

## CHARACTERISTICS OF COPPER AND COPPER – $Al_2O_3$ COMPOSITES PREPARED BY HIGH – ENERGY MILLING

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### ABSTRACT

The electrolytic copper powder, inert gas atomized prealloyed copper powder containing 3.5 wt.% Al, and the mixture of copper and commercial  $Al_2O_3$  powder particles (4 wt.%  $Al_2O_3$ ) were milled separately in the high-energy planetary ball mill up to 20 h in the air. Milling in the air of prealloyed copper powder promoted formation of fine dispersed  $Al_2O_3$  particles by internal oxidation. Hot-pressing was used for compaction (800 °C for 3 h in argon at pressure of 35 MPa). Compacts from 5 and 20 h milled powders were additionally subjected to hightemperature exposure (800 °C for 1 and 5 h in argon) in order to examine their thermal stability. The effect of different size and the amount of  $Al_2O_3$  particles on strengthening, thermal stability and electrical conductivity of the copper-based composites was studied. The results were discussed in terms of the effects of the grain size refinement along with micro- and nano-sized  $Al_2O_3$  particles on strengthening of the copper matrix.

**Keywords:** reinforced copper matrix ,  $Al_2O_3$  mechanical alloying, internal oxidation, properties

### INTRODUCTION

High-energy milling is a process applicable for production of powders various composites possessing a unique microstructure and properties. In recent years high energy milling is widely applied in processing of copper-based composites with a fine dispersion of various sized  $Al_2O_3$  particles accompanied by very fine grain structure. This structure contributes to copper matrix strengthening together with  $Al_2O_3$  particles. The uniform distribution of  $Al_2O_3$  particles can be accomplished by the processes of internal oxidation or by mechanical alloying. During high-energy milling of prealloyed copper powders aluminium, as more noble than copper, oxidizes first reacting with oxygen from the air and forming nano-sized  $Al_2O_3$  particles [1]. Applying mechanical alloying e.g. high-energy milling of a mixture of copper and various-sized  $Al_2O_3$  powder particles it is possible to reinforce copper matrix [2-4].

The object of this paper was to study the effect of grain refinement as well as size and amount of  $Al_2O_3$  particles during the processes of internal oxidation and mechanical alloying on strengthening, thermal stability and electrical conductivity of the copper-based composites.

### EXPERIMENTAL PROCEDURE

The electrolytic copper powder (Cu), the mixture of electrolytic copper powder with 4 wt.% of commercial Al<sub>2</sub>O<sub>3</sub> powder (average particle size – 0.75 μm) (Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub>) and the inert gas-atomized prealloyed copper powder containing 3.5 wt.% aluminium (Cu-3.5 wt. %Al) served as starting materials. The powders were separately milled in air up to 20 h in the high-energy planetary ball mill to obtain the fine grain structure and uniformly distribution of micro- and nano-sized Al<sub>2</sub>O<sub>3</sub> particles in the copper matrix. The weight ratio of powder to steel balls was 1:35. Milling in the air of prealloyed copper powder promotes formation of nano-sized Al<sub>2</sub>O<sub>3</sub> particles *in situ* by internal oxidation with oxygen from the air. Following milling, powders were treated in hydrogen at 400 °C for 1h in order to eliminate copper oxides formed at the surface during milling. Compaction was carried out by hot-pressing in an argon atmosphere at 800 °C for 1 h under the pressure of 35 MPa. Compacts from as-received Cu, non-milled Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> mixture and non-milled prealloyed Cu-3.5 wt. %Al were also synthesized under the same condition. Compacts processed from 5 and 20 h milled powders were additionally subjected to high temperature exposure in argon at 800 °C for 1 and 5h in order to examine their thermal stability.

The powders and compacts were characterized by X-ray diffraction analysis, optical and scanning electron microscope (SEM). X-ray diffraction analysis was performed using “Siemens D-500” X-ray powder diffractometer with CuK<sub>α</sub> 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 Willson and Hall [5]:

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

where the shape factor k=0.9 and radiation wave length λ=0.15405 nm. Δd/d presents the average lattice distortion, *i.e.* relative deviation of the lattice parameters from their mean value [6].

The strengthening of the copper matrix was estimated by microhardness measurement (applied load was 50g). The electrical conductivity (%IACS, IACS<sub>20°C</sub> = 0.5800 microhm<sup>-1</sup>cm<sup>-1</sup>) of polished compacts was measured using “Sigmatest” apparatus operating at 60 KHz with electrode diameter of 14mm, 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<sub>2</sub>O<sub>3</sub> 8.96 and 3.95 gcm<sup>-3</sup>, respectively.

