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INFLUENCE OF PRODUCTION PARAMETERS ON MICROSTRUCTURE AND PROPERTIES OF COPPER MATRIX COMPOSITES

WPŁYW PARAMETRÓW WYTWARZANIA NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MATERIAŁÓW KOMPOZYTOWYCH NA OSNOWIE MIEDZI

The paper presents results of studies into production of copper-based composites hardened with particles od Al_2O_3. Influence of chemical composition and process conditions on changes in structure and properties of the composites was examined. The following process parameters were examined: duration of powder composites milling, pressing pressure and temperature of sintering. Manufacturing process consisted of mechanical synthesis of copper powders and oxide of aluminium in the volume from 3 to 12%, and then their consolidation by two-side pressing followed by sintering. Sintering took place in the solid phases (T_s = 650°C) and with partial presence of liquid phase (T_s = 950°C). Pressing was conducted in cold conditions, using various pressures of 300 and 400 MPa. As a final operation a two-side pressing was applied under pressure of 500 MPa and recrystallization annealing. Evaluation of morphology of initial powders and structure of produced composites was done using scanning electron microscope (SEM), while the size of crystallites of Cu + Al_2O_3 powder mixture was determined by X-ray method. Density of the produced compacts was determined by geometrical method. Nasing on the density results also total porosity of the samples was determined.
Keywords: metal matrix composites, powder metallurgy, pressing, sintering, compact

W pracy przedstawiono wyniki badań dotyczące otrzymywania materiałów kompozytowych na osnowie miedzi umacnianych cząstkami Al_2O_3. Badano wpływ składu chemicznego oraz parametrów wytwarzania na zmiany struktury i właściwości badanych materiałów kompozytowych. Analizowano wpływ następujących parametrów wytwarzania: czasu mielenia komponentów proszkowych, ciśnienia prasowania oraz temperatury spiekania. Proces wytwarzania obejmował mechaniczną syntezę proszków miedzi oraz tlenku aluminium w ilości od 3 do 12% obj., a następnie ich konsolidację poprzez dwustronne prasowanie i następujące po nim spiekanie. Proces spiekania przebiegał w fazie stałej (T_{rms} = 650°C) oraz z częściowym udziałem fazy ciekłej (T_{rms} = 950°C). Zabieg prasowania prowadzono na zimno, stosując różne ciśnienie prasowania 300 oraz 400 MPa. Jako zabieg końcowy zastosowano prasowanie dwustronne pod ciśnieniem 500 MPa oraz wyżarzanie rekrystalizujące. Oceny morfologii proszków wyjściowych oraz charakterystyki struktury uzyskanych materiałów kompozytowych dokonano przy użyciu mikroskopu skaningowego (SEM), natomiast wielkość krystalitów mieszanki proszkowej Cu + Al_2O_3 określono metodą rentgenowską, Gęstość otrzymanych wyprasek wyznaczono metodą geometryczną. Na podstawie uzyskanych wyników gęstości wyznaczono również porowatość całkowitą próbek.

1. Introduction

Copper alloys strengthened with particles of ceramic phases present an interesting combination of mechanical and plastic properties and resistance to abrasion. They are also characterised by high electric and thermal conductivity. On that ground they found many applications, such as switches in low-voltage equipment, in aircraft relays, in engine starters and cutouts, as well as in materials used for electrode terminals for resistance welding. The hardening with particles not only changes mechanical properties of the composite when compared to the metallic matrix, but also modifies physical properties [1-5].

High-melting ceramic compounds of high hardness, in a form of metal oxides, carbides, borides, nitrides of titanium, hafnium, vanadium, tungsten, molybdenum or niobium, are used as hardening particles. The examples of such composites are: Cu/Al_2O_3, Cu/Si_3N_4, Cu/SiC, Cu/WC, Cu/graphite [5-7]. Conducted in the last years studies have shown that also particles of other oxides, such as: ZrO_2, Y_2O_3, Ce_2O_3 and Er_2O_3 can play the

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same role. Distribution of the particles in the matrix results in the increase of compression strength and wear resistance both in room and elevated temperatures [5 - 8].

The composites are manufactured by powder metallurgy methods using sintering with partial or complete participation of liquid phase or with application of internal oxidation. Sometimes also saturation of the porous skeleton, previously produced by pressing and sintering, by infiltration with metal or alloy to close the open pores is applied. Mechanical properties of the composites depend first of all on chemical composition of the powder mixture as well as on the technology of their production [7, 9, 10]. Proper grain size and purity of the components, e.g. powders of copper and oxide or carbide phases, is especially important as well as development of the methods for their mixing, forming and sintering.

