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PROCESSING, MICROSTRUCTURE AND PROPERTIES OF DIFFERENT METHOD OBTAINED Cu-Al_2O_3 COMPOSITES

WYTWARZANIE, MIKROSTRUKTURA I WŁAŚCIWOŚCI KOMPOZYTÓW Cu-Al_2O_3 OTRZYMYWANYCH RÓŻNYMI TECHNIKAMI

Alumina/copper composites are used where high thermal conductivity, high absorption and dissipation of heat, high resistance to thermal fatigue and good frictional wear resistance are required. The properties of these composites depend on a number of factors including the content, shape and distribution of the ceramic phase, the method of their obtaining, as well as the conditions under which they are obtained. All these variables have influence on mentioned properties and, in consequence, on the future applications of the final material. The aim of this paper was to develop Cu-Al_2O_3 composites, processed using two techniques, namely sintering (of Cu /Al_2O_3 high-energy mixed powders) and tape casting (of slurry of the following composition: 1, 3 and 5 vol.% of Al_2O_3 phase; the remaining part: Cu). The compositions were determined taking into consideration the planned applications. The paper presents newly developed technologies, the results of both microstructure investigations as well as of the measurements of selected physical and mechanical properties (microhardness, wear resistance, thermal conductivity etc.) and contains the analysis of the influence of selected techniques and processing conditions on the properties and the interface morphology between ceramic and copper.
Keywords: ceramic-metal composites, hot pressing, tape casting, microstructure, thermal properties

Kompozyty na bazie miedzi znajdują zastosowanie tam, gdzie jest wymagane: wysokie przewodnictwo cieplne, wysoka absorpcja i rozpraszanie ciepła, wysoka odporność na zmęczenie cieplne i dobra odporność na zużycie ścierne. Właściwości tych kompozytów zależą od wielu czynników tj. zawartości, kształtu i rozkładu fazy ceramicznej w metalowej osnowie jak również od samego sposobu (warunków) ich wytwarzania. Celem niniejszej pracy było otrzymanie kompozytów Cu-Al_2O_3 stosując dwie techniki: spiekania mieszaniny proszków pod ciśnieniem oraz odlewanie folii kompozytowych (*tape casting*), laminowanie oraz końcowe spiekanie otrzymanych materiałów. Ze względu na przyszłe zastosowania tych kompozytów (m.in. elementy w układach turbin w samolotach) wytypowane zostały następujące składy: $99\%_{obj.}$Cu-$1\%_{obj.}Al_2O_3$, $97\%_{obj.}$Cu-$3\%_{obj.}Al_2O_3$, $95\%_{obj.}$Cu-$5\%_{obj.}Al_2O_3$. W prezentowanej pracy przedstawiono dwie technologie otrzymania kompozytów na bazie miedzi. Przeprowadzone zostały badania mikrostruktury otrzymanych kompozytów ze szczególnym zwróceniem uwagi na możliwość pojawienia się warstwy przejściowej ceramika/metal. Przeprowadzone zostały również badania właściwości fizycznych (twardość, gęstość), badania właściwości cieplnych (dyfuzyjność cieplna, przewodnictwo cieplne) oraz badania właściwości mechanicznych (zużycie ścierne) otrzymanych kompozytów.

1. Introduction

Along with the development of various branches of industry, we have experienced a growing demand for new multiphase materials which could work in particularly difficult thermal conditions and in systems of high mechanical stress. The methods of manufacturing ceramic-metal composites enable obtaining materials which have properties of both ceramic materials (e.g. high hardness) and metals (e.g. high plasticity). This feature is crucial for instance for the development of technology of obtaining friction elements with increased resistance to cracking. Some metal-ceramic composites can possess particularly interesting physical properties such as high thermal conductivity, high electric conductivity or special magnetic characteristics. Copper-based composites, doped with the ceramic phase, showing, among others, high resistivity to sudden temperature changes, high thermal conductivity as well as increased mechanical strength, belong to the materials with the abovementioned properties [1-3]. Because of these superior features, Cu-Al_2O_3 composites have been used as resistance welding electrodes, lead frames, accelerators and electrical connectors [4,5]. Another possible application of a Cu-Al_2O_3 composite is to use it as a truster in turbines employed in the aerospace industry. Such parameters as thermal conductivity >300 W/(m*K), increased erosion, oxidation resistance and long life time are required in the case of these systems. Due to those requirement, materials of the following composition were selected: Cu/1%, 3%, 5 vol.% Al_2O_3.

