Characteristics of Cu–Al₂O₃ composites of various starting particle size obtained by high-energy milling

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(Received 9 December 2008)

Abstract: The powder Cu–Al₂O₃ composites were produced by high-energy milling. Various combinations of particle size and mixtures and approximately constant amount of Al₂O₃ were used as the starting materials. These powders were separately milled in air for up to 20 h in a planetary ball mill. The copper matrix was reinforced by internal oxidation and mechanical alloying. During the milling, internal oxidation of pre-alloyed Cu-2 mass %-Al powder generated 3.7 mass % Al₂O₃ nano-sized particles finely dispersed in the copper matrix. The effect of different size of the starting copper and Al₂O₃ powder particles on the lattice parameter, lattice distortion and grain size, as well as on the size, morphology and microstructure of the Cu–Al₂O₃ composite powder particles was studied.

Keywords: Cu–Al₂O₃ composite powders; high-energy milling; size of the starting powder particles.

INTRODUCTION

The copper-based matrix obtained by powder metallurgy (PM) techniques and reinforced applying the process of mechanical alloying has been extensively studied in recent years. The application of mechanical alloying as a method for obtaining a uniform distribution of dispersoids in a copper matrix accompanied with a fine-grained microstructure greatly improves the properties of such copper-based composites. The particle size of both the matrix alloy and the strengthening powders determines to a large extent many of the final properties of the produced PM compacts.

In this study, the copper matrix was reinforced with Al₂O₃ particles by internal oxidation and mechanical alloying. The effects of both the copper and Al₂O₃ particles size on the lattice distortion and grain size, as parameters with a considerable effect on the process of the sintering of copper-based composites, were the subject of this investigation. At the same time, the influence of these...
parameters on the evolution of the morphology and the microstructure of the Cu-based composite powder particles was also studied.

EXPERIMENTAL

Inert gas-atomized, pre-alloyed copper powder containing 2 mass %–Al and different mixtures of electrolytic copper powders and Al₂O₃ particles served as the starting materials for this investigation. The characteristics of the pre-alloyed copper powder and the powder mixtures used in this study are given in Table I. The starting powders are characterized by the same or different copper and Al₂O₃ powder particle size. These powders were separately milled in air for up to 20 h in a planetary ball mill. The weight ratio of the powder to steel balls was 1:35.

TABLE I. Size of the starting copper and Al₂O₃ powder particles

<table>
<thead>
<tr>
<th>Material</th>
<th>Size of pre-alloyed copper particles and size of copper particles, μm</th>
<th>Size of Al₂O₃ particles, μm</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-alloyed Cu–2 mass %–Al</td>
<td>30</td>
<td>0.010</td>
<td>Cu-2Al</td>
</tr>
<tr>
<td>Cu-4 mass %–Al₂O₃</td>
<td>30</td>
<td>0.75</td>
<td>Cu-4Al₂O₃</td>
</tr>
<tr>
<td>Cu*-4 mass %–Al₂O₃</td>
<td>15</td>
<td>0.75</td>
<td>Cu*-4Al₂O₃</td>
</tr>
<tr>
<td>*After internal oxidation</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The milled powders were characterized by X-ray diffraction analysis (XRD) using a Siemens D-500 X-ray powder diffractometer with CuKα Ni-filtered radiation. The lattice parameters were determined using the least square root method. The average lattice distortion, i.e., the relative deviation of the lattice parameters from their main value ($\Delta d/d$) and the grain size ($D$) were determined from the broadening ($\beta$) of the first four diffraction lines (111, 200, 220 and 311) using the approach developed by Williamson and Hall:

$$\beta \cos \theta = \frac{k \lambda}{D} + \frac{k \Delta d}{d} \sin \theta$$

where the shape factor $k = 0.9$ and the radiation wave length, $\lambda = 0.15405$ nm.