The efficiency of dispersion hardening depends on mechanical and geometrical parameters of dispersion phase, such as: hardness, dimensions and shape of particles, density, as well as their distribution in metallic matrix (dispersion coefficient) [11]. When very fine ceramic particles are used, representing large percentage of the composite, heterogeneous structures and badly condensed material is produced. It results in decrease of mechanical and electric properties. Therefore, when producing those types of materials special attention is paid to production of as homogenous as possible distribution of dispersive phase in the whole volume of the material, at the same time trying to reach the smallest dimensions and distances between particles [8-10].

The objective of the study was to determine influence of individual parameters of the production process on structure and properties of copper-based composite materials with fine-dispersion ceramic phases (Al_2O_3) produced by mechanical alloying method.

2. Experimental

The initial material used in investigationsas powder Cu, Al_2O_3. The investigations were conducted in two stages.

In the first stage the investigations were focused on production of Cu/Al_2O_3 composites according to the preliminary defined process conditions. Granularity of the used powders was $\leqslant 10\mu m$. Copper powder particles were of semi-spherical shape with shape coefficient 0.84 and relatively smooth surface.

The prepared powders were mixed during milling in a planetary Retsch PM 400 ball mill. The following conditions were applied during milling: rotational speed 275 rev/min, 60 minutes operation/ 5 seconds break. Bearing steel containers (of capacity 250 cm^3) and balls were used in milling. Diameter of the balls was about 10 mm, and balls to powder mass ratio was 5:1. To increase efficiency of the milling process a wetting agent was used in a form of acetone. The milling was conducted at the room temperature in air atmosphere. Milling time was 20 and 40 hours.

The mixture of powder Cu+Al_2O_3 components was subjected to compacting operations. Two-sided cold-pressing was applied, using pressure of 300 MPa. In the result of the pressing cylinder-shaped samples were produced of dimensions Ø10x15 mm. Operation of reduction annealing was applied (600°C/1h/atm. H_2) before the pressing. Sintering was conducted in a laboratory push-through furnace in the temperature of 650°C for 1 hour in hydrogen atmosphere. Additional cold-pressing was used to reduce porosity, with pressure of 500 MPa. The final operation was recrystallization annealing conducted for 1 hour in the temperature of 600°C.

In the second stage copper powder of highly developed surface produced by electrolytic method was used to increase formability of the powders. Particle size of the powders was also changed. The Cu, Al_2O_3 powders used in the investigations had grains ~3 μm. Complete characteristics of the powders is presented in Table 1. Morphology of the second stage powders is shown in Figure 1. Copper powder particles present dendrite structure of irregular shape. Some of the dendrites show also clusters of small spherical particles (1a). In the result of the high degree of fragmentation compact agglomerates built by spherical particles are observed in the structure of aluminium oxide powder (Fig. 1b).

TABLE 1

Physical properties of powders used to the research

Kind of powders	Purity, %	Theoretical density, g/cm^3	Specifiv surface m^{2}g^{-1}
Cu	99,8	9,17	0,57
Al_2O_3-typ α	99,99	4,16	3,27

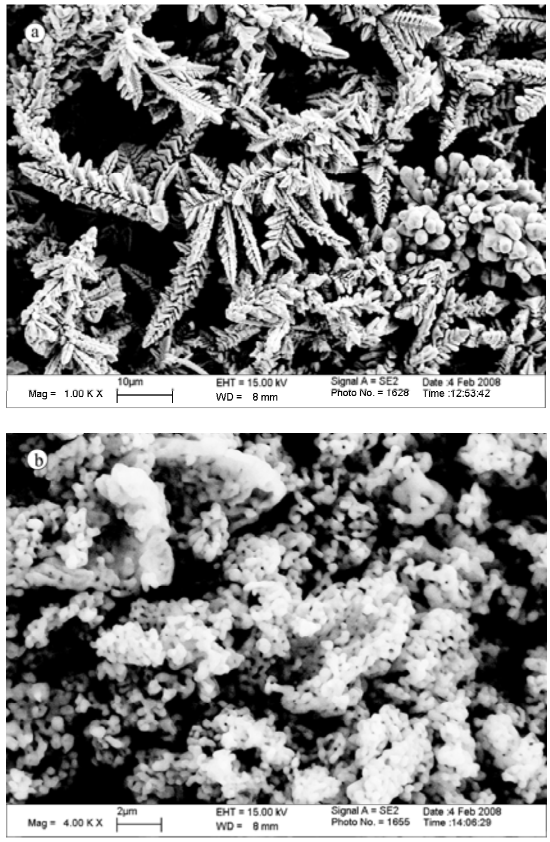

Fig. 1. Morphology of powder particles, SEM: Cu (a), Al_2O_3 (b)

The volume of the hardening phases represented 3, 8, 12% of Al_2O_3 volume, respectively. In the second stage of the investigations the milling bodies and steel containers were exchanged with their equivalents made of WC. Also milling time was changed and limited to 20h. The operations of compacting and consolidation were similar to the used in the first stage. Additionally two different pressures were applied 300 and 400 MPa as well as high-temperature sintering in the temperature of 950°C. The other process conditions were not changed.

