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Processing, characterization and properties of copper-based composites strengthened by low amount of alumina particles

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ABSTRACT

Copper-based composites strengthened by nano- and micro-sized alumina particles were fabricated by internal oxidation and mechanical alloying followed by hot-pressing. The effect of the simultaneous presence of nano- and micro-sized alumina particles on the microstructure and properties of the copper matrix was the object of this study. The inert gas-atomised prealloyed copper powder containing 0.5 wt.% Al and the mixture of inert gas-atomized prealloyed copper powder with 0.6 wt.% micro-sized alumina powder served as starting materials. Microstructure of composites was studied by X-ray diffraction analysis, scanning (SEM) and transmission electron microscopy (TEM). Microhardness, density and electrical conductivity were also applied for determination of properties. Microstructural characterization showed that nano-sized alumina particles significantly lower the grain size and inhibit the grain growth. Considerable increase of microhardness was also detected. At the maximum values (after 10 h of milling) the microhardness of both composites, Cu–0.5 wt.% Al and hybrid Cu–0.5 wt.% Al + 0.6 wt.% Al_2O_3, was approximately 3 times higher than microhardness of non-milled compacts processed from prealloyed copper and electrolytic copper powders. Micro-sized alumina particles play a twofold role in the strengthening of the copper matrix of the hybrid composite: together with the nano-sized particles they strengthen the matrix at shorter milling time, but with prolonged milling time the dislocation substructure formed around coarse particles serves as a trigger for the start of recrystallization processes provoking a decrease of microhardness. Both composites exhibit a much higher thermal stability at 800 °C than copper alloy processed by the method of vacuum melting and casting. The contribution of individual mechanisms such as the grain size, thermal expansion mismatch and Orowan hardening in strengthening of composites was evaluated and correlated with experimental results.

1. Introduction

The main problem of application of copper is its low intrinsic strength. Alloying with Ag, Nb, Cr and Zr the strength of the copper matrix was improved. Precipitation-hardened coppers, such as Cu–Cr–Zr (C18150) and Wieland K88 (C18080) showed good strength and high electrical conductivity up to 500 °C. However, at temperatures higher than 500 °C enhanced recrystallization was the main cause for the deterioration of these properties [1]. The addition of hard ceramic particles to soft copper matrix can significantly improve the mechanical properties and wear resistance, without any serious worsening of both thermal and electrical conductivities of copper. Alumina (Al_2O_3) particles have been mostly selected as the reinforcement phase [2–4]. This is due to the high wear resistance, superior high temperature mechanical properties and low cost. Alumina dispersion-strengthened copper alloys have been highly valued for their superior strength, electrical conductivity and thermal stability. This combination of mechanical and electrical properties has led to the application of dispersion-strengthened copper as welding electrodes, lead frames, accelerator electrodes and electrical connectors [5]. Dispersion-strengthened copper coatings, depending on the type and size of the dispersoid can also significantly improve certain properties of the base metal [6–8]. Nano-sized alumina particles affect the deformation and recrystallization of the copper matrix, i.e. small and closely spaced particles exert a pinning effect, also called Zener pinning, on the movement of dislocations and impede grain growth, resulting in retardation or even the complete suppression of recrystallization. Recently published results reported the effect of particle size, their distribution and amount as the most important parameters in strengthening of the copper matrix [9–16]. The applied powder metallurgy techniques may also have a significant impact on the properties of obtained composites [17].

High-energy milling has been proved as a very common technique for processing of copper-based composites since it allows the formation of ultrafine grained powder structures which are stable even after compaction at high temperature. Combination of internal oxidation

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and high-energy milling [18], as well as mechanical alloying, can provide uniformly distributed nano-sized alumina particles in the copper matrix.

In this paper, high-energy milling combined with mechanical alloying was used as a powder metallurgical technique to prepare the Cu-based composites strengthened with alumina particles. The objective was to provide a comparative study between the composite strengthened exclusively with nano-sized particles and the hybrid composite strengthened with the mixture of nano- and micro-sized alumina particles. The idea was to acquire information on the synergetic effect of nano- and micro-sized particles on the strengthening mechanism, thermal stability and electrical conductivity of copper-based composites. Prealloyed copper powder containing 0.5 wt.% Al and the commercial alumina powder served as a starting material.

2. Experimental procedure

Two copper-based composites were prepared. The inert gas-atomised prealloyed copper powder containing 0.5 wt.% Al served for processing of Cu–0.5Al composite (as referred in the following text), whereas the mixture of 0.5 wt.% Al prealloyed copper powder with addition of 0.6 wt.% alumina powder (commercial grade: average particle size — 0.75 μm) served for processing of Cu–0.5 wt.% Al + 0.6 wt.%Al_2O_3 composite (referred as hybrid composite). Powders were separately milled in air for 3, 5, 10, 12, 15 and 20 h in the planetary ball mill. The weight ratio of powder to steel balls was 1:35. During high-energy milling of prealloyed copper powder, aluminum is oxidized by internal oxidation through the reaction with oxygen from the air.

