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The Influence of Electrocorundum Granulation on the Properties of Sintered Cu/Electrocorundum Composites

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Abstract:
Copper/alumina composites are extensively used in automotive and aerospace industry for products that are subjected to severe thermal and mechanical loadings, such as rocket thrusters and components of aircraft engines. These materials are well-known for their good frictional wear resistance, good resistance to thermal fatigue, high thermal conductivity and high specific heat. In this paper, the sintering process of copper/electrocorundum composites reinforced by electrocorundum particles with diameters of 3 or 180 µm and 1, 3, 5 vol.% content is presented. The effects of different particle sizes of the ceramic reinforcement on the microstructure, physical, mechanical, tribological and thermal properties of the fabricated composites are discussed.
Keywords: *Copper/alumina composites, Sintering, Modeling of thermal properties, Microstructure, Mechanical properties.*

1. Introduction

Copper matrix composites reinforced with ceramic particles combine the high thermal and electrical conductivity and high plasticity of copper with the high stiffness, hardness and wear resistance of ceramic [1-6]. This combination of properties makes copper/alumina composites particularly interesting for wear applications, including automotive and aerospace industry. Copper is a material of high thermal conductivity ensuring good heat transfer inside the material, while the alumina component guarantees high wear resistance and hardness [7-10]. The Cu/Al_2O_3 composites can, thus, be used in applications where high thermal conductivity, high dissipation of heat, high resistance to thermal fatigue and good frictional wear resistance are required. These materials can be used as resistance welding electrodes, lead frames, accelerators and electrical contacts [9,10]. Another potential application of the Cu/Al_2O_3 composites are the exhaust systems in rocket thrusters and aircraft engines operating in severe thermal and mechanical loading conditions, which require structural materials of enhanced thermal conductivity (>300 W/(m·K)), increased resistance to erosion, oxidation and long life time [11]. In order to meet these material requirements, the following composition were selected for the copper-alumina MMCs in question: Cu/1%, 3%, 5% Al_2O_3 (vol.%). The properties of these composites depend on a number of factors including the content, shape and distribution of the ceramic phase, the processing method, as well as the conditions under which they are produced. All these variables have an influence on the

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aforementioned properties and, in consequence, on the future applications of the final material [12-13]. In the present paper, Cu/Al_2O_3 composites were obtained using powder metallurgy technique by mixing appropriate proportions of starting powders and sintering them at 1050°C under the pressure of 30 MPa. This technique has a considerable drawback. Aluminum oxide added as powder forms agglomerates and cannot be sintered at the process temperature (1050°C) as determined by the melting point of copper (1083°C). In addition this effect hinders the sintering of copper particles. The resultant porosity considerably affects, among other things, the thermal conductivity of composites, thus limiting their applicability.

This paper shows a solution to this problem consisting in using electrocorundum powder as the ceramic reinforcement for copper/alumina MMCs. Electrocorundum is formed by melting aluminum oxide powder (α-Al_2O_3) in an arc resistance furnace. The main objective is to investigate the effect of the particle size and amount of the reinforcement phase on the microstructure and selected physical, mechanical, tribological and thermal properties of Cu/Al_2O_3 composites.

2. Experimental procedure

The following commercially available powders were used as the starting materials: copper powder (Sigma Aldrich, 99.9% purity) with granulation 10 µm (Fig. 1a) and the BET specific surface area of 0.61 m^2/g, and two kinds of electrocorundum powder with considerably different particle sizes, i.e. fine powder < 3 µm and coarse powder of 180 µm (Polish company KOS, 99% purity). The morphology of the starting powders and particle size distribution are shown in Fig. 1.

a) b) c)