The size of crystallites of Cu + Al_2O_3 powder mixture produced in the milling process was determined by X-ray method. The crystallite size was measured on the basis of the broadening of X-ray diffraction lines according to Scherrer equation [12, 13]. Copper of 99.99 % purity was used as a reference. Phase composition of the studied composite materials was determined by Seifert-FPM X-ray diffractometer XRD 7, of vertical collimators.

Density and specific surface of the produced Cu+Al_2O_3 powder mixtures were measured by gas adsorption (BET) method using Gemini 2360 equipment. Density of compacts was measured by geometric method on the basis of sample sizes. Basing on the density results the total porosity was determined.

Characteristics of microstructure and morphology of the phases was done by optical microscope Olympus GX71F equipped with imaging analysis software AnalySIS. Electron scanning microscope LEO GEMINI 1525 was used in observation of microstructure at higher magnifications. The observations were conducted with accelerating voltage of 15 kV. Image analysis and quantitative metallography were used to determine basic geometric parameters of the microstructure. The quantitative analysis was done with computer software for image analysis Met-Ilo v. 9.07 and AnalySIS. The measurements were performed on images of microstructures registered with scanning microscope of magnifications from 3000 to 10000 x. All the measurements were done on the polished material. Methodological problems in the analysis of the produced images of microstructures, i.e. presence of artifacts, were solved by application of appropriate transformations of the image.

3. Results and discussion

Microscopic (SEM) observations showed that particles of powder mixture containing 3 vol% of Al_2O_3 form large, compact agglomerates after milling for 20 hours (Fig. 2a, b), while the powder with addition of 8 vol% of Al_2O_3 shows agglomerates of diversified size, mainly composed of a large amount of particles (Fig.

2c, d). Increase of the milling time to 40 hours results in comminution of agglomerates and changing of the shape from flake-shaped (Fig. 2a, b) to spherical (Fig. 2c, d), and in increase of the degree of individual particles dispersion. The degree of dispersion increases also with increase of hardening phase content.

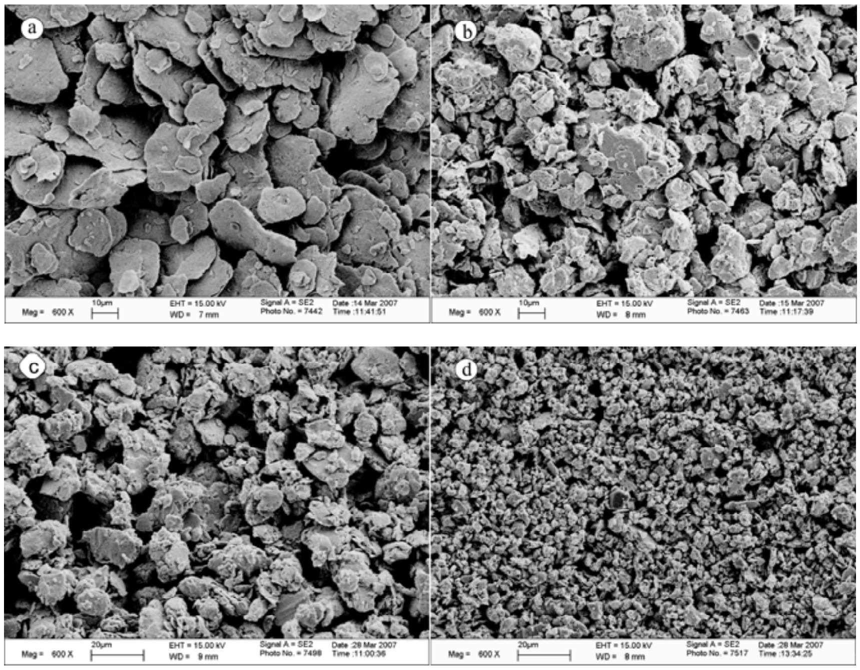

Fig. 2. Microstructures of powder mixture after 20 (a, b) and 40 h (c, d) milling; containing 3% Al_2O_3 (a, c), 8% Al_2O_3 (b, d)

The produced in the first stage powder mixtures were analysed for their phase composition. Figure 3 presents a sample diffractogram with marked reflexes of individual phases. XRD analysis showed that both increase of Al_2O_3 content to 8 vol% and elongation of milling time to 40 h leads to presence of, besides copper and aluminium oxide, iron of α type and formation of its oxides of Fe_3O_4 type (Fig. 3). The presence of iron in the powder mixture results from grinding of the aluminium oxide powder against the surface of balls and steel containers, and from transfer of their fragments into the mixture.

