Novel Functionally Gradient Composites Al₂O₃-Cu-Mo Obtained *via* Centrifugal Slip Casting

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The investigations applied the original concept of the formation of materials as hybrid gradient composites. Two innovative technologies were used: formation by centrifugal slip casting and sintering with varying proportions of the liquid phase. This allowed us to create a gradient microstructure. This article presents the study of Al₂O₃-Cu-Mo gradient composites. This work aimed to determine the effect of the metallic phase content on the composite's microstructure and basic properties. The most critical element of the study will be determining the ability to control the location and flow of the liquid phase during the sintering process. The research demonstrated that adding a third component in the form of Mo reduces the liquid Cu flow onto the surface of the composites during the sintering process. In this research, we achieve results with high cognitive value.

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I. INTRODUCTION

GRADIENT materials are characterized by a continuous change of properties along at least one direction. Their change of functional and structural properties is effected by variations in parameters, including chemical composition, size, morphology, and structure as a function of position.^[1–4] The gradient bond connecting the components of a given material is often the best type of connection, ensuring optimal composite properties. A smooth transition provides a gentle change of properties that directly reduces the stress in the adjoining area.^[5,6] Applications of gradient materials include, among other things, cutting tools, construction materials, and electronic components. Furthermore, gradient composites can also be used as biomedical materials and thermal shields.

Composites of the ceramic-metal system constitute an interesting group of gradient materials.^[7,8] Methods for obtaining gradient composites belonging to this system can be divided into three groups depending on the state of aggregation of the system during material synthesis. It can be distinguished that the processes are conducted

in gaseous, liquid, and solid phases. Those carried out in the gaseous phase include chemical vapor deposition (CVD)^[9–11] and physical vapor deposition (PVD).^[12,13] The CVD and PVD methods make it possible to obtain very thin gradient coatings.^[14,15] By changing the process parameters, *i.e.*, temperature, the chemical composition of the substrate, gas pressure, and energy of the bombardment ions, it is possible to obtain a controlled width and structure gradient. The gradient in composites obtained in the liquid phase is achieved by electroplating, plasma spraying, and eutectic reactions.^[16]

The product's requirements and application dictate the choice of technique for manufacturing gradient ceramic-metal composites. Other methods of producing such composites, which have enjoyed wide interest in recent years, are technologies for obtaining gradient materials using various slip casting techniques, *i.e.*, classical slip casting,^[17,18] tape casting,^[19] or centrifugal casting.^[20,21] The classical slip casting technique enables the formation of complex-shaped, solid, or thin-walled products. Tape casting enables the production of flat sheets,^[22] while the centrifugal casting of elements with symmetrical shapes in relation to the axis of rotation.^[23] At the same time, centrifugal casting ensures the highest density of the product compared to other casting methods and produces fewer defects.^[24] Given the quality of the products obtained and the advantages mentioned above, it can be concluded that the centrifugal casting method is the most effective technique for shaping gradient materials. What distinguishes this method from others is that it can achieve the desired material properties in a controlled fashion.

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Additionally, it is inexpensive and ecological. These qualities provide ceramics-metal system gradient materials with the potential to become competitive on the market in relation to currently available materials.

The objective of this work was to produce and characterize Al_2O_3 -Cu-Mo composites obtained by centrifugal slip casting. The choice of materials for testing, *i.e.*, powders of alumina, copper, and molybdenum, was deliberate. Based on previous publications concerning Al_2O_3 -Cu-Mo composites obtained by slip casting, it was found that the main problem encountered during the production of composites is the loss of liquid copper during the sintering process.^[25] The results of our research conducted on composites obtained by slip casting and centrifugal slip casting allowed us to conclude that the addition of the second metallic component, in this case, molybdenum, prevents or limits the escape of liquid copper and may provide better properties of the manufactured composites.^[26,27] Thermal analysis and dilatometric research results of the Al_2O_3 -Cu-Mo composite presented in ^[28] revealed decomposition and mass were increasing above the temperature of 600 °C, which is connected with Cu and Mo oxidation. Higher growth of mass is observed in composites with higher content of the metallic phase. Moreover, the higher amount of metallic phase results in increased temperature of densification start and the temperature of maximum densification. Decreased total shrinkage of the samples during sintering was observed as well. Mechanical properties of the slip cast Al_2O_3 -Cu-Mo composite depend on the volume content of the metallic phases. Lower hardness was revealed for composites with higher content of metallic phase. For these composites, increased tensile strength was observed. This is due to the lower hardness of Cu and Mo according to Al_2O_3 .

