The Influence of Powder Particle Size on Properties of Cu-Al$_2$O$_3$ Composites

V. Rajkovic[1*], D. Bozic[1], M. Popovic[2], M. T. Jovanovic[1]
[1] Institute of Nuclear Sciences "Vinca", P.O. Box 522, 11001 Belgrade, Serbia
[2] Faculty of Technology and Metallurgy, Karnegijeva 4, 11020 Belgrade, Serbia

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Abstract:

Inert gas atomized prealloyed copper powder containing 2 wt.% Al (average particle size ≈ 30 μm) and a mixture consisting of copper (average particle sizes ≈ 15 μm and 30 μm) and 4 wt.% of commercial Al$_2$O$_3$ powder particles (average particle size ≈ 0.75 μm) were milled separately in a high-energy planetary ball mill up to 20 h in air. Milling was performed in order to strengthen the copper matrix by grain size refinement and Al$_2$O$_3$ particles. Milling in air of prealloyed copper powder promoted formation of finely dispersed nano-sized Al$_2$O$_3$ particles by internal oxidation. On the other side, composite powders with commercial micro-sized Al$_2$O$_3$ particles were obtained by mechanical alloying. Following milling, powders were treated in hydrogen at 400 ^{0}C for 1h in order to eliminate copper oxides formed on their surface during milling. Hot-pressing (800 ^{0}C for 3 h in argon at pressure of 35 MPa) was used for compaction of milled powders. Hot-pressed composite compacts processed from 5 and 20 h milled powders were additionally subjected to high temperature exposure (800 ^{0}C for 1 and 5 h in argon) in order to examine their thermal stability. The results were discussed in terms of the effects of different size of starting powders, the grain size refinement and different size of Al$_2$O$_3$ particles on strengthening, thermal stability and electrical conductivity of copper-based composites.
Keywords: Cu-Al$_2$O$_3$ composite, internal oxidation, mechanical alloying, different size of starting powder particles, hot-pressing, properties.
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1. Introduction

Copper-based composites with a fine dispersion of Al$_2$O$_3$ particles produced by high-energy milling have been extensively studied in recent years [1-3] due to attained better properties than for pure copper and precipitation or solid solution hardened copper. Furthermore, high-energy milled powders are distinguished by a 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$_2$O$_3$ particles.

Since many parameters strongly influence the microhardness and other properties of a strengthened copper matrix, investigations in this area are not yet completed and many elements regarding strengthening phenomena of these composites still have to be explained.

Dispersion strengthened Cu- Al$_2$O$_3$ composite materials are extensively used as materials for products, which require high-strength and electrical properties, such as electrode

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[*] Corresponding author: visnja@vinca.rs

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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 [4]. The main requirement for structure of dispersion-strengthened materials is a homogenous distribution and small size of oxide particles.

The copper matrix was reinforced with Al_2O_3 particles applying two processes, i.e. internal oxidation and mechanical alloying. The effect of the various size of copper and Al_2O_3 powder particles on strengthening, thermal stability and electrical conductivity of Cu - Al_2O_3 composites obtained by hot-pressing was the object of this paper.

2. Experimental Procedure

Inert gas-atomized prealloyed copper powder (average particle size - 30 μm) containing 2 wt.% Al (designation: Cu-2 wt.% Al), and a 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 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 a 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 (the dew point of hydrogen was lower than - 69 ^{0}C) at 400 ^{0}C for 1 h in order to eliminate copper oxides formed at the surface during milling. X-ray diffraction analysis (XRD) with sensitivity of about 5% showed no presence of copper oxides. 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. Hot-pressed composites in the form of compacts (composites in further text) 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 density (ρ) of composites was determined by the Archimedes method. The theoretical density of compacts was calculated from the simple rule of mixtures, taking the fully dense values for copper (8.96 gcm^{-3}) and alumina (3.95 gcm^{-3}).

Before and after high-temperature exposure composites were characterized by XRD using a "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 [5]:

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

where the shape factor k=0.9 and the radiation wave length λ=0.15405 nm.