### RESULTS AND DISCUSSION

Distribution of Al<sub>2</sub>O<sub>3</sub> particles in Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> (powder) and Cu-3.5 wt. %Al (compact) is presented in Fig.1. While the size of Al<sub>2</sub>O<sub>3</sub> particles in Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> powder (Fig. 1a) is approximately between 1 and 2μm (as a result of agglomeration of previously added 0.75 μm particles), the size of Al<sub>2</sub>O<sub>3</sub> particles in Cu-3.5 wt. %Al compact (Fig. 1b) is in the range from 100 and 125 nm. It was previously reported [1] that during high-energy milling of prealloyed powders Al<sub>2</sub>O<sub>3</sub> particles formed by the process of internal oxidation are of nano-sized dimensions, *i.e.* the most of particles are

finer than 100 nm. Therefore, the structure of milled prealloyed and internally oxidized copper powders is characterized by much finer Al<sub>2</sub>O<sub>3</sub> particles than in the case of mechanically alloyed Cu-3 wt. % Al<sub>2</sub>O<sub>3</sub> milled powders. Since it was estimated that commercial Al<sub>2</sub>O<sub>3</sub> particles could not be fractured during milling [7], structure of Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> milled powders consists of micro-sized Al<sub>2</sub>O<sub>3</sub> particles (with average size of 750 nm) embedded in the copper matrix during milling.

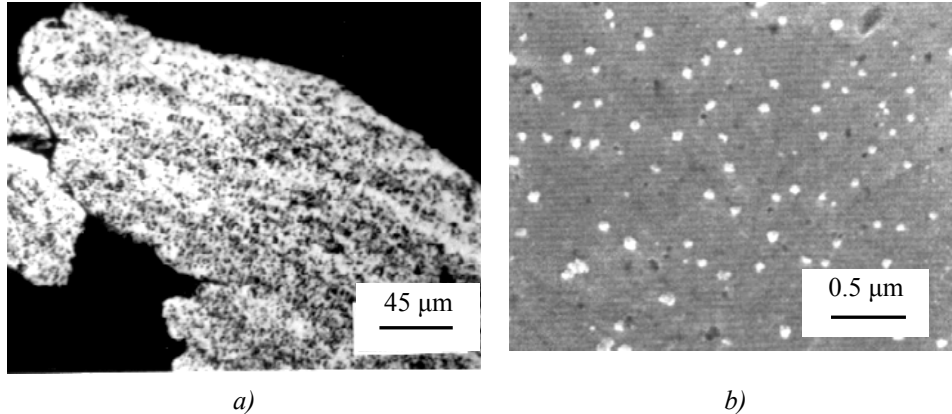
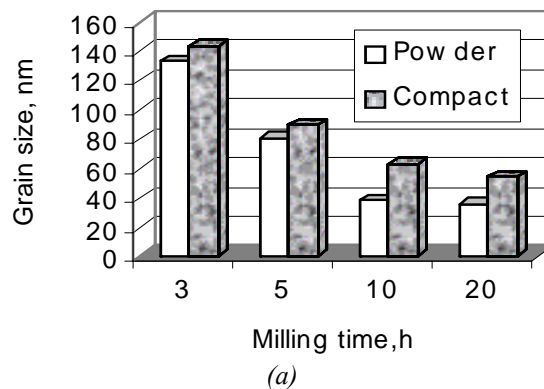
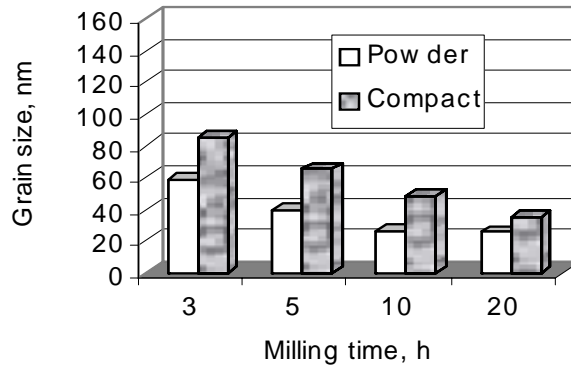


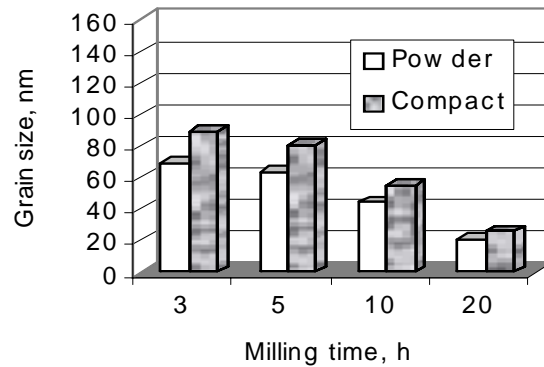
Fig.1. Light (a) and SEM (b) micrographs. (a) Microstructure of polished 5 h milled Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> powder particles; (b) microstructure of polished 5 h milled Cu-3.5 wt.% Al compact.