The main issues of manufacturing the composites using slip casting are not fully and regularly distributed metallic particles in the cross-section of the obtained composites.^[29] The author's own research results revealed that the microstructure of composites Al_2O_3 -Cu-Ni obtained by the slip casting method is characterized by few zones with different contents of metallic phase in the cross-section of the samples. At least one of these zones is characterized by a lack of metallic particles in the microstructure. To prevent this, a centrifugal slip casting was adapted. Previous research results of the authors revealed that the application of centrifugal slip casting for obtaining Al_2O_3 -Ni composites results in homogenization of the microstructure at the cross-section of the samples and prevents obtaining the zones deprived by the metallic phase.^[29] Other authors' research results on Al_2O_3 -Ni composites revealed that combining centrifugal slip casting and a magnetic field to determine the distribution of magnetic particles gives the possibility to obtain composites with different microstructures determined by the magnetic field. Application of magnetic field influence on the location of the metallic phase in the composite affects the physical properties of the composite.

In the current study, centrifugal slip casting was adapted to produce gradient materials from the Al_2O_3 -Cu-Mo system.

Aluminium oxide, which is characterized by high chemical and thermal resistance, high hardness, stiffness, and low density, was selected as a ceramic powder for the study. Copper was chosen for reinforcement since, being a plastic material, it improves the resistance to brittle cracking of the ceramic-metal composite.

Based on the Cu-Mo phase equilibrium system, it was found that metallic additives in the form of copper and molybdenum are mutually inert and do not form solid solutions or intermetallic phases between each other. The lack of reactivity between the components, therefore, constitutes another reason why they were selected for testing. After the sintering process, no new phase should appear at the interface of the metal particles, which could affect the properties of the composite. In addition, based on the literature, it was found that liquid copper effectively wettens molybdenum. Therefore, it will be interesting to determine whether adding molybdenum to the casting slip as a second metallic component will prevent the escape of copper in centrifugal slip cast composites during the sintering process. The idea behind combining the two types of reinforcement phases in the form of Cu and Mo in gradient composites is to improve the selected properties in relation to already known materials. Despite the many advantages of using pure Al_2O_3 , its applications are limited because of its low resistance to brittle cracking. Hybrid composites of the Al_2O_3 -Cu-Mo system can be a solution to this problem.

This study aimed to obtain and characterize in detail Al_2O_3 -Cu-Mo composites containing a gradient distribution of the metallic phase in the matrix, which have been formed by centrifugal slip casting. Composites with varying metallic phase content were produced. Analysis of the influence of metallic phase content change on the microstructure and selected properties of the composites was performed. Correlation among the microstructure, chemical composition, formation process parameters, and basic physical properties of the composites was investigated. The rheological characterization of the water-based slurries was performed. The microstructure of the samples was analyzed using SEM, EDS measurements, and XRD analysis. The quantitative description of the matrix grains in functionally graded materials was made. The effect of the metallic phase content on the growth of the matrix grains during the sintering process was determined. In addition, the Vickers microhardness of the samples was measured.

II. EXPERIMENTAL PROCEDURE

A. Research Techniques

To characterize the starting materials, the following steps were performed: microscopic observations using a scanning electron microscope, laser particle size distribution analysis, Brunauer-Emmett-Teller (BET) absorption isotherm analysis for measuring the surface of

powders, determination of the applied powders' density using a helium pycnometer, and X-ray fluorescence to confirm the purity of the metal powders. To characterize the obtained composites, the selected physical parameters were determined using the Archimedes method, microscopic observations, fractographic analysis, stereological analysis, and chemical composition analysis.

1. Particle size distribution measurement

For particle size distribution, the PSD of the powders used in the study was determined using the dynamic light scattering method with an LA-960 HORIBA laser scattering particle size distribution analyzer. Water was used as a dispersing medium in the experiment to examine aluminium oxide powder, while the copper and molybdenum metallic powders were analyzed using isopropanol.