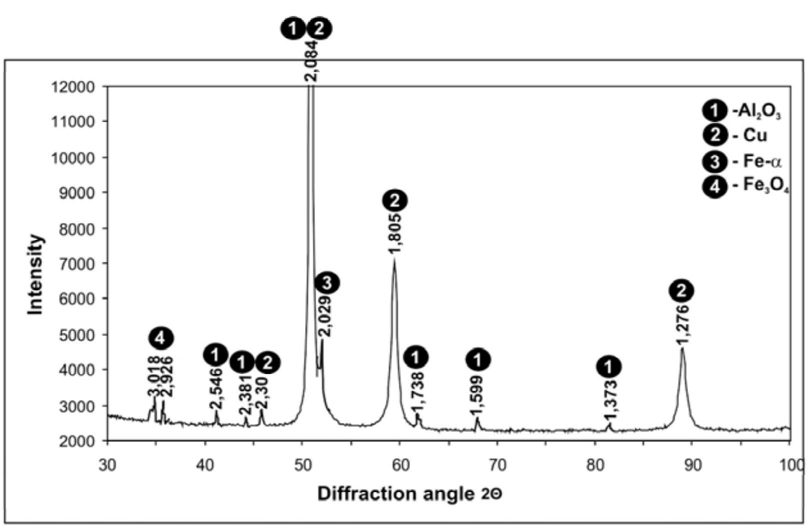

Fig. 3. X-ray diffraction of powder mixture containing 8% Al_2O_3 after 40 h milling

Changes in physical density and porosity of the compacts were adopted as a criterion for assessment of pressing and sintering efficiency. The presented relationships (Fig. 4) show that the increase in oxide phase content from 3 to 8 vol% results in the decrease of compact density by 12%. The similar effect was observed for elongation of the powder components milling time. With the change of density of compacts also their porosity changes. It was established that regardless of chemical composition, elongation of milling time to 40 h results in significant increase of the degree of compacts porosity (Fig. 5).

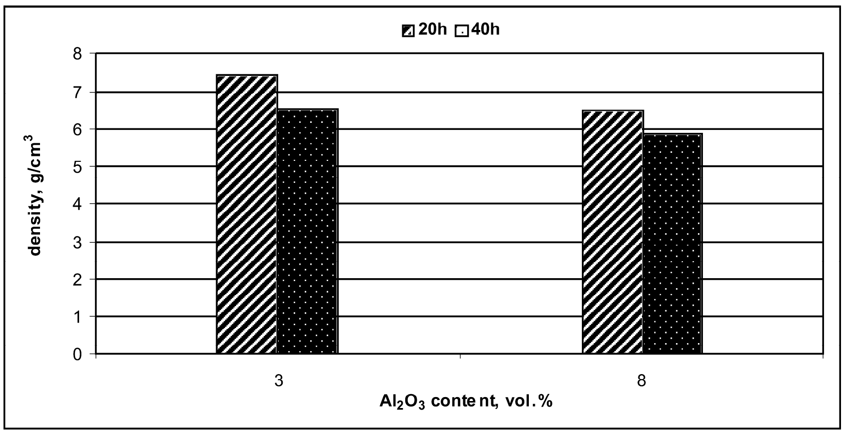

Fig. 4. Effect of Al_2O_3 content and milling time on density of compacts sintered at 650°C

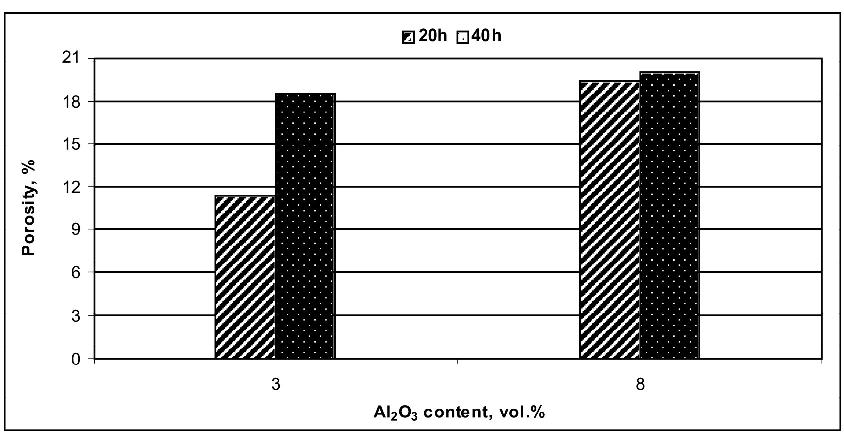

Fig. 5. Effect of Al_2O_3 content and milling time on porosity of compacts sintered at 650°C

