the local temperature at the collision points can be sufficiently high to ignite the combustion reaction. Our study [17] has shown that with simple blending of the CuO and Al powders the ignition temperature of the combustion is approximately 810 K, and that milling of the powder mixture for 1.5 min reduces the ignition temperature only slightly to approximately 800 K. This means that to ignite the combustion reaction, the local temperature at collision points has to be at least 800 K. Various studies [3, 4, 18] on ball milling using the SPEX Mixer/Mill have indicated that the temperature increase caused by the mechanical impacts of the collision is in the range of 50–350 K. Considering that the ambient temperature inside the vial is about 350 K, the maximum local temperature purely due to mechanical impact is very unlikely to be over 700 K. If the ignition temperature can be reduced to below 700 K by the ball milling as in the case of reaction between CuO and Fe [14], the combustion can be sufficiently ignited by the purely mechanical impacts. However, for the reaction between CuO and Al, this is unlikely to be the case for two reasons. The first reason is that the milling time prior to the combustion is too short to achieve the composite particle structure which is essential to reduce the ignition temperature substantially. Fig. 2 provides clear evidence for this. The second reason is that the actual measurement of ignition temperature shows that the short milling time reduces the ignition temperature only slightly. Therefore, there must be a second factor which contributes to the local temperature increase. This second factor is possibly low temperature reaction between CuO and Al. It is a well established fact that high energy ball milling can facilitate low temperature reactions. If it is assumed that the reaction temperature is 400 K, thermodynamic calculation shows that reaction between one mole of CuO and Al will release approximately 403 kJ of heat, while reaction between one mole of CuO and Fe will release approximately 124 kJ of heat. That is the former is more than three times the latter. With high intensity of heat release, the limited scale reaction between CuO and Al at the collision points could contribute substantially to the local temperature increase, and thus bring the local temperature up to more than 800 K. The 1.5–2.0 min incubation milling time is likely to be the time required to accumulate the statistical probability of achieving the right collision configuration for both the mechanical impact and the low temperature reaction, as suggested by Yang and McCormick [15]. On the other hand, since the magnitude of heat release from the reaction between CuO and Fe is much smaller, the contribution it makes to the local temperature increase would also be much smaller. This may account for the difference in milling times required to ignite the combustion reactions.

It appears that the large amount of heat released from the combustion reaction causes Cu and Al_2O_3 to melt and even evaporate. The melting and evaporation of Cu and Al_2O_3 are followed by their rapid solidification and condensation due to the low ambient temperature. The spherical Cu and Al_2O_3 particles with smooth surfaces are clear signs of the rapid solidification. The dimples on the surface of Cu particles which are caused by solidification shrinkage also indicate that the particles are formed from solidification of Cu liquid droplets.

Since the combustion reaction progresses at a high speed, it can be assumed that the combustion reaction occurs under an adiabatic condition. Under this condition, the maximum temperature, T_{ad}, can be estimated by using the following equation:

$$-\Delta H_r = (X_1 C_{p1} + X_2 C_{p2})(T_{\mathrm{ad}} - T_i) + X_1 \Delta H_{m1} + X_2 \Delta H_{m2} + X_2 \Delta H_{t2} \quad (1)$$

where ΔH_r is the heat released by the reaction between one mole of CuO and 2/3 mole of Al which can be described as $\mathrm{CuO} + \frac{2}{3}\mathrm{Al} \rightarrow \mathrm{Cu} + \frac{1}{3}\mathrm{Al_2O_3}$, ΔH_{m1} and ΔH_{m2} are enthalpy of melting of Cu and Al_2O_3 respectively, C_{p1} and C_{p2} are specific heat of Cu and Al_2O_3 respectively, $X_1 = 1$ and $X_2 = 1/3$ are the number of moles of Cu and Al_2O_3 in the reaction product respectively, and ΔH_{t2} is the enthalpy of crystal structure transition of Al_2O_3 from γ form to α form. T_i is the ignition temperature which can be taken as 800 K [17]. Assuming the reaction temperature to be 800 K, based on the thermodynamic data of all the substances involved [19], ΔH_r was calculated to be -405 kJ/mol. Taking $\Delta H_{m1} = 13.04$ kJ/mol, $\Delta H_{m2} = 108.68$ kJ/mol, $\Delta H_{t2} = 21.9$ kJ/mol, $C_{p1} = 31.35$ J/mol K and $C_{p2} = 131.67$ J/mol K [19], T_{ab} was calculated to be 5431 K. Since this temperature is well above the melting points of Cu and Al_2O_3, it is certain that complete melting of Cu and Al_2O_3 has occurred during the combustion reaction. This is in very good agreement with the observation of the spherical Cu and Al_2O_3 particles.

