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The possibility of producing graded Al_2O_3-Mo, Al_2O_3-Cu, Al_2O_3-W composites using CSC method

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Abstract. The subject of the study was the production and characterization of three ceramic-metal graded composites, which differed in addition of the metallic phase. The following composites systems were investigated: Al_2O_3-Mo, Al_2O_3-Cu, Al_2O_3-W. Composites were produced by centrifugal slip casting method. This technique combines the classic casting of the slurry into porous molds with the action of centrifugal force. As a result, sleeve-shaped shapes with a metallic phase gradient were obtained. X-ray phase analysis have not revealed new phases in the produced composites. The type of metallic phase and its distribution in the ceramic matrix influenced the hardness of the produced composites.

Key words: centrifugal slip casting, ceramic-metal composites, Al_2O_3 – molybdenum/copper/tungsten, SEM.

1. Introduction

The high demand for functionally graded materials (FGM) has forced significant demand for new materials in the materials science field [1–4]. The gradual transition between the properties of the constituent materials allows to full adaptation of the device to the anticipated conditions of its operation. The use of gradient materials reduces the cost of raw materials and the costs associated with maintenance of the structural components. Materials of this type can be used as thermal barriers, turbine blades, pipes for the transport of toxic medium or even biomaterials. Despite the significant contribution of these materials on the market, they are still the subject of basic research. Huge market demand for effective techniques to produce gradient materials such as ceramic-metal composites with a metallic phase gradient has led to the development of new methods to produce such materials. There are currently many techniques to produce functional gradient materials such as tape casting or electrophoretic deposition [5–12]. One of the newer methods of obtaining FGM is the centrifugal slip casting technique (CSC) [13]. This method combines the action of the centrifugal force with the classical slip casting technique [14]. The centrifugal casting method has been already used to compact ceramic materials such as alumina [15] or silicon nitride [16]. There are very few reports regarding the production of ceramic gradient composites, especially with the metallic phase as the reinforcement. Previous experimental work in the research team of the authors mainly concerned composites of the Al_2O_3-Ni system [14, 17–18]. The obtained results show many of the advantages of this technique in the manufacturing of gradient composites. Based on own research, it has been found that the method of slip centrifugal casting allows the formation of hollow-cylinder elements with a gradient concentration of metallic phase [17]. The results of the previous research indicated on that proper slurry selection influence on the width of the metal particles concentration in the composite [19]. Moreover, with the increase of solid content increases the width of the particle concentration in the composite zones [20]. Therefore, it would be useful to extend the research carried out so far to the new component systems. The metals that will be used together with the alumina matrix could be molybdenum, copper and tungsten. In addition, it should be noted that the composite molding process determines the contribution of the metallic phase in the ceramic matrix, the way they are arrange, their size and the presence of additional phases. Therefore, there is still need for the further research on the relationship between the process parameters and the composite structure. This is the subject of this article, its purpose and scope of research. The results give the base technology which may be a starting point to obtain other composite ceramics-metal by centrifugal slip casting. The purpose of this work is to determine the possibility of applying the centrifugal slip casting method to Al_2O_3-Mo, Al_2O_3-Cu, Al_2O_3-W composites.

2. Experimental

2.1. Materials. In the investigation, α-Al_2O_3 was used as ceramic powder with the average particle size 100 ± 20 nm, 99.99% purity and a density of 3.96 g/cm^3. Copper powder with 8.92 g/cm^3 and purity 99.99%, molybdenum powder with 10.28 g/cm^3 and purity 99.98%, tungsten powder with 19.25 g/cm^3 and purity 99.99% were used as metal powders to manufacture composites. The densities of the powders were determined by a helium pycnometer, AccuPyc 1340 II. The analysis of the particle size of the used metal powder was performed with the use of the HORIBA LA-950 analyzer (Horiba

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Ltd., Kyoto, Japan) and it is shown in Fig. 1. The analysis had shown that the used copper powder had an average size equal to 313.84 ±162.45 µm. In case of molybdenum it was found that average particles size has equal 46.56 ±27.74 µm. In the case of tungsten, it was found that a particle size was 60.08 ±49.56 µm.