Because of the presence of impurities in the produced in the first stage of investigation composite materials and their high porosity the parameters of production were changed and chemical composition was expanded. Application of milling bodies and containers of tungsten carbide and reduction of milling operation time to 20 hours resulted in relatively homogenous powder mixtures with no impurities, as confirmed by phase composition analysis (Fig. 6).

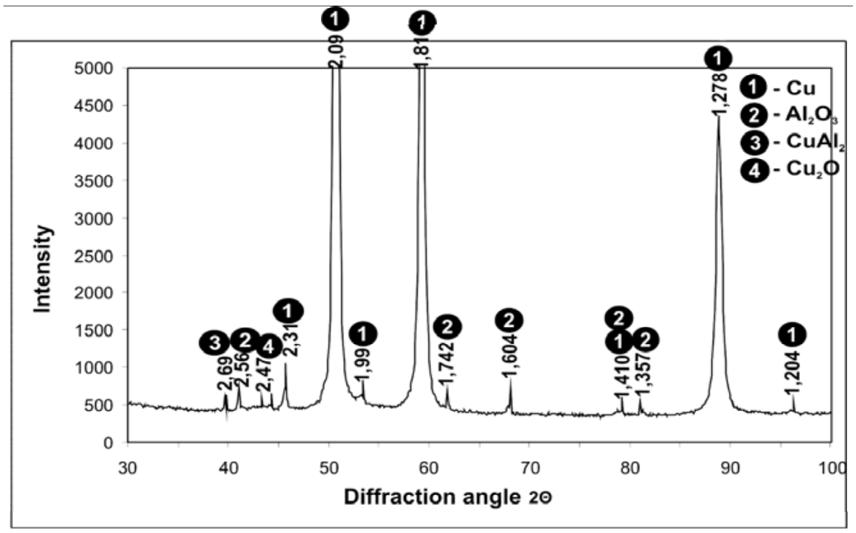

Fig. 6. X-ray diffraction of powder mixture containing 12% Al_2O_3

Density and specific surface measurement were performed on the produced $Cu+Al_2O_3$ powder mixtures. The results are presented in Table 2. Increase of oxide phase content results in increase of specific surface which, for the mixture of Cu+12 vol% of Al_2O_3, reaches the value of 1.308 m^2/g. It arises from high degree of dispersion obtained with this content of the components. Density of powder mixture depends not only on the composition, but also on the form of the ceramic powder used. It was also established that energy intensive comminution in a planetary ball mill leads to formation of nanocrystalline structure in powder particles of crystallite size 40-48 nm (Table 2). During milling the copper powder particles undergo strong deformation, comminution, agglomeration and subsequent processes of fragmentation.

TABLE 2

Properties of the powder mixture

Composition of powder mixture	Density, g/cm^3	Specific surface m^{2}g^{-1}	Crystallites size	
			Cu	Al_2O_3
$Cu/3Al_2O_3$	8,777	1,219	40	48
$Cu/8Al_2O_3$	8,539	1,300	–	–
$Cu/12Al_2O_3$	8,32	1,308	40	46

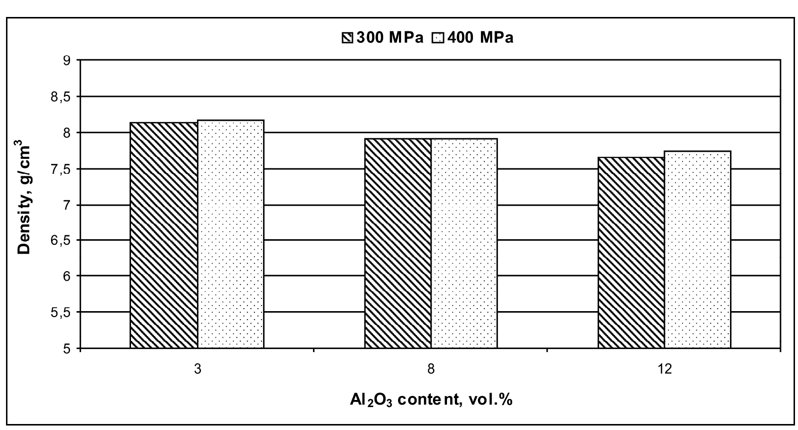

Fig. 7. Effect of Al_2O_3 content and compaction of metal powders on density of compacts sintered at 950°C

