Role of mechanical alloying parameters on powder distribution of Al/Cu alloy and Al/Cu composite

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The aim of the current study is to investigate the effect of milling time and speed on mixing properties of aluminium (Al)/copper (Cu) alloy and Al/Cu composite. Ethanol and argon gas were employed as process control agent and milling atmosphere. Mechanical alloying process by means of high-energy ball milling was performed to produce alloy and composite metal powder. This process proceeds through repeated deformation, cold welding and fracturing of powder particles mixture with a controlled fine microstructure. X-ray diffraction and particle size analyser confirmed particle size reduction of Al/Cu alloy with increasing milling time and speed. On the other hand, the addition of reinforcement particles was found to accelerate the milling process of Al/Cu composite. Scanning electron microscope micrographs revealed homogeneous distribution of powder mixture particles by mechanical alloying process at changing milling conditions.

Keywords: Al/Cu alloy, Al/Cu alloy composite, Mechanical alloying, Milling time, Milling speed, Ethanol, Argon gas

Introduction

Mechanical alloying (MA) by means of ball milling technique has attracted considerable attention for manufacturing complex materials including amorphous alloys, intermetallic compounds, quasicrystalline materials, nanocomposite and composite materials.1–5 As part of powder metallurgy technique, MA involves a simple and low-cost fabrication method that cannot be obtained by other conventional melting or casting techniques. John Benjamin6 originally invented MA, which later was widely utilised to produce powders with controlled microstructure. The basic mechanism of the MA process involves ball to powder collision. During the MA process, the powder particles are continuously trapped between colliding balls and container. This high-energy impact resulted in repeated deformation, cold welding and fracturing process of powder particles, enhancing its mechanical and physical properties. These processes continuously proceed until a steady-state equilibrium condition is reached.6 This equilibrium condition refers to a balance reaction between the rate of welding (average particle size tends to increase) and the rate of fracturing (average particle size tends to decrease).

According to Suryanarayana,7 deformation leads to a change in particle shape, cold-welding results in an increase in particle size while fracture causes a decrease in particle size contributing to the formation of fine dispersed alloying particles in the grain-refined soft matrix. On the other hand, to guarantee a desirable equilibrium reaction achievement between welding and fracturing processes, selection of starting materials is important before performing the MA process. The raw powders for the MA process are usually commercially available pure powders having particle sizes between 1 and 200 μm. The particle size of the starting powders is not a critical factor, as long as it is smaller than the diameter of the grinding balls. This is due to the decreasing particle size of starting powders with time during the MA process; particle size reaches a small value of a few microns after only a few minutes of the milling process.7

From a MA perspective, powders can be categorised as either ductile–ductile, ductile–brittle or brittle–brittle systems. Mechanical alloying also depends on other milling parameters such as milling speed, milling time, process control agents (PCA) and milling atmosphere. It is important to note that the use of PCA for ductile metallic materials is essential to ensure the successful process of MA. Moreover, only a small amount of PCA is needed to obtain a balance process between cold welding and fracturing.1–9 The absence or insufficient content of PCA often results in larger particle size of milled powder, indicating the absence of the fracturing process. For fabrication of composite material, it is not necessary to introduce PCA because of the addition of reinforcement, but the use of PCA is widely applied to
prevent powder segregation and to obtain homogeneous distribution of reinforcement in the matrix material. Previously, several studies were performed to investigate the effects of milling parameters on the MA process. Adamiak suggested that homogeneous reinforcement particles were obtained by controlling the milling parameters, which resulted in mechanical properties enhancement. Moreover, Ghasemi and Najafzadeh-Khoei concluded that Al nanocomposite with finer microstructure was successfully synthesised at 10-hour milling time whereas prolonged milling time might result in decreasing crystallite size with homogeneous reinforcement particles distribution. On the other hand, Ramezani and Neitzert studied the MA process involving pure aluminium powder. The authors found that repeated processes of cold welding and fracturing affect the morphology of Al powder, including particle size and particle shape, with longer milling time effectively reducing the powder particles’ size. As most studies involving milling parameters focused on ductile–brittle system, this study was done to investigate the effects of milling time and speed on mixing properties of ductile–ductile system for Al/Cu alloy and Al/Cu composite.