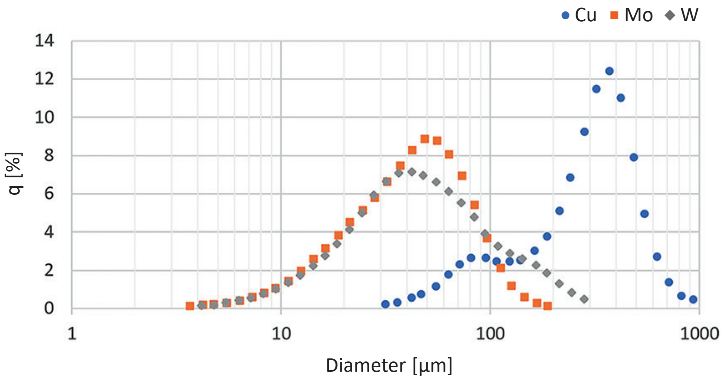

Fig. 1. Size distribution of the used metal powders

The micrographs of the base powders were shown in Fig. 2. It was found that ceramic powder was characterized by a high tendency to create agglomerates. It was observed that the surface of the metal particles is highly irregular with numerous cavities in contrast to ceramic powder which is characterized by a regular surface similar to spherical.

Diammonium hydrocitrate (DAC) and citric acid (CA) were used as dispersants in the ceramic suspension. Ceramic water-based slurries contained: diammonium hydrocitrate (0.3 wt.%) and citric acid (0.1 wt.%), respectively, with respect to the total solid weight.

2.2. Fabrication of the composites. Three types of samples were prepared: Al_2O_3-Mo, Al_2O_3-Cu, Al_2O_3-W. During the first stage of composites preparation the aqueous slurry containing 50 vol.% of the solid phase and 10 vol.% of the metal particles (molybdenum, cooper or tungsten) was prepared by adding the alumina and selected metal powders to the solvent with the dispersants. Afterwards, milling the mixture in a planetary ball mill PM100 (Retsch) for 60 min with a speed of 300 rpm was performed. Slurries were degassed in a THINKY ARE-250 Mixer and Degassing Machine for 5 min with a speed of 1600 rpm. The equipment allows to release bubbles >1 µm from the slurry. Then, the slurry was poured into a gypsum mold of 20 mm in inner diameter. Subsequently, the tubular mold was centrifuged in the radial direction with a speed of 3000 rpm for 70 minutes. After the centrifugation, the sample together with the gypsum mold was removed from the metal mold and was dried in a dryer at 35°C for 24 hours in order to evaporate water. The dried sample could be easily removed from the gypsum mold thanks to drying shrinkage. Then, the samples were sintered at 1400°C for 2 h in H_2/N_2 atmosphere with heating and cooling rate equal to 5°C/min. The composite samples were obtained according to the centrifugal slip casting method schematically shown in Fig. 3. This process allowed to obtain composites in the shape of a hollow cylinder with a gradient concentration of the metal particles.

