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# Solid-state reactions between Cu and Al during mechanical alloying and heat treatment

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**Abstract**

Solid-state reactions between Cu and Al during mechanical alloying and heat treatment of the as-milled powder with compositions of Cu–14at.%Al and Cu–35at.%Al has been studied by using scanning electron microscopy, differential scanning calorimetry and X-ray diffractometry. It was found that Cu and Al could be easily mechanically alloyed by ball milling of a mixture of Cu and Al powders, forming a Cu(Al) solid solution when the composition of the mixture was 14at.%Al; and forming $\gamma$-$Cu_9Al_4$ intermetallic compound when the composition was 35at.%Al. It was demonstrated that the same final outcome of the alloying can also be achieved through heat treating the as-milled composite powders. However, it was identified that for Cu–14at.%Al powder, the first phase formed was $\theta$-$CuAl_2$ or $\gamma$-$Cu_9Al_4$, whereas for Cu–35at.%Al, the first phase was $\theta$-$CuAl_2$. The refinement of Cu/Al composite structure through milling does not change the nucleation temperature of the first phase during heating but it significantly decreases the peak and end temperature of the nucleation and growth of the dominating phase. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Alloys; Mechanical alloying; Solid-state reaction; Phase transformation; X-ray diffraction

## 1. Introduction

The binary Al–Cu phase diagram shows several equilibrium intermediate phases, such as $\theta$-$Al_2Cu$ and $\gamma$-$Cu_9Al_4$, as well as terminal Al(Cu) and Cu(Al) solutions [1]. This means that when a Al/Cu diffusion couple is heated up to activate the solid-state reaction between Al and Cu, there are several possibilities in terms of the first phase formed and the sequence of phase formation. Depending on the thermodynamic, kinetic and other factors, the first phase formed could be one of the equilibrium intermediate phases or one of the solid solutions, or perhaps a metastable phase such as an amorphous phase. The diffusion couples can be established in many ways. They could be formed by preparing multilayer Al/Cu thin films, by rolling Cu and Al sheets together, by blending and compacting Al/Cu powders, or by high energy mechanical milling Al and Cu powder mixtures. Similar to multi-pass cold rolling, high energy ball milling is capable of creating a Al/Cu composite structure in each of the powder particles [2,3]. Such composite structure can be considered as a stack of numerous Al/Cu diffusion couples. Once the composite structure is established, continued milling leads to refinement of the composite structure and eventually activate solid-state reactions between Al and Cu. At this point, real sense mechanical alloying is started.

Solid-state reactions between Al and Cu are of great interest to materials scientists as Al–Cu base alloys (Al rich) and Cu–Al base alloys (Cu rich) are important engineering materials. Some research has been done to investigate solid-state reactions between Cu and Al under different conditions. Jiang et al. [4] and Liu et al. [5] studied the solid-state reactions between Cu and Al during heating of Al/Cu multilayer thin films, and they showed that $\theta$-$CuAl_2$ was the first phase to form. The temperature required to activate the reaction in thin films was 157°C. Peng et al. [6] investigated the solid-state reactions between Cu and Al in Al/Cu laminate formed by cold rolling and they found that the first phase formed was also $\theta$-$CuAl_2$. The diffusion couples in this case were bulk diffusion couples, and the temperature required to activate the reaction was 300°C. On the other hand, Lima et al. [7] have shown that $\gamma$-$Cu_9Al_4$ intermediate phase can be formed by high energy ball milling of a Cu and Al powder mixture with a normal composition of 33at.%Al for

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sufficiently long time. It was not clear whether this phase was the first phase to be formed during mechanical alloying.

This paper describes the result of an investigation into the solid-state reactions during heating of powders produced by high energy milling of Al and Cu powder mixtures with two nominal compositions: Cu–14at.%Al and Cu–35at.%Al. The purpose of this study was to demonstrate the first phase formed and temperature required to activate the reaction under different conditions, and to establish the sequence of phase formation in this system.

## 2. Experimental technique

The materials used in the experiments were Cu powder (99.5% pure; particle size, <150 μm), Al powder (99.8% pure; particle size, 50–300 μm). Cu/Al powder mixtures with a nominal composition of Cu–14at.%Al or Cu–35at.%Al were milled. To prepare for the milling, four stainless steel balls with a diameter of 12.7 mm together with 7.5 g of Cu–14at.%Al powder mixture or 5.5 g of Cu–35at.%Al powder mixture were sealed in a hardened steel vial in a glove box filled with high purity argon. The ball milling was performed using a SPEX 8000 Mixer/Mill. The milling process was interrupted from time to time to take a small amount of samples for analysis using X-ray diffractometry (XRD), differential scanning calorimetry (DSC) and microstructural examination of the powder particles. The XRD analysis was performed in a Philip's X-pert system diffractometer using Cu Kα radiation and a copper single crystal monochromator. The DSC analysis was performed in a TA Instruments 2920 Differential Scanning Calorimeter under flowing argon. The heating rate used was 20°C/min. The polished and etched cross-sections of powder particles at different stages of milling were examined by using an optical microscope and a Hitachi S400 scanning electron microscope (SEM). The SEM is also equipped with an energy dispersive X-ray spectrum analyser (EDAX).

