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PROPERTIES OF Cu-Al_2O_3 POWDER AND COMPACT COMPOSITES OF VARIOUS STARTING PARTICLE SIZE OBTAINED BY HIGH-ENERGY MILLING

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Abstract

Copper-based composites were obtained using high energy milling. The inert gas-atomized prealloyed copper powder (average particle size - 30 μm) containing 2 wt.% Al, and the mixture of electrolytic copper powder (average particle size – 30 and 15 μm) with 4 wt.% comertial Al_2O_3 powders (average particle size –0.75μm) served as starting materials. These powders were separately milled in air up to 20 h in the planetary ball mill. Milling of prealloyed copper powder promotes formation of nano-sized Al_2O_3 particles by internal oxidation with oxygen from air**.** It was calculated that by internal oxidation of 2 wt.% aluminum approximately 3.7 wt.% Al_2O_3 was generated in the copper matrix. Milled powders were treated in hydrogen at 400 ^{0}C for 1 h in order to eliminate copper oxides formed at the surface during milling. Compaction executed by hot-pressing was carried out in an argon atmosphere at 800 ^{0}C for 1 h under the pressure of 35 MPa. Compacts obtained from 5 and 20 h milled powders were additionally subjected to high-temperature exposure in argon at 800 ^{0}C for 1 and 5 h. The results were discussed in terms of the effects of different size of starting powder particles on structure, strengthening of copper matrix, thermal stability and electrical conductivity of the Cu - Al_2O_3 composite.

Key words: Cu-Al_2O_3 composite, mechanical alloying, internal oxidation, structure, microhardness, thermal stability, electrical conductivity

1. Introduction

Dispersion strengthened Cu - Al_2O_3 composite materials are extensively used as materials for products which require high-strength and electrical properties, such as electrode materials for lead wires, relay blades, contact supports and electrode materials for spot welding. Electrode tips made of this composite material which operating temperature is approximately 800°C demonstrate much higher softening (recrystalization) temperature than tips made of standard high-strength and high-conductivity copper alloys [1]. Copper-based composites with a fine dispersion of Al_2O_3 particles produced by high-energy milling has been extensively studied in recent years due to attained better properties than pure copper and precipitation or solid solution hardened copper [1-5]. Further, high-energy milled powders are characterized by very fine, nano-scaled grain structure, which may be retained even during compaction. This fine-grained structure contributes to copper matrix strengthening together with Al_2O_3 particles.

In this study the copper matrix was strengthened by Al_2O_3 particles by internal oxidation and mechanical alloying. The effect of the various size of copper and Al_2O_3 powder particles on structure, strengthening, thermal stability and electrical conductivity of Cu - Al_2O_3 composite was the object of this paper.

2. Experimental

The inert gas-atomized prealloyed copper powder (average particle size - 30 μm) containing 2 wt.% Al (designation: Cu-2 wt.% Al), and the mixture of electrolytic copper powder (average particle size – 30 and 15 μm) with 4 wt.% Al_2O_3 (designation: Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3**,** respectively) served as starting materials. Commercial grade of Al_2O_3 powder with average particle size of 0.75 μm was used. These powders were separately milled in air up to 20 h in the planetary ball mill. The weight ratio of powder to steel balls was 1:35.

Milling of prealloyed copper powder promotes formation of nano-sized Al_2O_3 particles by internal oxidation with oxygen from air**.** Assuming that the complete amount of aluminum was oxidized**,** it was calculated that by internal oxidation of 2 wt.% aluminum approximately 3.7 wt.% Al_2O_3 was generated in the copper matrix.

In the next process, powders were treated in hydrogen at 400 ^{0}C for 1 h in order to eliminate copper oxides formed at the surface during milling. Compaction executed by hot-pressing was carried out in an argon atmosphere at 800 ^{0}C for 1 h under the pressure of 35 MPa. Compacts obtained from 5 and 20 h milled powders were additionally subjected to high-temperature exposure in argon at 800 ^{0}C for 5 h in order to examine their thermal and electrical stability.