2. Total specific surface area measurement

The study investigated the specific surface area of the initial powders by nitrogen sorption at liquid nitrogen temperature using an ASAP2020 Micromeritics Instrument analyzer. Initially, each sample was degassed under reduced pressure at 90 °C for 1 h and then at 300 °C for another 4 h. The total specific surface area (S_{BET} [m^2/g]) of the powders was determined by approximating the results of five-point measurements in the range of $p/p_0 = 0.05\text{--}0.3$ for samples Al_2O_3 and $p/p_0 = 0.01\text{--}0.1$ for the metallic samples Cu and Mo to the BET adsorption isotherm.

3. Density measurement using a helium pycnometer

A helium pycnometer was used to determine the actual density of the Al_2O_3 , Cu, and Mo powders. Density measurement using a helium pycnometer was determined based on the standard ASTM D3766.^[30] The density determined by this method is the ratio of the mass of the solid material to the sum of the volumes of the solid material and closed pores within the material. The test was carried out using a Micrometrics Accu Puc II helium pycnometer in 800 cycles and 10 rinses in the presence of helium. The equipment measures the skeletal volume of the powder by gas displacement using the volume-pressure relationship of Boyle's law.^[31] During the measurement, the powder was placed in a firmly closed cup with a known volume. Subsequently, this cup with powder was situated in the sample chamber. Throughout the measurement, helium is introduced to the sample chamber and afterward expanded into a second empty chamber with a noted volume. During the investigation, the pressure observed after filling the sample cell and the pressure discharged into the expansion chamber were measured. Afterward, based on the obtained measurements, the volume was determined. The density was defined as dividing the sample weight by the designated volume.^[32]

4. X-ray fluorescence measurement

X-ray fluorescence (XRF) was used to characterize the metallic powders, *i.e.*, copper and molybdenum, used in the study. The chemical composition of copper

and molybdenum powders used in the experiment was investigated with an XRF X-MET 8000 spectrometer.

5. Rheological behavior of composite suspensions

The rheological behavior of the composite suspensions was examined by using a AMETEK Brookfield DV3TRV EXTRA Viscometer. The AMETEK Brookfield Viscometer is accurate within ± 1.0 pct of the range in use, and it characterized a reproducibility within ± 0.2 pct. The viscosities of the suspensions as a function of the shear rate were measured. The shear rate was raised from 1 to 130 s^{-1} and then decreased to 1 s^{-1} . The rheological study was carried out in an air-conditioned laboratory at 23 °C.

6. Determination of the slurry's tendency to sedimentation

Observations were carried out on the process of sedimentation of the suspensions used in the investigation. For this goal, the slurries were observed for 2 h from the time they were obtained. Monitoring of the composite suspensions was carried out at 23 °C.

7. Microstructure observations

Observations of the microstructure of gypsum mold fractures and the morphology of the source Al_2O_3 , Cu, and Mo powders and of the manufactured composites were made using a JEOL JSM-6610 scanning electron microscope equipped with secondary electron (SE) and back-scattered electron (BSE) detectors. A voltage of 15 kV was applied during the observations.

The SEM observations made it possible to determine the distribution of the metallic phase in the ceramic matrix. Metallographic sections were prepared for microscopic examination. The sintered sleeves were cut into 1-cm-high fragments and then mounted. The fragments for the metallographic sections were selected from the central part of the sample. Mounting was performed hot using conductive resin. The specimens were then ground and polished. Photos taken with SEM were assembled into panoramic images showing detailed cross-sectional fragments of the obtained samples. Moreover, fractographic observations of $\text{Al}_2\text{O}_3\text{--Cu--Mo}$ system fractures were made. Fractographic observations were carried out to determine the influence of the metallic phase content in the produced composites on the growth of matrix grains.

8. Energy-dispersive X-ray spectroscopy measurement

Analyses of the chemical composition of $\text{Al}_2\text{O}_3\text{--Cu--Mo}$ samples produced by centrifugal slip casting were performed using a JEOL JSM-6610 SEM equipped with an Oxford X-Max energy-dispersive X-ray spectroscope (EDS).

