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PROPERTIES OF Cu-Al_2O_3 COMPOSITES OBTAINED BY HIGH-ENERGY MILLING AND INTERNAL OXIDATION

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Abstract

The inert gas atomized prealloyed copper powders containing 3.wt.%Al was milled up to 20 h in the planetary ball mill to oxidize aluminium *in situ* with oxygen from air. The microhardness of compacts processed from the as-received Cu-3 wt.%Al powder was 104 HV, while in the case of composites microhardness increases up to 300 HV. The grain size of compacted Cu-3 wt.%Al powder after 5 and 20 h of milling were 55 and 30 nm, respectively. Increased microhardness and improved thermal stability of compacted composites are the result of very small grain size of compacts and alumina particles formed by internal oxidation during high-energy milling. The values of electrical conductivity of compacted Cu-3 wt.%Al powder (37 and 38 % IACS after 5 and 20 h of milling, respectively) imply that the electrical conductivity depends not only on the presence of alumina particles but also on density of composites.
Key words: Cu-Al_2O_3 composite, high-energy milling, internal oxidation, structure, microhardness, electrical conductivity, thermal stability

Introduction

Reinforced copper matrix has been extensively studied in recent years due to attained better properties than pure copper and copper alloys reinforced by precipitation and solid solution hardening. Obtaining copper-based composites with a fine dispersion of alumina particles by high energy milling and internal oxidation [1-4] is mainly applied and seems to be a very common technique in powder metallurgy for processing this type of a material. Although much work has been done, the results reported in the literature are rather inconsistent and the influence of many parameters regarding reinforcing phenomena of these composites still has to be explained.

In this study the effect of Al_2O_3 particles processed by internal oxidation during high – energy milling of prealloyed copper powders containing 3 wt.%Al on

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strengthening, thermal stability and electrical conductivity of Cu - Al_2O_3 composite was examined.

Experimental

The inert gas atomized prealloyed copper powders containing 3 wt.%Al were milled in air in the planetary ball mill for 3 h and then in steps of 5 h up to 20 h in order to obtain a fine grain structure and formation of alumina dispersoids by internal oxidation. The weight ratio of powders to steel balls was 1:35. During high-energy milling of prealloyed copper powders, aluminium being more noble than copper oxidizes first reacting with oxygen from the air and forming a uniform distribution of nano-sized alumina particles [1]. It was calculated that by internal oxidation of 3 wt.% aluminium 5.6 wt.% of alumina was generated in the copper matrix. After milling, all powders were treated in hydrogen at 400 ^{0}C for 1 h in order to eliminate copper oxides. Composites (1 cm in diameter and 1cm in height) were obtained by hot pressing in an argon atmosphere at 800 ^{0}C for 3h under the pressure of 35 MPa. Composites from 20 h-milled powders were treated in argon at 800 ^{0}C for 5 h with the idea to examine their thermal and electrical stability. Composites processed from electrolytic copper powder were also prepared under the same conditions as prealloyed compacts.

Cu-3 wt.%Al powders and composites were characterized by X-ray diffraction analysis and optical microscopy. Samples for optical microscopy were mounted in 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.

The lattice parameter was determined using the least square root method.

The average lattice distortion, *i.e.* relative deviation of the lattice parameters from their mean value ($\Delta d/d$) and the grain size (D) of Cu-3 wt.%Al powder and compact was determined from the broadening (β) of the first four diffraction lines (111, 200, 220 and 311) using the approach developed by Williams and Hall [5]:

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

where the shape factor k = 0.9 and radiation wave length λ=0.15405 nm, $\Delta d/d$ is the average lattice distortion, i.e. relative deviation of the lattice parameters from their mean value [6]. X-ray diffraction analysis was performed using a "Siemens D-500" X-ray powder diffractometer with Cu-K_α Ni filtered radiation.

Microhardness, electrical conductivity and density of composites were measured. Detailed information of these measurements were presented in a previous paper [7]. Values of density, microhardness and electrical conductivity represent the mean value of five measurements performed on the same compact.