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Metal matrix composite materials can be produced by many methods including hot pressing (HP), casting techniques (TC), internal oxidation and infiltration, et. [2,4,6,7]. There are several limitations on obtaining this kind of materials, e.g. a high sintering temperature of ceramic or its low wettability by liquid metals [8,9]. Therefore, special procedures are needed. In the present paper Cu-Al_2O_3 composites were obtained by sintering a powder mixture in a hot press and by sintering laminated foil cast materials (tape casting). These techniques fail to give a good uniformity of dispersion.

Tape casting is a low-cost process for making high-quality laminated materials, in the case of which an adequate thickness control and a good surface are achieved [10,11]. The tape casting method allows the production of a thin layer of a composite material (ceramic/metal and organic) by coating a carrier surface with casting slurry as it passes under a doctor blade [12]. Tape casting slurries are complex systems which contain inorganic and organic components. The inorganic component is a powder, whereas organic components are dispersing agents, binders and other surfactants. These organic additives impart a variety of properties to the slurry and the green foil [13,14]. The task of the liquidizer is to dissolve organic additives such as the dispersant and the binder in order to achieve homogeneous slurry. Dispersants assure the stability of the suspension by keeping particles apart. The task of the binder addition is to make the tape flexible for handling in subsequent processing steps [11,14]. The tape casting technique has advantages over the method entailing sintering of powders due to the fact that it enables formation of flat fittings with a large surface. Rough foil is a semi-finished product, from which fittings of different sizes can be cut out. In the present paper, the properties of Cu-Al_2O_3 composite materials obtained by the two methods are compared.

2. Experimental procedure

A high purity (99,99%) aluminium oxide powder (α-form) from NewMet was used in the present work. The mean particle size (d_{50}) of this powder was in the range 2-3 μm (Fig. 1a) and the BET specific surface area was 3,66 m^2/g. The copper powder (99,9% purity) was a commercial product of Sigma Aldrich, with the grain size of about <10 μm (Fig. 1b) and the BET specific surface area was 0,61 m^2/g. The morphology of the starting powders is shown in Fig. 2.

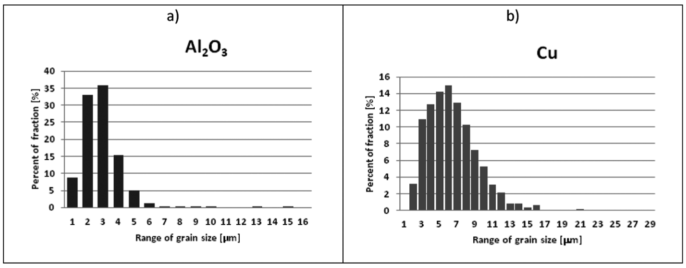

Fig. 1. Distributions of the grain size of (a) Al_2O_3 and (b) Cu

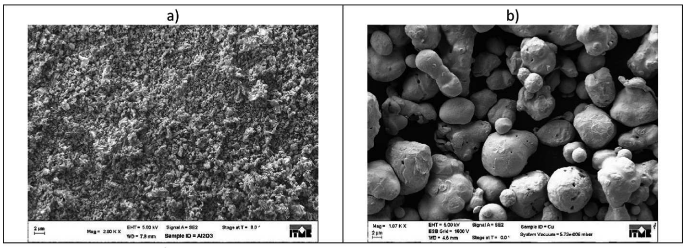

Fig. 2. SEM image of the starting powders (a) Al_2O_3 and (b) Cu

The remaining components of the slurry were: a binder (PVB), surface-active agents (di-octylo-phtalane) and a liquidizer (alcohol-POCH).

Three compositions of the powder mixture with the following Cu to Al_2O_3 ratio (in vol.%): 99Cu-1Al_2O_3, 97Cu-3Al_2O_3 and 95Cu-5Al_2O_3, were prepared. They were obtained in a mechanical mixing process in a planetary ball mill (Pulverisette 6, Fritsch) with a tungsten carbide balls (Ø 5 mm). High-energy mechanical milling experiments were performed at a room temperature in air atmosphere, at the rotation speed of 200 rpm and at the time of mixing of 6h. The weight ratio of balls to powder (BPR) was 3:1.

