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MICROSTRUCTURE AND PROPERTIES OF HOT-PRESSED MOLYBDENUM-ALUMINA COMPOSITES

SPIEKANE KOMPOZYTY MOLIBDEN-Al_2O_3 – STRUKTURA I WŁAŚCIWOŚCI

Brittleness is the main technical limitation on a wide use of advanced ceramic materials. To overcome this problem, ceramic-metal composites are commonly applied. A principal advantage of ceramic-metal composite materials is their higher resistance to brittle fracture. An increase of fracture toughness depends on the type, amount, size and shape of a metallic component. The metallic phase can additionally modify physical, mechanical and thermal properties of materials.

The results of experiments concerning a manufacturing process of Mo-Al_2O_3 composite materials obtained by the hot pressing method were presented. Two powder mixtures with different volume fraction of aluminium oxide were prepared in a planetary ball mill. The hot pressing process allowed to obtain well-densified metal matrix composites (~99% of a theoretical density). Microstructural observations of sinters were conducted using scanning electron microscopy, energy-dispersive X-ray spectroscopy, and transmission electron microscopy. Very stable bonding between metal and ceramic grains was observed. Complex investigations of the physical and mechanical properties of obtained molybdenum-alumina composite materials seem to be very promising from an application point of view.

Keywords: ceramic-metal composites, hot pressing, microstructure, interface, mechanical properties

Główną przyczyną ograniczenia stosowalności zaawansowanych materiałów ceramicznych jest ich kruchość. W celu pokonania tego problemu powszechnie stosuje się kompozyty ceramiczno-metalowe, których zaletą jest wyższa odporność na kruche pękanie w porównaniu z materiałami ceramicznymi. Zależy ona od wielu czynników m.in. rodzaju, ilości, wielkości oraz kształtu zastosowanego metalu. Ostatecznym zmianom ulegają również inne właściwości tj. fizyczne, mechaniczne, termiczne.

W pracy przedstawiono wyniki technologicznych prób otrzymywania materiałów kompozytowych Mo-Al_2O_3 przy wykorzystaniu techniki spiekania pod ciśnieniem. Mieszaniny proszków o różnych udziałach objętościowych fazy ceramicznej przygotowano w planetarnym młynku kulowym. Ostateczny proces zagęszczania pozwolił uzyskać materiały o wysokiej gęstości względnej (powyżej 99% gęstości teoretycznej). Analizowano mikrostrukturę spieków z wykorzystaniem skaningowej i transmisyjnej mikroskopii elektronowej. Stwierdzono występowanie bardzo dobrego połączenia fazy ceramicznej z osnową metalową. Przeprowadzono szeroka analizę właściwości fizycznych i mechanicznych uzyskanych kompozytów, co powinno pozwolić na rozszerzenie możliwości aplikacyjnych opracowanych tworzyw.

1. Introduction

Ceramic-metal composites are highly-processed materials whose design and production are aimed at achieving such physicochemical features that will permit their stable and reliable operation under complex, sometimes extreme, exploitation conditions. One of the advantages of these materials is their increased fracture toughness compared to that of traditional ceramic materials [1,2]. This parameter depends on a variety of factors, including the type, number, size and shape of metallic phase particles, and also on uniformity of their distribution within the matrix of a composite [3,4]. Among materials that are most often used for modifying the properties of alumina ceramics one can mention copper, nickel, chromium, molybdenum and tungsten. We have been interested in molybdenum since it has a relatively high specific weight (10.22 g/cm^3), high HV hardness (2.3 GPa) and high tensile strength R_m (about 700 MPa), also at elevated temperatures. Its linear thermal expansion coefficient α (5.35×10^{-6} 1/K) is close to that of alumina ceramic (5.5×10^{-6} 1/K), which may be beneficial from the point of view of the residual stress state induced in a composite. A high melting temperature of molybdenum