The powders and compacts were characterized by X-ray diffraction analysis, optical and scanning electron microscope (SEM). Samples for optical microscope were mounted in acrylic resin. Polishing was performed using the standard procedure, whereas the mixture of 5 g $FeCl_3$ and 50 ml HCl in 100 ml distilled water was used for etching.

X-ray diffraction analysis was performed using “Siemens D-500” X-ray powder diffractometer with CuK_α Ni filtered radiation. The grain size (D) 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 [6]:

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

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 [9].

The strengthening of the copper matrix was estimated by microhardness measurements (applied load was 50 g). The electrical conductivity (%IACS, $IACS_{20°C}$ = 0.5800 $microhm^{-1}cm^{-1}$) of polished compacts was measured using "Sigmatest" apparatus operating at 60 KHz with electrode diameter of 14 mm, whereas the density of compacts (ρ) was determined by the Archimedes method. The theoretical density of compacts was calculated from the simple rule of mixtures, taking the full dense values for copper and Al_2O_3 8.96 and 3.95 gcm^{-3}, respectively.

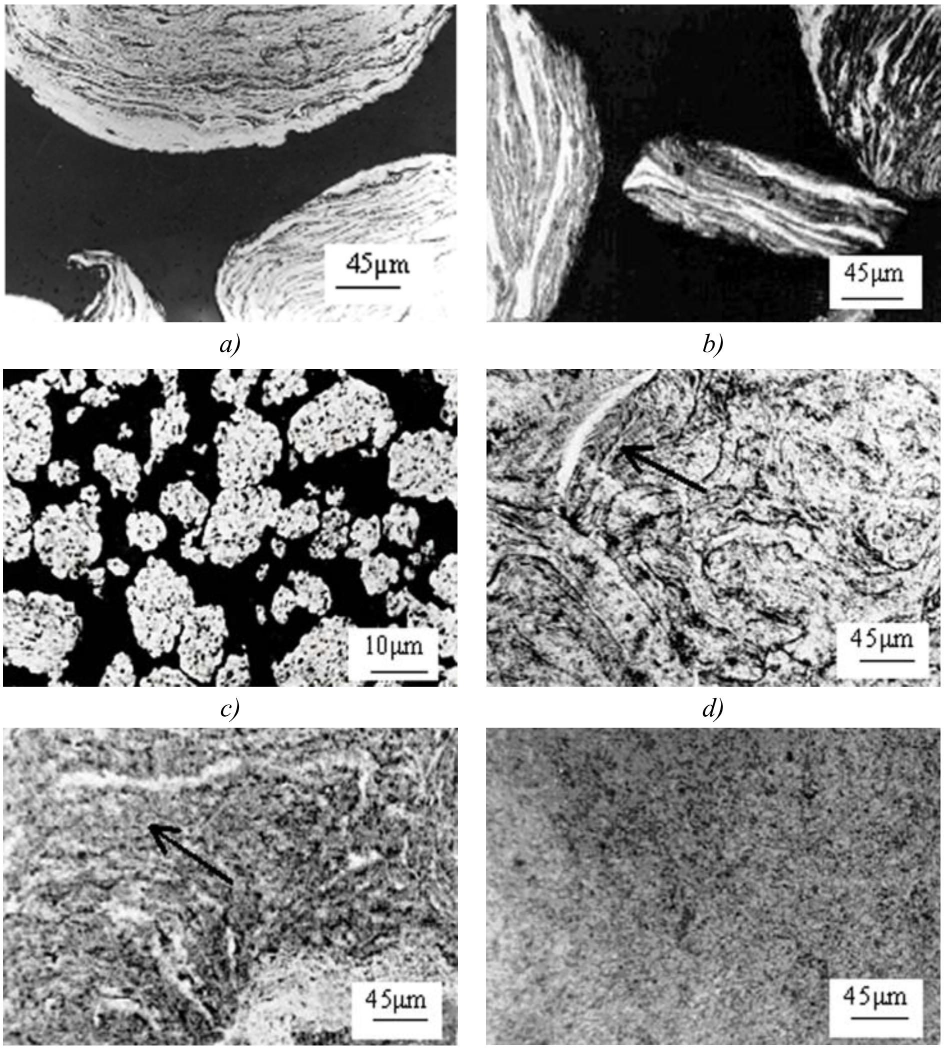
Values of density, microhardness and electrical conductivity represent the mean value of five measurements performed on the same compact.

