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## Characteristics of Cu–Al<sub>2</sub>O<sub>3</sub> composites of various starting particle size obtained by high-energy milling

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**Abstract:** The powder Cu–Al<sub>2</sub>O<sub>3</sub> composites were produced by high-energy milling. Various combinations of particle size and mixtures and approximately constant amount of Al<sub>2</sub>O<sub>3</sub> 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 % Al<sub>2</sub>O<sub>3</sub> nano-sized particles finely dispersed in the copper matrix. The effect of different size of the starting copper and Al<sub>2</sub>O<sub>3</sub> powder particles on the lattice parameter, lattice distortion and grain size, as well as on the size, morphology and microstructure of the Cu–Al<sub>2</sub>O<sub>3</sub> composite powder particles was studied.

**Keywords:** Cu–Al<sub>2</sub>O<sub>3</sub> 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.<sup>1–4</sup> 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 Al<sub>2</sub>O<sub>3</sub> particles by internal oxidation and mechanical alloying. The effects of both the copper and Al<sub>2</sub>O<sub>3</sub> 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,<sup>4</sup> were the subject of this investigation. At the same time, the influence of these

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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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> powder particles

| Material                                    | Size of pre-alloyed copper particles and size of copper particles, μm | Size of Al <sub>2</sub> O <sub>3</sub> particles, μm | Designation                         |
|---|---|--|-------------------------------------|
| Pre-alloyed Cu-2 mass %-Al                  | 30  | 0.010  | Cu-2Al                              |
| Cu-4 mass %-Al <sub>2</sub> O <sub>3</sub>  | 30  | 0.75   | Cu-4Al <sub>2</sub> O <sub>3</sub>  |
| Cu*-4 mass %-Al <sub>2</sub> O <sub>3</sub> | 15  | 0.75   | Cu*-4Al <sub>2</sub> O <sub>3</sub> |

\*After internal oxidation<sup>8</sup>

The milled powders were characterized by X-ray diffraction analysis (XRD) using a Siemens D-500 X-ray powder diffractometer with CuK<sub>α</sub> 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 ( $\Delta d/d$ )<sup>5</sup> 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:<sup>6</sup>

$$\beta \cos \theta = \frac{k\lambda}{D} + \frac{k\Delta d}{d} \sin \theta \quad (1)$$

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 FeCl<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub>. 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 ( $a_{\text{Cu-2Al}} = 0.3624$  nm) and after 20 h of milling ( $a_{\text{Cu-2Al}} = 0.36167$  nm) is 0.20 %. This difference is similar to the difference (0.24 %) in the theoretical lattice parameters of the pre-alloyed powder ( $a_{\text{Cu-2Al}} = 0.36210$  nm) and the copper powder ( $a_{\text{Cu}} = 0.36150$  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 Al<sub>2</sub>O<sub>3</sub> 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 % Al<sub>2</sub>O<sub>3</sub>. On the other hand, the slight increase of the lattice parameters of the mixtures containing Al<sub>2</sub>O<sub>3</sub> particles might be the result of contamination of the copper matrix with steel balls debris during milling.<sup>7</sup>

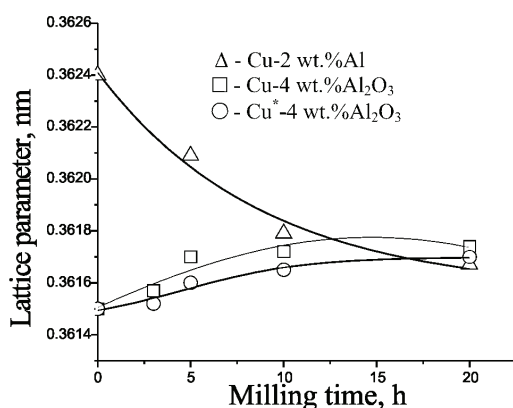


Fig. 1. Lattice parameter vs. milling time for pre-alloyed copper powder and copper Al<sub>2</sub>O<sub>3</sub> powder mixtures.