Samples for optical and SEM microscope were mounted in acrylic resin. Polishing was performed using the standard procedure, whereas a mixture of 5 g $FeCl_3$ and 50 ml HCl in 100 ml distilled water was used for etching.

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The reinforcing of copper matrix was estimated by the microhardness[1] measurements applying load of 50 g. The electrical conductivity, expressed in % IACS, ($IACS_{20 °C} = 0.5800$ microhm^{-1}cm^{-1}) was measured at 60 kHz on polished composites using "Sigmatest" apparatus with electrode diameter of 14 mm.

All values of experimental results represent the average value of at least three tests measurements.

3. Results and discussion

The average value of density of Cu-2 wt.%Al, Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 composites was 8.23, 6.88 and 7.21 gcm^{-3}, respectively. According to this result the density of composites depended on the size of starting copper powder particles as well as on the size of Al_2O_3 particles. The lower extent of densification of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 composites may be the result of high dislocation accumulation around coarser Al_2O_3 particles. The higher density of Cu^*-4 wt.% Al_2O_3 composites in relationship to the density of Cu-4 wt.% Al_2O_3 is a consequence of smaller size of starting copper powder particles. Thus, the average value of density of Cu-2 wt.%Al, Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 composites in comparison with theoretical density (8.56 gcm^{-3}, calculated for 4 wt.% Al_2O_3) was 96.14, 80.37 and 84.22 %, respectively, indicating that the densification by hot-pressing of milled powders was not completely terminated. The reason for such an inadequate consolidation could be related to the copper matrix hardening and dislocation generation by alumina particles [6]. Also, the applied pressure of 35 MPa was probably insufficient to accomplish better compaction. Hot-extruding seems to be a common method of compaction because the measured density of the extruded materials is greater than 99.3% [7].

The microstructure of composites after 5 h of milling time is shown in Fig. 1. The compacts retained lamellar structure characteristic for high-energy milled powder particles. Compared with Cu-2 wt.%Al and Cu-4 wt.% Al_2O_3 composites (Fig. 1a and b, respectively), lamellae in Cu^*-4 wt.% Al_2O_3 composite are much finer (Fig. 1c). The light areas (denoted by arrows) in the microstructure of Cu-2 wt.%Al and Cu-4 wt.% Al_2O_3 composite indicate that the recrystalization occurred during hot-pressing contrary to Cu^*-4 wt.% Al_2O_3 composite. 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 composites 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 composites. According to Fig.2a, the size of most Al_2O_3 particles formed during high energy milling of prealloyed powders by internal oxidation is approximately 100 nm or even less. 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.