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(2610°C) also permits the use of Mo-Al_2O_3 composites in high-temperature applications. Available literature data indicate that Mo-Al_2O_3 composites are most often produced by the powder metallurgy technique (with the use of micro- or, more rarely, nano-powders), but starting materials differ by the method of their preparation – beginning with commercial materials and ending at materials specially produced in various forms by chemical methods. The authors of refs [5-7] obtained starting powders by dry-sputtering a suspension of a molybdenum oxide solution in ammonia water added with 5 to 20 vol% of Al_2O_3. The granulate thus prepared was subjected to reduction in a hydrogen atmosphere and, then, to hot-pressing. Al_2O_3 composites were sintered at a temperature between 1550°C and 1700°C in a vacuum or in an atmosphere of a protective gas. The authors of refs [8-12], on the other hand, examined how the composition and morphology of starting materials affected the microstructure and properties of final materials (fracture toughness, bending strength, and frictional wear resistance, etc.).

The present paper discusses the results of examinations concerning the technology of Mo-Al_2O_3 composites and contains an analysis of mechanisms that accompany the sintering process. It is also concerned with characterization of the composites.

2. Experimental procedure

In the present work, an aluminum oxide powder of α-form (average grain size ~1μm – Fig. 1a.) and a molybdenum powder (~10μm – Fig. 1b.) were used. Two compositions of powder mixtures with the following Al_2O_3 to Mo ratio (in vol.%) were prepared: 75Mo/25Al_2O_3 and 60Mo/40Al_2O_3. They were obtained in a mechanical mixing process using a planetary ball mill (Pulverisette 6, Fritsch) with tungsten carbide balls (Ø 10mm). The process was conducted in an air atmosphere at the rotational speed of 200 rpm and at the time of mixing between 1h and 8h. The ratio of the ball to the powder (BPR) was approximately 5:1.

SEM observations of the powder mixtures were performed for different mixing times. It was found that a homogeneous powder mixture is not certain to occur if the mixing time is too short (below 2 hours), while extending it to beyond 8 hours results in the growth of Al_2O_3 agglomerates on the surface of the molybdenum powder. The tests showed that the optimal mixing time to obtain homogeneous powder mixtures without vast quantities of aluminium oxide powder agglomerates was 4 hours. Exemplary Mo-Al_2O_3 powder mixtures are presented in Fig. 2.

The grain size distribution examined after selected stages of the mixing process and for the powder mixtures was determined using a television image analysis system (Clemex). It was calculated as a function of the Feret diameter (d) and, in consequence, the average Feret diameter (d_{AVG}) was obtained. Fig. 3. shows exemplary grain size distributions of Mo-Al_2O_3 powder mixtures.

The analysis proved that the Mo-Al_2O_3 grain size varies considerably depending on the mixing time. As it is increased, the average grain size decreases even to below 5 μm.