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 Al<sub>2</sub>O<sub>3</sub> particles (Fig. 2a) were higher than those of a mixture of Cu–4Al<sub>2</sub>O<sub>3</sub> with an average Al<sub>2</sub>O<sub>3</sub> particle size of 0.75 μm (Fig. 2b; the size of the copper powder ≈ 30 μm). The FWHM of the Cu\*–4Al<sub>2</sub>O<sub>3</sub> mixture (Fig. 2c; size of copper powder ≈ 15 μm) were significantly higher than the FWHM of Cu–4Al<sub>2</sub>O<sub>3</sub>. The higher FWHM of the Cu\*–4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> were slightly higher than those of Cu–2Al. These results suggest

that the influence of the smaller starting copper powder particles (15  $\mu\text{m}$ ) on the FWHM prevails over the effect of the  $\text{Al}_2\text{O}_3$  particles size.

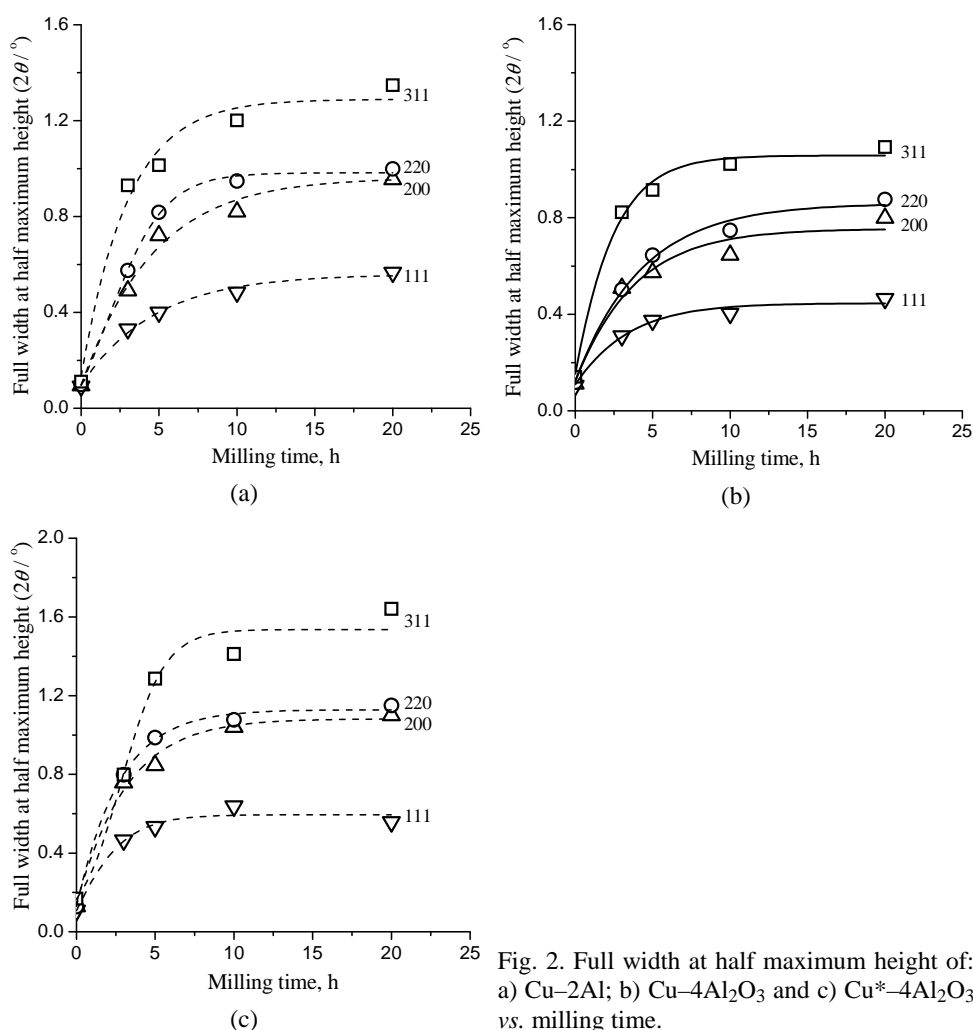


Fig. 2. Full width at half maximum height of: a) Cu-2Al; b) Cu-4 $\text{Al}_2\text{O}_3$  and c) Cu\*-4 $\text{Al}_2\text{O}_3$  vs. milling time.