The change of the grain size of powders and corresponding compacts processed from 3, 5, 10 and 20 h milled powders was calculated using equation 1 and the results are shown in Fig.2. It is obvious that the grain size of powders and compacts decreases with the milling time. The grain size of compacts is higher than the grain size of milled powders as a consequence of grain growth during the compaction at 800 °C. Although the grains of milled powders grow during compaction they still remain in the range of nano-sized dimensions. The most intensive grain refinement in both powders and compacts occurs in the early stage of milling, becoming slower with the prolonged milling time.





(b)



(c)

Fig. 2. Effect of milling time on grain size. (a) Cu; (b) Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and (c) Cu-3.5wt.% Al

The microstructure of compacts processed from Cu, Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al powders after 20 h of milling is shown in Fig. 3. The light areas (denoted by arrows) in the microstructure of Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5wt.% Al compacts (Fig. 3b and c, respectively) indicate that the recrystallization occurred during hot-pressing contrary to Cu compact (Fig. 3a). The extent of recrystallization in Cu-4 wt.% Al compact is higher in the relation to Cu-3.5 wt.% Al compact. It is interesting to note that the recrystallization in Cu-3.5 wt.% Al compact was initiated at the corners of the particle powder where the concentration of stresses imposed during compaction was highest.

Fig. 4 shows the effect of milling time on microhardness of compacts. Microhardness of all compacts increases with the previous milling time of powders showing that 20 h milled compacts exhibit significantly higher microhardness than compacts processed from as-received powders. The change of microhardness with milling time is different depending on the composition of compacts. The increase in microhardness of Cu compacts is slow during first 10 h of milling becoming rapid with prolonged milling time.

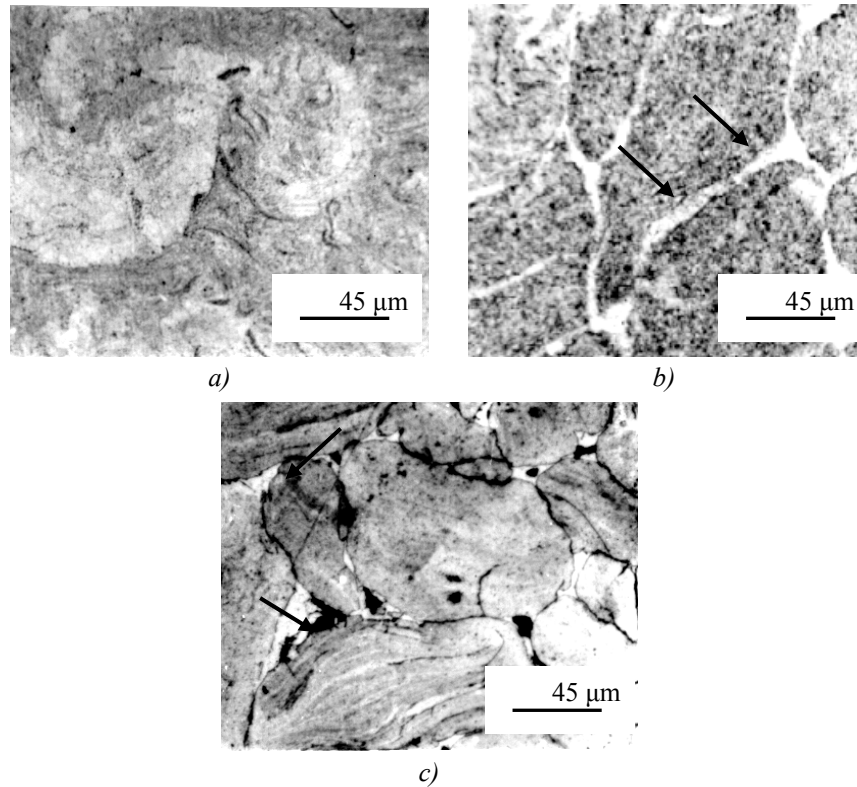


Fig. 3. Light micrographs. Microstructure of compacts processed from 20 h milled powders. (a) Cu; (b) Cu-4 wt.%  $\text{Al}_2\text{O}_3$  and (c) Cu-3.5 wt.% Al.