Large content of ceramic phases makes production of good quality compacts difficult, therefore sintering process in the second stage of investigations was conducted with some content of liquid phase. Measurements of compacts density showed that with the increase of sintering temperature up to 950°C significant increase in density of compacts is observed (Fig. 4, 7). The increase of pressing pressure to 400 MPa does not bring such significant changes in the value of density of the examined composite sinters. The higher pressure has, however, a positive effect on porosity of sintered composite compacts (Fig. 8).

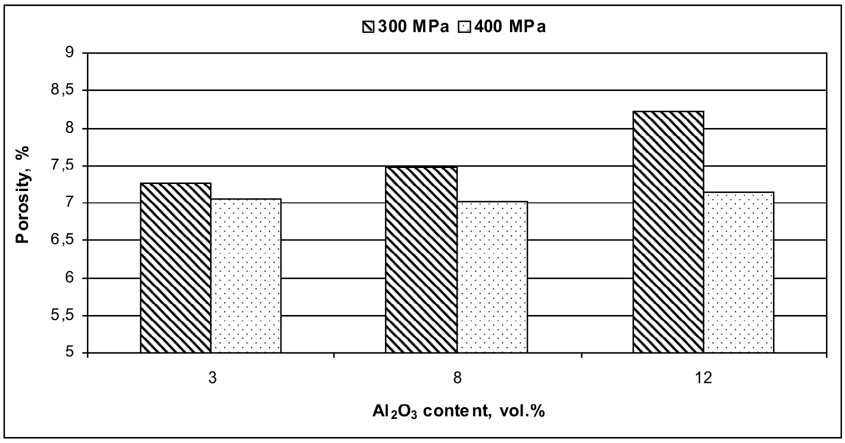

Fig. 8. Effect of Al_2O_3 content and compaction of metal powders on porosity of compacts sintered at 950°C

Sintering temperature has also significant influence on porosity of the examined sinters. Porosity of the composites sintered in the temperature of 950°C decreased on the average by 10% when compared to their equivalents sintered in 650°C. At the same time porosity of compacts increases with the increase of content of ceramic phase particles, which arises from more difficult contact of metal grains through small precipitates of those phases. The presented results confirm that with respect to the physical properties the higher sintering temperature is more advantageous.

Microscopic observations of the composites produced in the second stage showed that the distribution of Al_2O_3 phase particles in the matrix is relatively homogenous, and the degree of the homogeneity increases with the increase of the pressure (Fig. 9, 10). Additionally, in the microstructure of Cu/Al_2O_3 composites numerous recrystallisation twins formed during the final annealing. It seems probable that the location of Al_2O_3 particles correspond to the convenient places for generation of nuclei of recrystallisation. Analysis of microstructure of the produced composites showed that they have compact and homogenous structure within the whole volume. They also show high degree of sintering.

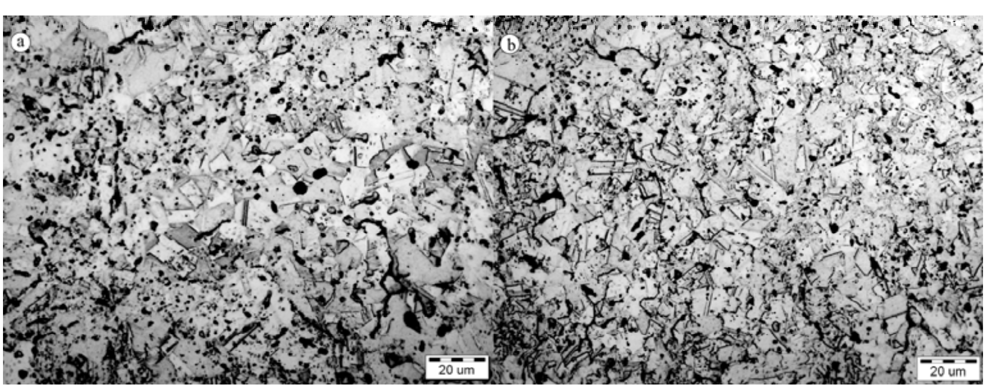

Fig. 9. Microstructure of composite $Cu/3Al_2O_3$ pressed with pressure: 300 MPa (a), 400 MPa (b) and sintered at 950°C