## 3. Results

### 3.1. Cu–14at.%Al

Fig. 1 shows the XRD patterns of the powder produced at different stages of milling a Cu/Al powder mixture with a composition of Cu–14at.%Al. After 1 h of milling, the XRD pattern (Fig. 1a) shows Cu peaks and the Al {111} peak. The positions of Cu and Al peaks remained the same as those of pure Cu and Al peaks, indicating no significant reaction occurred during this initial period of milling. After 2 h of milling, the Al peak disappeared, and the positions of the Cu peaks still remained unchanged, as shown in Fig. 1b. This indicates that the amount of Al diffusing into the Cu phase is insignificant. After 4 and 8 h of milling, the position of Cu {111} peak shifted from $2\theta = 43.35°$ to $2\theta = 43.19°$ and $2\theta = 43.07°$, respectively. The final Cu peak shift corresponds to an increase of the Cu lattice parameter from 3.613 to 3.639 Å, i.e. by 0.7%. This lattice parameter increase suggests that a solid solution of Al in Cu formed as a result of mechanical alloying of Cu and Al. It was also noted that with increasing the milling time from 2 to 4 h, the Cu peaks became substantially widened. The widening of the XRD peaks was due to residual strain in the Cu-rich phase and decrease of grain size. Neglecting the contribution of straining, the average grain size of the Cu-rich phase was estimated using the half height width of Cu {111} peak and Scherrer's equation [8]. The result showed that the average grain size of the Cu-rich phase decreased slightly from 25 to 24 nm as the milling time increases from 1 to 2 h and decreased substantially from 24 to 11 nm as the milling time increased from 2 to 4 h. However, as the milling time increases from 4 to 8 h, the average grain size remained unchanged.

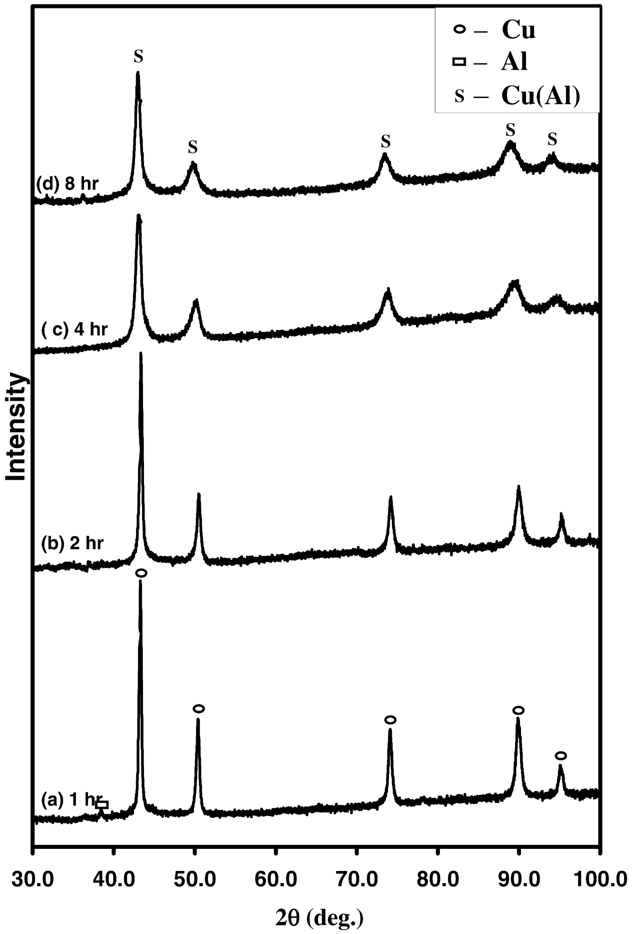

Fig. 1. XRD patterns of the powders produced after milling a Cu/Al mixture with 14at.%Al for different times.

Fig. 2a,b shows the typical microstructure of particles in the Cu–14at.%Al powder after being milled for 1 and 2 h,