In the above calculation of the maximum temperature T_{ad}, the enthalpy of evaporation of Cu and Al_2O_3 is not considered. However, since T_{ad} is well above the boiling point of Cu, it is very likely that part or all of the Cu phase evaporates as a result of the heat release. The heat taken by evaporation of Cu is quite substantial, being approximately 303 kJ/mol [19], hence it is possible that the maximum temperature is limited to the boiling point of Cu, T_{b1}, which is 2846 K [19]. Assuming that this is true and that the copper phase is only partially evaporated, the fraction of Cu to be evaporated can be calculated by using the following equation:

$$-\Delta H_r = (X_1 C_{p1} + X_2 C_{p2})(T_{b1} - T_i) + X_1 \Delta H_{m1} + X_2 \Delta H_{m2} + X_2 \Delta H_{t2} + X_3 \Delta H_{v1} \quad (2)$$

where X_3 is the number of moles of Cu to be evaporated by the heat, and ΔH_{v1} is the enthalpy of evaporation of Cu. Taking $\Delta H_{v1} = 303.47$ kJ/mol, X_3 was calculated to be approximately 0.64 mol. Since $X_3 < 1$, it is true that Cu is only partially evaporated. Therefore, the maximum possible temperature caused by the combustion reaction is 2846 K. It should be pointed out that in the paper by Schaffer and McCormick [10], T_{ad} was estimated to be 5151 K for the combustion reaction between CuO and Al, much higher than our estimate. This large discrepancy may be caused by whether evaporation of Cu is considered.

Based on the observation and calculation, it is envisaged that the microstructure of the product of the combustion reaction between CuO and Al is evolved through rapid condensation of Cu vapour and rapid solidification of Cu and Al_2O_3 liquid. It is interesting to note that Al_2O_3 particles and Cu phase are clearly separated in the final microstructure. This can be partly attributed to the fact that the density of Cu is more than twice of that of Al_2O_3. It is also likely that the liquid phases of Cu and Al_2O_3 are immiscible. For these reasons, the shaking force in the ball mill could cause the Cu liquid droplets to be deposited onto the wall of the vial well before Al_2O_3 particles. Similar to this observation, Lai *et al.* [20] have also observed that the Al_2O_3 particles and Cu phase formed by CuO/Al combustion reaction are separated by a centrifugal force. The second possible reason which could contribute to the phase separation is that the Cu/Al_2O_3 interfacial energy might be such that the Al_2O_3 particles are pushed to the front of the solid phase during solidification of the Cu liquid.

5. Conclusions

The combustion reaction between CuO and Al can be easily ignited within a very short time (a few minutes) of high energy ball milling with a fairly low ball to powder charge ratio. The reaction product consists of polycrystalline Cu in bulk and particle forms and a large number of nanometer sized spherical Al_2O_3 particles attached to the surface of the Cu pieces. It is clear that this microstructure is evolved through rapid solidification of Cu and Al_2O_3 melts and perhaps rapid condensation of Cu vapour during and after the combustion reaction. The separation of Cu and Al_2O_3 phases in the microstructure is mainly due to the large density difference between the two phases and the shaking force of the ball mill.

Acknowledgements

The authors would like to thank Mr Yuanji Zhang and Mr Alf Harris for their assistance in the experimental work.

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Received 16 June
and accepted 8 October 1998