Materials
Elemental powders of aluminium (Al) (99.97% purity and <70 μm particle size) and copper (Cu) (99.98% purity and <70 μm particle size) were used as starting materials to produce Al/Cu alloy and Al/Cu composite. For the composite system, polymethylmethacrylate (PMMA) having a particle size less than 150 μm with 99.99% purity was introduced as reinforcement. All these starting materials were purchased from Novascientific Sdn Bhd, Malaysia. For Al/Cu alloy, the amount of Al and Cu were fixed at 95 and 5 wt-% whereas for Al/Cu composite, PMMA amount was fixed at 50 wt-%.

Experimental method
Mixing of Al, Cu and PMMA powders to produce Al/Cu alloy and Al/Cu composite were performed in a planetary high-energy ball milling (Pulverisette 5, 4 grinding station mill) by the MA process. During the MA process, a ball to powder (B/P) ratio of 10:1, ball diameter of 20 mm, ball material of tungsten carbide and 250 ml capacity of stainless steel vial were fixed.

1 Average percentage of various ranges of particle sizes at different milling times and speeds
throughout the process to obtain homogeneous distribution of powders mixing. First, Al and Cu powders were mixed at various milling times and speeds. These milling times and speeds were varied between 120 and 200 rev m$^{-1}$ and 4–16 hours. For the Al/Cu composite system, the PMMA was mixed along with Al and Cu powders. A total of 3 wt-% of ethanol was added as PCA during the MA process to avoid intermetallic compound formation and powder sticking to the wall vial and ball. In addition, PCA was also used to lessen the cold-welding effect of blending different powder materials, especially soft materials such as Al and Cu. Argon gas was supplied to the vial for a short time to minimise powder contamination before conducting the MA process. In order to prevent overheating, the high-energy ball milling was stopped periodically every 30 minutes and resumed after 30 minutes until the MA process completed. Finally, once the MA process completed, the mixed powders were cooled inside the vial for a few hours before being carefully transferred into a plastic container.

**Characterisation techniques**

A particle size analyser (PSA), X-ray diffraction (XRD) analysis and SEM were used to determine the properties of the milled powders. Beckman Coulter LS 200 laser PSA with a measurement range between 3.9 and 125 μm was used to monitor the change in particle size of Al/Cu alloy and Al/Cu composite under various milling conditions. The alloying behaviour and phase changes after the MA process were evaluated by a pan-analytical empyrean 1032 (60 kV) XRD with Cu Ka radiation ($\lambda = 0.15406$ nm). The XRD patterns were documented in the 20 range of 20–100°. The morphology, microstructure and distribution of Al/Cu alloy and Al/Cu composite were examined using a Quanta 250 FEG SEM with capacity of 40 nA probe current.

**Results and discussion**

**Particle size analysis**

The PSA for Al/Cu alloy and Al/Cu composite was based on the average percentage of different particle size ranges between 3.9 and 125 μm. Based on these ranges, material having particle sizes of 15-6 μm and below are classified as the smaller particle size group while material having particle sizes of 62 μm and above are classified as the bigger particle size group. For the Al/Cu alloy system, during the initial MA process of 4 and 7 hours, most of the powder particles were bigger in size, about 85 and 75%, respectively, as depicted in Fig. 1a. Only low average percentage of smaller particle size was detected at about 7 and 5% at 4 and 7 hours of milling duration, respectively. This indicates short milling time and slow milling speed were insufficient to break up the powder particles because of the effects of the cold-welding process. Therefore, agglomeration of powder particles with formation of flaky structure was observed as shown in Fig. 3a and 3b. Similar results...
were also reported by Ramezani and Neitzert, where flattening and work hardening of Al particles occurred at an early stage of MA because of powder welding, thus increasing the particle size. As milling time and speed were increased to between 10 hours (160 rev min\(^{-1}\)) and 13 hours (180 rev min\(^{-1}\)), the average percentage of bigger particle size began to decrease about 69% for both milling states. At this stage, the average percentage of smaller particle size was increased about 30% for both milling conditions. As milling time and milling speed were prolonged up to 16 hours and 200 rev min\(^{-1}\), the average percentage of bigger particle size was reduced about 27% whereas the average percentage of smaller particle size rose about 73%. At longer milling time, fracturing dominates over cold welding thus resulted in smaller particle size and finer particle structure. Moreover, homogeneous distribution of powder particles due to the reachable in steady-state condition was achieved as demonstrated in Fig. 3c.