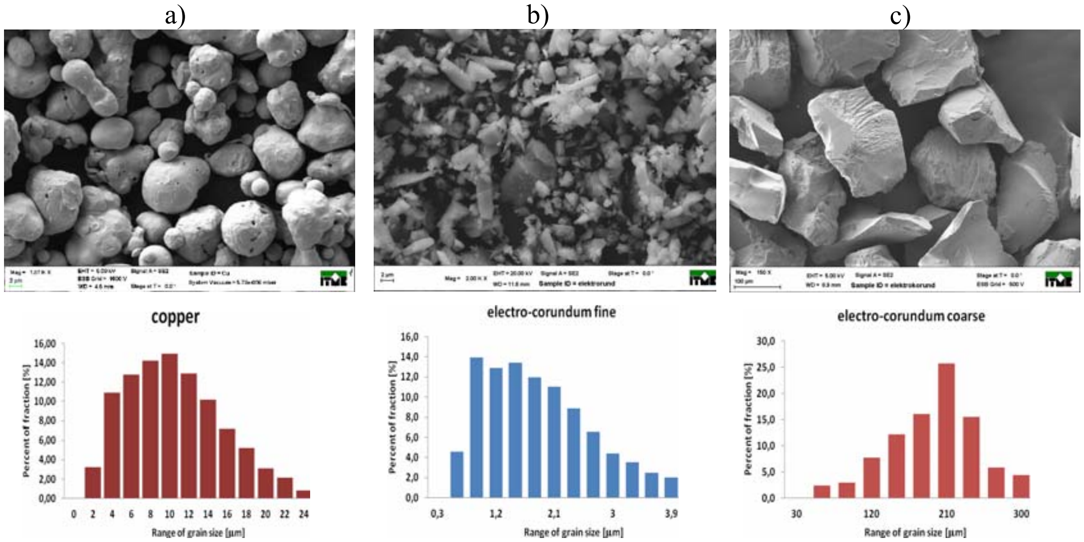

Fig. 1. Particle size distribution and SEM images of the starting powders, i.e. a) copper, b) fine electrocorundum and c) coarse electrocorundum.

The particle size distribution of the starting powders was studied using a CLEMEX television image analysis system (Fig. 1). It was calculated as a function of the Feret diameter (d) and, in consequence the average Feret diameter (d_{avg}) was obtained. The average particle size of copper, fine electrocorundum and coarse electrocorundum were determined to be d_{Cu} = 9 µm, $d_{elek.fine}$ = 2.5 µm and $d_{elek.coars}$ = 180 µm, respectively. The microscopic examinations showed a relatively high scatter of results, ranging from 2 to 11 µm, for the particle size of copper. Both copper and electrocorundum powders do not form powder agglomerates. It was observed that copper particles are rather spherical in shape (ball-shaped), whereas those of electrocorundum have sharp edges (Fig. 1).

Three compositions of the powder mixture were prepared with the following Cu to ceramic phase content (vol.%): 99%Cu-1%Al_2O_3, 97%Cu-3%Al_2O_3 and 95%Cu-5%Al_2O_3. They were obtained in a mechanical mixing process in a planetary ball mill (Pulverisette 6, Fritsch) with tungsten carbide balls (Ø5 mm). The high-energy mechanical mixing process was performed at room temperature in air atmosphere, at the rotation speed of 200 rpm and the time of mixing of 6 h. The balls to powder weight ratio (BPR) was 3:1. The mixing conditions were adopted from authors' previous experiments reported in [14].

The morphology of the powder mixtures was studied using scanning electron microscopy. Fig. 2 shows examples of the morphology of a fine powder mixture of 95%Cu-5%Al_2O_3 obtained by mechanical alloying.