Results and discussion

The relationship between Cu-3 wt.%Al lattice parameter and milling time is shown in Fig. 1. The rapid decrease in lattice parameter occurs at the very beginning of the milling process, then the change in lattice parameter decreases slowly with the prolonged milling. The decrease in lattice parameter is assumed to be due to the

oxidation of dissolved aluminium, which forms alumina dispersoids. Since the difference in lattice parameters (0.32 %) of prealloyed Cu-3 wt.%Al powders before ($a_{Cu\text{-}3\ wt.\%Al}$ = 0.36385 nm) and after milling ($a_{Cu\text{-}3\ wt.\%Al}$ = 0.36270 nm) is similar to the difference (0.30 %) in theoretical lattice parameters of the prealloyed powder ($a_{Cu\text{-}3\ wt.\%Al}$ = 0.36260 nm) and the copper powder (a_{Cu} = 0.36152nm), it is assumed that after 20 h of milling almost all aluminium diffused from the copper matrix. Considering that the complete amount of aluminium was oxidized**,** it was calculated that 5.6 wt.% of alumina was generated in the copper matrix by internal oxidation of prealloyed coper with 3 wt.% aluminium.

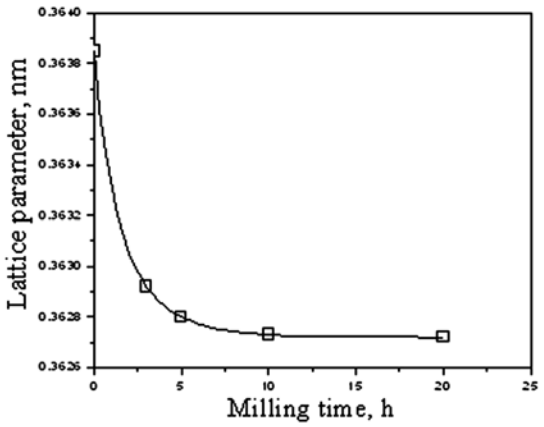

Figure 1. Lattice parameter vs. milling time for Cu-3 wt.%Al powders.

X-ray diffraction pattern of Cu-3 wt.%Al powder shows a progress in line broadening with milling time (Fig. 2) as a result of a severe lattice distortion and grain size refinement [6,8].

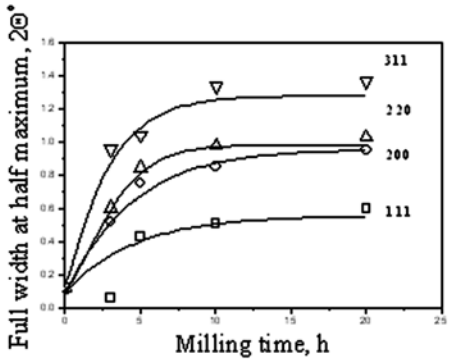

Figure 2. Full width at half maximum (FWHM) vs. milling time for Cu-3 wt.%Al powders.

The effect of milling time on the grain size and lattice distortion of examined powder particles is presented in Fig. 3. As can be seen, the most intensive grain refinement occurs in the

early stage of milling when the grain size abruptly decreases from about 542 to about 55 nm, whereas in the period from 5 h to 20 h the grain size remains practically constant, *i.e*. approximately 30 nm. Fig. 3 also illustrates a strong increase of lattice distortion during 5 h of milling. At longer milling time the lattice distortion becomes less evident. This result is in agreement with some earlier hypothesis that the deformation of particles occurs during the early stage of milling [8]. The effect of milling time on the grain size and lattice distortion of examined powder particles is presented in Fig. 3. As can be seen, the most intensive grain refinement occurs in the

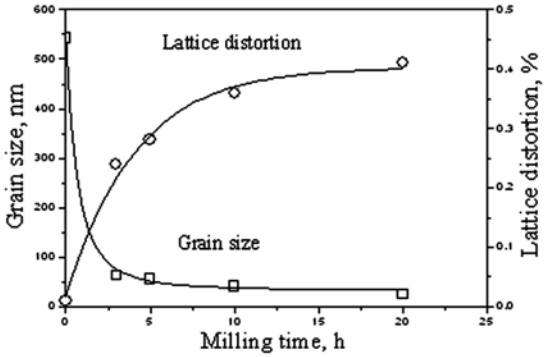

Figure 3. Effect of milling time on grain size and lattice distortion of Cu-3 wt.%Al

Microhardness of composites depends on the previous milling time of prealloyed copper powder (Fig. 4). Microhardness of all composites increases with the milling time showing that 20 h milled composites exhibit significantly higher microhardness (up to 300 HV) than composites processed from as-received powders (104 HV). The change in microhardness occurs within 5 h of milling and prolonged milling results in a negligible change in microhardness. Since after 5 h of milling (see Fig. 3), the grain size was significantly decreased, this observation suggests that small grain size has a very strong effect on hardening of Cu-3 wt.%Al. In spite to the fact that the data on alumina particles formed during internal oxidation were not known, the effect of these particles on microhardness cannot be neglected. The microhardness (260 HV) of composite processed from 5 h-milled powder with grain size of about 55 nm is 3.5 times greater than that processed from as-received electrolytic copper powder (68 HV) compacted under the same conditions. The coarsening of alumina particles leads to lowering of microhardness, but since in the case of this study microhardness remains constant up to 20 h of milling, it may be assumed that the coarsening of alumina dispersoids did not occur, or the effect of small grain size dominates over the process of hardening. This assumption confirms the results published by Mehta *et al.* [9] and Nadkarni and Synk [10] who reported that alumina content above 0.65wt.% did not result in increase of hardening.