In contrast, for the Al/Cu composite system, the average percentage of bigger particle size was higher as compared to Al/Cu alloy. This is in agreement with the formation of composite material associated with bigger particle size, whereas smaller particle size corresponded to the elemental particle of Al and Cu powders. As illustrated in Fig. 4a and b, the early stage of MA process for Al/Cu composite led to the formation of bigger particle size even up to milling time and speed of 10 hours and 160 rev min\(^{-1}\). This could be associated with the non-uniform distribution of reinforcement particles (PMMA) inside the metallic matrix materials, resulting in agglomeration of Al/Cu composite particles. Moreover, as exemplified in Fig. 4b, coarse structure with a lot of clustering particles was also detected during this early MA process. At milling time and speed of 13 hours and 180 rev min\(^{-1}\), the average percentage of smaller particles was enhanced up to 56%. However, a slight increase in average percentage of bigger particle size with a slight decrease in average percentage of smaller particle size was found at 16 hours and 200 rev min\(^{-1}\) of milling parameters. This shows that the duration needed to accomplish steady state for Al/Cu composite had become shorter as compared to the Al/Cu alloy system.\(^{10}\) This is believed to be due to the addition of hard reinforcement particles in the soft metallic matrix material, which acts as a small milling agent. For that reason, the work hardening rate and local deformation of the matrix around the reinforcement particle was enhanced, and thus accelerated the fracturing process of the composite system during milling.\(^{10}\) As a result, the time needed to achieve
equilibrium or steady-state condition decreased. Despite a slight increase in average percentage of bigger particle size and a decrease in average percentage of smaller particle size, agglomeration of powder particles was found to improve with a stable distribution in powder particle size and shape as shown in Fig. 4c.

**Elemental analysis of the mixture**

Figure 2a–c demonstrates XRD patterns of as-milled powders with and without PMMA and unmilled powders. By comparing the peaks intensities of milled and unmilled powders, a decline pattern in peaks intensity of milled powders was evidenced suggesting that a decrease in powder particle size occurred after the MA process. Fig. 2a and b show that Al and Cu peaks remained unchanged for Al/Cu alloy and Al/Cu composite during the initial 4 hours of milling time. As the milling time increased to 7 hours, Al peaks for Al/Cu alloy became slightly weaker, suggesting a decrease in particle size.1,4,6,8 It is also observed that intensity of the powders slightly reduced due to the decrease of the powder’s crystallinity. As milling time and speed were prolonged up to 16 hours, the intensity of Al peaks continuously declined implying a decrease in powder particle size. As mentioned in the previous section, the changing pattern in powder particle size with respect to milling time and speed could be attributed to the repeated phenomenon of cold-welding and fracturing processes during the MA process. A similar trend was also observed for Cu peaks except that some of the Cu peaks (311, 222) diminished gradually after 13 hours of milling. This shows dissolution of the Cu phase in the Al phase occurred owing to alloying of Al and Cu.1 For the variation in milling speed, equal pattern as milling time was evidenced between milling speed of 120 and 200 rev min⁻¹. This is due to the high impact kinetic energy of the stainless steel ball leading to the decrease in the particle size via crushing and amorphisation effects of powder particles.3 The XRD patterns for the Al/Cu composite system are partially similar to those of Al/Cu alloy. This is because the XRD patterns for Al/Cu composite do not really vary between one another, even at higher milling conditions. This finding is in agreement with PSA result as shown in Fig. 1b. As stated in the previous section, this might be due to the reinforcement effect of PMMA particles that led to a minimal change in XRD patterns. These reinforcement particles resulted from a decrease in cold-welding effect domination and thus reduced the time to reach steady-state condition.10 In addition, the PMMA peak is also
hardly accessible because of the amorphous nature of PMMA, while all Cu peaks still exist even after milling time of 16 hours. This shows successful fabrication of Al/Cu composite. It should be noted that no additional phases were observed for either system.