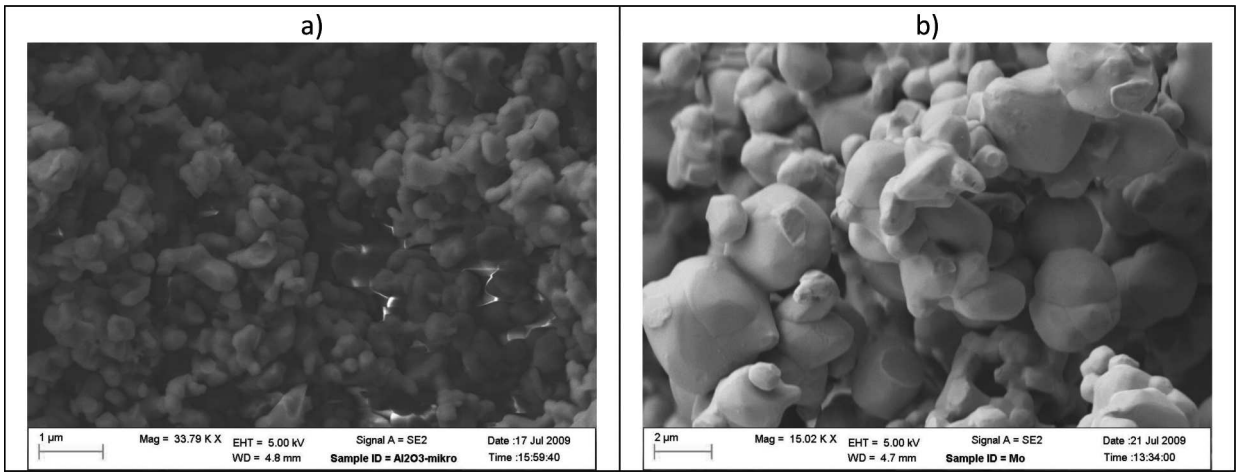

Fig. 1. SEM images of starting materials: a) aluminum oxide, b) molybdenum powder

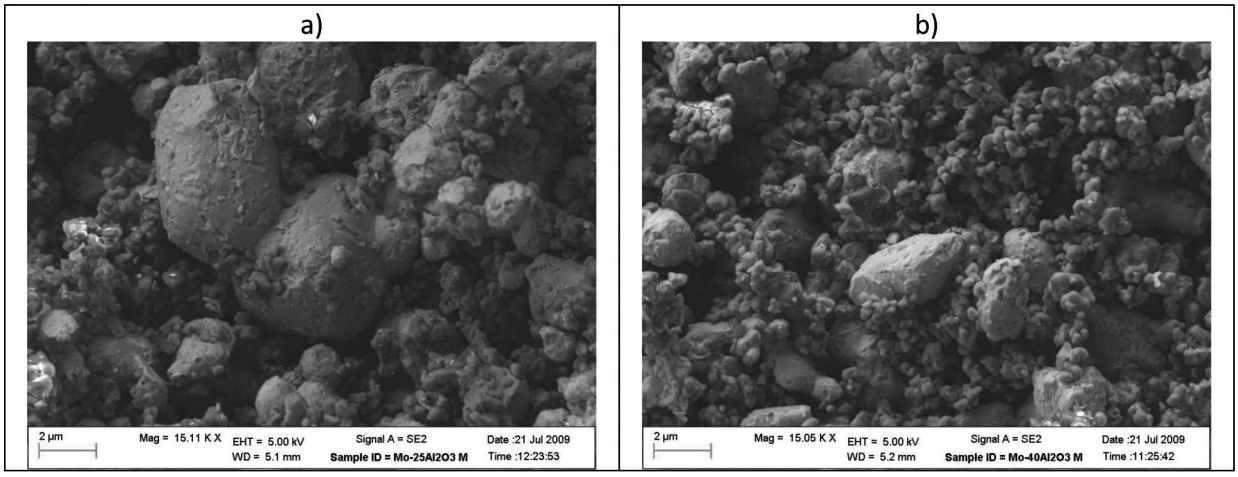

Fig. 2. SEM images of Al_2O_3-Mo powder mixtures after a 4-hour long mixing process in a planetary ball mill: a) 75Mo/25Al_2O_3 and b) 60Mo/40Al_2O_3