9. Study of selected physical properties by the Archimedes method

The Archimedes' method according to European Standard EN623-2^[33] was used to determine the apparent density, relative density, open porosity, and absorbability of the obtained composites. To determine the selected physical parameters, the samples were cut

into 1-cm-high fragments. A Secotom 15 saw with a diamond blade was used for cutting. The dry cut elements were weighed and then boiled for 1 h in distilled water to allow water to absorb into the material. In the next stage, the samples were weighed again in water and air. Moreover, the physical parameters of the composites such as linear and volumetric shrinkage were determined. To determine these values, measurements of height, external diameter of the shapes, and inner diameter of the holes as measured with a calliper were used.

10. Stereological analysis

A quantitative description of the microstructure of the samples was made based on SEM images of randomly selected areas on the fracture of samples carried out by a micrometer computer image analyzer.^[34] This method allows obtaining information about the actual size and distribution of the Al_2O_3 grain size in the sample. The SEM analysis of images included: image processing, measurement, and explanation of received scores. Microstructure observations were carried out using magnification $\times 10,000$ and $\times 20,000$. The average values were calculated from the measurement of 15 pictures. Moreover, based on the stereological analysis, the shape parameters of Al_2O_3 grains were determined: elongation ($\alpha = d_{\text{max}}/d_2$), convexity ($W = p/p_c$) coefficient describing the surface development ($R = p/p_c \cdot d_2$), where d_{max} = the maximum diameter of Al_2O_3 grain projection [μm], d_2 = diameter of the circle of the same surface as the surface of the analyzed grain [μm], p = the perimeter of Al_2O_3 grains [μm], and p_c = the Cauchy perimeter [μm].^[34]

11. X-ray diffraction measurement

To determine the phase composition, a Rigaku MiniFlex II diffractometer (Japan) with a CuK radiation wavelength of $\lambda = 1.54178 \text{ \AA}$ was used, set to the following recording parameters: voltage 30 kV, current 15 mA, angular range 2θ 20 to 100° , step $D2\theta$ 0.02° , and counting time 3 s. The test was carried out to characterize the phases present in the composites before and after the sintering process.

12. Microhardness measurement

The Vickers method was used to establish the microhardness of the obtained samples. To perform the test, a Struers DURA SCAN 70 hardness tester was used. The surfaces of the samples were prepared by hand grinding using abrasive paper with decreasing gradation starting from P240 and ending with P1200. The investigation was then conducted at a load of 9.8 N for 15 s. The hardness results were obtained from about 25 measurements carried out along the radial direction in an equal interval of distance (0.2 mm) to confirm the compositional changes.

B. Materials

The main component of the produced composites was an $\alpha\text{-Al}_2\text{O}_3$ matrix. Taimicron Chemicals' TM-DAR powder was used in the study. According to its

manufacturer, the powder has the following parameters: average particle size $100 \pm 25 \text{ nm}$, 3.98 g/cm^3 density, and 99.99 pct purity. Based on microscopic observations, the Al_2O_3 powder used was spheroidal (Figure 1). The observations revealed that Al_2O_3 tends to form agglomerates. This is because nanometric powders have a high surface area to single particle volume ratio. Figure 2 shows the particle size distribution of Al_2O_3 powder determined by the dynamic light scattering method. Analysis of the obtained histogram revealed that the particle size distribution is unimodal (Figure 1). The average particle size is 219 nm, with a median of 214 nm and standard deviation of 50 nm. The obtained results confirm the tendency of Al_2O_3 powder to form agglomerates. The actual density determined by the pycnometric method was $4.06 \pm 0.04 \text{ g/cm}^3$. The obtained density value was higher than the theoretical density given by the manufacturer (3.98 g/cm^3). The discrepancy in the results may be caused by a measurement error, which correlates with insufficient desorption of the ceramic powder before the measurement. BET absorption isotherm analysis showed that the average S_{BET} total specific surface area of the powder particle is estimated at $10.85 \pm 0.07 \text{ m}^2/\text{g}$. The obtained values indicate that the Al_2O_3 powder has a developed surface. The obtained density and total specific surface area values for Al_2O_3 (TM-DAR) are consistent with the literature data published by A. Wieclaw-Midor and her team.^[35]