The progress in the broadening of the FWHM with milling time is a result of a severe lattice distortion and grain size refinement.<sup>9</sup> 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.<sup>9</sup> 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 Al<sub>2</sub>O<sub>3</sub> particles, whereas the lowest lattice distortion was observed in the powder mixture Cu\*–4Al<sub>2</sub>O<sub>3</sub>. 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 Al<sub>2</sub>O<sub>3</sub> strengthening particles increased the lattice distortion, *i.e.*, very small (0.01 μm) Al<sub>2</sub>O<sub>3</sub> 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.<sup>10</sup> The smallest distortions in the Cu\*–4Al<sub>2</sub>O<sub>3</sub> 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 powders<sup>10</sup> 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.

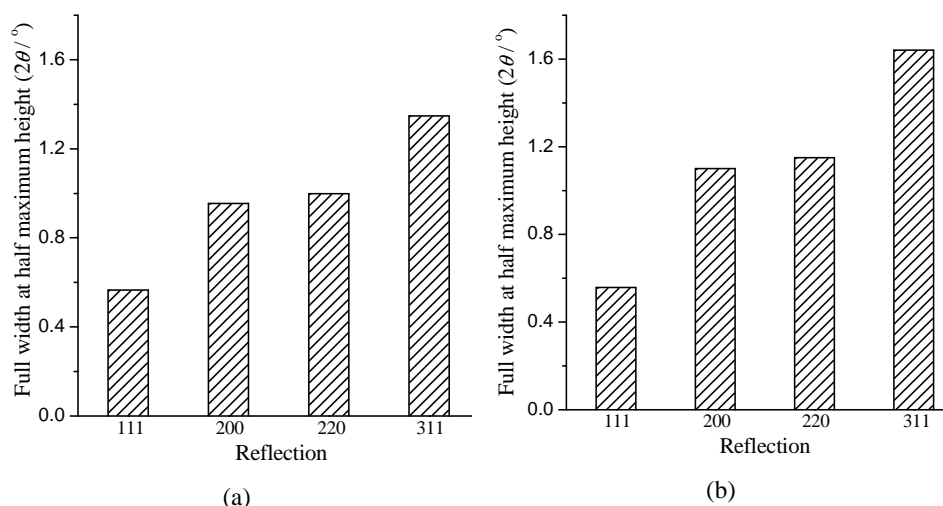


Fig. 3. Full width at half maximum (FWHM) height of: a) Cu–2Al and b) Cu–4 Al<sub>2</sub>O<sub>3</sub> after 20 h of milling.

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\*–4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> particle size, but also the decreasing influence of the elastic strain energy on the lattice distortion of Cu\*–4Al<sub>2</sub>O<sub>3</sub> 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\*–4Al<sub>2</sub>O<sub>3</sub> 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\*–4Al<sub>2</sub>O<sub>3</sub> mixture may be ascribed to the fact that smaller powder particles are more easily subjected to higher deformation during milling than coarser particles.

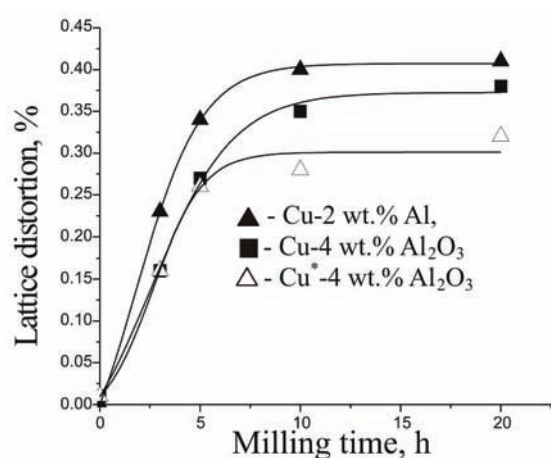


Fig. 4. Effect of milling time on the lattice distortion.

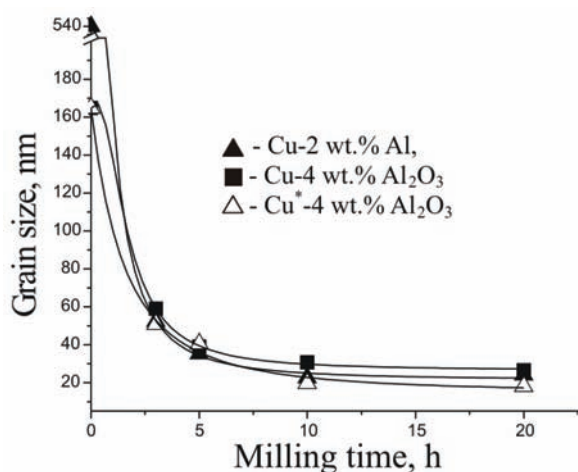


Fig. 5. Effect of milling time on the grain size.