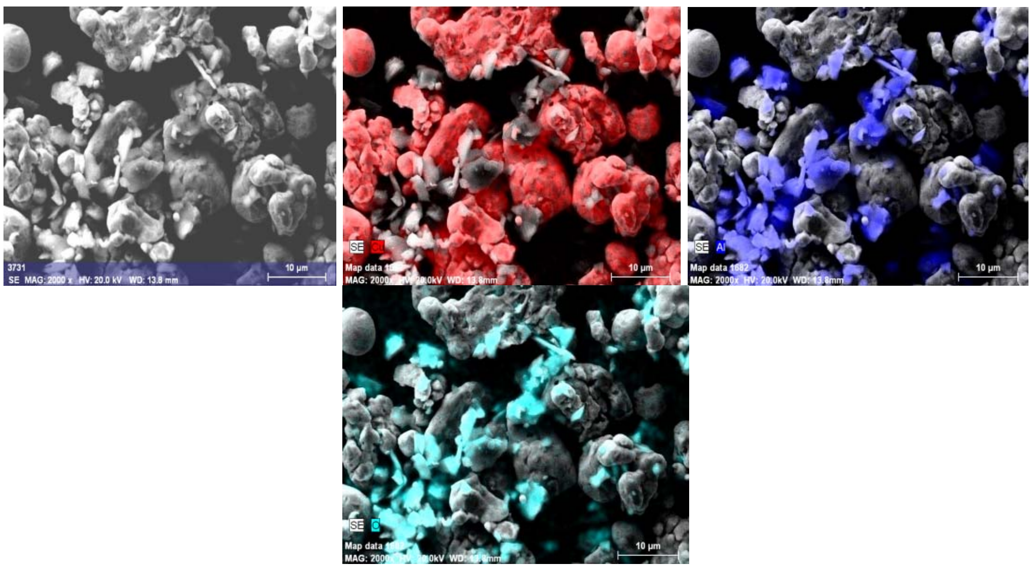

Fig. 2. The morphology of powders and the surface distribution of elements in composite mixtures after the mixing process for Cu-5vol.%Al_2O_3 fine: red-copper, blue-Al_2O_3, green-oxygen.

The powder mixtures were placed in a graphite die and sintered in an Astro Thermal Technology hot press for 30 min in argon atmosphere at 1050°C under the external pressure of 30 MPa. After the holding time (30 min), the samples were cooled inside the furnace down to the room temperature, with the external load removed. Then, they were removed from the furnace, mechanically cut, ground and polished.

The morphology of both the starting powders and the powders after mixing as well as the microstructure of the composite materials were examined using a scanning electron microscope (SEM) AURIGA CrossBeam Workstation (Zeiss) with an integrated EDS microanalysis system. The density of the obtained composites was measured according to the Archimedes method. The theoretical density was calculated using the densities of Al_2O_3 (ρ_{Al2O3}= 3.97 g/cm^3) and copper (ρ_{Cu}= 8.97 g/cm^3). The hardness (HV1) was measured using Durascan 10/Emcotest with a Vickers diamond indenter applying a load of 9.81 N for 10 s. The results of hardness were averaged over 5 indentations per specimen. Thermal conductivity was measured at the temperature of 50°C using the Laser Flash Analyser LFA457/Netzsch in argon atmosphere for the sample size of 10x10x3 mm. The surface of the samples was covered by a thin layer of graphite. The entire set of experimental data was fitted applying the Cape-Lehman theoretical model with pulse correction, which takes into consideration radiative heat loss. The measurements of the specific heat (used in the calculation of thermal conductivity) of the Cu/Al_2O_3 composites were performed by a STA 449 Jupiter Netzsch fine thermal analyzer – using the differential scanning calorimetric method with heat flow (DSC). The measurements were made for 4x4x1 mm samples at the temperature of 50°C. The obtained values of specific heat for composite materials were compared with the theoretical values estimated from the rule of mixtures: $Cp_{comp} = 1/\rho_{comp} (V_m\rho_m Cp_m + V_r\rho_r Cp_r)$; where: Cp is the specific heat, ρ is the density, V is the volume fraction of a component, and superscripts comp, m and r stay for the properties of the composite, matrix and reinforcement, respectively. The bending strength of the composite was determined in a three-point bending test using ZWICK 1446 testing machine at a support spacing of 30 mm and a head travel speed of 10 mm/min. The size of the test specimens was 30x4x2.5 mm. The average values of the bending strength were calculated from five test realizations.

Tribological tests (ball-on-flat) were conducted applying the following parameters: the force F_n – 5 N (steel ball) and velocity – 5 mm/s. The friction force F_t thus generated was measured with a piezoelectric displacement sensor 24 times per second. It was induced and recorded in 30 min long friction processes. The friction coefficient was analyzed using a special software. After the test, the surface of the groove was analyzed using scanning electron microscopy and wear volume of the groove of the samples was measured with a scanning profile-gauge (Veeco).

3. Results and discussion

The density and hardness of the Cu/Al_2O_3 composites obtained by hot pressing (HP) are presented in Tab. I.

Tab. I The properties of pure sintered copper and Cu/Al_2O_3composite materials.