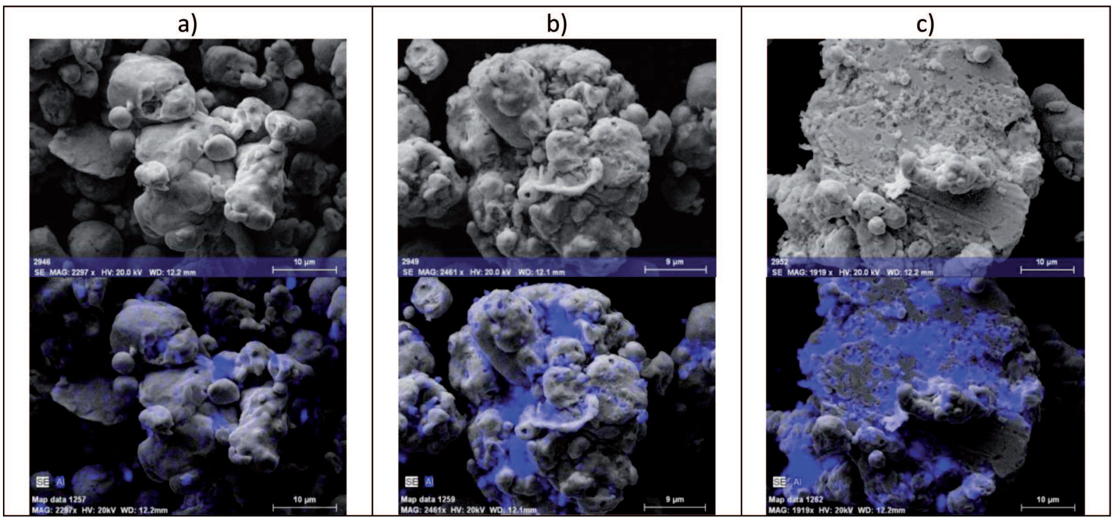

Fig. 3. SEM and EDS images of powder mixtures after mechanical alloying for different compositions: (a) Cu+1%Al_2O_3, (b) Cu+3%Al_2O_3, (c) Cu+5%Al_2O_3

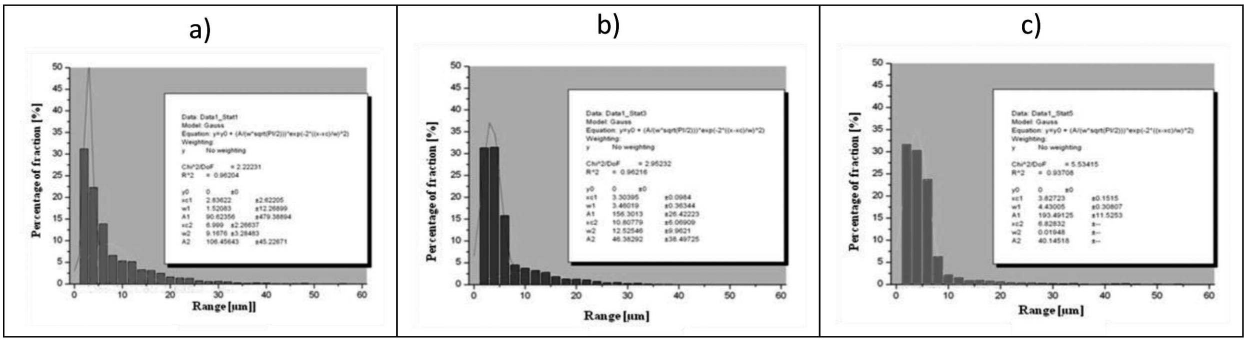

Fig. 4. Grain size distribution of (a) $Cu+1\%Al_2O_3$, (b) $Cu+3\%$ Al_2O_3, (c) $Cu+5\%Al_2O_3$ powders mixture

The mixing conditions were chosen after earlier experiments of authors [15,16]. The morphology of the powder mixtures after mixing and EDS maps are shown in Fig. 3. Particle size distribution analysis after the mixing process is shown in Fig. 4.