3. Results and discussion

The microstructure of powder particles and compacts after 5 h of milling time is shown in Fig. 1. Fig.(1a-c) illustrates the microstructure of composite powder particles. It was confirmed that milled composite powder particles, except Cu^*-$4Al_2O_3$ particles, exhibit lamellar structure typical for high-energy milled powders (Fig. 1a,b). Lamellae represent individual plastically deformed prealloyed copper (Fig. 1a) and electrolytic copper powder particles (Fig. 1b). Applying higher magnification the uniform distribution of commercial Al_2O_3 particles embedded in the matrix of agglomerated copper particles may be seen in the microstructure of Cu^*-$4Al_2O_3$ composite powder particle (Fig. 1c). In these milled powder particles lamellae are non visible probably due to very small powder particle size.

The compacts retained lamellar structure of high-energy milled powder particles which is illustrated in Fig.1(d-f). Compared with Cu-2 wt.%Al and Cu-4 wt.% Al_2O_3 compacts (Fig. 1d and e, respectively), lamellae in Cu^*-4 wt.% Al_2O_3 compact are much finer (Fig. 1f). The light areas (denoted by arrows) in the microstructure of Cu-2 wt.%Al and Cu-4 wt.% Al_2O_3 compacts indicate that the recrystalization occurred during hot-pressing contrary to Cu^*-4 wt.% Al_2O_3 compact. These microstructural variations are the consequence of different starting copper particle size.

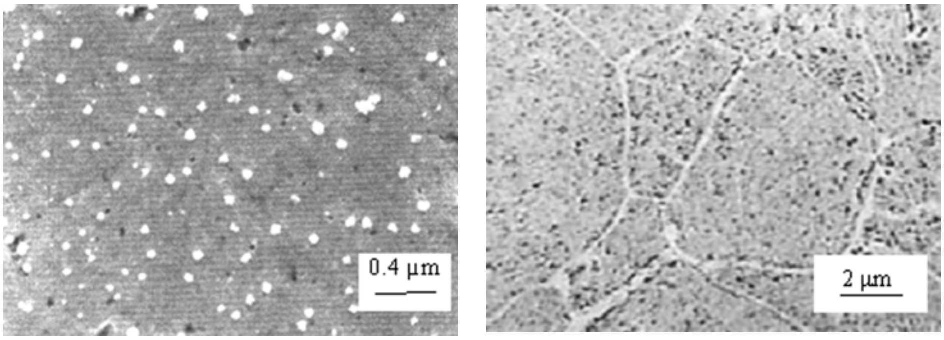
The presence and distribution of Al_2O_3 particles in the copper matrix of Cu-2 wt.% Al and Cu-4 wt.%Al_2O_3 compacts processed from 5 h-milled powders is shown in Fig.2a and b, respectively. A very uniform distribution of Al_2O_3 particles exists in both compacts. According to Fig.2a, the size of most Al_2O_3 particles formed by internal oxidation during high energy milling of prealloyed powders is approximatly 100 nm or even smaller. Fig.2b shows that commercial Al_2O_3 particles size was practically unchanged suggesting that fracture or agglomeration of these particles did not occur during high-energy milling.



a) b) c) d) e) f)

Fig . 1. Light microscopy. Microstructure of powder particles and compacts after 5 h of milling time (a) and (d) Cu-2 wt.%Al, (b) and (e) Cu-4 wt.% Al_2O_3, (c) and (f) Cu^*-4 wt.% Al_2O_3

The size of grains, i.e crystallites formed inside powder particles during milling abruptly decreases with milling time (Fig. 3). This decrease was highest up to 5 h of milling when the grain size is between 40 and 60 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^*-$4Al_2O_3$ powders with the grain size somewhat smaller, i.e. 15 nm. Generally, the smallest grain size found in the Cu^*-$4Al_2O_3$ mixture may be ascribed to the fact that smaller powder particles are more easily subjected to higher deformation during milling than coarser particles.



a) *b)*

Fig . 2. SEM and light microscopy. (a) SEM micrograph of polished Cu-2 wt.% Al and (b) light micrograph of polished Cu-4 wt.%Al_2O_3 compacts processed from 5 h-milled powders.