The increase in microhardness of Cu-4 wt.%  $\text{Al}_2\text{O}_3$  compacts is slow and continuous during the whole interval of milling, whereas the highest increase in microhardness of Cu-3.5 wt.% Al occurs in compacts processed from 5 h milled powders and further milling results in negligible increase in microhardness. After 20 h of milling microhardness of Cu, Cu-4 wt.%  $\text{Al}_2\text{O}_3$  and Cu 3.5 wt.% Al compacts is 2580, 1730 and 3060 MPa, respectively. In general, the increase in microhardness of compacts is either the consequence of the grain refinement (Cu compacts) or the synergetic effects of grain refinement and the strengthening of copper matrix by  $\text{Al}_2\text{O}_3$  particles (Cu-4 wt.%  $\text{Al}_2\text{O}_3$  and Cu-3.5 wt.% Al compacts). It is interesting to note that the microhardness of 20h milled Cu compact is higher than Cu-4 wt.%  $\text{Al}_2\text{O}_3$  compact which may be ascribed to the much finer grain size of Cu compact. In this situation the effect of grain refinement prevails over the strengthening effect of micro-sized  $\text{Al}_2\text{O}_3$  particles. In spite that the grain size is larger than in Cu compacts, the highest microhardness of Cu-3.5 wt.% Al compacts is the result not only of the influence of nano-sized  $\text{Al}_2\text{O}_3$  particles, but in this case the effect of solution hardening of the copper matrix by aluminium should be considered. It is also confirmed that nano-sized  $\text{Al}_2\text{O}_3$  particles in internally oxidized Cu-3.5 wt.% Al compacts act as a much stronger strengthening parameter of the copper matrix than micro-sized  $\text{Al}_2\text{O}_3$  particles in mechanically alloyed Cu-4 wt.%  $\text{Al}_2\text{O}_3$  compacts.

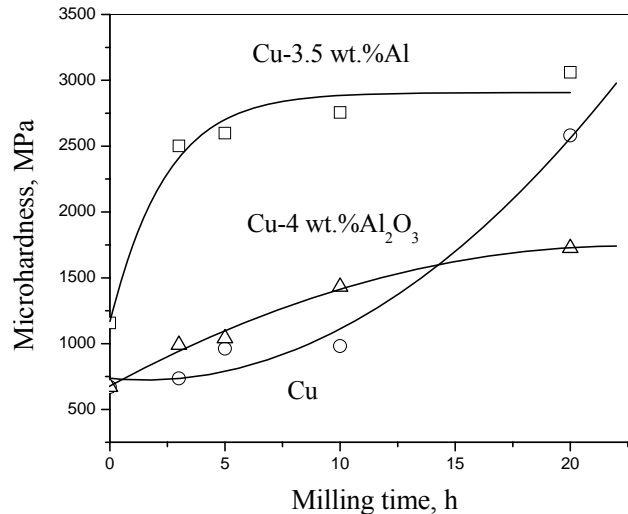


Fig.4. Effect of milling time on the microhardness of compacts

Table 1 illustrates the effect of different time of high temperature exposure at 800 °C on the thermal stability (expressed through the change of microhardness) of compacts processed from 5h and 20h milled powders. The microhardness of Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al compacts decreases in some extent with time. The decrease of microhardness of these compacts may be explained by grain growth processes occurring during the high temperature. Retained enhanced microhardness during high temperature exposure suggests good thermal stability of Cu-3.5 wt.% Al compacts contrary to Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> compacts. Namely, the grain growth increases at lower extent in Cu-3.5 wt.% Al compacts since it is obstructed by nano-sized Al<sub>2</sub>O<sub>3</sub> particles. On the other side, the micro-sized Al<sub>2</sub>O<sub>3</sub> particles are less efficient barrier in preventing grain growth in Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub>. The results from Table 1 reveal that the microhardness of Cu compacts first increases and then a decrease occurs with longer time of exposure. The increase of microhardness after 1 h of exposure could be the consequence of the formation of small grains during recrystallization. After 5 h of exposure the microhardness decreases due to the growth of previously recrystallized grains.