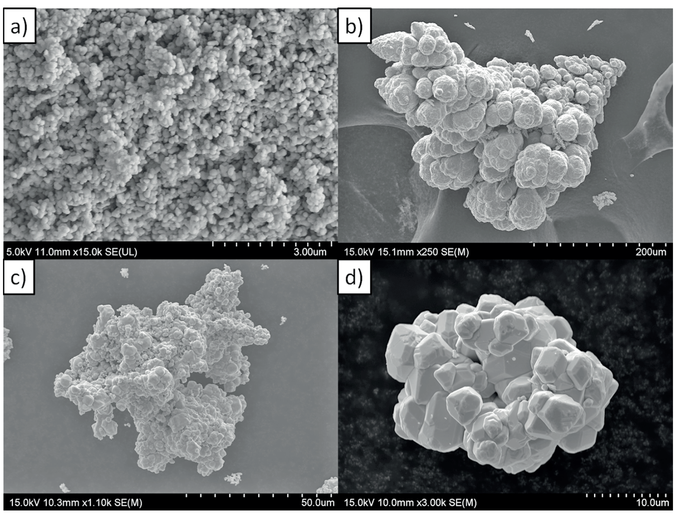

Fig. 2. Morphology of started powders: a) Al_2O_3, b) Mo, c) Cu, d) W

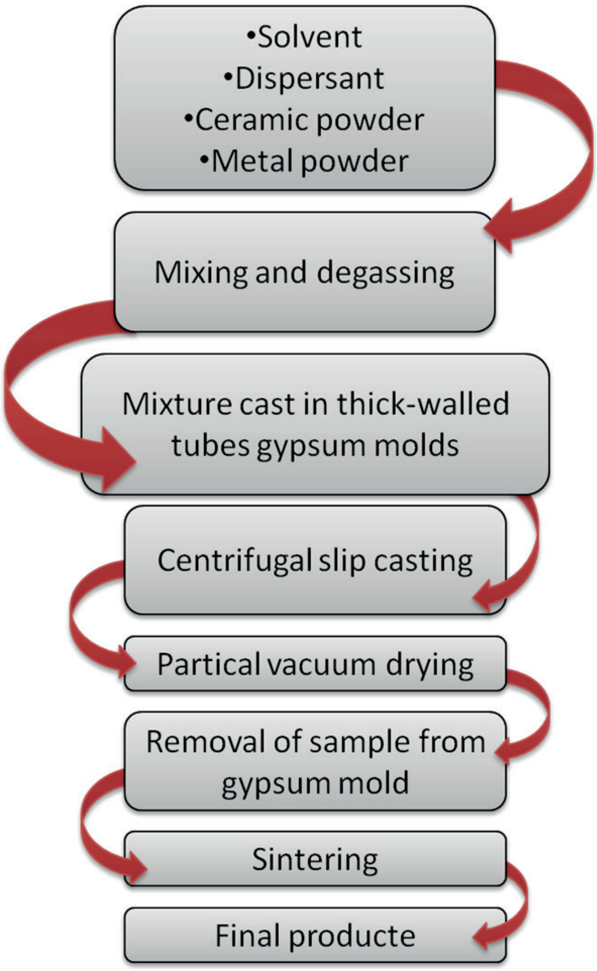

Fig. 3. Schematic diagram of centrifugal slip casting process

2.3. Characterizations methods. The X-ray phase analysis was performed by X-ray diffractometer Rigaku MiniFlex II with filtered cooper radiation $\left(\lambda_{CuK\alpha} = 1.54178\ \text{Å}\right)$. Bragg-Brentano and grazing incidence angles diffraction geometry were used for the phase analysis. The diffraction pattern was obtained at a rate of 1 deg/min in the range $2\theta = 20$–$100°$.

The microstructure of the cross section of the sintered specimens was investigated by scanning electron microscope Hitachi SU-70 equipped with energy-dispersive x-ray spectroscopy (EDS) and back-scattered electron (BSE) detector. SEM was used to observe the surfaces and the distribution of metal particles in composites matrix. EDS was used to perform linescan measurements of chemical composition distribution through cross-sections of samples. Observations were performed using acceleration voltages in the range of 10–15 kV. Observations of the structure of the composites zones were carried out along their cross-sections. Linescans were performed at 20 kV acceleration voltage. The cross sections were prepared by cutting the samples across the axial direction with diamond saw. Before structural examinations all samples were subjected to the metallographic preparation involving grinding on SiC papers with granulations of 320, 800, 1200, 2400 and polishing with diamond suspensions 3 μm and 1 μm. Observations for each sample were conducted from the central part of the composite signed as a "CP" in Fig. 5, 7, 9. The microscopic observations mainly concerned the occurrence of the metallic gradient in the samples.

The hardness of the Al_2O_3/Ni composites was determined by using Zwick/Roell Vickers hardness tester. Vickers hardness was measured on the polished surface. Each of zones observed in the composites were measured. In the measurements load of 9.8 N was used.

3. Results and discussion

The X-ray diffraction patterns of composites after sintering at 1400°C in a H_2/N_2 atmosphere (20% hydrogen, 80% nitrogen) revealed that the resulting moldings contained the base phases, i.e. Al_2O_3 and the appropriate metals (Fig. 4). It was found that using of the reductive atmosphere (H_2/N_2) during sintering avoid the formation of the new phase in all types of composites.