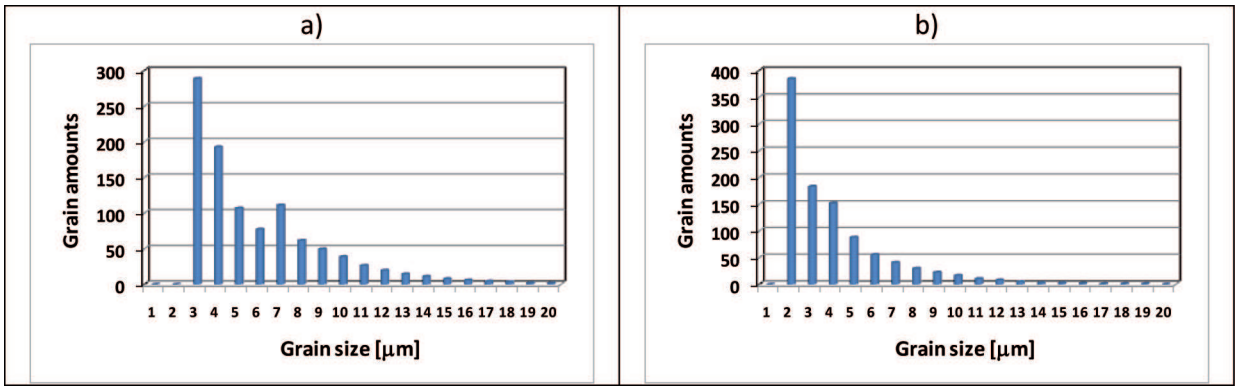

Fig. 3. Grain size distribution in Mo-Al_2O_3 powder mixtures after the mixing process in a planetary ball mill (mixing time 4.0 h): a) 75Mo/25Al_2O_3 and b) 60Mo/40Al_2O_3

The prepared powder mixtures were finally densfied by the hot pressing method. The process was performed in a Thermal Technology Astro press in an argon atmosphere using a graphite mould. An optimal sintering temperature and time of holding were fixed experimentally and chosen as follows: 1600°C and 30 min. After reaching the sintering temperature, the pressure of 30 MPa was applied. The heating rate was 10°C/min. After the holding time the samples were naturally cooled with the furnace to room temperature before removal.

Microstructural investigations included scanning electron microscopy (SEM, Hitachi S4100) and transmission microscopy (TEM, Tecnai G2). The samples were mechanically cut, grinded and polished. For the purpose of SEM observations they were covered with a thin layer of carbon. This foils for TEM were cut using FIB Quanta 200 3D FEI instruments.

Density studies of Mo-Al_2O_3 composites were made according to the hydrostatic method. Hardness (HV10) was tested with a Vickers diamond indenter using 98 N load with loading time of 10 s. Each indentation was placed at least ten diagonal lengths away from an adjacent indentation. The hardness results were averaged over ten indentations per specimens. The flexure strength, fracture toughness and Young's modulus measurements of the obtained Mo-Al_2O_3 composites were performed using a Zwick 1446 testing machine. For the bending test, the samples were cut (dimensions 5×5×50 mm). The measurements were made using a three-point bending mode with a span of 45 mm and a displacement rate of 1.0 mm/min. Average values of the bending strength, fracture toughness and Young's modulus were calculated from five tests.

3. Results and discussion

For the assumed volume content, theoretical densities of composites were specified, adopting the density of aluminium oxide ρ_{Al2O3} = 3.97 g/cm^3 and of molybdenum ρ_{Mo} = 10.22 g/cm^3. The above density values were chosen for the composition 75Mo/25Al_2O_3 – ρ_T =

8.66 g/cm^3 and 60Mo/40Al_2O_3 – ρ_T = 7.72 g/cm^3 respectively.

The densities of Mo-Al_2O_3 composites obtained by the hot pressing method are presented in Table 1. Density tests confirmed the possibility of obtaining Mo-Al_2O_3 composites of density close to the theoretical density for a different volume content of the ceramic phase.

TABLE 1
Densities of hot-pressed Mo-Al_2O_3 composites

Chemical composition (vol.%)	Theoretical density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)
75Mo-25 Al_2O_3	8.66	8.62	99.5
60Mo-40 Al_2O_3	7.72	7.70	99.7

The next step of experiments included a microstructural analysis of Mo-Al_2O_3 composites obtained by the hot pressing method. In Figure 4 selected results of the microstructure examination using scanning electron microscopy are presented.

Microstructural observations confirmed high densities of hot pressed Mo-Al_2O_3 composites. Some porosity was visible in the structure of the composites, yet it was low and not significant, which proves that the obtained materials exhibit a very high relative density. Moreover, in all cases, their structure was characterized by a singularly good homogeneity.