Createc's copper powder with an average particle size of $< 150 \mu\text{m}$, a density of 8.94 g/cm^3 , and a purity of 99.98 pct was used to produce the composites. Based on microscopic observations, it was found that the copper particles are characterized by micrometric size and feature numerous appendices with rounded edges (Figure 2). PSD analysis showed that their average particle size is $72.53 \pm 1.81 \mu\text{m}$ (Figure 2). Histogram analysis showed that the powder has a unimodal distribution. The actual density of the copper powder, as measured by the pycnometric method, is $9.04 \pm 0.02 \text{ g/cm}^3$, which is higher than the value given by the manufacturer. The discrepancies in the values obtained may result from the presence of impurities on the powder surface, which was contaminated during preparation. Chemical analysis of the powder sample using a fluorescent X-ray spectrometer (XRF) showed that it contains $100.0 \pm 0.2 \text{ pct Cu}$ (Figure 2). The BET method revealed that the average total specific surface area of the Cu powder is $0.09 \pm < 0.01 \text{ m}^2/\text{g}$.

The second metal used for obtaining the composites was molybdenum (Createc). The manufacturer defines this powder as micrometric with an average particle size of 3 to $8 \mu\text{m}$, a density of 10.28 g/cm^3 , and 99.99 pct purity. Microscopic observations showed that molybdenum particles have a regular surface with an elongated shape (Figure 3). The BET method revealed that the average total specific surface area of the Mo powder is $0.24 \pm < 0.01 \text{ m}^2/\text{g}$. The average particle size of Mo was $8.00 \pm 0.95 \mu\text{m}$ as determined according to the particle size distribution histogram (Figure 3).

Fig. 1—Microstructure and histogram of the particle size distribution of Al_2O_3 powder.

C. Sample Preparation

The centrifugal slip casting method was used to obtain gradient composites from the Al_2O_3 -Cu-Mo system. Commercially available alumina, copper, and molybdenum powders were used to obtain the composites. Three series of samples with different contents of metallic phase in the casting slip were produced: Series I—5 vol pct metallic phase, Series II—10 vol pct metallic phase, and Series III—15 vol pct metallic phase. Each of the prepared casting slips contained 50 vol pct solid phase. DURAMAX D-3005, a commercial dispersant consisting of a 35 pct ammonium salt solution in water with a density of 1.16 g/ml, was used as a liquidizer.^[36,37] In the experiments, 1.5 wt pct DURAMAX D-3005 was used in relation to the total solid content of the casting slip. Distilled water was used as a solvent for economic and ecological reasons. The molding process was carried out at room temperature ($T = 23^\circ\text{C}$) for 130 min at 3000 rpm. Gypsum molds obtained in a reverse hydration reaction of modeling gypsum were used for casting. The addition of water caused the degree of hydration to change, which led to the precipitation of fine gypsum crystallites. During the preparation of the molds, a mixture of powder and water at a 2:3 ratio was used. Selected physical properties of the gypsum molds were measured by the Archimedes' method in accordance with EN-623-2:1993. The sintering process of the Al_2O_3 -Cu-Mo system composites was carried out in a Carbolite STF 16/75/450 furnace in a reducing

atmosphere consisting of N_2/H_2 . The sintering was done with varying properties of the Cu liquid phase. During the sintering process at temperatures up to 1083°C to 1400°C , 100 pct copper had already accrued in the liquid form. Steps of the sintering process were:

- heating to 120°C , heating rate: $5^\circ\text{C}/\text{min}$,
- heating in the temperature range of 120°C – 750°C , heating rate: $2^\circ\text{C}/\text{min}$,
- heating in the temperature range of 750°C – 1400°C , heating rate: $5^\circ\text{C}/\text{min}$,
- storage at 1400°C , duration: 2 h,
- cooling rate: $5^\circ\text{C}/\text{min}$.