When it comes to the particle size distribution for the Al_2O_3 content of 1% and 3%, there is a clear separation between the matrix and the reinforcing phase. For the Al_2O_3 content of 5%, the degree of homogeneity of the mixture is the biggest, as evidenced by the lack of spectra for both components.

The powder mixtures were used to obtain composite materials with the same compositions (1, 3 and 5 vol.% of Al_2O_3 phase; the remaining part: Cu) by two techniques: sintering the powder mixture in a hot press and sintering of laminated foils. For the first technique, the composite powder mixture was placed in a graphite die and sintered at 1050°C by 30 min in nitrogen atmosphere and the pressure of 30 MPa by using an ASTRO press. The tape casting process was more complex. The stable slurry consisting of the powder mixture, a binder, a liquidizer and surface-active agents was cast on the laboratory belt using a doctor blade method and underwent a one day long drying process at a room temperature. After the green foil of the composite material was removed from the belt and cut into the size of 67×67 mm, the stack (10 single foils) was formed and finally placed in the metal die where the laminated process was performed. The thickness of a single foil was 0.4 mm. The lamination process was carried out at 100°C by 5 min in air atmosphere using a pressure 30 MPa. The sintering process of the laminated stacks of composite materials was conducted in two stages. The first step included burning organic additives during a long-lasting process in air atmosphere. Next, the final density of the samples was obtained by their sintering under a hydrogen atmosphere at the temperature of 1050°C in a Batch furnace.

The morphology of both the starting powders and the powders after milling as well as the microstructure of the composite materials were examined by using a scanning electron microscope (SEM) AURIGA CrossBeam Workstation (Zeiss) with an integrated EDS microanalysis system. Characterization of the grain-size distribution of the starting powders and the powders after milling was performed employing a CLEMEX television image analysis system.

The density of the $Cu\text{-}Al_2O_3$ composites was measured according to the Archimedes method. The theoretical density was calculated on the basis of densities of Al_2O_3(ρ_{Al2O3} =3.97 g/cm^3) and Cu (ρ_{Cu} = 8.97 g/cm^3). The hardness (HV1) was tested by Durascan 10/Emcotest with a Vickers diamond indenter applying a loud 9,81 N with the loading time of 10 s. The hardness results were averaged over 5 indentations per a specimen.

Thermal properties (thermal diffusivity and thermal conductivity) were measured within the temperature range 50-600°C using the Laser Flash Analyser LFA457/Netzsch. The measurement principle is as follows. The front side of a plane parallel solid sample is heated by a short laser pulse (Nd-YAG). The heat induced propagates through the sample and causes a temperature increase on the rear surface. This temperature rise is measured versus time using an infrared detector. Thermal diffusivity (a) and, in most cases, the specific heat (c_p) can be ascertained using the measured signal. If the density (ρ) and the specific heat are known, thermal conductivity (λ) is determined from the relation:

$$\lambda = c_p \cdot a \cdot \rho \tag{1}$$

where: λ – thermal conductivity in W/(m·K), ρ – density in g/cm^3, c_p – specific heat in J/(g·K), a – thermal diffusivity in mm^2/s.

The measurement conditions were the following: the size of samples 10×10×3 mm, the surface of samples was covered by a thin layer of graphite in spray and the measurement was carried out in protective argon atmosphere. The values of the specific heat for composite materials were determined from the rule of mixtures.

Tribological tests were conducted according to the following process. The samples were pressed against a stainless steel ball with 6.5 mm in diameter with force F_n =5 N. A holder together with a ball attached to it were set in a reciprocating motion driven by an electro-dynamic generator. The two components between which the friction appeared slid on one another at a velocity of 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 30.0 min long friction processes. The friction coefficient was analyzed using special software. After the test, the surface of the groove was analysed using scanning electron microscopy.

3. Results and discussion

The physical properties (density and hardness) of $Cu\text{-}Al_2O_3$ composites which were obtained by two methods:

hot pressing (HP) and sintering of laminated green foils (TC) are presented in Table 1.

For the composites obtained by hot pressing, we managed to get a better material density. The lower density of the composites was achieved by tape casting due to the presence of additional pores created after the removal of organic additives.