The microstructure of the treated powders was characterized by light microscopy using a Zeiss Axiovert 25 microscope and scanning electron microscopy (SEM) using a Philips XL30 instrument. Samples for light microscopy were mounted in an acrylic resin. Polishing was performed using the standard procedure and a mixture of 5 g FeCl₃ and 50 ml HCl in 100 ml distilled water was used for etching.

RESULTS AND DISCUSSION

Change of powder particles parameters

During milling of the pre-alloyed Cu–2Al powder, the lattice parameter decreased with milling time, whereas the lattice parameters of the other starting powder mixtures slightly increased (Fig. 1). The decrease in the Cu–2Al lattice parameter results from the oxidation of the aluminum during internal oxidation, which precipitates from pre-alloyed copper forming a fine dispersion of Al₂O₃. The decrease in the lattice parameter was rapid during the first 10 h of milling but become slower with prolonged milling. This indicates that the most of alu-
minum precipitates from the copper matrix at the beginning of the milling process due to facilitation of the oxidation process through the severe deformation of the copper matrix in this period of milling. The difference in the lattice parameter of the pre-alloyed Cu–2Al powders before ($a_{\text{Cu-2Al}} = 0.3624 \text{ nm}$) and after 20 h of milling ($a_{\text{Cu-2Al}} = 0.36167 \text{ nm}$) is 0.20 %. This difference is similar to the difference (0.24 %) in the theoretical lattice parameters of the pre-alloyed powder ($a_{\text{Cu-2Al}} = 0.36210 \text{ nm}$) and the copper powder ($a_{\text{Cu}} = 0.36150 \text{ nm}$), indicating that after 20 h of milling almost all the aluminum had been precipitated from the copper matrix. Assuming that the complete amount of aluminum was oxidized, it was calculated that 3.7 mass % of Al₂O₃ was generated by internal oxidation of 2 mass % Al in the copper matrix. This result shows that the amount of the strengthening particles was kept nearly constant in pre-alloyed copper and the powder mixtures, being around 4 mass % Al₂O₃. On the other hand, the slight increase of the lattice parameters of the mixtures containing Al₂O₃ particles might be the result of contamination of the copper matrix with steel balls debris during milling.

The full width at half maximum (FWHM) height measured from X-ray the diffraction patterns of the examined powders showed a progressive line broadening with milling time (Figs. 2a–2c). From Figs. 2a and 2b, it may be seen that the FWHM of the pre-alloyed Cu–2Al powder strengthened with 0.01 μm Al₂O₃ particles (Fig. 2a) were higher than those of a mixture of Cu–4Al₂O₃ with an average Al₂O₃ particle size of 0.75 μm (Fig. 2b; the size of the copper powder ≈ 30 μm). The FWHM of the Cu*–4Al₂O₃ mixture (Fig. 2c; size of copper powder ≈ 15 μm) were significantly higher than the FWHM of Cu–4Al₂O₃. The higher FWHM of the Cu*–4Al₂O₃ sample implies that the starting size of copper powder particles had a great influence on the FWHM during the milling process. The separate diagram (Figs. 3a and 3b) shows that the values of the FWHM of Cu*–4 Al₂O₃ were slightly higher than those of Cu–2Al. These results suggest
that the influence of the smaller starting copper powder particles (15 µm) on the FWHM prevails over the effect of the Al$_2$O$_3$ particles size.

![Graphs showing FWHM vs. milling time for different powder mixtures](image)