The composites made by centrifugal slip casting have the shape of hollow cylinders. A typical microstructure of composite after sintering is shown at Fig. 5, 7, 9. The dark areas on the micrograph correspond to the ceramic matrix (Al_2O_3), while the bright areas are the metallic phase. The microscopic observations were carried out on fragments of composites from the middle part of the sinters. The scanning electron microscopy studies have revealed not homogeneous distribution of the metallic phase in all composites. The differences in distribution of metallic phase was observed in all materials. It was found based on microscopic observations that the content of the metallic phase decreases with the increased distance from the outside to the inner edge of the sample in all case. It was noted that each of the samples had a maximum metallic phase content in the middle part of the composite.

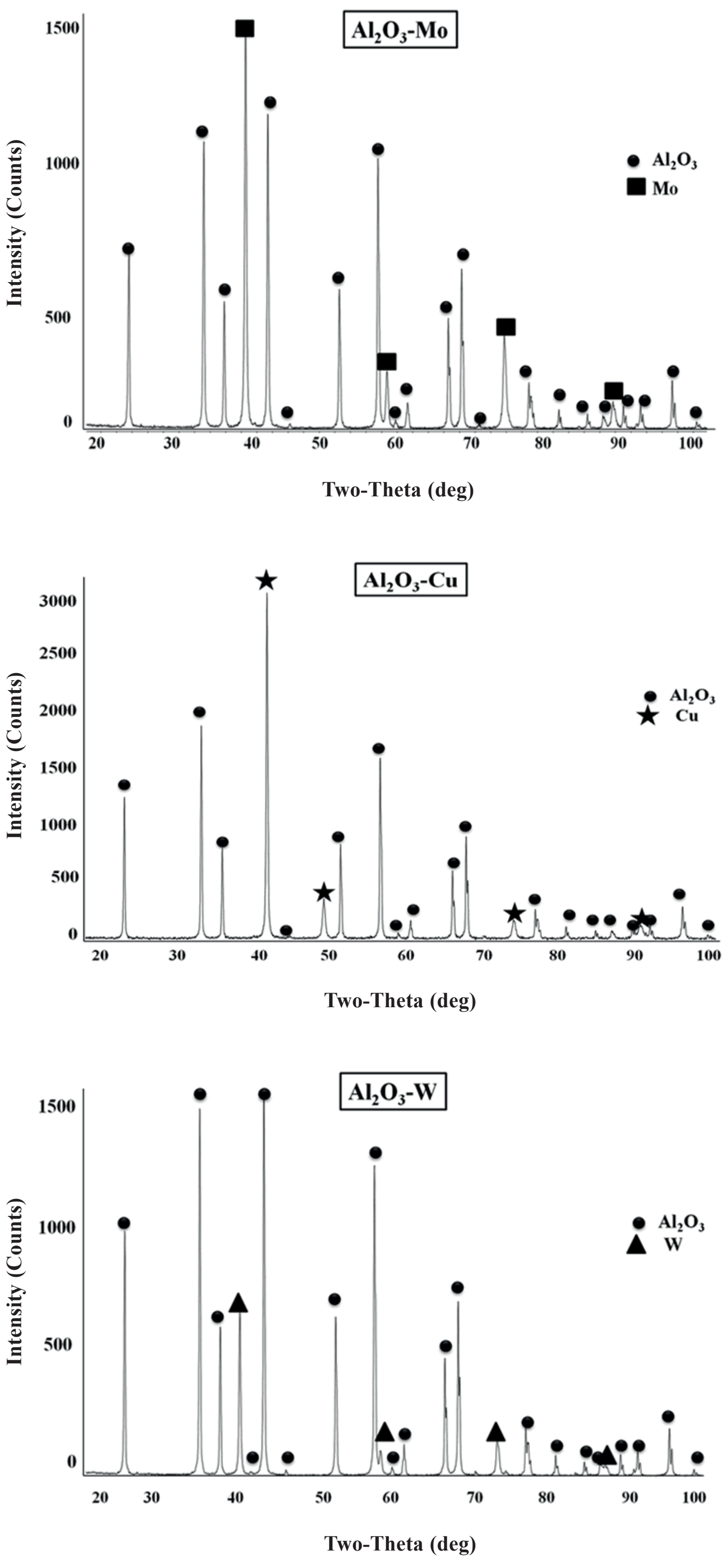

Fig. 4. XRD of samples

Macroscopic observation and linescan result revealed that the gradation of molybdenum content change from outer surface towards the inner side of composites (Fig. 5, 6). In the Al_2O_3-Mo composite, four zones (I–IV) with varying molybdenum content