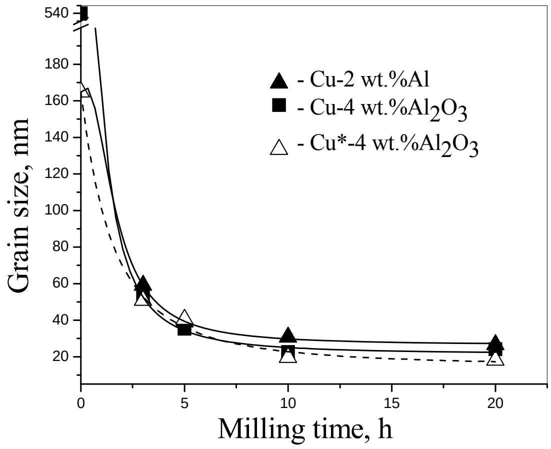


Fig. 3. Effect of milling time on grain size inside powder particles.

The effect of the milling time of powders on microhardness of compacts processed from these powders is shown in Fig. 4. The microhardness of compacts increases with milling time. This increase in microhardness is a consequence of a fine dispersion of Al_2O_3 particles and refined grain structure. While the microhardness of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 compacts increases continuously with milling time, the largest increase in microhardness of Cu-2 wt.% Al compacts occurs at 5 h milling. Further milling results in negligible change in microhardness of Cu-2 wt.% Al compacts. The maximum microhardness values of compacts processed from 20 h-milled Cu-2wt.%Al, Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 powders attains 2310, 1730 and 1790 MPa, respectively.

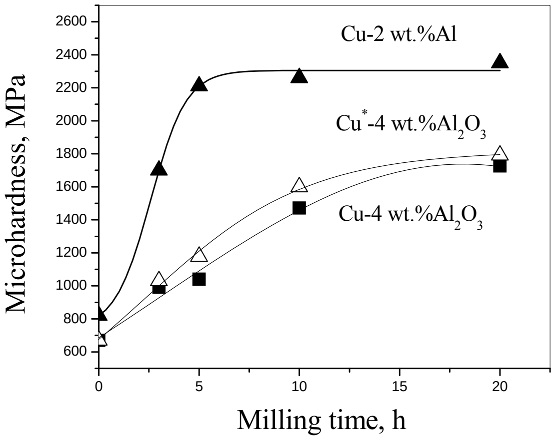


Fig. 4. Effect of milling time on micro- hardness of compacts

The microhardness of Cu-2 wt.% Al compacts is higher than microhardness of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 compacts as a consequence of the fact that nano-sized Al_2O_3 particles act as a stronger strengthening parameter of the copper matrix than the micro-sized Al_2O_3 particles.

The difference in the microhardness of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 compacts is the result of difference in grain size of compacted particles (Table 1). The smallest grain size measured in Cu*-4Al_2O_3 compacts may be ascribed to the smaller particle size of milled powders [7]. Although the grain size of Cu-2 wt.% Al compacts is bigger than other compacts (see Table 1), the fact that this compact exibits highest microhardness indicates that the effect of nano-sized Al_2O_3 particles in raising hardness is more pronounced than the grain size.

Table 1. Grain size of compacts processed from 5 and 20 h-milled powders before and after high-temperature exposure at 800°C.

Compact	Grain size, nm			
	Before exposure (at room temperature)		After exposure	
	Milling time, h		Milling time, h	
	5	20	5	20
Cu-2 wt.%Al	45	61	53	62
Cu-4 wt.%Al_2O_3	65	36	69	72
Cu^*-4 wt.%Al_2O_3	57	29	60	65

Table 2 shows the thermal stability through the change of microhardness of 5 and 20 h-milled compacts during high-temperature exposure at 800 ^{0}C. The results indicate that compacts still retain enhanced microhardness in different extent mainly depending on Al_2O_3 particle size and grain size**.**