The above sintering curve profile was applied based on previous study findings for this system.^[28]

III. RESULTS

A. Rheological Characterization

The viscosity curves of the Al_2O_3 -Cu-Mo slurries contained 5 vol pct, 10 vol pct, and 15 vol pct of the metallic phase in the prepared suspension. Figure 4 shows the viscosity curves of Al_2O_3 -Cu-Mo slurries. All suspensions showed shear thinning behavior. The measurements demonstrate that the value of the viscosity at a shear rate of 10 s^{-1} was 17,890 mPa·s, 14,560 mPa·s, and 11,070 mPa·s for the suspensions containing 5 vol

Fig. 2—Microstructure, XRF, and histogram of the particle size distribution of Cu powder.

pct, 10 vol pct, and 15 vol pct metallic phase, respectively. These results demonstrated that the value of viscosity decreases with the increase of the metallic phase in the slurry. It was found that the highest viscosity value was obtained for the slurry containing 5 vol pct metallic phase. The average size of the particles used in the experiment is correlated with the changes in the viscosity value. In the investigation, the authors used a ceramic powder with an average particle size of about $0.2\ \mu\text{m}$ and two types of metallic powder with an average particle size of about $85.6\ \mu\text{m}$ and range of 3 to $8\ \mu\text{m}$ for Cu and Mo, respectively.

Figure 5 demonstrates the flow curves of Al_2O_3 -Cu-Mo slurries containing 5 vol pct, 10 vol pct, and

15 vol pct metallic phase in the prepared suspension. Results are discussed in the Discussion section.

B. Characterization of Suspension Sedimentation

The authors' previous research shows that to obtain an effective composite molding process and to produce specimens with the appropriate properties, the suspension must be dispersed and stable over time.^[28] Studies have shown that suspensions containing 50 vol pct solid content with 10 vol pct and 15 vol pct of metal particles (Cu and Mo) with respect to the total solid-phase content were stable for 24 h from the moment of mass preparation.^[28] In this investigation, the sedimentation

Fig. 3—Microstructure, XRF and histogram of the particle size distribution of Mo powder.

studies were extended to include another slurry that contained 5 vol pct metallic phase. To determine the stability of the slurries over time, a sedimentation test was performed for three suspensions with different metallic phase contents (5 vol pct, 10 vol pct, 15 vol pct). Figure 6 presents photos documenting the state of the suspensions at specified intervals of time. The observations of the suspensions showed that the $\text{Al}_2\text{O}_3\text{-Cu-Mo}$ slurries were stable during the experiment. During the examination, no sedimentation of the suspensions was observed. It can be concluded that the use of DURAMAX D-3005 as a dispersant ensured obtaining a stable suspension from the preparation of slurries to the start of the molding process. The change

of the metallic phase content in the prepared suspensions did not affect the rate of sedimentation.

C. Gypsum Mold Characterization

The type of gypsum mold used in the experiment plays a significant role in the formation of composites.^[38] Its porosity determines the rate of removal of the liquid medium from the prepared casting slip and thus the density of the suspension. Based on previous experiments performed to determine the influence of gypsum mold porosity on the properties of the product obtained by centrifugal slip casting, it was found that the higher the porosity of the mold, the greater the width

Fig. 4—Viscosity curves of Al_2O_3 -Cu-Mo slurries containing 5 vol pct, 10 vol pct, and 15 vol pct metallic phase in the prepared suspension.

Fig. 5—Flow curves of Al_2O_3 -Cu-Mo slurries containing 5 vol pct, 10 vol pct, and 15 vol pct metallic phase in the prepared suspension.

of the metallic zone in the product.^[38] The reason for this is that at a higher porosity of the gypsum mold, the liquid medium is removed from the casting slip more quickly. In the current study, STODENT II gypsum was used. This made it possible to produce gypsum molds with an open porosity of 26.9 pct and an absorbability of 15.4 pct. A typical microstructure of the gypsum molds used in this experiment is shown in Figure 7. The gypsum molds used in the formation of the composites were characterized by a linear shrinkage equal to 0.2 pct. Moreover, it was found that the gypsum used had a compressive strength equal to 10 MPa. The values of linear shrinkage and compressive strength for STODENT II gypsum were determined based on ISO 6873: 2013.^[39]

D. Macroscopic Characterization of Sintered Samples

Macroscopic observations of the produced shapes showed that the centrifugal slip casting method makes it possible to form composites with a gradient distribution of metallic particles in the matrix. Composites of the ternary system (Al_2O_3 -Cu-Mo) obtained by centrifugal casting are shown in Figure 8. No microcracks or

delamination was found on the surface of the produced samples before sintering. The observations (Figure 8(a)) revealed that the sample containing 5 vol pct metallic phase (Series I) was characterized by an absence of cracks that would be formed during sintering, as opposed to the other two series. However, the surfaces of the samples with a higher content of metallic phase (Series II—Figure 8(b) and III—Figure 8(c)) contained microcracks.