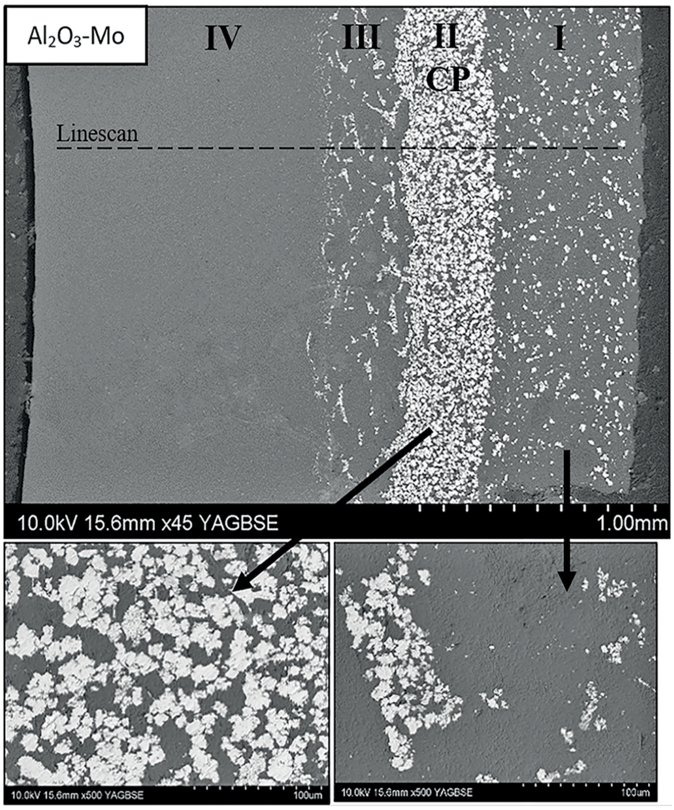

Fig. 5. Microstructure of the composites Al_2O_3-Mo

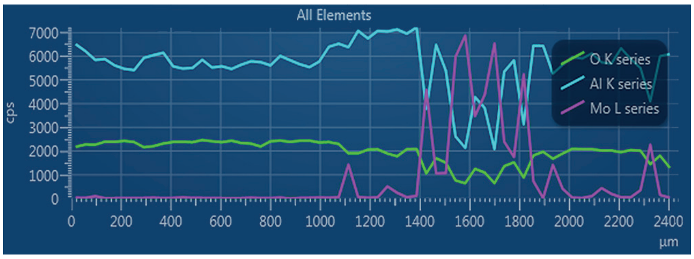

Fig. 6. EDS Linescan results through the zones of Al_2O_3-Mo (measurements line at Fig. 5)