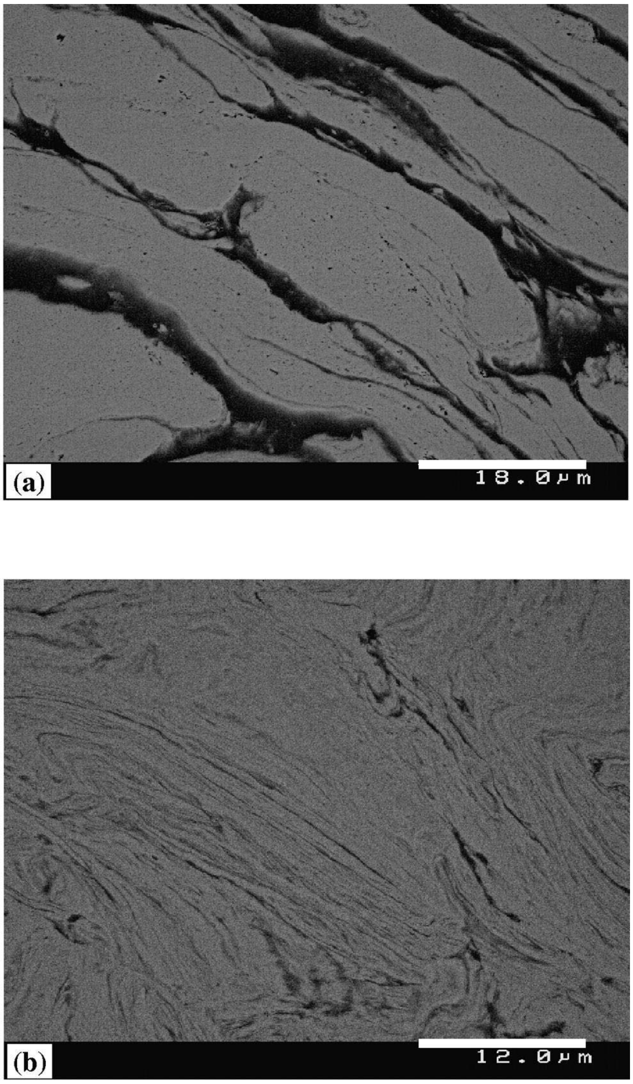

Fig. 2. SEM micrographs of the cross-sections of powder particles produced by milling Cu–14at.%Al powder mixture for (a) 1 h and (b) 2 h.

respectively. It was proved by EDAX analysis that the dark phase is Al and the light phase is Cu. After 1 h of milling, an irregular multilayer structure consists of alternating Al and Cu layers was formed in each powder particle as shown in Fig. 2a. The thickness of Al layer ranges from 0.5 to 5 μm. A few thicker elongated pieces of Al phase with a thickness ranging from 10 to 20 μm were also observed. While, after 2 h of milling, Cu and Al phases were well mixed and the multilayer structure was more clearly defined, as shown in Fig. 2b. The Al-rich phase was still present in the microstructure even though the XRD pattern did not show any Al peaks. The thickness of Al layers ranges from 0.05 to 0.2 μm. After 4 h of milling, the microstructure became much finer and could not be resolved using SEM.

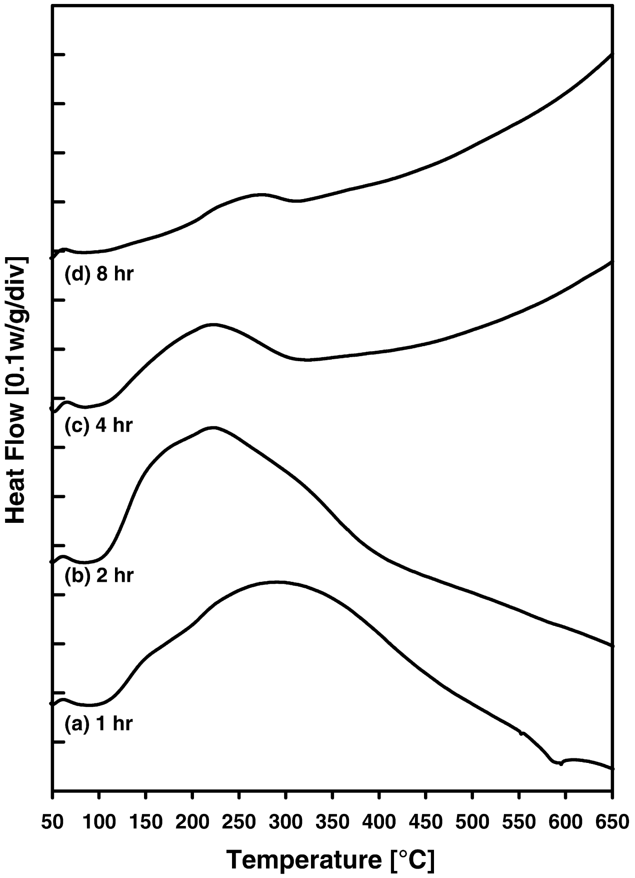

Fig. 3. DSC traces of the powders produced after milling a Cu/Al mixture with 14at.%Al for different times.