E. Microscopic Characterization of Sintered Samples

Figure 9 demonstrates sample images of cross-sectional fragments of Al_2O_3 -Cu-Mo composites. Observation of the images revealed an uneven distribution of the metallic phase in the ceramic matrix. The observations confirmed that a microstructure gradient was obtained in all produced series of samples. All composites are characterized by a similar microstructure. It was also found that the shapes produced are characterized by a three-zone structure. Three zones with different metallic phase contents were distinguished. It was found that the metallic areas are characterized by irregular shape and size.

Starting from the outer edge, the following were distinguished: Zone I, Zone II, and Zone III. In the micrographs, in all samples tested, the gray areas correspond to the matrix, while the bright areas are the metallic phase. The observations reveal that Zone I is characterized by an even distribution of metallic particles in the matrix. It was observed that in this area particles of various sizes, both small and large, were located. For the composites produced in the experiment, a zone without metallic particles was not obtained.

The focus then moved on to determining the width of the individual zones in the composites. Microscopic observations revealed that the width of Zone II changed depending on the content of the metallic phase in the casting slip used to make the shapes. Based on the images shown in Figure 10, the total width of the shape's wall and the width of the distinguished zones were determined. The results are presented in Table I. It was shown that the total width of individual zones is similar for all samples. In the case of Series II and III, the widths of individual zones are slightly lower, probably as a result of the loss of liquid copper during the sintering process.

F. Energy-dispersive Spectroscopy Mapping of Composites

Investigating the microstructure of the composites revealed the gradient of two types of metallic phases. Copper in BSE images (Figure 10) is characterized by a darker gray color, while molybdenum is lighter. Moreover, copper particles in the composites are larger than the molybdenum phase. Based on the results of observations using a scanning electron microscope, it was found that the copper particles had melted during the sintering process and filled up the pores of the matrix. The characteristic appearance of copper and molybdenum particles is shown in Figure 10, which also presents

Slurry containing 5 vol.% of metal

Slurry containing 10 vol.% of metal

Slurry containing 15 vol.% of metal

Fig. 6—Photograph of the performance and colloidal stability of the slurries.

Fig. 7—Typical microstructure of the gypsum mold used in the study.

the distribution of elements in the composites in the form of mapping analysis of selected areas. The microstructure observed in Figure 10 is characteristic for all zones observed in the composites macrostructure (Figure 9) and is a result of surrounding the matrix particles by liquid copper during the sintering process. The smaller,

brighter particles of phase, molybdenum, are separated from the larger particles. Besides the larger copper phases and smaller molybdenum particles, an additional area is observed and indicated by the arrow. This area is characterized by ultrafine molybdenum particles, which are often located on the copper-ceramic interface.

Fig. 8—Photographs of manufactured ternary-graded hollow cylinder composites: (a) Series I: 5 vol pct metal phase, (b) Series II: 10 vol pct metal phase, (c) Series III: 15 vol pct metal phase.

G. Physical Properties

The selected physical properties of the obtained materials are listed in Table II. Composites sintered in a reducing atmosphere were characterized by a density of between 90 pct and 95 pct. It was shown that Series I samples containing a 5 vol pct content of metallic phase had the highest density. Moreover, in the case of Series II and III, it was noticed that approximately 3 pct–5 pct of copper in relation to the total copper content flowed out in the samples during the sintering process and, as a consequence, poor densification of the samples after sintering. It was concluded that the gained density results for Series II and III are not satisfying and have to be optimized in the future to obtain improved properties of the fabricated samples. The highest values of open porosity and absorbability were achieved by the samples from Series III, which contained 15 vol pct metallic phase. This result can be attributed to the presence of surface defects caused by the highest loss of liquid copper in this series during sintering. Direct measurements showed the maximum linear shrinkage of composites observed for Series II equaled 15.68 ± 0.25 pct, while the lowest for samples containing 15 vol pct metallic phase (Series III).