Table 2. Microhardness of compacts processed from 5 and 20 h-milled powders before and after high-temperature exposure at 800°C

Compact/ Milling time	Microhardness, MPa		
	Before exposure (at room temperature)	After exposure	
		800°C/1h	800°C/5h
Cu-2 wt.%Al/5h	2250	1810	1390
Cu+2 wt.%Al/20h	2310	2200	1500
Cu-4wt.%Al_2O_3/5h	1050	640	410
Cu-4wt.%Al_2O_3/20h	1730	680	570
Cu^*-4 wt.%Al_2O_3/5h	1180	720	600
Cu^*+4 wt.%Al_2O_3/20h	1790	840	650

The change of grain size of compacts processed from 5 and 20 h-milled powders after high-temperature exposure at 800 ^{0}C for 5 h is also shown in Table 1. The smallest grain size attained in Cu-2 wt.% Al compacts after exposure at 800 ^{0}C may be ascribed to nano-sized Al_2O_3 particles acting as barrier to grain growth under the influence of enhanced diffusion processes at high temperature.

Table 3. The effect of high-temperature exposure at 800 ^{0}C for 5 h on electrical conductivity of compacts processed from 5 and 20 h-milled powders.

Compact	Electrical conductivity, % IACS			
	Before exposure		After exposure	
	Milling time, h		Milling time, h	
	5	20	5	20
Cu-2 wt.%Al	30.5	32.1	33	33.2
Cu-4 wt.%Al_2O_3	47	46	48	48
Cu-4* wt.%Al_2O_3	46.8	45.4	47.7	48.3

The effect of milling time (5 h and 20h) and high-temperature exposure (800 ^{0}C for 5 h) on the electrical conductivity of compacts is summarized in Table 3. According to these results, the electrical conductivity of compacts does not depend on the milling time. Also, electrical conductivity remained practically unchanged after high-temperature exposure. The average values of electrical conductivity of compacts processed from milled prealloyed powders (Cu-2 wt.% Al) are lower than the conductivity of compacts processed from the milled powder mixtures (Cu-4 wt.%Al_2O_3 Cu^*-4 wt.%Al_2O_3). These results suggest that nano-sized Al_2O_3 particles have higher effect on the electrical conductivity then micro-sized particles, i.e. very small Al_2O_3 particles form a great number of interfaces considered as a possible source of additional electron scatter, which is a significant factor in reducing conductivity [8]. Thus, the extent of reduction of the electrical conductivity of Cu-2 wt.%Al compacts with nano-sized Al_2O_3 particles (3.7 wt.%) is higher than in Cu-4 wt.%Al_2O_3 and Cu^*-4 wt.%Al_2O_3 compacts with approximatelly the same (4 wt.%) amount micro-sized Al_2O_3 particles.

4. Conclusion

- The mixing of approximately the same amount of different Al_2O_3 particle size and the copper particles of various size (30 μm and 15 μm) induces different effects on the microstructure and properties of Cu - Al_2O_3 composite.
- Internal oxidation of aluminum during high-energy milling generated in prealloyed Cu-2 wt.% Al powders approximately the same amount of Al_2O_3 particles (3.7 wt.% and 100nm in size) in the copper matrix as in the case when 4 wt% Al_2O_3 commercial particles (0.75 μm in size) were added to electrolytic copper powders.
- The microhardness of Cu-2 wt.% Al composite is higher than microhardness of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 compacts as a consequence due to nano-sized Al_2O_3 particles acting as a stronger strengthening parameter of the copper matrix.
- The Cu^*-4 wt.% Al_2O_3 composite showed better combination of the microhardnes and thermal stability than Cu-4 wt.% Al_2O_3 composite due to smaller starting copper powder particle size.
- The electrical conductivity of compacts does not depend on the milling time. The average values of electrical conductivity of compacts processed from milled prealloyed powders (Cu-2 wt.% Al) are lower than the conductivity of compacts processed from the milled powder mixtures (Cu-4 wt.%Al_2O_3 Cu^*-4 wt.%Al_2O_3). These results suggest that nano-sized Al_2O_3 particles have higher effect on the electrical conductivity then micro-sized particles.

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