Figure 5 shows two micrographs taken at a thin section of the composite. One can see the growth of ceramic particles up to a few micrometers as compared to the initial size of the ceramic powder, which is (Fig. 1) a fraction of a micrometer. There are some cracks (marked by arrows) at Mo/Al_2O_3 or Al_2O_3 interfaces which may be the effect of the preparation of thin samples, but it may be due to not satisfied sintering level of ceramic particles; however, at the same time, they indicate that adhesion at the Mo/Al_2O_3 interface is not too strong and, most probably, because no diffusion layer is present. The contrast change at the interface also suggests that no diffusional interface layer is formed.

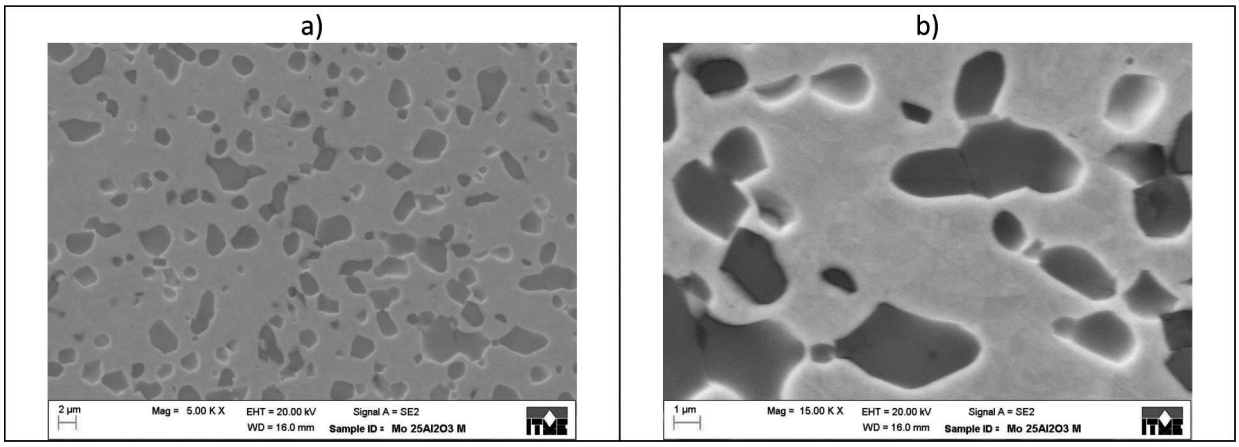

Fig. 4. SEM images of hot pressed Mo-25Al_2O_3 composites (T=1600°C, p=30 MPa, t=30 min)

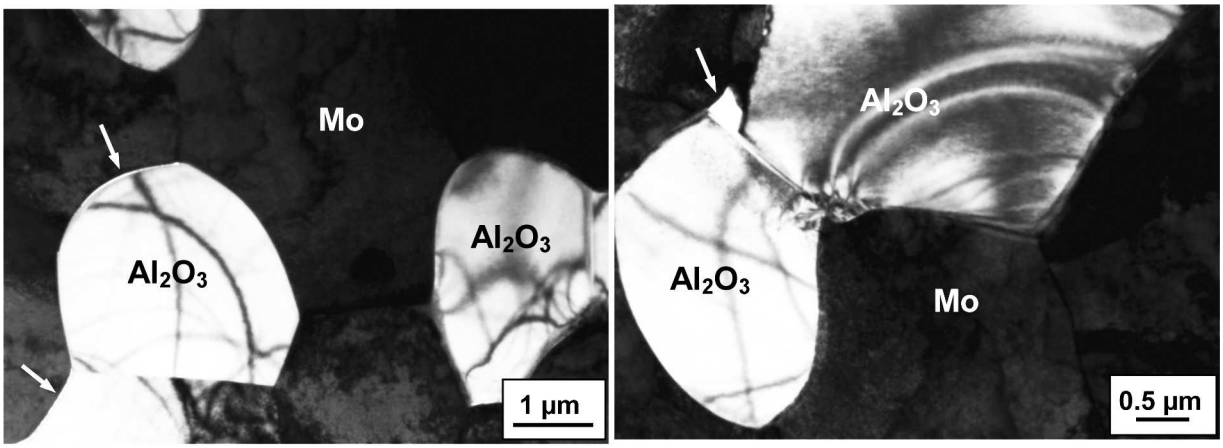

Fig. 5. TEM micrographs of composites with addition of 25% of Al_2O_3 ceramic particles