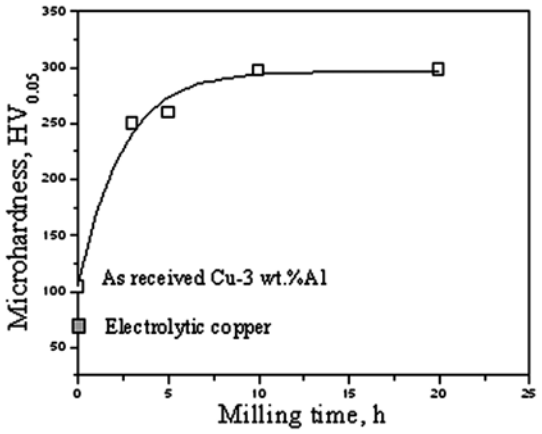

Figure 4. Effect of milling time on microhardness of Cu-3 wt.%Al composites.

The results of effect of the high temperature exposure at 800°C for 5 h on the grain size and microhardness of composites processed from 5 and 20 h-milled powders are shown in Table 1. In general, Cu-3 wt.%Al composites are characterized by low increase in the grain size and by low decrease in the microhardness as a consequence of the presence of very fine Al_2O_3 particles. A previous investigation [1] showed that the most of alumina particles formed *in situ* by oxygen from the air are finer than 100 nm and well within the range required for the dispersion hardening [11].

Table 1. The effect of high temperature exposure at 800°C for 5 h on the grain size and microhardness of Cu-3 wt.% Al composites processed from 5 and 20 h milled powders.

Properties	Before exposure		After exposure	
	Milling time, h		Milling time, h	
	5	20	5	20
Grain size, nm	75	45	82	49
Microhardness, HV	260	300	182	285

As far as properties of composites are concerned, the measured densities of compacted Cu-3 wt.%Al powder after 5 h and 20 h of milling (7.74 and 7.85, respectively) in comparison with theoretical density (8.46 gcm-3) were 93.1 % and 94.5 % indicating that the densification by hot pressing of milled prealloyed powder was not completed. Hot extru**sion** seems to be a common method of compaction because the measured density of Cu-based extruded composites is greater than 99.3% [12].

The results of electrical conductivity of composites after different time of milling are summarized in Table 2. No significant change in electrical conductivity was detected with increase of milling time. The electrical conductivity of compacted Cu-3 wt.%Al powder after 5 and 20 h of milling were 37 and 38 % IACS. It should be noted that the conductivity requirement for the copper-based alloys for higher temperature

applications is 50% IACS [13]. On the other side, electrical conductivity of commercially available Cu - Al_2O_3 based composites ranging between 78 and 92% IACS, is related to the lower content of alumina (less than 3wt. %) [10]. Much lower values of electrical conductivity measured in this work were not only the consequence of the presence of higher amount of alumina particles in the copper matrix, but are also the result of inadequate density of Cu-3 wt.%Al composites.

Table 2. The effect of milling time on electrical conductivity of Cu-3 wt.%Al composites.

Electrical conductivity, %IACS				
Milling time, h				
0*	3	5	10	20
27	34.5	37	37.5	38

* composites processed from as-received and non-milled powders

The effect of high-temperature exposure on the electrical conductivity of composites processed from 5 and 20 h milled powders is summarized in Table 3. Somewhat higher electrical conductivity after exposure is related to the slight increase in the grain size [14] (see Table 1). In any case this result shows high temperature stability at 800°C.

Table 3. The effect of high-temperature exposure at 800°C for 5 h on electrical conductivity of Cu-3 wt.%Al composites processed from 5 and 20 h milled powders.