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[1] In this situation the expression of "microhardness" was used, although in some cases during measurements it is statistically probable that Al_2O_3 particle may be encountered by the indentor and the method becomes reversed from microhardness to (macro)hardness. However, during measurements the high values of microhardness possibly ascribed to Al_2O_3 particle have not been detected.
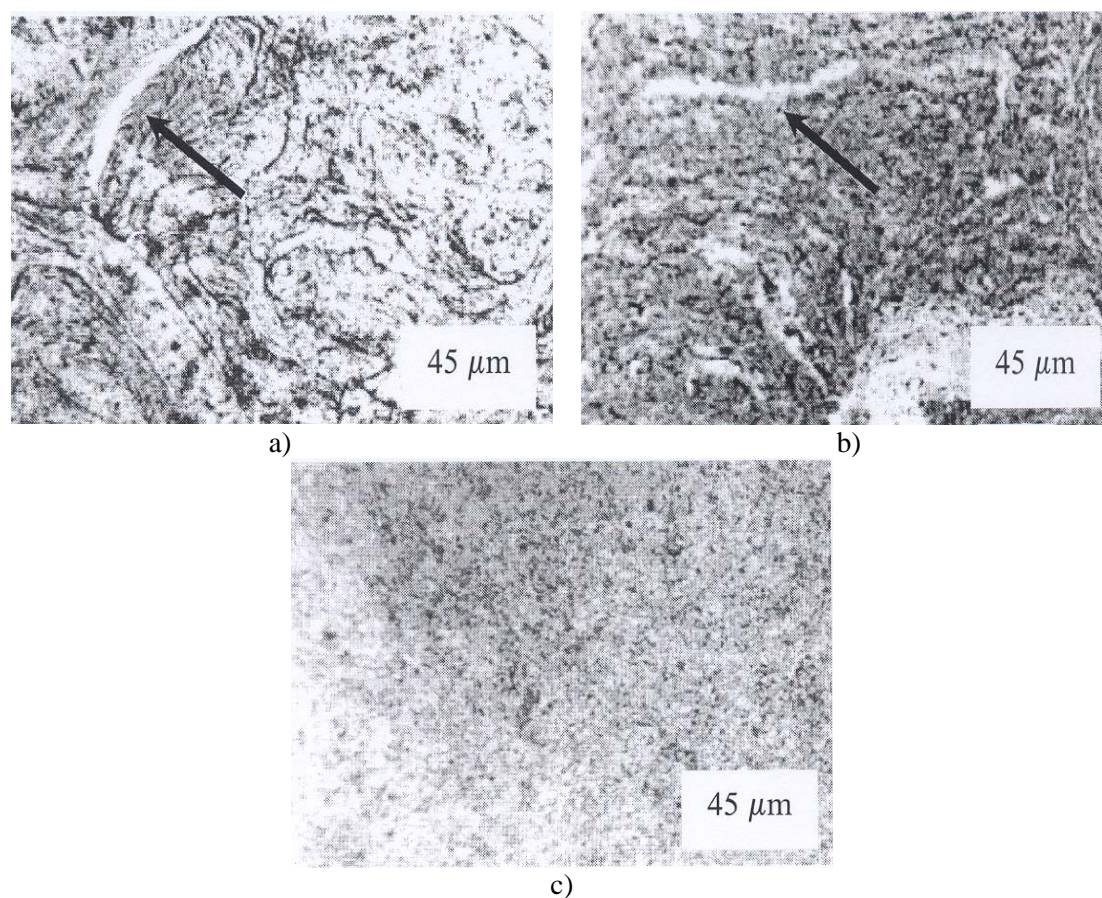
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Fig. 1 Optical micrographs of hot pressed composites based on (a) internally oxidized prealloyed Cu-2 wt.%Al powder; (b) and (c) powder mixtures based on 0.75 μm Al_2O_3.particles and 30 and 15 μm copper powders, respectively.
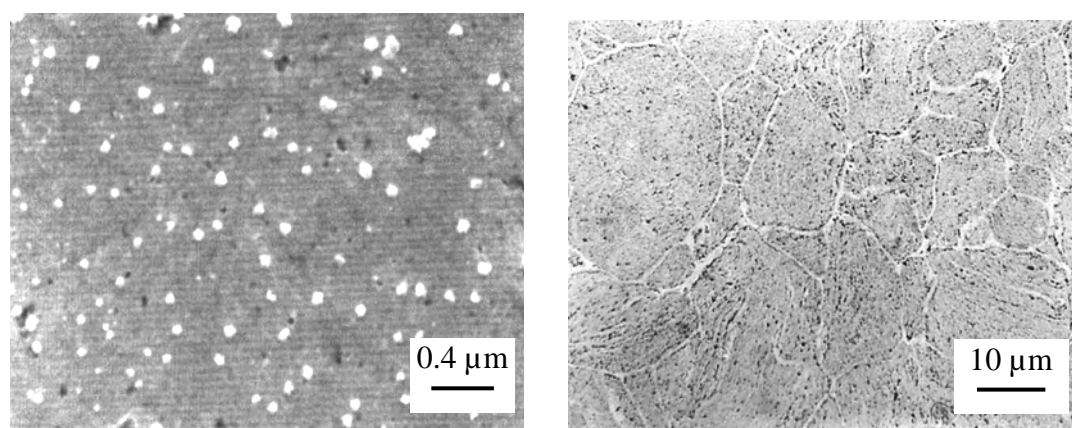

Fig. 2 (a) SEM micrograph of hot-pressed composite based on internally oxidized prealloyed Cu-2 wt.%Al powder; (b) optical micrograph of composite based on 30 μm copper powder.