Fig. 3 shows DSC traces of Cu–14at.%Al powders produced after milling for different times. As shown in Fig. 3a, the DSC trace of 1-h milled powder exhibited two overlapping exothermic peaks and an endothermic peak at high temperatures. The first exothermic peak was rather small and its onset and peak temperatures were approximately 125 and 150°C, respectively. The second exothermic peak was very large and broad, and its onset and peak temperature were approximately 150 and 300°C, respectively. The endothermic peak was small, and its onset and peak temperatures were 550 and 580°C, respectively. It is likely that the endothermic peak was caused by melting of an Al(Cu) solution with very high Cu content [1]. This solution might be formed during heating due to inhomogeneous distribution of Al and Cu among different powder particles. After the powder was milled for 2 h, the endothermic peak disappeared from the DSC trace. The onset and peak temperatures of the first exothermic peak remained unchanged, but the area clearly increased. The onset temperature of the second exothermic peak also seemed unchanged, but the peak temperature decreased significantly from 300 to 210°C. The second exothermic peak also became sharper. After the powder was further milled to a total time of 4 h, the onset and peak temperatures of both exothermic peaks remained unchanged, but their area became substantially smaller. After 8 h of milling, the first exothermic peak disappeared, while only a small fraction of the second peak was left. In order to identify the reactions which caused the first and second exothermic peaks, the 2-h milled powder was first heated in DSC to 200°C, i.e. just above the peak temperature of the first exothermic peak but below that of the second exothermic peak, and then cooled. Fig. 4a shows the XRD pattern of this powder. It showed strong Cu peaks, weak Al {111} peak and two new peaks which were weak but clear. These two new peaks were indexed as $\gamma$-$Cu_9Al_4$ {330} peak and {600} peak, respectively. This shows that the first exothermic peak was caused by reaction between Al and Cu forming $\gamma$-$Cu_9Al_4$. The position of the Cu {111} peak in this XRD pattern was at $2\theta=43.4°$, the same as that of pure Cu. The 2-h milled powder heated to 650°C and then cooled to room temperature in DSC was also analyzed using XRD. Fig. 4b shows the XRD pattern of this powder. It showed that all the powder was converted to Cu(Al) solid solution. The position of Cu{111} peak in the XRD pattern is at $2\theta=43.07°$ which means that the lattice parameter of the fcc phase was $a=3.635$ Å, almost same as that of the solid solution produced by mechanical alloying. The heat released during heating the Cu–14at.%Al powder as a function of milling time is plotted in Fig. 5. The heat released from the 1-h milled Cu–14at.%Al powder was 8.72 kJ/mol. The amount of heat released decreases with increase of milling time, and became close to zero after 8 h milling.

### *3.2. Cu–35at.%Al*

Fig. 6 shows the XRD patterns of the powders produced at different stages of milling a Cu/Al powder mixture with a composition of 35at.%Al. After milling for 1 h, the XRD pattern (Fig. 6a) shows Cu and Al peaks. The positions of

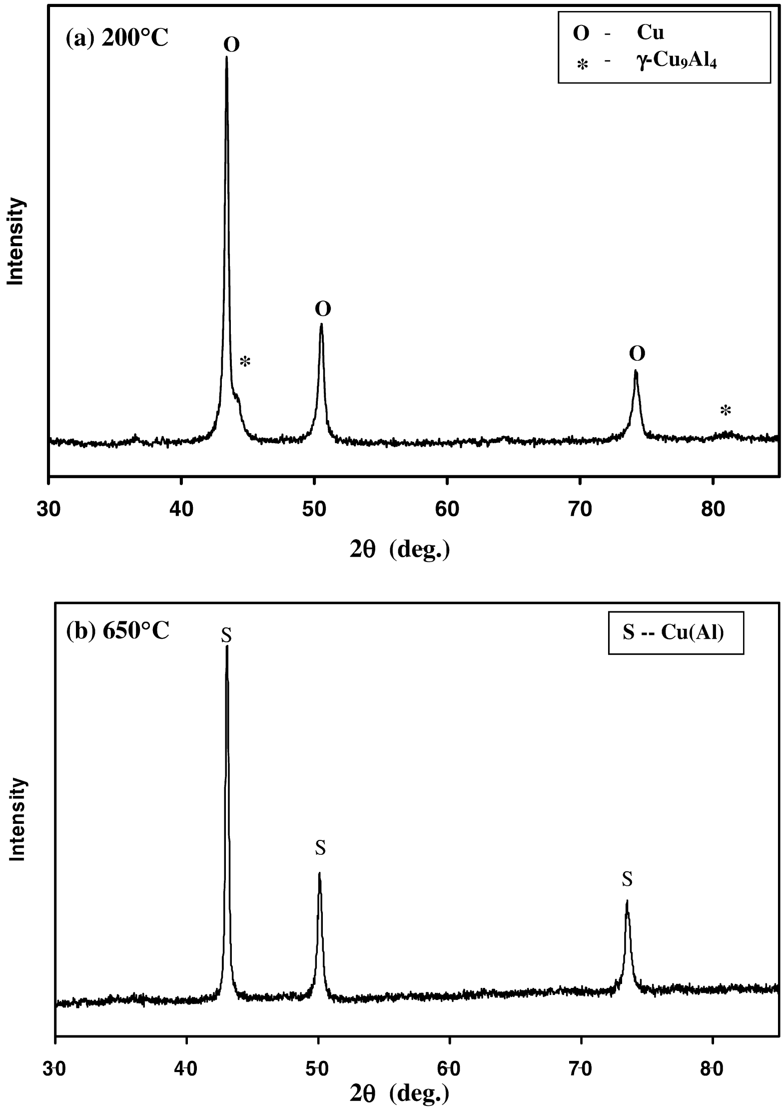

Fig. 4. XRD patterns of the powders produced after milling a Cu/Al mixture with 14at.%Al for 2 h and then heated to different temperatures and then cooled in DSC.