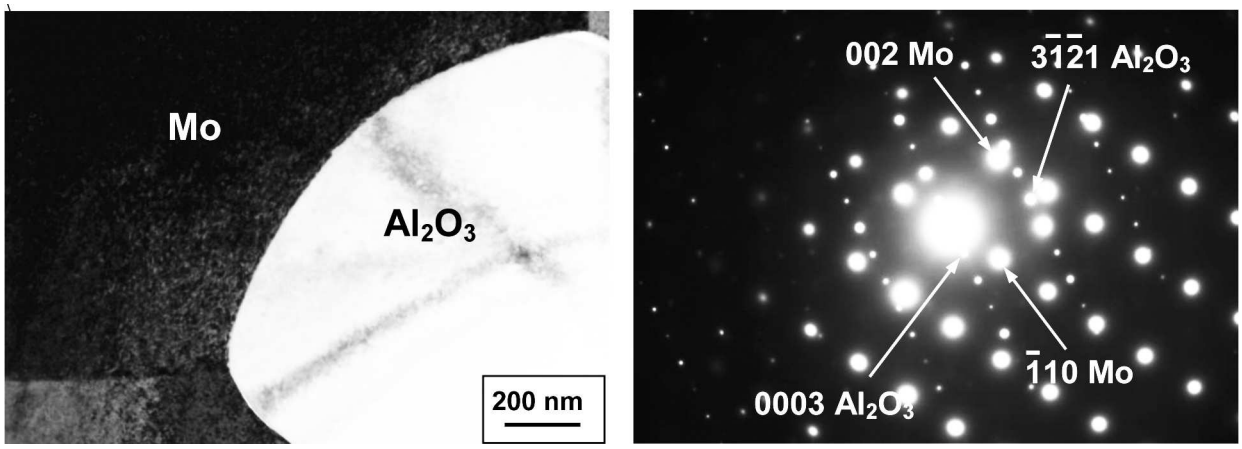

Fig. 6. TEM micrograph of the composite Mo-40Al_2O_3 (a) and selected area diffraction pattern at the area visible in 6a (b)

Figure 6 shows a TEM micrograph and a Selected Area Diffraction Pattern (SADP) taken at the area visible in the micrograph. The microstructure is similar to that of a composite containing 25% of Al_2O_3, with a difference that a strong, darker contrast is visible within Mo grains. It is the most probably due to diffraction contrast, but this thesis is not confirmed by the SADP, which shows reflections only from Mo at [110] zone axs and Al_2O_3 single crystals. The orientation relationship between Mo and Al_2O_3 is the following: $[\bar{1}\bar{5}40]$ Al_2O_3 ||[110] Mo and $(3\bar{1}\bar{2}1)$ Al_2O_3 ||$(\bar{1}12)$ Mo. It does not seem to be reproducible and in other cases other relationships, also far from basic ones such as $[\bar{1}100]$ Al_2O_3 ||[110] Mo and $(11\bar{2}3)$ Al_2O_3 ||$(01\bar{1})$ Mo are observed. The lack of simple crystallographic relationship between Mo and Al_2O_3 may be responsible for a weak adhesion force between metallic and ceramic particles. The microanalysis of particles basically agrees with the composition of components; however, some oxygen content was observed in the molybdenum part, which also can be seen in Table 2 showing the results of chemical analysis from EDS spectra. Relatively high 1.2 at.% of oxygen may result from contamination during the process of preparation using a FEG instrument. On the other hand, the contrast visible in Figure 6 in molybdenum crystals may suggest surface oxidation. The Cu radiation results from the FIB prepared sample holder.