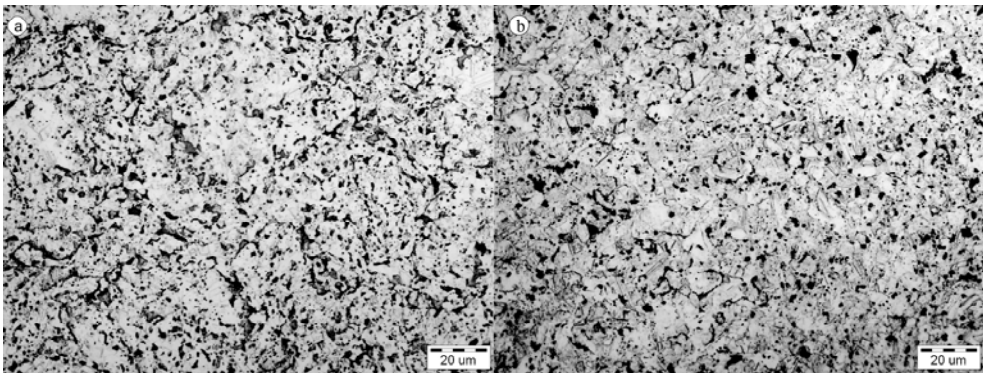

Fig. 10. Microstructure of composite Cu/12Al_2O_3 pressed with pressure: 300 MPa (a), 400 MPa (b) and sintered at 950°C

For a detailed characteristics of microstructure of the produced composite materials its quantitative analysis was performed basing on the images registered with scanning microscope. Figure (11) presents structure of the composite and corresponding computational binary image. The quantitative evaluation of equivalent diameter of particles plane section showed that with the increase of Al_2O_3 content the value of that parameter decreases, regardless of the applied pressing pressure (Fig. 12). The analysis of particle size of Al_2O_3 phase showed that production process conditions have no significant influence on the value of the determined stereological parameters. To determine the degree of dispersion of hardening phase particles a dispersion coefficient was determined (C) which represents the total surface of a phase per unit volume (C = SV/VV). It was established that the value of this parameter is significantly higher in the case of sinters containing 12 vol% of Al_2O_3 (Fig. 13), which results from the higher degree of comminution of oxide phase particles in those materials.

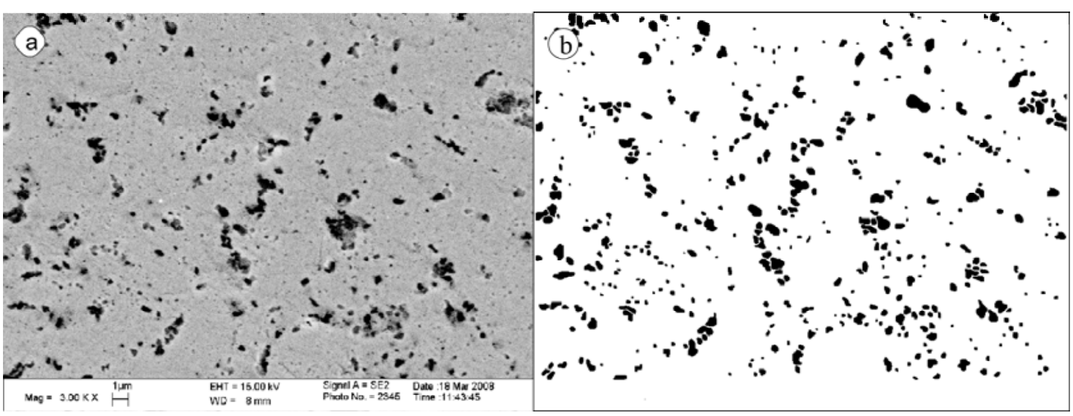

Fig. 11. Microstructure of composite Cu/12Al_2O_3: real image (a), binary image (b)

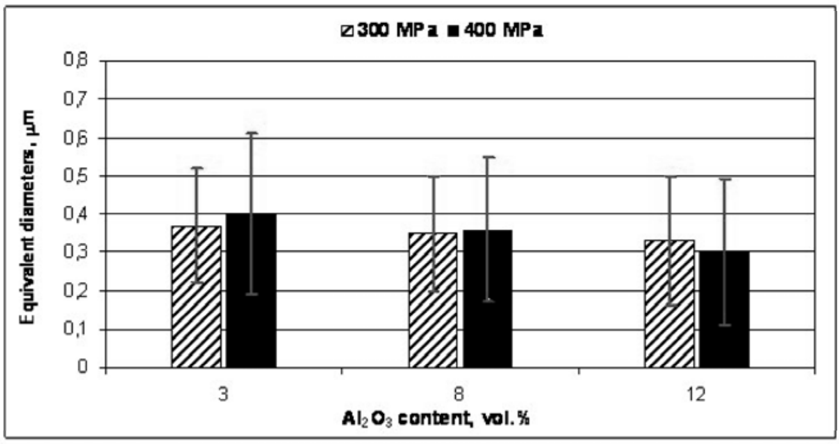

Fig. 12. Effect of Al_2O_3 content and compaction of metal powders on equivalent diameters of phase particles Al_2O_3