Material composition (vol.%)	Theoretical density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)	Hardness HV1
Cu	8.96	8.7	97.1	39.7±3.2
Cu+1%Al_2O_3fine	8.87	8.6	96.9	42.1±2.4
Cu+3%Al_2O_3fine	8.77	8.5	96.9	43.1±1.8
Cu+5%Al_2O_3fine	8.67	8.3	95.7	54.7±3.4
Cu+1%Al_2O_3coarse	8.87	8.6	96.9	42.4±2.1
Cu+3%Al_2O_3coarse	8.77	8.6	97.8	55.2±1.8
Cu+5%Al_2O_3coarse	8.67	8.4	96.8	60.2±2.7

The data reveal higher relative density for composites with electrocorundum having a coarse particle size. This is because the specific surface of coarser particles is smaller and the powder compressibility is higher. The residual porosity was observed only between copper particles. Most probably, electrocorundum used as the reinforcing phase eliminates intergranular porosity formed between α-Al_2O_3 powder particles [15-16]. This fact can be easily explained by the rule of mixtures. The higher hardness of the composites can also be attributed to the fact that alumina particles prevent the movement of dislocations [17]. It is obvious that by increasing the amount of alumina phase, with hardness much higher than that of pure copper, the hardness of composites also increases. The obtained results are consistent with the density results for the developed composites.

SEM and EDS images of the cross-sections of the composite materials are shown in Fig. 3-4.

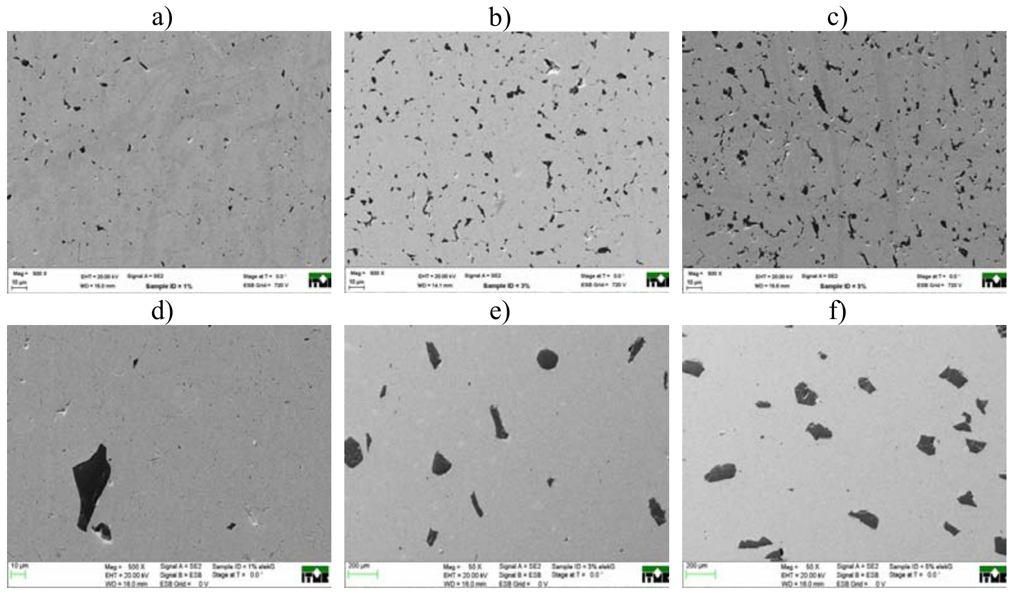

Fig. 3. SEM images of Cu/Al_2O_3 composite materials: (a) Cu-1%Al_2O_3 fine, (b) Cu-3%Al_2O_3 fine, (c) Cu-5%Al_2O_3 fine, (d) Cu-1%Al_2O_3 coarse, (e) Cu-3%Al_2O_3 coarse, (f) Cu-5%Al_2O_3 coarse.

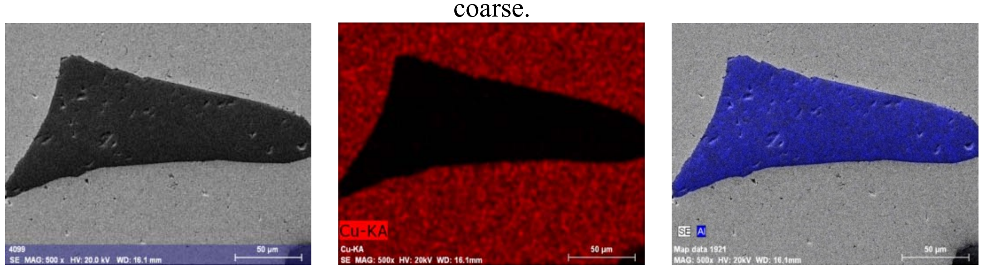

Fig. 4. SEM/EDS maps of the distribution of elements on the surface for Cu-5%Al_2O_3 coarse.