The hardness values increased when raising the amount of Al_2O_3. Higher hardness was achieved for the composite materials obtained by the tape casting technique. A possible reason for this phenomenon can be a better (more homogenous) distribution of the ceramic phase in the metal matrix in this case.

SEM and EDS images of the cross-sections of composite materials obtained by two techniques are shown in Fig. 5 and Fig. 6.

TABLE 1

The physical properties of $Cu\text{-}Al_2O_3$ composite materials

Material composition (in vol%)	Theoretical density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)	Hardness HV_1 (MPa)
$Cu+1\%Al_2O_{3\,HP}$	8.90	8.40	94.4	39.7
$Cu+3\%Al_2O_{3\,HP}$	8.81	8.31	94.3	42.8
$Cu+5\%Al_2O_{3\,HP}$	8.72	8.24	94.4	49.5
$Cu+1\%Al_2O_{3\,TC}$	8.90	8.25	92.7	42.9
$Cu+3\%Al_2O_{3\,TC}$	8.81	8.14	92.4	47.7
$Cu+5\%Al_2O_{3\,TC}$	8.72	7.90	90.1	50.0

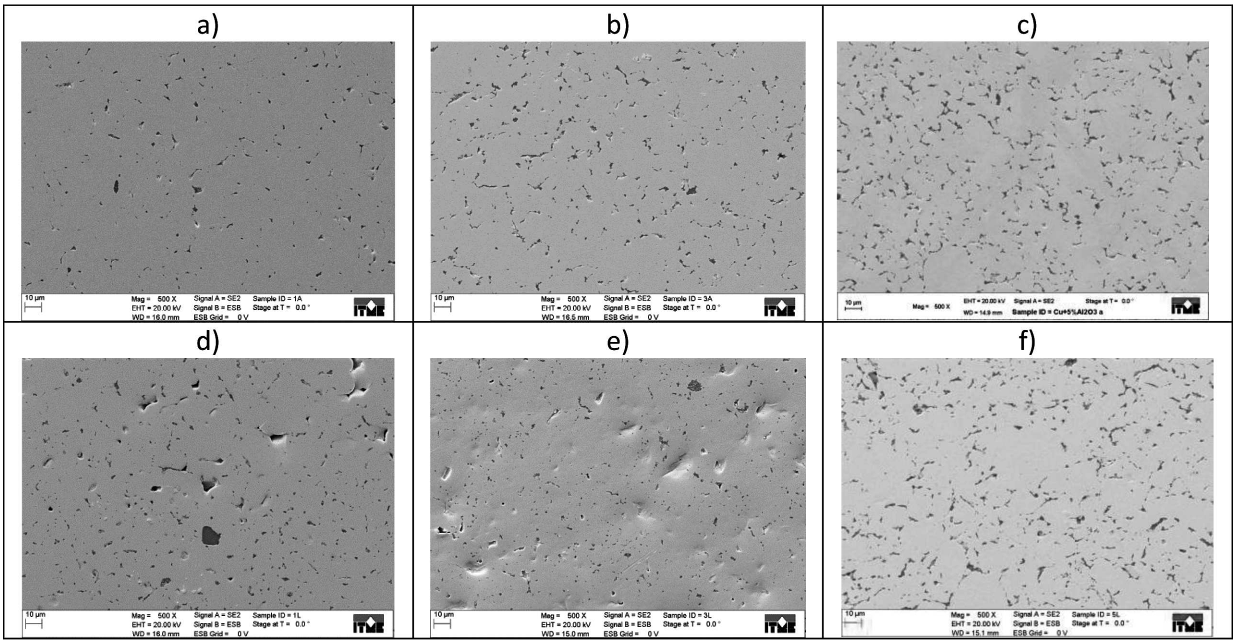

Fig. 5. SEM images of $Cu\text{-}Al_2O_3$ composite materials: (a) $Cu+1\%Al_2O_{3HP}$, (b) $Cu+3\%Al_2O_{3HP}$, (c) $Cu+5\%Al_2O_{3HP}$, (d) $Cu+1\%Al_2O_{3TC}$, (e) $Cu+3\%Al_2O_{3TC}$, (f) $Cu+5\%Al_2O_{3TC}$