#### *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

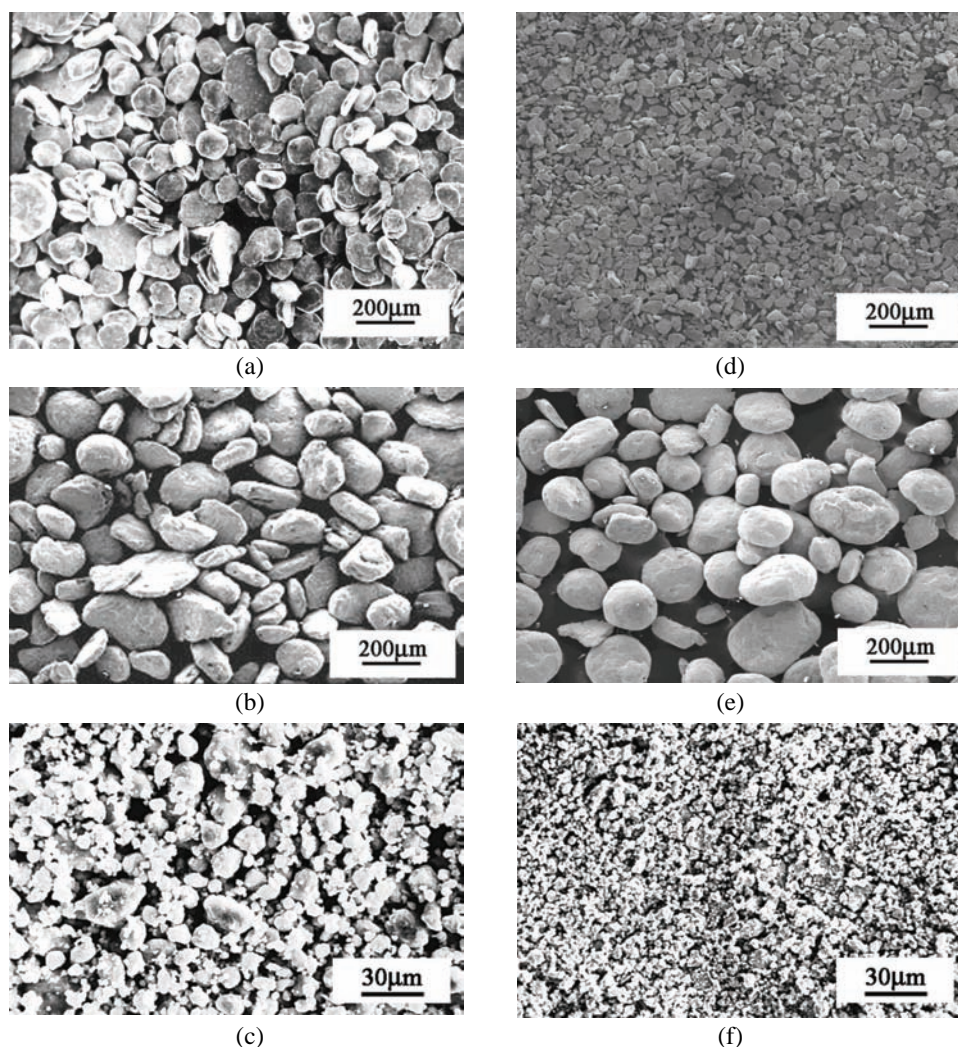


Fig. 6. SEM microphotographs. Morphology of Cu–2Al, Cu–4Al<sub>2</sub>O<sub>3</sub> and Cu\*–4Al<sub>2</sub>O<sub>3</sub> composite powder particles after 5 (a–c) and 20 h (d–f) of milling.