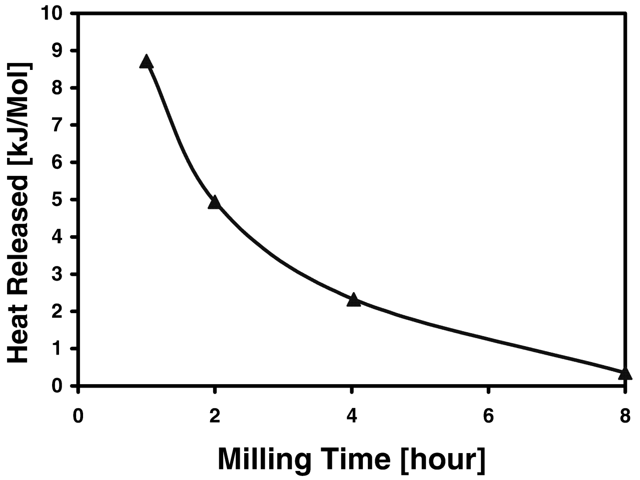

Fig. 5. The heat released during heating the milled Cu–14at.%Al powder as a function of milling time.

the Cu and Al peaks were same as those of pure Cu and Al, indicating no significant reaction occurred during milling. After 2 h of milling, the Cu and Al peaks remained in the pattern, and in the mean time, two new peaks emerged as shown in Fig. 6b. These peaks were indexed as γ-$Cu_9Al_4$ {330} and {600} peaks. After 4 h of milling, the γ-$Cu_9Al_4$ peaks dominated the pattern as shown in Fig. 6c. Although the Cu peaks still remained in the pattern, they became significantly weaker. After 8 h of milling, the XRD pattern only showed γ-$Cu_9Al_4$ peaks as shown in Fig. 6d. Using the half height width of the γ-$Cu_9Al_4$ {330} peak and Scherrer's equation [8] the average grain size of the γ-$Cu_9Al_4$ phase was estimated to be approximately 10.5 nm.

Fig. 7a,b shows the typical microstructure of particles in the Cu–35at.%Al powder after being milled for 1 and 2 h, respectively. Again, the dark phase is Al and the light phase is Cu. After 1 h of milling, an irregular multilayer structure consisting of alternating Cu and Al layers formed in each powder particle as shown in Fig. 7a. The layer

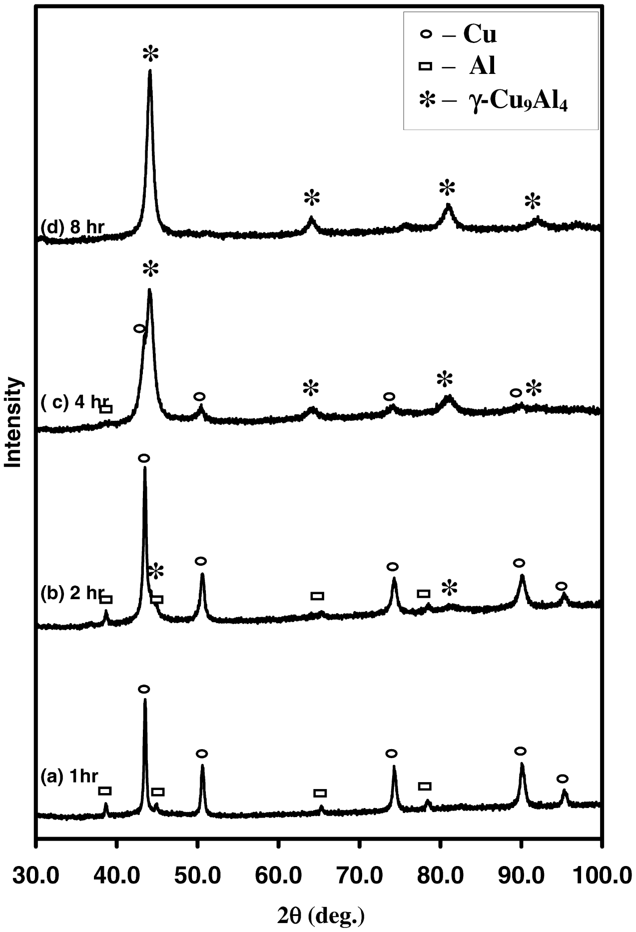

Fig. 6. XRD patterns of the powders produced after milling a Cu/Al mixture with 35at.%Al for different times.