TABLE 2
Quantitative results of chemical composition in points marked 1 and 2 in Fig. 7 calculated from EDS spectra visible in Fig. 7

Element	Point 1		Point 2	
	Wt %	At %	Wt %	At %
O (K)	43.7	56.7	0.2	1.2
Al (K)	56.3	43.3	0	0
Mo (K)	0	0	99.8	98.8

EDS results were confirmed by the XRD analysis. The X-ray phase analysis (Fig. 8) showed the presence of both molybdenum and alumina phases. Only on the surface level of the material, small amounts of molybdenum oxide were found, probably as a result of reaction with oxygen from the atmosphere.

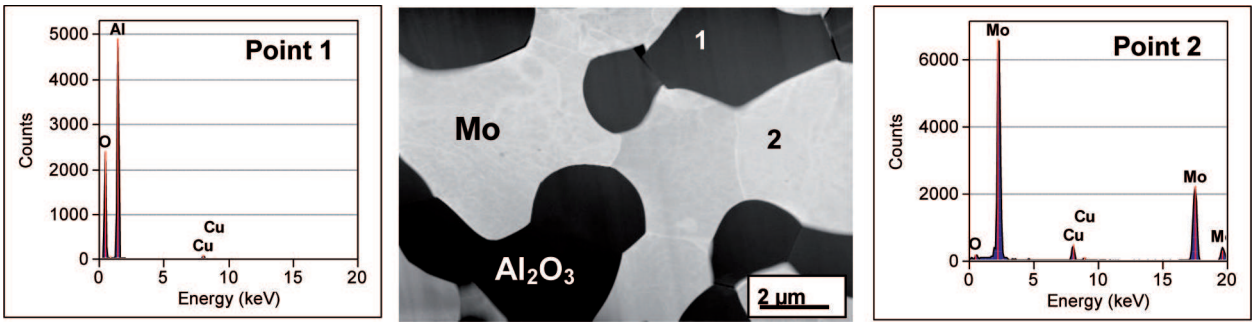

Fig. 7. TEM micrograph and EDS spectra of both components of the composite measured in points 1 and 2

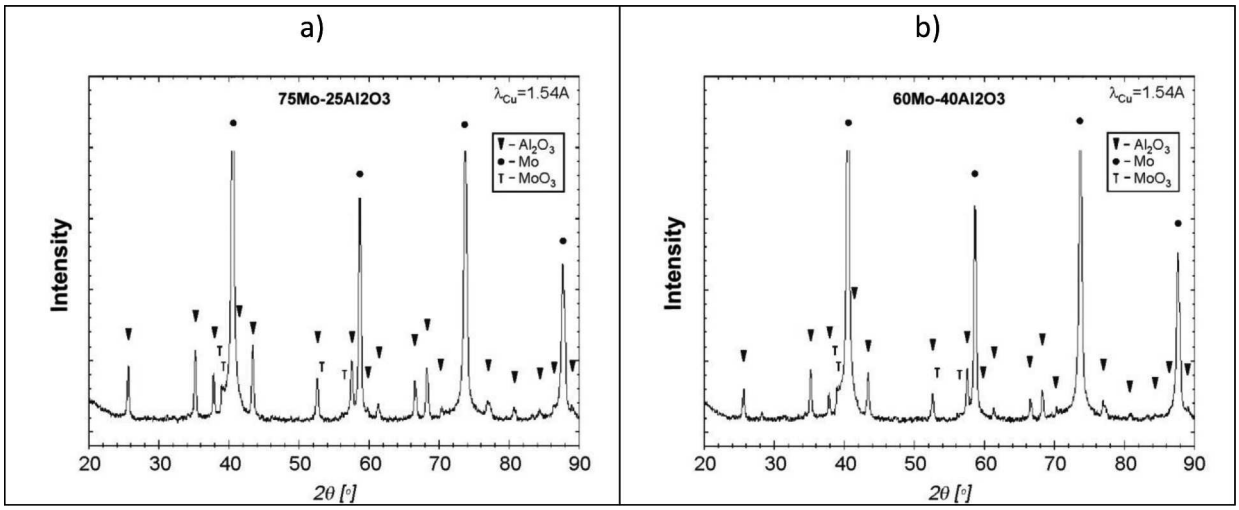

Fig. 8. XRD patterns of hot pressed Mo-Al_2O_3 composites

Table 3 presents the selected results of the mechanical properties of hot pressed Mo-Al_2O_3 composite materials.