Cu-2Al particles (Fig. 6a) are flattened, whereas the Cu-4Al<sub>2</sub>O<sub>3</sub> and Cu\*-4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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-4Al<sub>2</sub>O<sub>3</sub> 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\*-4Al<sub>2</sub>O<sub>3</sub> particles (Fig. 6f). The results presented in Fig. 6 suggest that the size of the starting copper particles, as well as the Al<sub>2</sub>O<sub>3</sub> 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-4Al<sub>2</sub>O<sub>3</sub> 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\*-4Al<sub>2</sub>O<sub>3</sub> 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

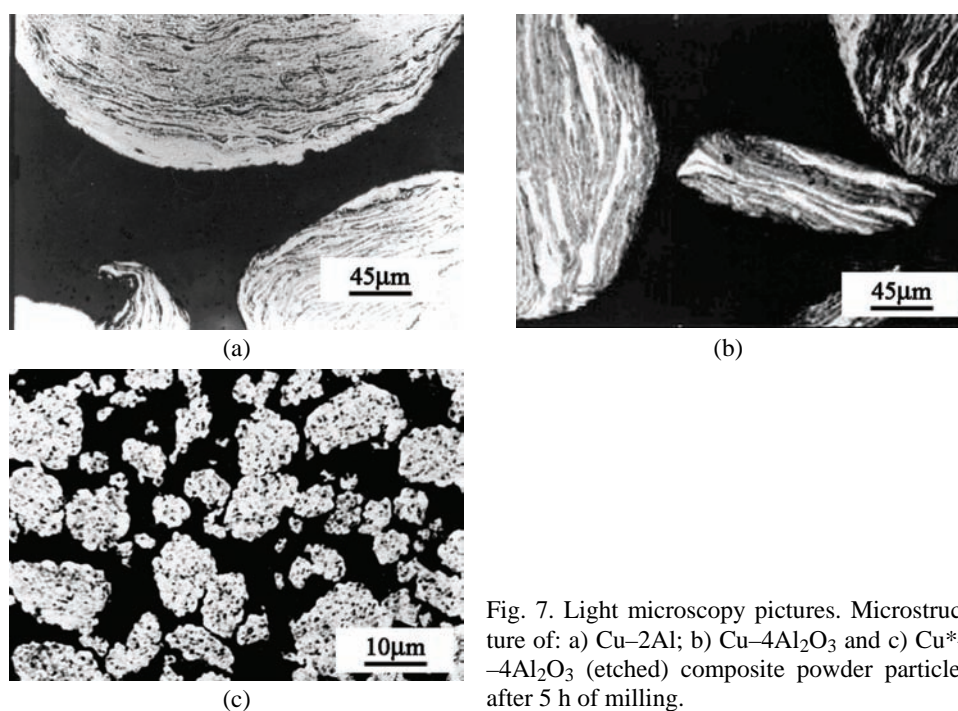


Fig. 7. Light microscopy pictures. Microstructure of: a) Cu-2Al; b) Cu-4Al<sub>2</sub>O<sub>3</sub> and c) Cu\*-4Al<sub>2</sub>O<sub>3</sub> (etched) composite powder particles after 5 h of milling.



particles, except the Cu\*–4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> particles embedded in a matrix of agglomerated copper particles may be seen in the microstructure of the Cu\*–4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> particles in the Cu–4Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> particles were higher, the uniform distribution of Al<sub>2</sub>O<sub>3</sub> particles between deformed copper particles, typical for composites obtained by high-energy milling, may be clearly seen.

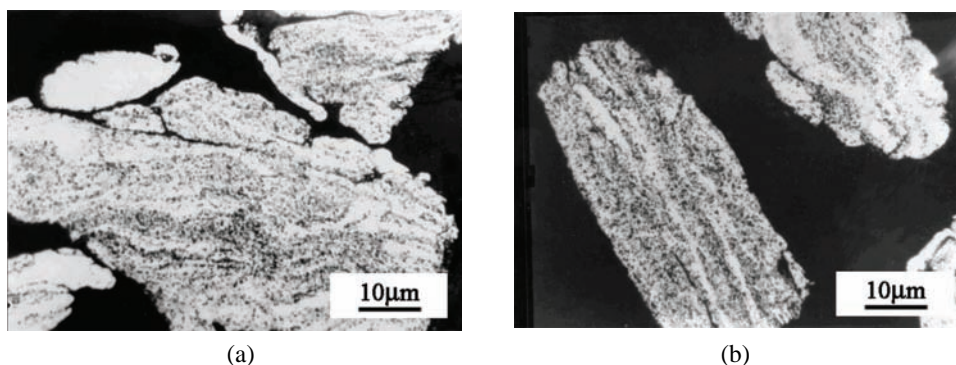


Fig. 8. Light microscopy pictures of Cu–4Al<sub>2</sub>O<sub>3</sub> after: a) 5 and b) 20 h of milling (polished).