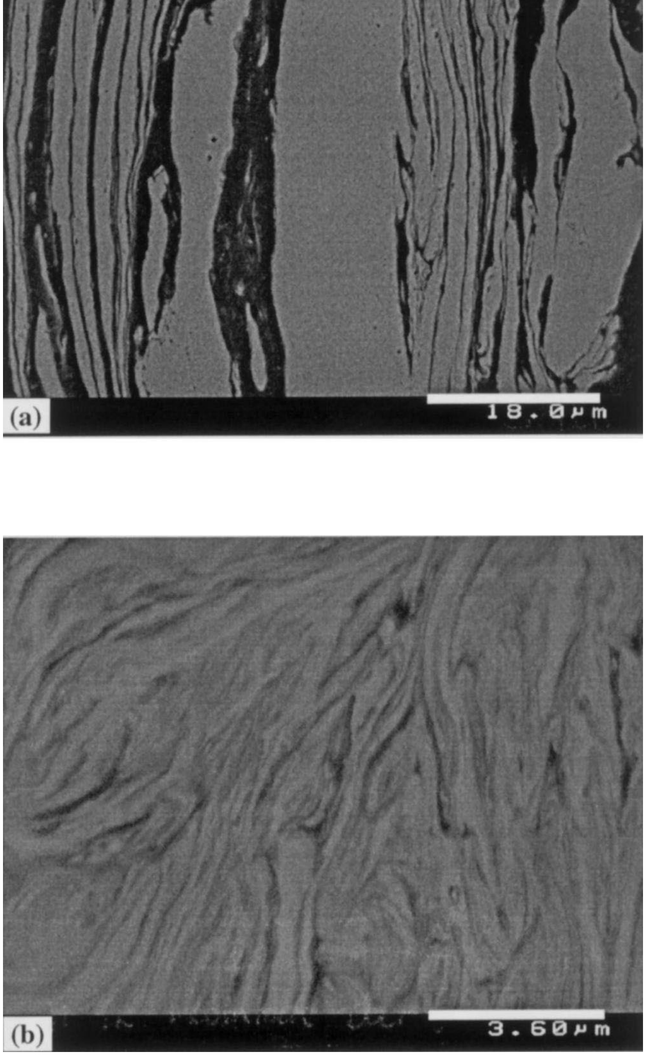

Fig. 7. SEM micrographs of the cross-sections of powder particles produced by milling Cu–35at.%Al powder mixture for (a) 1 h and (b) 2 h.

thickness of Al phase ranged from 1 to 6 μm. A few larger elongated particles of Al with a thickness ranging from 10 to 20 μm were also observed. After 2 h of milling, the Cu and Al phases were well mixed and the multilayer structure was more clearly defined, as shown in Fig. 7b. The thickness of Al layers ranged from 0.05 to 0.2 μm. After 4 h of milling, the multilayer structure became significantly refined and could not be clearly resolved using SEM.

Fig. 8 shows DSC traces of Cu–35at.%Al powders produced after milling for different times. As shown in Fig. 8a, the DSC trace of 1-h milled powder exhibited two overlapping exothermic peaks and four endothermic peaks at high temperatures. The first exothermic peak was very small and its onset and peak temperatures were approximately 105 and 160°C, respectively. The second exothermic peak was very large and broad and its onset and peak temperatures were approximately 150 and 300°C, respectively. The endothermic peaks were in the temperature range of 540–650°C, and they were likely caused by melting of Al rich phases formed through diffusion of Cu into Al during heating. After the powder was milled for 2 h, the endothermic peaks disappeared from the DSC trace. The first exothermic peak became stronger, and its onset and peak temperatures remained unchanged. The second exothermic peak became much sharper and its onset temperature seemed unchanged. The peak temperature of the second exothermic peak decreased significantly from 300 to 230°C. After the powder was further milled to a total time of 4 h, the first exothermic peak almost disappeared, and the second exothermic peak became substantially smaller. The onset temperatures of these peaks seemed unchanged, but the peak temperature of the second peak decreased to 200°C. This suggests that a substantial fraction of Al phase and Cu phase already reacted during milling from 2 to 4 h. After 8 h of milling, the first exothermic peak disappeared, while only a small fraction of the second peak was left. This suggests that almost all of the elemental phases were reacted during 8 h of milling. In order to identify the reactions corresponding to the exothermic peaks, the 2-h milled powder was heated in DSC to 190°C, i.e. just above the first peak temperature but below the second peak temperature and then cooled. Fig. 9a shows the XRD pattern of this powder. It showed that $\gamma$-$Cu_9Al_4$ peaks, $\theta$-$CuAl_2$ peaks as well as elemental Cu and Al peaks. The 2-h milled powder heated to 650°C and then cooled to room temperature in DSC was also analyzed using XRD. Fig. 9b shows the XRD pattern of this powder. It showed only $\gamma$-$Cu_9Al_4$ peaks. This suggests that the first exothermic peak corresponds to reaction between Al and Cu forming $\theta$-$CuAl_2$ while the second peak corresponds to reaction between $\theta$-$CuAl_2$ and Cu forming $\gamma$-$Cu_9Al_4$. The heat released during heating the Cu–35at.% as a function of milling time was plotted in Fig. 10. The reaction heat for the 1-h milled Cu–35at.%Al powder was 15.02 kJ/mol. The amount of heat released decreases with increase of milling time and became close to zero after 8 h milling.