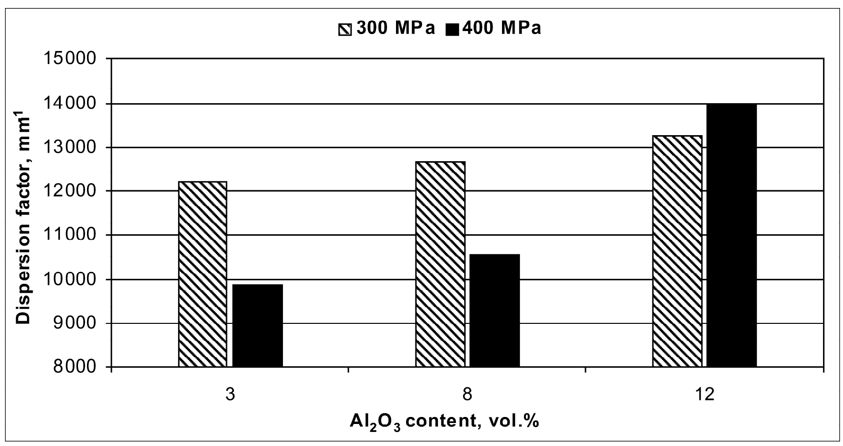

Fig. 13. Effect of Al_2O_3 content and compaction of metal powders on dispersion factor of phase particles Al_2O_3

Comparative studies of electric conductivity and mechanical properties were done with the produced samples of composite materials (Table 3). The results show significant changes in conductivity of examined materials depending on the applied production process conditions. The sinters in which higher pressure of pressing was applied (400 MPa) have on average about 3 MS/m higher conductivity than the compact pressed with the pressure of 300 MPa, regardless of the hardening phase content. Despite the fact that electric conductivity of copper is higher than ceramic particles conductivity by several orders of magnitude, their presence significantly lower electric properties of the whole composite.

TABLE 3

Mechanical and physical properties of examined composites

Composition of powder mixture	Compaction of metal powders	Porosity, %	Mechanical proprieties			Electrical conductivity, MS/m
			HV3	$R_{c0,2}$, MPa	A_c, %	
$Cu/3Al_2O_3$	300 MPa	7,3	72	220	45	45
$Cu/8Al_2O_3$		7,6	79	251	41	41
$Cu/12Al_2O_3$		8,2	83	268	39	39
$Cu/3Al_2O_3$	400 MPa	7	67	125	47	47
$Cu/8Al_2O_3$		7	73	171	44	44
$Cu/12Al_2O_3$		7	78	178	42	42

The conducted experiments of Cu/Al_2O_3 composites deformation in the compression tests performed in room temperature showed that sinters of higher content of ceramic phases present higher mechanical properties than the respective composites of lower amount of those phases (Table 3). At the same time, with the increase of strength worsening of plasticity of the sinters is observed (Table 3) resulting from the hardening of the material. The strength increase results from hindering the freedom of dislocation movement by fine, densely packed particles of ceramic phases. The highest level of plasticity with simultaneous high hardness is observed in composites pressed with the pressure of 400 MPa. That results from low level of porosity (Table 3) reached in Cu/Al_2O_3 sinters in those production conditions. Application of higher pressing pressure results in fairly uniform level of plasticity (a_c) in the composites, at the level of 63 %, regardless of their chemical composition.

4. Conclusions

1. Application of steel containers and milling bodies in the milling process contaminates the powder mixture with iron resulting from grinding away steel mill components during milling. The level of impurities increases with the increase of Al_2O_3 content as well as with elongation of milling time.
2. Extended milling time (40h) of powder components and low temperature of sintering (650°C) leads to production of sinters of high porosity at the level of 20%.
3. Selection of technological conditions has a significant influence on the quality of the final product. Sintering process conducted with some content of liquid phase (950°C) brings significant increase of density and decrease of total porosity. The increase of pressing pressure has similar influence.
4. The increase of pressing pressure has also positive influence on physical properties of the composites. Application of the pressure of 400 MPa during the pressing operation significantly improves conductivity of the produced composite materials, regardless of their content of ceramic.

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