The average values of density of Cu, Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al compacts (8.1, 7.11 and 7.2 gcm<sup>-3</sup>, respectively) were 90.4, 83.06 and 85.1 %, respectively, in comparison with theoretical density, which indicates that the densification by hot-pressing of milled prealloyed powders was not completely terminated. The reason for such an inadequate consolidation could be also related to the copper matrix strengthening and dislocation generation by Al<sub>2</sub>O<sub>3</sub> particles [8] as well as the particle size and shape of milled powders. Also, the applied pressure of 35 MPa was 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 % [9].

Table 1. Microhardness of compacts before and after high temperature exposure (HTE) at 800 °C for 1 h and 5 h.

Compact/ milling time	Microhardness, MPa		
	Before HTE	After HTE	
		1h	5h
Cu/5 h	960	1890	343
Cu/20 h	2580	1600	730
Cu-3.5wt.%Al/5 h	2600	2355	1850
Cu-3.5wt.%Al/20 h	3060	2920	2830
Cu-4wt.%Al <sub>2</sub> O <sub>3</sub> /5 h	1050	640	410
Cu-4wt.%Al <sub>2</sub> O <sub>3</sub> /20 h	1730	680	570

The results of electrical conductivity of compacts 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 Cu compacts is higher than electrical conductivity of Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al compacts. Further, the electrical conductivity of compacts processed from Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> milled powders is higher than the conductivity of the compacts processed from the Cu-3.5 wt.% Al powders. These results suggest that electrical conductivity depends not only on the presence of Al<sub>2</sub>O<sub>3</sub> particles, but also on their size and density. In the same time, aluminium in the copper-solid solution also contributes to the reduction of the conductivity of Cu-3.5 wt.% Al compacts. The increase of electrical conductivity of milled Cu-3.5 wt.% Al compacts compared to non-milled compacts is due to a decrease of aluminium concentration in the copper-solid solution promoted by diffusion processes during compaction at 800 °C.

Table 2. Effect of milling time on electrical conductivity of compacts.

Compact	Electrical conductivity, %IACS				
	Milling time, h				
	0*	3	5	10	20
Cu	87	75	75	72	72
Cu-3.5 wt.% Al	25	31	36.5	38	39
Cu-4 wt.% Al <sub>2</sub> O <sub>3</sub>	-	47	47	46	46

\*Compacts processed from as-received and non-milled powders

## SUMMARY

The effect of different size and the amount of Al<sub>2</sub>O<sub>3</sub> particles on strengthening, thermal stability and electrical conductivity during internal oxidation and mechanical alloying of the copper-based composites was studied. The electrolytic copper powder

(Cu), inert gas atomized prealloyed copper powder (Cu-3.5 wt.% Al) and the mixture of copper and commercial Al<sub>2</sub>O<sub>3</sub> powder particles (Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub>) served as starting materials:

- After 20 h of milling microhardness of Cu, Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al compacts was 2580 MPa, 1730MPa and 3060MPa, respectively.
- Increase in the microhardness of compacts is consequence of refinement grain structure (Cu compacts) as well as refinement of grain structure and presence of nano-sized (Cu 3.5 wt.% Al compacts) and micro-sized (Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub>) Al<sub>2</sub>O<sub>3</sub> particles.
- The microhardness of compacts decreases in different extent after high temperature exposure. Retained enhanced microhardness during high temperature exposure suggests higher thermal stability of Cu-3.5 wt.% Al compacts than Cu and Cu-4 wt.%Al<sub>2</sub>O<sub>3</sub> compacts.
- The highest microhardness and the best thermal stability of Cu-3.5 wt.% Al compacts are the consequence of uniformly distributed Al<sub>2</sub>O<sub>3</sub> particles obtained by internal oxidation. Nano-sized Al<sub>2</sub>O<sub>3</sub> particles in internally oxidized Cu-3.5 wt.% Al compacts act as a much stronger strengthening parameter of the copper matrix than micro-sized Al<sub>2</sub>O<sub>3</sub> particles in mechanically alloyed Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> compacts.
- The electrical conductivity of Cu compacts is higher than electrical conductivity of Cu-4 wt.% Al<sub>2</sub>O<sub>3</sub> and Cu-3.5 wt.% Al compacts. After 20 h of milling electrical conductivity of Cu, Cu-4 wt.%Al<sub>2</sub>O and Cu-3.5 wt.% Al compacts was 72 %IACS, 46 %IACS and 39 %IACS These results imply that the electrical conductivity depends not only on the presence of Al<sub>2</sub>O<sub>3</sub> particles, but also on their size and density.

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