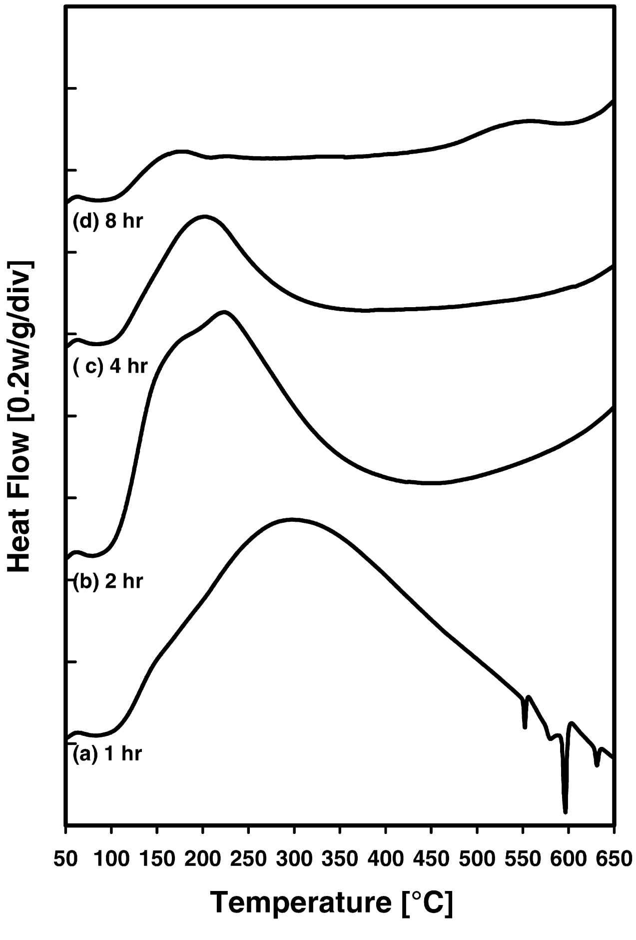

Fig. 8. DSC traces of the powders produced after milling a Cu/Al mixture with 35at.%Al for different times.

## 4. Discussion

The present study shows that alloying between Cu and Al can be achieved either mechanically through ball milling of a mixture of Cu and Al elemental powders or thermally through heat treating the milled powder. With a low Al composition of 14at.%, the mechanical alloying results in formation of a Cu(Al) solid solution. With a high Al composition of 35at.%, the mechanical alloying results in formation of $\gamma$-$Cu_9Al_4$. This is in agreement with Lima at al.'s observation [7]. Monitoring of the phase development of the process only reveals a progressive conversion of a mixture of elemental phases into a solid solution or an intermediate phase. So it is not clear whether the formation of the final product is preceded by formation of one or more other intermediate phases such as $\theta$-$CuAl_2$. The mechanical alloying process is slow and progressive, so it is difficult to clarify this issue.

On the other hand, heating the milled powder in DSC can reveal the kinetic of the reactions which can occur in

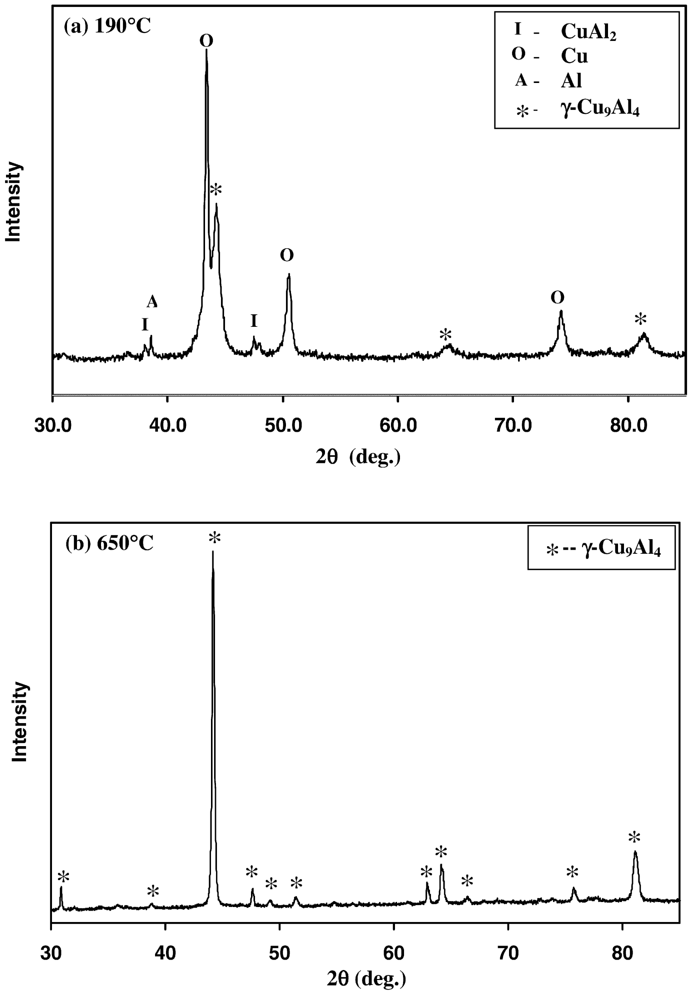

Fig. 9. XRD patterns of the powders produced after milling a Cu/Al mixture with 35at.%Al for 2 h and then heated to different temperatures.

the Cu–Al system. For both compositions, the DSC trace of the milled but not extensively reacted powder shows two heavily overlapping exothermic peaks. With low Al composition, it is identified that at low temperatures Cu and Al react forming $\gamma$-Cu$_9$Al$_4$, while at high temperatures $\gamma$-Cu$_9$Al$_4$ is dissolved into Cu forming Cu(Al) solid solution. With high Al composition, it is identified that at low temperatures Cu and Al react, forming $\theta$-CuAl$_2$, while at high temperatures CuAl$_2$ and Cu react, forming $\gamma$-Cu$_9$Al$_4$. It seems that with low Al composition, the first phase formed by reaction between Cu and Al is $\gamma$-Cu$_9$Al$_4$, while with high Al composition, the first phase is $\theta$-CuAl$_2$. However, the Al composition in the powder mixture only affects the volume ratio of Al phase and Cu phase in the Cu/Al composite. It would be unlikely for the change of volume ratio of the two elemental phases to alter the formation of the first phase which is controlled by the state of Cu/Al interface. The fact that in the Cu/Al composite powder with high Al volume fraction, formation of CuAl$_2$ precedes formation of $\gamma$-Cu$_9$Al$_4$ shows that it is easier for $\theta$-CuAl$_2$ to nucleate at the Cu/Al interfaces than $\gamma$-Cu$_9$Al$_4$. The crystal structure of $\theta$-CuAl$_2$ is also simpler than $\gamma$-Cu$_9$Al$_4$. This is also a favorable factor to determine that CuAl$_2$ is easier to nucleate. Therefore, it is likely that even with low Al composition, $\theta$-CuAl$_2$ may still be the first