Electrical conductivity, % IACS			
Before exposure		After exposure	
Milling time, h		Milling time, h	
5	20	5	20
37.5	38	40.3	44

Figure 5 illustrates the microstructure of as-received and milled Cu-3 wt.% Al powder particles (Fig. 5a and c**,** respectively) and composites after 0 h and 20 h of milling (Fig. 5b and d, respectively). Comparing the microstructure of the as-received powder (Fig. 5a) with the milled powder particles (Fig. 5c) it is evident that milled powder particles exhibit lamellar structure typical for high energy treated powders, where lamellae represent individual plastically deformed prealloyed copper particles. Fig. 5d shows that the lamellar structure of particles is retained in composite, i.e. following hot-pressing. The light areas (denoted by arrows) in the microstructure of Cu-3 wt.% Al composite (Fig. 5d) indicate that recrystallization occurred during hot-pressing. The recrystallization in Cu-3 wt.% Al composite was initiated at the corners of the particle powder where the concentration of stresses imposed during compaction was highest.

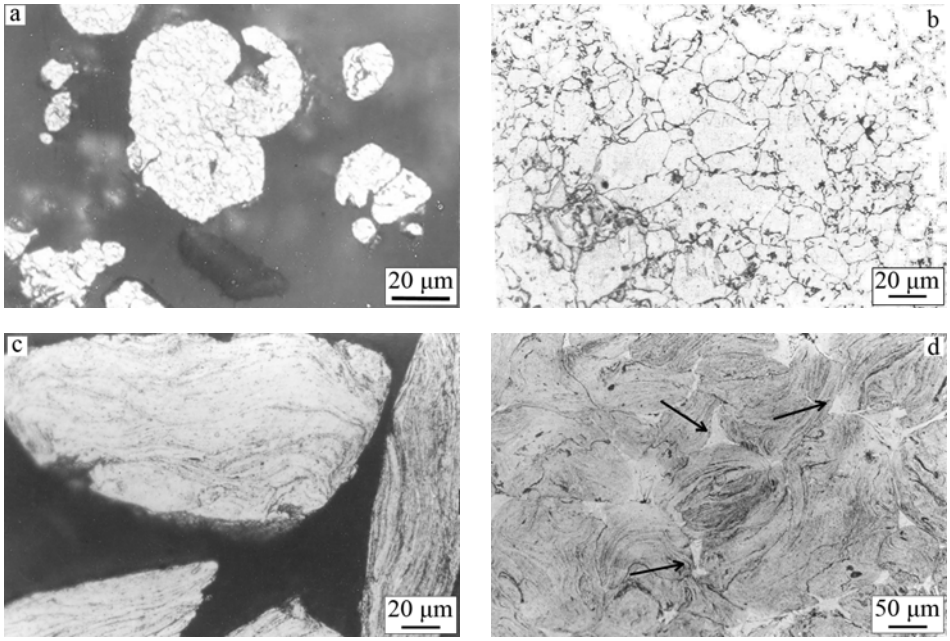

Figure 5. Light microscopy. Microstructures of Cu-3 wt.% Al powders and composites. (a) as-received powder; (b) as-received hot compacted powder; (c) 20 h-milled powder and (d) hot compacted 20 h- milled powder.

Conclusions

The following conclusions can be drawn from the present study:

1. The decrease of Cu-3 wt.%Al lattice parameter with milling time was the result of oxidation of aluminum which precipitated from prealloyed copper forming a fine dispersion of alumina particles. Assuming that the complete amount of aluminum was oxidized, it was calculated that 5.6 wt.% of Al_2O_3 was produced in the copper matrix by internal oxidation of 3 wt.% Al.
2. Increase in microhardness of Cu-3 wt.%Al composites is a consequence of very small grain size formed during high energy milling of starting and the presence of very fine alumina particles generated by internal oxidation. The microhardness of compacts processed from the as-received Cu-3 wt.%Al powder was 104 HV, while in the case of composites originating from milled powders microhardness increases up to 300 HV.
3. During high-temperature exposure at 800°C Cu-3 wt.%Al composites retain relatively high microhardness which indicates their high thermal stability.
4. The electrical conductivity of Cu-3 wt.%Al composites does not depend on the milling time and remained practically unchanged after high-temperature exposure. The values of electrical conductivity of compacted Cu-3 wt.%Al powder (37 and 38 % IACS after 5 and 20 h of milling, respectively) imply that the electrical

conductivity depends not only on the presence of alumina particles, but also on density of composites.

5. The milled Cu-3 wt.%Al powder particles exhibit lamellar structure typical for high energy treated powders where lamellae represent individual plastically deformed prealloyed copper particles. The lamellar structure of particles is retained in composites, i.e. following hot-pressing.

Acknowledgments

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