The SEM examination has revealed a homogeneous distribution of the ceramic phase in the composite. A good quality bonding (adhesion type) was observed between the copper matrix and the ceramic reinforcement, especially for the samples made with the coarse alumina powder. No significant structural discontinuities were observed at the copper-ceramics boundaries and there was no evidence of the presence of the third phase (Fig. 4).

Tab. II Thermal properties (at 50°C) and mechanical properties of pure sintered copper and Cu/Al_2O_3 composites with two kinds of Al_2O_3 particles.

Material composition (vol.%)	Thermal Conductivity (W/m·K)	Measured Specific heat (J/g·K)	Theoretic Specific heat (J/g·K)	Bending Strength (MPa)
Cu	359.2±4.8	-	0.39	-
Cu+1%Al_2O_3fine	333.5±2.1	0.40±0.1	0.42	291.0±7.7
Cu+3%Al_2O_3fine	315.2±2.8	0.41±0.1	0.43	275.4±7.9
Cu+5%Al_2O_3fine	303.5±1.6	0.42±0.1	0.44	294.4±9.1
Cu+1%Al_2O_3coarse	330.1±3.4	0.40±0.1	0.42	284.5±9.2
Cu+3%Al_2O_3coarse	320.1±3.4	0.42±0.1	0.43	300.1±8.9
Cu+5%Al_2O_3coarse	305.5±1.1	0.43±0.1	0.44	289.6±8.3

The particle size and the amount of the reinforcement have a pronounced effect on the mechanical properties of the composites. Selected properties of the fabricated Cu/Al_2O_3 composites are shown in Tab. II.

As expected, the thermal conductivity of composites decreased when increasing the ceramic content. No significant differences in the thermal conductivity and the specific heat were observed for the composites made with fine or coarse Al_2O_3 powders. In both cases, the measured thermal conductivity was higher than 300 W/(m·K).

The influence of the size of ceramic reinforcement and its distribution within the copper matrix on the thermal properties of the obtained composites was also examined by modelling. To this end, a numerical analysis (FEAP) was performed for two models of the Cu-5%Al_2O_3 composite taking into account the porosity of 1%, 3% and 5% [18,19]. In model 1 it was assumed that the reinforcement phase is uniformly distributed in the metal matrix and a porosity of 3% was randomly introduced (Fig.5-Model 1- b). Model 2 required random distribution and multiple grinding of the reinforcement phase, with porosity arranged just like in model 1 (Fig. 5-Model 2- b).

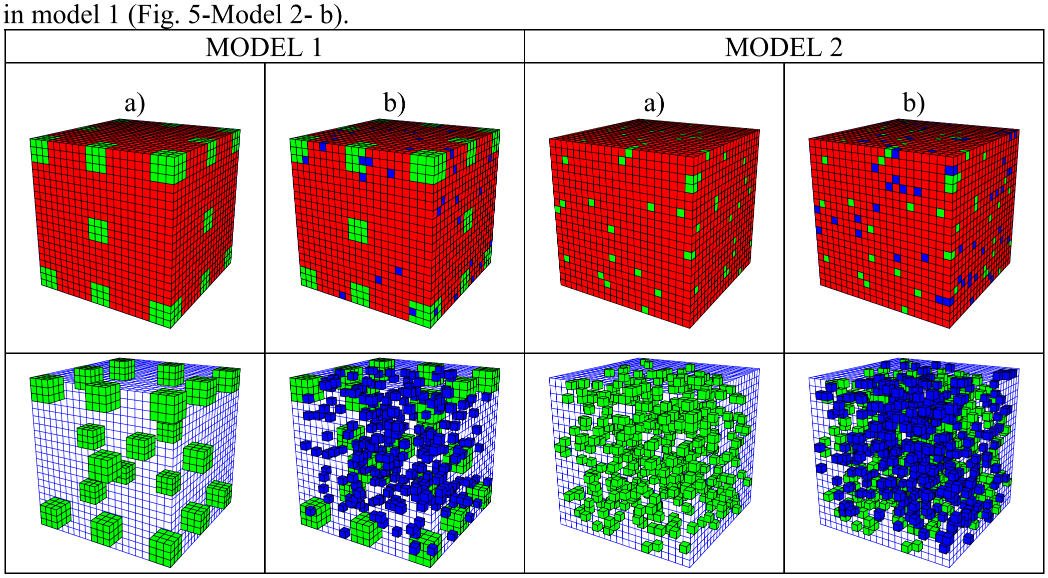

Fig. 5. FEM mesh for models 1 and 2; blue voxels – porosity, green – ceramic phase, red – copper; a) 0% porosity, b) 3% porosity.