#### CONCLUSIONS

Powders composites of Cu–Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> 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 Al<sub>2</sub>O<sub>3</sub> particles. Assuming that the all the aluminum was oxidized, it was calculated that 3.7 mass % of Al<sub>2</sub>O<sub>3</sub> 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 effect on the FWHM than the larger  $\text{Al}_2\text{O}_3$  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  $\text{Al}_2\text{O}_3$  particles, *i.e.*, nano-sized (0.01  $\mu\text{m}$ )  $\text{Al}_2\text{O}_3$  particles caused a higher lattice distortion than the coarser micro-sized (0.75  $\mu\text{m}$ ) particles. The crystal lattice of the smaller (15  $\mu\text{m}$ ) starting copper powder was distorted to a lesser extent than the lattice of the coarser (30  $\mu\text{m}$ ) particles.

The Cu– $\text{Al}_2\text{O}_3$  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  $\mu\text{m}$  copper powder particles, in which case the grain size was 15 nm.

The starting copper particles size and size of the  $\text{Al}_2\text{O}_3$  particles affected the morphology, size and microstructure of the composite powders formed during milling.

The Cu\*–4 $\text{Al}_2\text{O}_3$  composite powder particles did not exhibit a characteristic lamellar structure, due to the small starting copper powder particles (15  $\mu\text{m}$ ).

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#### ИЗВОД

#### КАРАКТЕРИСТИКЕ КОМПОЗИТА Cu– $\text{Al}_2\text{O}_3$ СА РАЗЛИЧИТИМ ПОЧЕТНИМ ЧЕСТИЦАМА ПРАХА ДОБИЈЕНОГ МЛЕВЕЊЕМ У ВИСОКО-ЕНЕРГЕТСКОМ МЛИНУ

ВИШЕСЛАВА РАЈКОВИЋ, ДУШАН БОЖИЋ и МИЛАН Т. ЈОВАНОВИЋ

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Прахови композита на бази Cu– $\text{Al}_2\text{O}_3$  добијени су млевењем у високо-енергетском млину. Почетни материјал представљале су комбинације прахова различитих величина као и смеше различитог састава. Прахови су одвојено млевени у планетарном млину са куглама и то на ваздуху при чему је време млевења било 20 h. За ојачавање основе бакра примењени су унутрашња оксидација и механичко легирање. За време млевења под утицајем унутрашње оксидације у предлегираном праху Cu–2 мас %–Al настало је 3,7 мас % фино диспергованих нано-честица  $\text{Al}_2\text{O}_3$ . Испитиван је утицај почетне величине честица бакра и честица  $\text{Al}_2\text{O}_3$  на параметар кристалне решетке и њену дисторзију, као и на величину кристалног зрна. Такође су испитивани величина честица праха, морфологија и микроструктура композита Cu– $\text{Al}_2\text{O}_3$ .

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## REFERENCES

1. C. Jianyi, W. Mingpu L. Zhou, W. Yanhui, in *China-EU Forum on Nano-sized Technology*, Beijing, 2002, <http://www.863.org.cn/english/Forum/17.doc> (accessed 2002)
2. L. Shuhua, F. Liang, X. Lei, F. Zhikang, *J. Comp. Mat.* **38** (2004) 1495
3. B. Tian, P. Liu, K. Song, Y. Li, Y. Liu, F. Ren, J. Su, *Mat. Sci. Eng. A* **435–436** (2006) 705
4. D. L. Zhang, S. Rayanova, C. C. Koch, R. O. Scattergodd, K. M. Youssef, *Mat. Sci. Eng. A* **410–411** (2005) 375
5. G. Ziegler, *Powder Met. Int.* **10** (1978) 70
6. K. G. Williams, H. W. Hall, *Acta Met.* **1** (1953) 22
7. R. H Palma, A. O. Sepulveda, *Mat. Sci. Forum* **416–418** (2003) 162
8. V. Rajković, D. Božić, M. T. Jovanović, *J. Alloys Compd.* **459** (2008) 177
9. B. Lonnberg, *J. Mat. Sci.* **29** (1994) 3224
10. Y. Kanno, *Powder Met.* **44** (1985) 93.