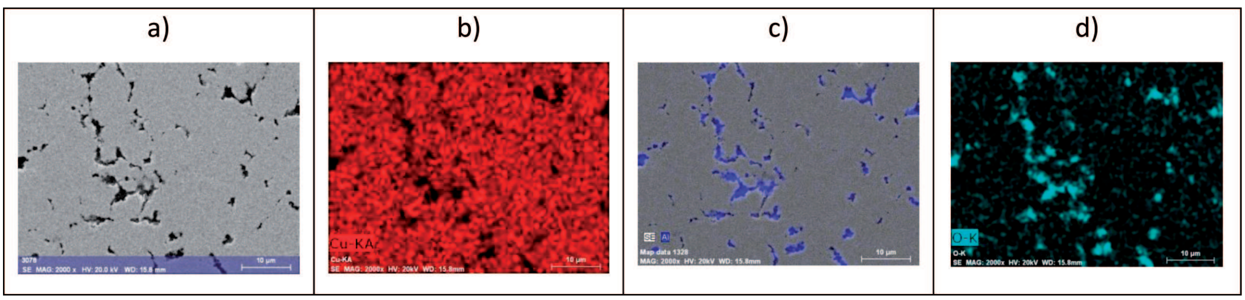

Fig. 6. SEM/EDS maps of the distribution of elements on the surface for $Cu+5\%Al_2O_{3HP}$ (a) SEM image, (b) Cu, (c) Al (d) O

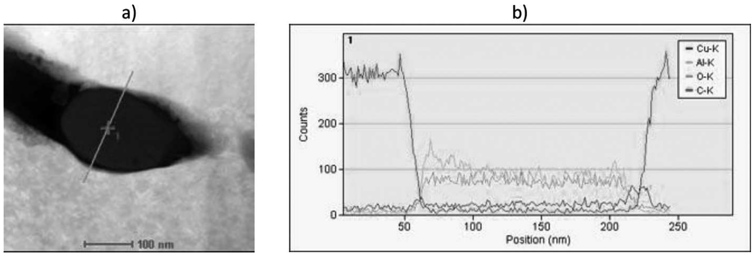

Fig. 7. STEM image (a) and linear elements distribution (b) in Cu-5%Al_2O_{3HP}

As a result of the conducted analysis, a good binding was reported between the copper matrix of the composite and ceramic particles of the reinforcing phase. No significant structural discontinuities were observed in the area of the copper/ceramics boundary. In all instances, the structure was characterized by high homogeneity. The presence of holes was a direct consequence of the process of samples processing, i.e. cutting and polishing, which caused pulling ceramics out of the copper matrix. Composites obtained by tape casting possessed additional porosity, which resulted from eliminating organic additives used in the preparation of slurry. No structural discontinuity linked with the bonding of foils was identified in the cross section of the samples, what proves that lamination took place in appropriate conditions.

Microstructural investigations (Fig. 7) of interface appeared a clean ceramic-metal boundary, there is no evidence of presence the third phase. However, in the case of hot-pressed composites locally some amounts of CuO_x phase was observed.

The results of both the measured thermal diffusivity and the estimated thermal conductivity at 50°C of obtained composite materials are presented in Table 2 and in Fig. 8.

TABLE 2

Thermal properties of Cu-Al_2O_3 composite materials

Material composition (in vol%)	Thermal Conductivity (W/(m·K)	Thermal Diffusivity (mm^2/s)
Cu+1%Al_2O_{3HP}	339.5	95.7
Cu+3%Al_2O_{3HP}	316.4	90.2
Cu+5%Al_2O_{3HP}	296.5	87.0
Cu+1%Al_2O_{3TC}	308.5	90.4
Cu+3%Al_2O_{3TC}	265.2	78.6
Cu+5%Al_2O_{3TC}	220.2	68.2

The results of the diffusivity and thermal conductivity of Cu-Al_2O_3 composites depend greatly on the methods of their obtaining. Higher thermal diffusivity values were observed for materials sintered under press. As was stated above, materials obtained by tape casting exhibit higher porosity, which in turn substantially lowers the thermal conductivity value. Consistent with expectations, an increase in the ceramic phase rate in a composite brings a drop in thermal conductivity and stems from the rise in the share of the phase with lower thermal conductivity.