The results of the numerical calculations of thermal conductivity for the assumed models are shown in Tab. III.

Tab. III Results of numerical calculations of thermal conductivity for Cu-5%Al_2O_3 composites.

	0% porosity		3% porosity	
	Model 1	Model 2	Model 1	Model 2
Thermal Conductivity W/(m·K)	362.0	362.1	348.4	348.7

It is noted that the numerically predicted values of the thermal conductivity of Cu-5%Al_2O_3 composites (Tab. III) are overestimated when compared with the experimental data in Tab. II. Another conclusion that can be drawn from Tab. III is that distribution of the reinforcement phase in the composite as well as multiple grinding of the ceramic phase grains do not exert a strong influence on thermal conductivity. On the other hand, porosity significantly affects the thermal properties of these composite materials.

When compared with the Cu/Al_2O_3 composites (α-Al_2O_3) developed in [15], using the same hot press and under analogous process conditions, the mechanical and thermal properties of the present composites are superior to those reported in [15]. This fact is linked with the elimination of the intergranular porosity which typically forms between non-sintered Al_2O_3 grains. From the point of view of prospective applications, the tribological properties of composites are particularly important.

The comparison of the time-dependent friction coefficient for Cu/Al_2O_3 composites is presented in Fig. 6 for the two groups of materials under investigation. It can be concluded that as a result of an increase in the composite's hardness with the raise of the ceramic phase content, the resistance to motion and, in consequence, the friction coefficient are also increased. The measured values of the friction coefficient for composites with 1 vol.% of Al_2O_3 content were similar to those for pure copper (μ = 0.3). For composites with 3 and 5 vol.% of Al_2O_3 content the friction coefficient vs. time measurements are depicted in Fig. 6. It can be seen that Cu/Al_2O_3 composites have a relatively high and sTab. friction coefficient.