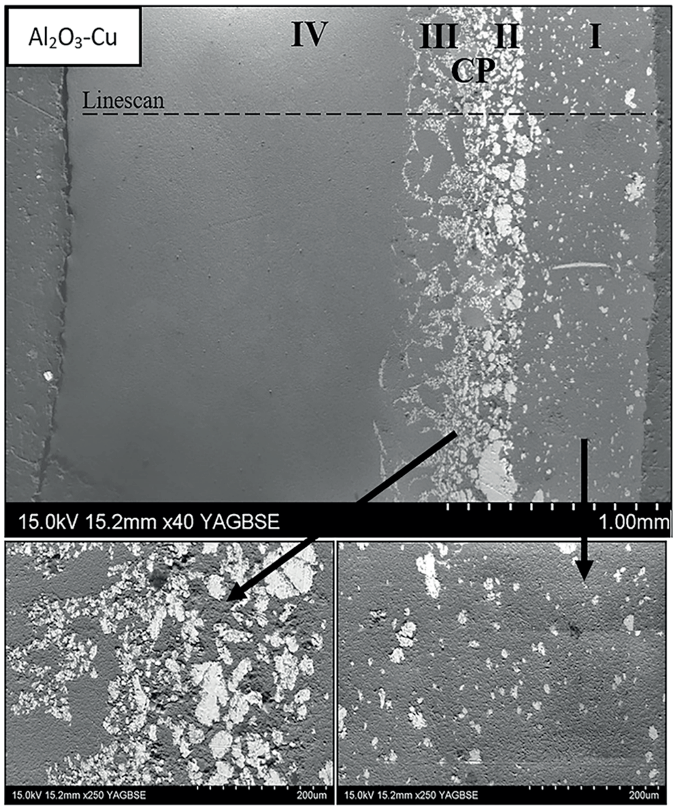

Fig. 7. Microstructure of the composites Al_2O_3-Cu

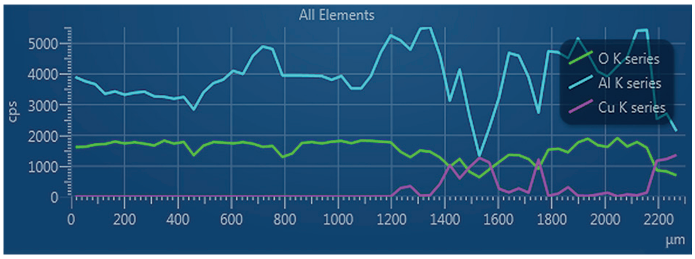

Fig. 8. EDS Linescan results through the zones of Al_2O_3-Cu (measurements line at Fig. 7)

on the cross-section of the samples was distinguished (Fig. 5). Content of the particles in the outer part of composites (zone I) was a result of removing fluid through capillary action in the gypsum mold. The observation of graded hollow composites reveal that the maximum content of Mo particles was in zone II. It was observed that with decreases distance from the central part of the sample, the content of molybdenum particles decreases. As a consequence, inner part of Al_2O_3-Mo composite was composed of alumina oxide (zone IV).

It was found that Al_2O_3-Cu composite have similar microstructure as previously studied Al_2O_3-Ni composites [14–16]. Namely, the Al_2O_3-Ni composites was described by three zones on the cross section of the samples obtained by CSC. The distribution of metallic phase in composites are represented by four zones (I–IV) in the sample, from the outer surface towards inner side of the graded hollow tubes. Typical microstructure of obtained hollow cylinders was shown in Fig. 7. The first zone of the graded region was a result of removing fluid through capillary action in the gypsum mold. According to the previous research it was observed that this zone in each sample was characterized by the content of the metallic phase which was used to prepare the starting slurry (eg 10% vol.) [13–16]. The central zone (II–III) has a higher content of metal particles than average contribution of metal particles in the composite (Fig. 8). This zone was obtained as a result of centrifugal acceleration. In this part of composites, the metallic particles move toward faster than the Al_2O_3 particles. At the same time, due to removal of solvent, the viscosity of the slurry increases. In the consequence in this region the distances between the particles were quite short. Moreover, the particles could interfere with each other which also reduced their mobility during formation in this part of composites. Finally, a zone with the maximum