The progress in the broadening of the FWHM with milling time is a result of a severe lattice distortion and grain size refinement. Lattice distortion and grain size are important parameters of milled powders since they have a significant effect on both compacting the powders during the sintering process and the properties of the finely dispersed strengthened copper matrix. Lattice distortion normally increases with milling time. However, there are exceptions to this behavior and some literature results claim that the lattice distortion may decrease during milling. The results of this study show that the lattice distortion increased with time of milling (Fig. 4), being the highest in the powder mixture Cu–2Al.
strengthened with very small Al₂O₃ particles, whereas the lowest lattice distortion was observed in the powder mixture Cu*-4Al₂O₃. According to the results in Fig. 4, it is obvious that the lattice distortion decreased with decreasing particle size of the starting copper powders. The presence of smaller Al₂O₃ strengthening particles increased the lattice distortion, i.e., very small (0.01 μm) Al₂O₃ particles caused higher lattice distortion than the coarse (0.75 μm) particles. These changes of lattice distortion are probably due to polygonized dislocation structures of the highly deformed small particles during high-energy milling. The smallest distortions in the Cu*-4Al₂O₃ powders suggest that the dislocations formed during milling of small copper powder particles due to the very low amount of stored elastic energy are arranged in configurations that reduce the strain energy. However, in the case of such small-sized powders, a contributing factor to the low strain energy due to partial amorphization of the powders¹⁰ cannot be excluded, in spite of the fact that the diffraction peaks remained sharp up to 20 h of milling, as in the present case.

In view of these facts, the results presented in Figs. 3a and 3b and Fig. 4 should not be regarded as contradicting. Namely, the slightly higher values of the FWHM of the Cu*-4Al₂O₃ powders compared to those of Cu-2Al may be considered from the view that the influence of grain refinement on the FWHM surmounts not only the effect of the Al₂O₃ particle size, but also the decreasing influence of the elastic strain energy on the lattice distortion of Cu*-4Al₂O₃ powders.

The size of the grains, i.e., the crystallites, formed inside the powder particles during milling abruptly decreased with milling time (Fig. 5). This decrease
was the highest up to 5 h of milling, when the grain size was between 30 and 40 nm. After 20 h of milling, the grain size was slightly changed, ranging between 20 and 30 nm, except for the grain size of Cu*-4Al2O3 powders, for which the grain size was somewhat smaller, i.e., 15 nm. This result is in accordance with the FWHM results (see Figs. 3a and 3b). Generally, the smallest grain size found in the Cu*-4Al2O3 mixture may be ascribed to the fact that smaller powder particles are more easily subjected to higher deformation during milling than coarser particles.

Fig. 4. Effect of milling time on the lattice distortion.

Fig. 5. Effect of milling time on the grain size.

Size, morphology and microstructure of the composite powders

The composite powder particles formed from the starting powders change their morphology, size and microstructure during high-energy milling as a consequence of repeated deformation, fracture and welding processes. Generally, at the beginning of milling, the average particle size of composite powders in-
creases until welding of the particles powders dominates the milling process, but the size of particles starts to decrease when the fracture process prevails. In the case of balance of fracture and welding processes, the particles are rather uniform in size and similar in shape.

SEM microphotographs showing the morphology of the composite powder particles after 5 and 20 h of milling are presented in Figs. 6a–6c and Figs. 6d–6f, respectively. Detailed observations of the morphology and particle size showed that the composite powders based on pre-alloyed powders and mixtures had a different size and morphology after 5 h of milling, Figs. 6a–6c. The composite powders...
Cu–2Al particles (Fig. 6a) are flattened, whereas the Cu–4Al2O3 and Cu*–4Al2O3 composite particles are more rounded (Figs. 6b and 6c, respectively). The flattened shape of the Cu-2Al composite particles is a consequence of the fact that the nano-sized Al2O3 particles formed by internal oxidation generate a higher resistance to the strong plastic deformation occurring at the beginning of the milling than the micro-sized commercial Al2O3 particles. During prolonged milling (20 h), the size of Cu–2Al particles (Fig. 6d) significantly decreased, becoming more rounded in shape. On the other hand, the size of Cu–4Al2O3 particles (Fig. 6e) increased to some extent and they had a completely rounded shape. No significant change in the size and morphology could be detected in the Cu*–4Al2O3 particles (Fig. 6f). The results presented in Fig. 6 suggest that the size of the starting copper particles, as well as the Al2O3 particle size, has an influence on the different morphologies and particle sizes of the composite powders during milling.