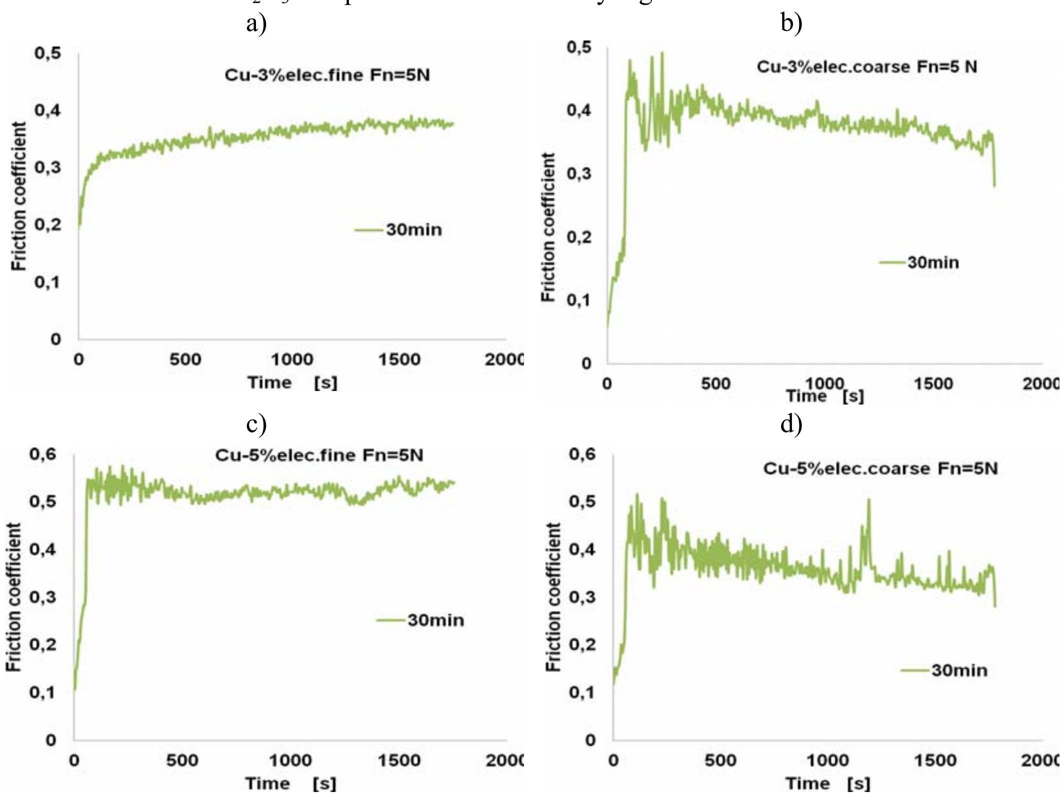

Fig. 6. The friction coefficient for Cu/Al_2O_3: a) Cu-3%Al_2O_3 fine, b) Cu-3%Al_2O_3 coarse, c) Cu-5%Al_2O_3 fine, d) Cu-5%Al_2O_3 coarse.

For 5 N load, the final value of the friction coefficient (between the steel and composite) for fine Cu/Al_2O_3 composites is 0.3 (3% ceramic phase) and 0.5 (5% ceramic phase), whereas for coarse Cu/Al_2O_3 composites it equals 0.4 (3% ceramic phase) and 0.4 (5% ceramic phase). In several initial friction cycles, both the instantaneous value of the friction force and the amplitude of its changes increased for each friction cycle (when movement was made in one direction).

No significant differences in the friction coefficient values in relation to the number and size of electrocorundum particles were observed. Temporary changes in the friction coefficient values of the order of $\Delta\mu$ = ~ 0.1 resulted from variable resistance to motion accompanying friction for friction pairs, originating from numerous small broken-out sections and transported wear products (mass transfer).

Exemplary images of the groove area are presented in Fig. 7. The macrostructure of the groove is very inhomogeneous: gaps, chipping and accretion are present, which causes rapid friction. In all analyzed cases, tiny ceramic and metal particles, removed during the friction process, were observed.

a) b) c) d)

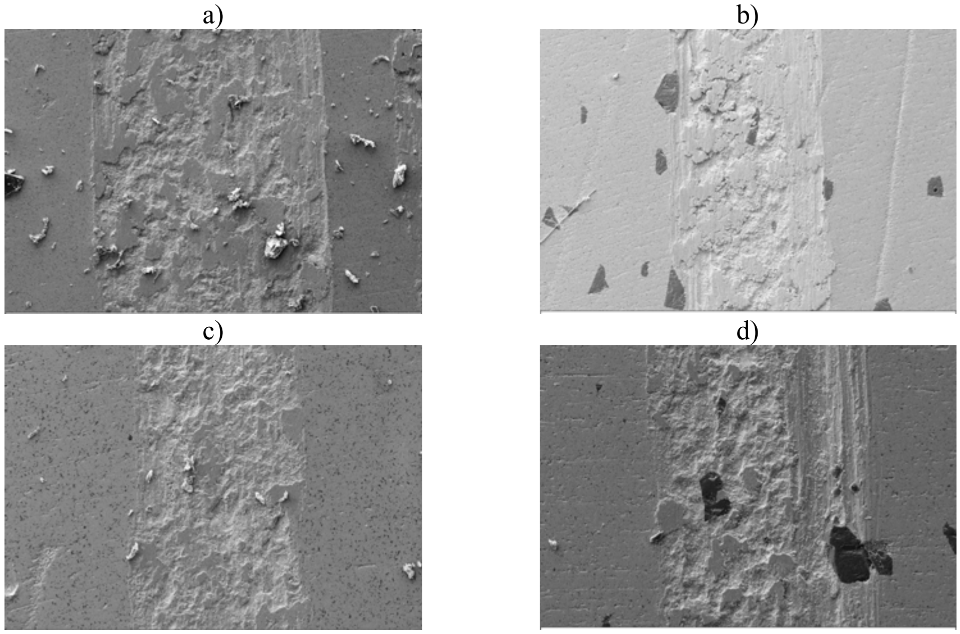

Fig. 7. SEM images of the groove area for the time of friction test (F_n=5 N) for composites: a) Cu-3%Al_2O_3 fine, b) Cu-3%Al_2O_3 coarse, c) Cu-5%Al_2O_3 fine, d) Cu-5%Al_2O_3 coarse.