TABLE 3
Mechanical properties of Mo-Al_2O_3 composites

Composition (vol. %)	Hardness (GPa)	Bending strength (MPa)	Fracture toughness (MPa·m$^{1/2}$)	Young's modulus (GPa)
75Mo – 25Al_2O_3	3.44	769.7	14.9	295.0
60Mo – 40Al_2O_3	4.55	547.0	11.8	291.7

The obtained mechanical properties of molybdenum-alumina composite materials should be analyzed with respect to the properties of pure alumina, which is one of the most commonly used advanced ceramic materials. High-temperature stability and retention of strength at elevated temperatures are enumerated among its most important attributes. On the other hand, brittleness is a major technical limitation to a wide application of alumina. The addition of a metallic component causes a significant decrease in both the Young's modulus values and hardness of obtained Mo-Al_2O_3 composites. When compared to the properties of pure alumina (E=400 GPa and H_V =13-15 GPa), their elastic properties and hardness are drastically reduced with the increase of the metallic phase content. Because the hardness of the Mo phase (H_V =2.1 GPa) is lower than that of Al_2O_3, the hardness of composites shall decrease once the molybdenum content is increased. It was found that the obtained values of the elastic modulus were lower than in the case of pure Mo and Al_2O_3, which could be caused by the presence of some porosity in the composites. But, most importantly promising changes were observed in the bending strength and fracture toughness. It was found that the bending strength reaches 547.0 and 769.7 MPa for 40% and 25% of alumina respectively. It is the increase of over 100% and 200% for each composition compared to pure alumina (σ_b =250 MPa). Since it is known that the addition of ductile metals improves the mechanical properties of ceramics [4], some plastic deformations during the bending test are acceptable. These results can be explained on the basis of TEM investigations, during which good adherence between molybdenum and alumina particles was observed.

Alumina ceramics show a mean value of K_{1c} of around 2.5-3.0 MPa·m$^{1/2}$, whereas in the case of the Mo-Al_2O_3 composite material containing 75% of molybdenum by volume it increases to almost 15 MPa·m$^{1/2}$. This important raise could be attributed to different mechanisms, including crack bridging, crack deflection, particle pull-out, microcracking and plastic deformation of the metallic phase, which are most commonly observed. The analysis of fracture samples allows to confirm the presence of crack bridging in the areas of ceramic particles. When adherence at the interface is high, a large amount of energy is lost in order to propagate the crack at the composite material. Crack propagation towards the interface and its passing through metallic grains was observed.

4. Conclusions

On the basis of this study, the following conclusions can be drawn.

1. The hot pressing method is a technique particularly suitable for obtaining Mo-Al_2O_3 composite materials with a wide range of the ceramic phase content. The process conducted at 1600°C at 30MPa allow to produce materials with a very high related density (over 99%).
2. Microstructural observations confirmed a high density of composite materials. Some porosity was ob-

served in the area of the ceramic phase. The structure was characterized by a very good homogeneity. It was found that there is no simple crystallographic relationship between Mo and Al_2O_3, which may be responsible for the presence of a weak adhesion between metallic and ceramic phases. Such a character of the ceramic-metal grain boundary affects the mechanical properties of Mo-Al_2O_3 composites.

3. Mechanical properties are strongly related to the volume content of composite components. The hardness of Mo-Al_2O_3 composites is decreasing with the raise of the molybdenum content. Moreover, the bending strength and fracture toughness are increasing when the volume fraction of the alumina phase is lowered. Although the microstructural analysis (TEM) did not show diffusion between the components of composites at ceramic/metal grain boundaries, a substantial improvement of mechanical properties, compared to pure alumina, was observed.

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