Following milling, powders were treated in hydrogen at 400 °C for 1 h to eliminate copper oxides formed at the surface during milling. Compaction executed by hot-pressing was carried out in an argon atmosphere at 800 °C for 3 h under the pressure of 35 MPa. Samples (in the following text referred as compacts) processed from non-milled electrolytic copper and prealloyed Cu–0.5Al were also synthesized under the same condition. Dimensions of compacts and composites were as follows: 10 mm height and 10 mm diameter. Table 1 gives an overview of investigated materials.

Microstructure of composites was investigated by the scanning electron microscope (SEM) (JEOL JSM-6610LV). Electron dispersive X-ray spectroscope (EDS) was used for chemical analysis of particles present in the copper matrix. Polishing of samples was performed applying the standard method, whereas the mixture of 5 g $FeCl_3$ and 50 ml HCl in 100 ml distilled water was used for etching. Only few composites, corresponding to samples processed from 10 and 20 h-milled powder, were investigated with the transmission electron microscope (TEM) JEOL JEM-7. For TEM characterization, thin slices (about 1 mm) of the material were cut from the central cross-section of each compact. The slices were further thinned to 100 μm by conventional grinding. Disks with 3 mm in diameter were punched from the central part of the slices and electropolished in a twin-jet electropolisher. The electropolishing was performed in the solution mixture CH_3OH–HNO_3 with the ratio 3:1, at the following conditions: T = −35 °C, U = 9 V and I = 20 mA.

Milling in air of prealloyed copper powder promoted the formation of 0.95 wt.% of finely dispersed alumina particles by internal oxidation. Assuming that the complete amount of aluminum was oxidized, it was calculated that 0.95 wt.% alumina was produced in the copper matrix by internal oxidation of 0.5 wt.% Al. This calculation was made using the simple equation:

$$4Al + 3O_2 = 2Al_2O_3. \quad (1)$$

Given that $4 \times 27 = 48$ g of aluminum oxide produce 204 g of Al_2O_3, i.e. $2 \times (2 \times 27 + 3 \times 16) = 204$ g, then oxidation of 0.5 g of aluminum, contained in the prealloyed copper, will generate 0.95 g of alumina. As previously mentioned, this is only a calculation and there is no proof that the whole aluminum was oxidized during internal oxidation. Composites processed from 10 h-milled powder showed the highest level of microhardness. To examine their thermal stability these composites were additionally subjected to the high-temperature exposure (HTE) in argon at 800 °C for 1 and 5 h.

The grain size (D) of composites was determined by X-ray diffraction analysis (XRD) using "Siemens D-500" X-ray powder diffractometer with CuK_α Ni filtered radiation. The broadening (β) of the first four diffraction lines (111, 200, 220 and 311) was used for calculation according to the approach developed by Williams and Hall [19]:

$$\beta \cos\theta = \frac{k\lambda}{D} + \frac{k\Delta d}{d} \sin\Theta \quad (2)$$

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

Strengthening of the copper matrix was estimated by microhardness measurement with applied load of 50 g and time of indentation 20 s. Electrical conductivity (% IACS; where $IACS_{20\,°C} = 0.5800\ \mu\Omega^{-1}\ cm^{-1}$) of polished composites was measured with "Sigmatest", with electrode diameter of 7 mm and operating at 120 kHz. Density (ρ) of the composites was determined by the Archimedes method; the theoretical density of composites was calculated from the simple rule of mixtures, taking the fully dense values for copper and alumina 8.96 and 3.95 g cm^{-3}, respectively.

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

3. Results

3.1. Microstructure

The grain size change of Cu–0.5Al and hybrid composites as a function of milling time is shown in Fig. 1.

The grain size was calculated using Eq. (1). Compared to non-milled compacts the grain size of both composites drastically decreases even after 3 h of milling and reaches minimum value after 10 h of milling, where the grain size of Cu–0.5Al composite is somewhat lesser than that of hybrid. A negligible increase of the grain size of Cu–0.5Al composite occurs with the milling time, whereas the grain size of hybrid composite steeply increases with the prolonged milling.

SEM micrographs illustrating the microstructure of Cu–0.5Al and hybrid composites processed from 10 h-milled powder are shown in Fig. 2.

The presence of mainly globular nano-sized alumina particles (approximately less than 100 nm in size) obtained by internal oxidation

Table 1
Materials used for investigation.

Starting material, composition, wt.%	Designation	Processing	Final form
Prealloyed Cu–0.5Al powder	Cu–0.5Al	Milled for 3, 5, 10, 12, 15, 20 h + hot-compacted	Composite
Mixture: prealloyed Cu–0.5Al + 0.6 Al_2O_3 powder	Hybrid	Milled for 3, 5, 10, 12, 15, 20 h + hot-compacted	Composite
Electrolytic Cu powder	Electrolytic Cu	Non-milled, hot-compacted	Compact
As-received prealloyed Cu–0.5Al powder	As-received Cu–0.5Al	Non-milled, hot-compacted	Compact