Since the particles of the milled composite powders Cu–2Al and Cu–4Al2O3 were neither similar nor uniform in size, it is obvious that the balance of the fracture and welding processes of the powder particles has not been attained during 20 h of milling. Concerning this aspect, the situation with the Cu*–4Al2O3 composite powders is not quite clear.

The microstructure of the composite powder particles after 5 h of milling are illustrated in Fig. 7. Thereby, it was confirmed that the milled composite powder
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particles, except the Cu*–4Al₂O₃ particles, exhibit a lamellar structure (Figs. 7a and 7b), typical for high-energy milled powders. The lamellae represent individual plastically deformed starting pre-alloyed copper (Fig. 7a) and copper powder particles (Fig. 7b). Applying higher magnification, the uniform distribution of the commercial Al₂O₃ particles embedded in a matrix of agglomerated copper particles may be seen in the microstructure of the Cu*–4Al₂O₃ composite powder particle (Fig. 7c). In these milled powder particles, lamellae are not visible, probably due to very small powder particle size.

The structural observations showed that a very homogenous distribution of Al₂O₃ was achieved after 5 h of milling in the majority of the mechanically alloyed copper particles and that this distribution improved with increasing milling time. The distribution of Al₂O₃ particles in the Cu–4Al₂O₃ particles after 5 and 20 h of milling is illustrated in Figs. 8 a and 8b, respectively. In this case, when the size of the starting copper and Al₂O₃ particles were higher, the uniform distribution of Al₂O₃ particles between deformed copper particles, typical for composites obtained by high-energy milling, may be clearly seen.

![Fig. 8. Light microscopy pictures of Cu–4Al₂O₃ after: a) 5 and b) 20 h of milling (polished).](image)

CONCLUSIONS

Powders composites of Cu–Al₂O₃ were obtained using high-energy milling in air. Inert gas-atomized pre-alloyed copper powder containing 2 mass % Al and mixtures of various combinations of particle size with an approximately constant content of Al₂O₃ were used as the starting materials. Depending on the characteristics of the starting powders, the milled powders possessed different properties.

The decrease of the Cu–2Al lattice parameter with milling time was the result of oxidation of aluminum, which precipitated from the pre-alloyed copper forming a fine dispersion of Al₂O₃ particles. Assuming that all the aluminum was oxidized, it was calculated that 3.7 mass % of Al₂O₃ was produced in the copper matrix by internal oxidation of 2 mass % Al.
The full width at half maximum (FWHM) height of the peaks in the X-ray diffraction patterns of the examined powders showed a progressive line broadening with milling time. The effect of the smaller copper particles had a more pronounced affect on the FWHM than the larger Al2O3 particles.

The lattice distortion was found to increase with increasing milling time. The lattice distortion was highest in the Cu–2Al sample strengthened with very small Al2O3 particles, i.e., nano-sized (0.01 μm) Al2O3 particles caused a higher lattice distortion than the coarser micro-sized (0.75 μm) particles. The crystal lattice of the smaller (15 μm) starting copper powder was distorted to a lesser extent than the lattice of the coarser (30 μm) particles.

The Cu–Al2O3 composite powder showed high grain size refinement. The most intensive grain refinement occurred in the early stage (up to about 5 h) of milling. In the period from 5 to 20 h of milling, the grain size of the powders remained practically constant (between 20 and 30 nm), except for the powders with 15 μm copper powder particles, in which case the grain size was 15 nm.

The starting copper particles size and size of the Al2O3 particles affected the morphology, size and microstructure of the composite powders formed during milling.

The Cu*–4Al2O3 composite powder particles did not exhibit a characteristic lamellar structure, due to the small starting copper powder particles (15 μm).

Acknowledgement. Authors are indebted to the Ministry of Science and Technological Development of the Republic of Serbia for financial support of this investigation realized through the Project No. 142027.
REFERENCES

5. G. Ziegler, Powder Met. Int. 10 (1978) 70