The effect of the milling time of powders on microhardness of composites processed from these powders is shown in Fig. 3.
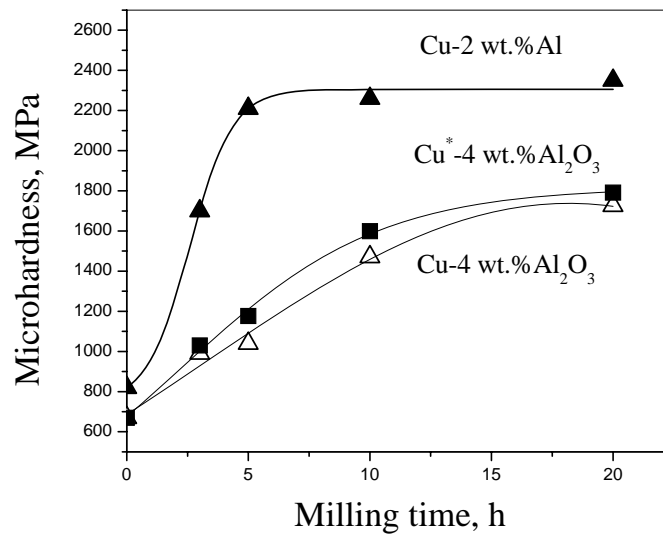
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Fig. 3 Effect of milling time on microhardness of hot-pressed composites: ▲ - based on internally oxidized Cu-2 wt.%Al prealloyed powder; ■ - based on 30 μm copper powder; △ - based on 15 μm copper powder.

The microhardness of composites 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 composites increases continuously with milling time, the largest increase in microhardness of Cu-2 wt.% Al compacts occurs at 5h milling. Further milling results in negligible change in microhardness of Cu-2 wt.% Al compacts. The maximum microhardness values of composites processed from 20 h-milled Cu-2wt.%Al, Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 powders attains 2510, 1726 and 1791 MPa, respectively.

The microhardness of Cu-2 wt.% Al composites is higher than microhardness of Cu-4 wt.% Al_2O_3 and Cu^*-4 wt.% Al_2O_3 composites as a consequence of the fact that nano-sized Al_2O_3 particles act as a stronger reinforcing 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 composites is the result of difference in grain size of compacted milled particles (Tab. I). The smallest grain size measured in Cu*-4Al2O3 composites may be ascribed to the smaller particle size of milled powders [8]. Namely, smaller powder particles are more easily subjected to higher deformation during milling than coarser particles.

Tab. I. The effect of high-temperature exposure at 800 ^{0}C for 5 h on grain size of composites processed from 5 and 20 h-milled powders.

Compact	Grain size, nm			
	Before exposure		After exposure	
	Milling time, h		Milling time, h	
	5	20	5	20
Cu-2 wt.%Al	45	61	53	62
Cu-4 wt.%Al$_2$O$_3$	65	36	69	72
Cu*-4 wt.%Al$_2$O$_3$	57	29	60	65

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

Tab. II. Microhardness of composites processed from 5 and 20 h-milled powders before and after high-temperature exposure at 800^{0}C.