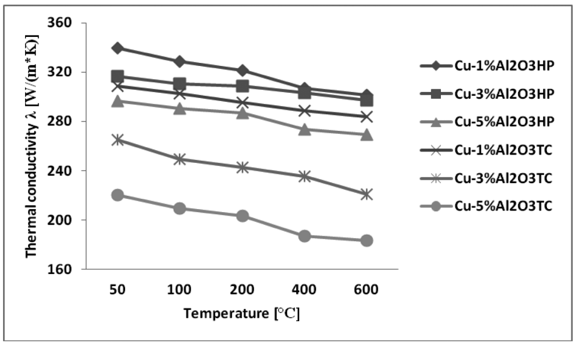

Fig. 8. Thermal conductivity of Cu-Al_2O_3 composite materials

The comparison of the time-dependant friction coefficient of copper-alumina composites is presented in Fig. 9.

When comparing the obtained results of the friction coefficient for both groups of composite materials, it can be concluded that as a result of an increase in the composites hardness with the raise of the ceramic phase rate, resistance to motion and, in consequence, the friction coefficient also

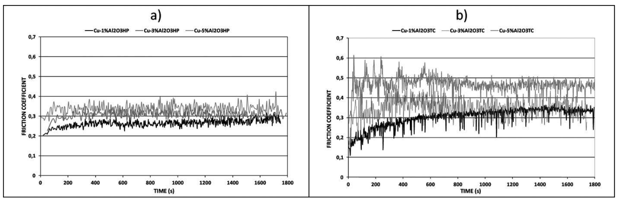

Fig. 9. The friction coefficient of copper-alumina composites: (a) HP and (b) TC

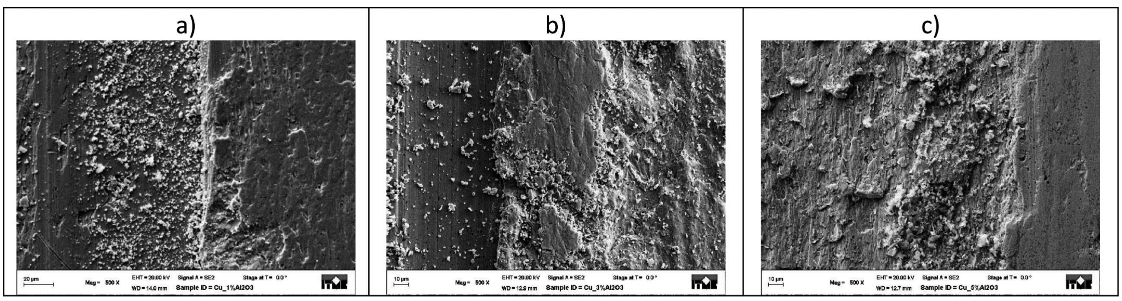

Fig. 10. SEM images of the groove area for the Cu-Al_2O_3 TC: (a) Cu+1%Al_2O_{3TC}, (b) Cu+3%Al_2O_{3TC}, (c) Cu+5%Al_2O_{3TC}

increase. In the case of materials obtained by sintering powder mixtures, the friction process is rather mild, with no substantial differences and the friction coefficient value is around 0.25-0.35, depending on the dopant rate. Materials obtained from laminated foil are characterized by faster wear. During the friction process, considerable changes in resistance to motion, which significantly affect the friction coefficient value (the value varies between 0.3 and 0.6), were noted.

Examplary images of the groove area are presented in Fig. 10. The macrostructure of the groove is very unhomogeneous; gaps, chipping and accretion are present, which causes rapid friction. In all analyzed cases, tiny ceramic and metal particles, removed in the friction process, were observed.

4. Conclusions

On the basis of the presented results following conclusion can be drawn:

- It is possible to obtain good quality Cu-Al_2O_3 composite material by following techniques: hot pressing the powder mixture in a hot press and sintering of laminated foil casted materials.
- There was not observed the presence of interphase at the ceramic-metal boundary. However some local presence of CuO_x phase was observed in the case of hot-pressed materials.
- Developed of the Cu-Al_2O_3 composite materials are characterized by relatively high thermal conductivity. Thermal conductivity depends greatly on the Al_2O_3 content and the methods of their obtaining. Higher thermal diffusivity values were observed for hot pressed materials (>300 W/(m·K)).
- Increasing of the ceramic rate in composite caused the increase of resistance to wear and also, in consequence, the friction coefficient.

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