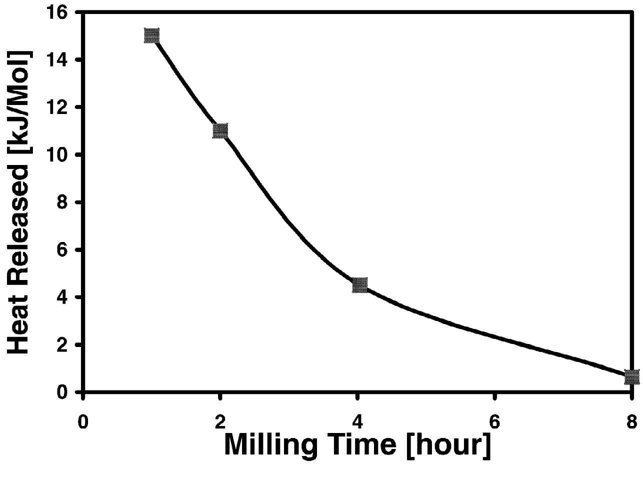

Fig. 10. The heat released during heating the milled Cu–35at.%Al powder as a function of milling time.

phase formed. But since the $CuAl_2$ is Al rich, the amount of $CuAl_2$ is too small to be revealed by DSC and XRD analysis.

The DSC analysis of the milled powder shows that $\theta$-$CuAl_2$, as the first phase to be formed by reaction between Cu and Al, nucleates and grows at temperatures ranging from 100 to 190°C. This temperature range is very similar to that observed by Jiang et al. [4] during annealing Cu/Al multilayer thin films. The DSC analysis also reveals that $\gamma$-$Cu_9Al_4$ start to nucleate at about 150°C. These temperatures are also similar to those observed by Jiang et al. during annealing of multilayer thin films. These similarities suggest that after sufficient time of milling (1–2 h in this case), the behavior of the Cu/Al composite powder during heating is very much similar to that of the multilayer thin films, even though the layer thickness has not been as small as a few nanometers. Another aspect of this study is about the effect of Cu/Al composite structure on the reaction kinetics. When the composite structure is refined by increasing milling time from 1 to 2 h, the onset temperature of the formation of the first phase remains unchanged, as shown in Figs. 3a,b and 8a,b, respectively. However, with the refinement of the composite structure, the fraction of the first phase formed increases and the temperature range for completing formation of the second phase became narrower. It is not difficult to envisage that the $\theta$-$CuAl_2$ phase nucleates at Cu/Al interfaces. With refinement of the composite structure, the total area of the interfaces becomes larger, so the number of nucleation sites per unit weight of powder becomes larger. This would, with no doubt, lead to an increase of the nucleation rate. On the other hand, the onset temperature of nucleation is controlled by interface diffusivity rather than the total area. So it is quite understandable to see that the onset temperature remains unchanged. Likewise, the narrowing of the temperature range for formation of the $\gamma$-$Cu_9Al_4$ phase or the solid solution is caused by decrease of layer thickness. The layer thickness determines the required growth distance. With smaller layer thickness, the required growth distance is smaller, so it is faster for the reaction to come to completion.

In the Cu–Al system, formation of a metastable phase has not been observed in mechanical alloying, in heat treating of milled Cu/Al composite powder or in annealing of multilayer thin films. This seems to be characteristic of this system. The likely cause of this is the difficulty of preventing formation of intermediate phase like $\theta$-$CuAl_2$.

The heat released measured by DSC during heating the milled powder particles is very useful information on the progress of reaction which occurs during milling. This information is complementary to XRD patterns. This measurement shows that for both 14at.%Al and 35at.%Al, reaction in the powder completes by milling for 4–8 h. This is in good agreement with the XRD patterns.

## 5. Conclusion

1. Cu and Al are mechanically alloyed during ball milling of a mixture of Cu and Al powders. When the composition of the mixture is 14at.%Al, Cu(Al) solid solution forms as a result of mechanical alloying. When the composition is 35at.%Al, the intermetallic compound $\gamma$-$Cu_9Al_4$ forms.
2. The same final outcome of the alloying can also be achieved through heat treating the as-milled composite powders. However, it was identified that for Cu–14at.%Al powder, the first phase formed was $\theta$-$CuAl_2$ or $\gamma$-$Cu_9Al_4$, whereas for Cu–35at.%Al, the first phase formed was $\theta$-$CuAl_2$.
3. The refinement of Cu/Al composite structure through milling does not change the nucleation temperature of the first phase during heating but it significantly decreases the peak and end temperature of the nucleation and growth of the dominating phase.

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