Compact/ Milling time	Microhardness, MPa		
	Before exposure (at room temperature)	After exposure	
		800^{0}C/1h	800^{0}C/5h
Cu-2 wt.%Al/5h	2354	1810	1390
Cu+2 wt.%Al/20h	2510	2200	1500
Cu-4wt.%Al$_2$O$_3$/5h	1050	638	410
Cu-4wt.%Al$_2$O$_3$/20h	1726	677	569
Cu*-4 wt.%Al$_2$O$_3$/5h	1177	720	601
Cu*+4 wt.%Al$_2$O$_3$/20h	1791	843	650

The effect of milling time (5 h and 20h) and high-temperature exposure (800 ^{0}C for 5 h) on the electrical conductivity of composites is summarized in Tab. III. According to these results, the electrical conductivity of composites does not depend on the milling time. Also, electrical conductivity remained practically unchanged after high-temperature exposure. The average values of electrical conductivity of composites processed from milled prealloyed powders (Cu-2Al wt.% Al) are lower than the conductivity of composites processed from the milled powder mixtures (Cu-4 wt.%Al$_2$O$_3$ Cu*-4 wt.%Al$_2$O$_3$). These results suggest that nano-sized Al$_2$O$_3$ particles have higher effect on the electrical conductivity then micro-sized particles. Very small Al$_2$O$_3$ particles form a great number of interfaces considered as a possible source of additional electron scatter, which is a significant factor in reducing conductivity [9]. Thus, the extent of reduction of the electrical conductivity of Cu-2 wt.%Al composites with nano-sized Al$_2$O$_3$ particles (3.7 wt.%) is higher than in Cu-4 wt.%Al$_2$O$_3$ and Cu*-4 wt.%Al$_2$O$_3$ composites with the same (4 wt.%) amount micro-sized Al$_2$O$_3$ particles.

Tab. III. The effect of high-temperature exposure at 800 ^{0}C for 5 h on electrical conductivity of composites 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$_2$O$_3$	47	46	48	48
Cu-4* wt.%Al$_2$O$_3$	46.8	45.4	47.7	48.3

Summary

• Internal oxidation of aluminum during high-energy milling generated in prealloyed Cu-2 wt.% Al powders approximately the same amount of Al$_2$O$_3$ 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 composites as a consequence of nano-sized Al_2O_3 particles acting as a much stronger reinforcing parameter of the copper matrix than micro-sized Al_2O_3 particles.

• The electrical conductivity of composites does not depend on the milling time. The average values of electrical conductivity of composites processed from milled prealloyed powders (Cu-2Al wt.% Al) are lower than the conductivity of composites 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.

Acknowledgement

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Садржај:Предлегирани прах бакра са 2 mas.% Al добијен гасном атомизацијом у аргону (средња величина честица праха≈ 30 тт) и смеше прахова бакра (средње величине ≈ 15 и 30 тт) и 4 mas.% комерцијалног праха Al_2O_3 (средње величине ≈ 0.75 тт) одвојено су млевени на ваздуху у високо-енергетском планетарном млину. Трајање времена млевења било је до 20 h. Циљ млевења био је да се изврши ојачавање основе бакра помоћу уситњавања зрна, као и под дејством честица Al_2O_3. Млевењем на ваздуху и под утицајем унутрашње оксидације у предлегираним честицама праха бакра образоване су фино дисперговане нано-честице Al_2O_3. С друге стране, прахови композита са комерцијалним честицама Al_2O_3 микро-величине добијени су применом процеса механичког легирања. Прахови су затим жарени 1 h на 400 ^0C у атмосфери водоника како би се са површине честица одстранио оксид бакра створен током механичког легирања. Да би се извршило компактирање прахова примењено је топло пресовање (3 h на 800 ^0C у атмосфери аргона и при притиску од 35 МРа). Компакти

добијени од прахова који су претходно били млевени 5 и 20 h изложени су утицају повишене температуре (1 и 5 h на 800 ^{0}C у атмосфери аргона) са циљем да се испита њихова топлотна стабилност. У раду је разматран утицај почетне величине честица бакарних прахова и честица Al_2O_3, као и утицај уситњавања зрна на топлотну стабилност и електричну проводност композита на основи бакра.

Кључне речи: *Cu-Al_2O_3 композити, механичко легирање, унутрашња оксидација, почетна величина честица праха, топло пресовање, особине.*