Figure 8 shows the 3-D profiles of the composite surface after the wear test. The increased content of fine Al_2O_3 results in an improved frictional wear resistance: the volume of the material abraded during the 30 min test was 0.5×10^{-6} cm^3, 0.41×10^{-6} cm^3 and 0.36×10^{-6} cm^3 for Cu-1%Al_2O_3, Cu-3%Al_2O_3 and Cu-5%Al_2O_3, respectively. As can be observed, there is a significant improvement in the wear resistance when compared with pure copper for which the volume of the groove was 8.1×10^{-6} cm^3. Similar wear results were obtained for composites with electrocorundum having bigger grains.

a) b) c)

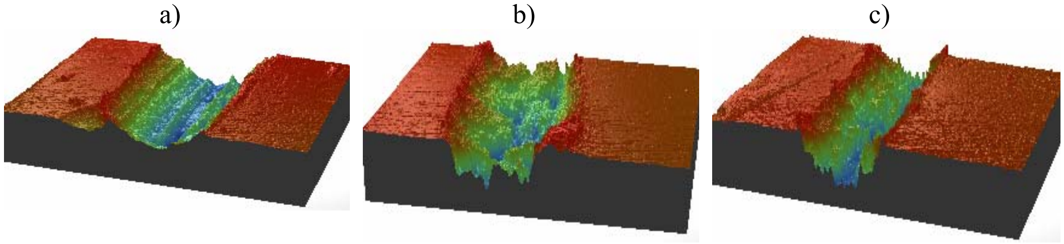

Fig. 8. Wear profiles after the friction test for: a) Cu-1%Al_2O_3 fine, b) Cu-3%Al_2O_3 fine, c) Cu-5%Al_2O_3 fine.

4. Conclusions

The use of an electrocorundum made it possible to obtain favourable properties of the composites, as compared to composites made with α-Al_2O_3 powder as the reinforcement phase. The manufacturing process of copper-based composites reinforced with electrocorundum particles of significantly different granulation (fine 3 μm and coarse 180 μm) was developed. As a result, composite materials with decreased porosity, as compared with the composites reinforced with a non-sintered aluminium oxide powder (α-Al_2O_3), were obtained. Eliminating intergranular porosity, which is undesirable from the point of view of the material properties, will enable manufacturing of graded Cu/Al_2O_3 composites (FGM) using hot pressing or tape casting method for target applications in e.g. rocket thrusters.

The obtained Cu/Al_2O_3 composite materials are characterized by relatively high thermal conductivity (over 300 W/(m·K)). Thermal conductivity depends significantly on the ceramic content - as the volume fraction of the ceramic phase increases, the thermal conductivity decreases. Higher values of thermal conductivity values were measured for composites containing coarse electrocorundum.

No significant differences in the friction coefficient values in relation to the number and size of grains of electrocorundum were observed. On the other hand, an addition of the ceramic phase leads to increased wear resistance when compared with that of pure copper.

By using electrocorundum (polycrystalline material) as ceramic reinforcement in copper-based composites it was possible to decrease porosity in the ceramic phase (electrocorundum used as the reinforcing phase eliminates intergranular porosity formed between α-Al_2O_3 powder particles, [15]). Finally the improvement of composite properties was obtained, which is so crucial from their future applications point of view.

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Садржај: *Композити бакар/алумина су у широкој употреби у аутомобилској и космичкој индустрији као производи који су подвргнути термичким и механичким оптерећењима, као што су ракетни потисници и компоненте ваздухопловних мотора. Ови материјали су добро познати због доброг трења и отпорности на хабање, добре отпорности на термички умор, велике термичке проводљивости и високе специфичне топлоте. У овом раду испитиван је процес синтеровања бакар/корунд композита који је ојачан са честицама корунда величине 3 или 180 μm и уделом од 1, 3, 5 запреминских %. Испитиван је утицај различите величине честица на микроструктуру, физичка и механичка својства, као и на термална својства композита.*

Кључне речи: *бакар/алумина композити, синтеровање, моделовање термичких својстава, микроструктура, механичка својства.*