**Microstructure analysis**

Figures 3 and 4 reveal the micrographs of as-milled powders for Al/Cu alloy and Al/Cu composite at various milling times and speeds by SEM. For the Al/Cu alloy system, powder particles with coarse structure were obtained after initial milling time as shown in Fig. 3a. At this stage, most of the powder particles were found to be flaky in shape. It should be noted that different PCA will result in different morphology (shape and size) of milled powders as reported by Ramezani and Neitzert. Moreover, the powder particles were also found to be bigger in size with various ranges of particle sizes. According to Benjamin, most powder particles at the early stage of milling are still soft and tend to weld together, forming larger particle sizes with some powder particles having two to three times greater diameter than the original size. As milling time and speed were increased up to 10 hours and 160 rev min$^{-1}$, agglomeration of powder particles became clearly visible along with formation of smaller particle sizes as depicted in Fig. 3b. This indicates that at a longer milling time, the powder particles became harder thus reducing their capacity to deform without fracturing due to the collision between the milling balls and powder friction. At this level, the flake-like structure also remained unchanged. In addition, the powder particle size continuously decreases at higher milling time and speed up to 16 hours and 200 rev min$^{-1}$. Furthermore, a low degree of agglomeration with finer powder particles was also identified under these milling conditions. This promotes homogeneous distribution of powder particles as evidenced in Fig. 3c. It can be observed that the variation in powder particle sizes became narrow with disappearance of the flaky structure. Consistent results with past studies of changing milling conditions was also reported earlier.

An almost similar morphology pattern as that of Al/Cu alloy was also observed for Al/Cu composite in terms of flattening of powder particles, welding and fracturing of flaky powder particles, except that the degree of agglomeration of Al/Cu composite powder particles was higher than that of Al/Cu alloy. Moreover, the flake-like powder particles are also hardly accessible in the milling process of the Al/Cu composite system. As discussed in the PSA section, this could be due to the formation of composite material (PMMA addition). Adamiak also mentioned that during the MA process involving soft metallic material and hard reinforcement particles, the brittle reinforcement tends to undergo fragmentation while ductile metallic particles are likely to undergo deformation. Once the ductile particles begin to weld, the brittle reinforcement will enter the soft metallic particles forming a flattened composite material resulting in a real composite formation. Fig. 4a shows that the powder particles are not as flattened as in the Al/Cu alloy system after the initial MA process. As mentioned before, at this stage the presence of PMMA particles decreased the predominant mechanism of cold-welding effect, thus changing the morphology of the powder particles by building up laminar particles. At prolonged milling parameters (13 hours and 180 rev min$^{-1}$), fracturing succeeds over cold welding and reduces the powder particles ability to accept continuous plastic deformation. At higher milling time and speed of 16 hours and 200 rev min$^{-1}$, a slightly bigger particle size was observed. This signifies that an equilibrium condition was reached at 13 hours of milling time. Nevertheless, powder distribution improvement with a narrow distribution in particle size and shape was evidenced at longer milling time as shown in Fig. 4c. This finding is in agreement with previous studies where powder particles continued to refine with a stable distribution in particle size and shape even after steady-state condition had been reached.

**Conclusion**

It can be concluded that the average percentage of smaller and bigger particle sizes for Al/Cu alloy and Al/Cu composite was found to decrease with an increase in lattice strain at higher milling time and speed. The optimum milling time and speed were found at 16 hours (200 rev min$^{-1}$) and 13 hours (180 rev min$^{-1}$) indicating adequate mixing of Al/Cu alloy and Al/Cu composite. In addition, the presence of reinforcement particles was discovered to accelerate the milling process for the Al/Cu composite system. Scanning electron microscopy analysis confirmed homogeneous distribution of powder particles with controlled microstructure under changing milling conditions. Moreover, mechanical alloying can be considered as an economical technique to produce various powders with unique properties.

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**References**