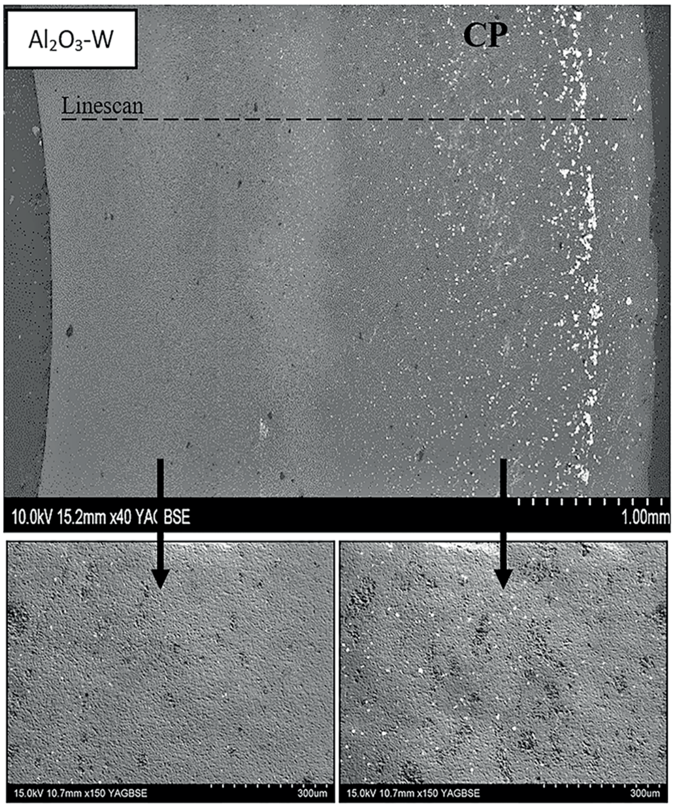

Fig. 9. Microstructure of the composites Al_2O_3-W

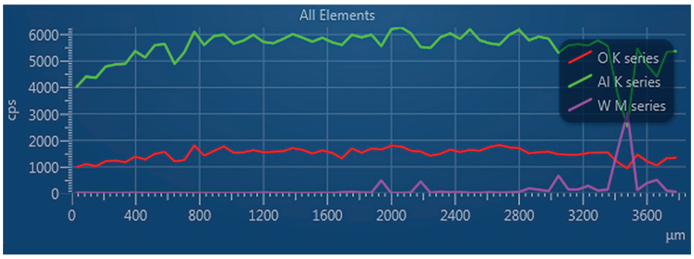

Fig. 10. EDS Linescan results through the zones of Al_2O_3-W (measurements line at Fig. 9)

amount of metal particles was obtained. However, proportion of metal particles were reduced simultaneously with the distance from the outer of surface of samples [13–16]. It was observed that the zone located close to inner part (IV) of composites did not contain the metal particles.

It was found that the Al_2O_3-W composite was characterized by slightly visible gradient of metallic phase compared to the other composites (Fig. 9). This is due to the fact that tungsten is characterized by much higher density than aluminum oxide. Part of sample used for microscopic observation were cut from the middle of the moldings similar to other composites. Sedimentation process were stated for the tungsten particles as a result of the large difference in density between the components. The results revealed that the use of powders differing significantly in density $\left(\rho Al_2O_3 = 3.96\ g/cm^3,\ \rho W = 19.25\ g/cm^3\right)$ have a significant effect on the distribution of the metallic phase on the cross section of the composite. In the case of the Al_2O_3-Cu and Al_2O_3-Mo composites the sedimentation process were not observed on the longitudinal section of the samples.

The results of Vickers hardness measurement (Table 1) revealed that the hardness of each composite depends on content of metallic phases. It can be seen that the maximum of hardness values was observed in part of samples without metallic phases, approximately 2000 HV1 in each sample. Hardness of zone I in sample Al_2O_3 reaches nearly 1800 HV1. Due to the highest content of molybdenum particles in zone II the lowest hardness approximately 450 HV1 was reached. Similar to zone I, hardness of zone III reaches nearly 1800 HV1. The value of the hardness measured in the zone I reaches 1650 HV1 and decrease to 129 HV1 in zone II due to the maximum amount of metal particles. In composite Al_2O_3-W hardness of outer part of sample is approximately 1200 HV1 and decrease to 773 HV1 in direction to central part of sample.

Table 1
The results of Vickers hardness measurement of the fabricated composites

	Hardness of composites [HV1]		
	Al_2O_3-Mo	Al_2O_3-Cu	Al_2O_3-W
Zone I	1821	1640	2077
Zone II	364	129	
Zone III	1794	1271	
Zone IV	2075	2020	

4. Conclusions

It was found that the centrifugal casting method can be used to obtain composites Al_2O_3-Mo, Al_2O_3-Cu, Al_2O_3-W. However, it should be stated that the difference in density between composite components plays a key role. Too large difference in density between the matrix phase and the metallic phase do not allow to obtain a homogeneous gradient of metallic phase on the cross section of the obtained hollow cylinder.
Moreover, based on results of the X-ray phase analysis, it was found that the reducing atmosphere prevents the formation of new phases in the produced composites. The hardness measurements indicated a direct relationship between matrix and volume fraction of metal particles.

It was concluded that this research can give a starting point for work with application character for centrifugal slip casting method for producing functionally graded composites. The obtained results allow to create a basis principal for controlling the properties of ceramic matrix composites by the planned distribution of the reinforcing phase formation graded materials.

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