H. Fractography Observations of Samples

Fractography investigation was performed to reveal the fracture mechanism of the composites depending on the metal phase content. Surfaces of the fractured

samples were used to characterize the mechanism. SEM images in Figure 11(a) through (c) show the fracture surfaces of the composites manufactured with 5 to 15 vol pct metal phase.

Next, the effect of the metallic phase content on the growth of the matrix grains during the sintering process was determined. For this purpose, fractographic investigations were performed to observe Al_2O_3 grains in the entire sample volume using SEM, based on which a stereological analysis was performed. Figure 12 shows the sample microphotographs depicting the matrix areas of Series I, II, and III.

I. Stereological Analysis

The size distributions of alumina grains in the sintered samples depending on the metal content in the series are shown in the histograms in Figure 13. Analysis of the obtained histograms revealed a unimodal distribution of Al_2O_3 grains for all shapes. For Series I, the average grain size was in the range of 0.1 to 2.0 μm . For Series II, the average grain size was in the range of 0.1 to 1.3 μm , while for Series III it was in the range of 0.1 to 1.0 μm . It was discovered that the size ranges of Al_2O_3 after sintering are larger than those of the initial Al_2O_3 powder. Stereological analysis made it possible to determine the average size of Al_2O_3 grains after sintering. The measurements showed that the average grain size of Al_2O_3 for series I, II, and III is 0.7 ± 0.2 , 0.65 ± 0.3 , and 0.5 ± 0.2 μm , respectively.

Fig. 9—SEM images of cross-sectional fragments of Al_2O_3 -Cu-Mo composites: (a) Series I (5 vol pct metal phase), (b) Series II (10 vol pct metal phase), and (c) Series III (15 vol pct metal phase).

In the next step, the shape factors were determined, such as: the curvature of the grain boundary, elongation, and convexity. The obtained results of the analysis are presented in Table III. The shape factors should be interpreted in relation to the shape of the circle. If the parameter value is close to one, this means that the grain shape is similar to a circle. Based on the obtained results, it was found that the matrix grains, regardless of the volume fraction of the metallic phase in the materials, are characterized by similar shapes. The stereological analysis indicated that the alumina grains in all series are characterized by elongation, no convexity, and a very developed surface. This is evidenced by the values of shape parameters (curvature of the grain boundary, elongation, convexity presented in Table III).

J. XRD

The analysis of the phase composition was carried out on samples both in the raw state (Figure 14(a)) and after sintering (Figure 14(b)). The results presented in Figure 14(a) show that the sintering process for this composite system does not result in the appearance of any new phases in the material. Regardless the metallic phase content both before and after sintering, the composite samples contained three phases: Al_2O_3 , Cu and Mo.

XRD analysis also revealed that in all prepared samples both Cu and Mo can be characterized by a cubic structure (Fm-3m and Im-3m, respectively), regardless of the metallic phase content. These results are consistent with the literature data presented in previous works.^[28,40,41]

K. Microhardness Test

Figure 15 shows the results of the microhardness test. The results revealed a nonhomogeneous distribution of hardness along the radial direction of the samples. This is due to the different sizes of the metallic phase particles, different distances between particles, and different distributions of the particles along the samples. The indenter pressed during the hardness test covers a relatively large area in relation to the particle size influence on the microhardness test results. Another reason for the results observed in Figure 15 is the uneven distribution of the pores in the matrix on the surface of the samples. Consequently, the area directly under the indenter is deformed inconsistently during the measurement, which results in a significant standard deviation of the test results. Nevertheless, the microhardness test results revealed the maximum hardness of the samples at a level of 765 HV1 for Series I, 689 HV1 for Series II, and 532 HV1 for Series III. Minimum hardness values were: 224 HV1 for Series I, 169 HV1 for Series II, and 167 HV1 for Series III.

IV. DISCUSSION

A. Rheological Analysis of Slurry

All slurries prepared in the experiment contained the same solid content in the suspension. However, each of the prepared slurries differs in the metallic phase content (5 vol pct, 10 vol pct, 15 vol pct). With the increasing content of the metallic phase in the slurry, micropowders with large particles occupy increasing space in the total volume of the solid phase in the suspension. This means that the number of small particles decreases and the number of large particles in the suspension increases. By definition, viscosity is defined as the friction appearing between individual molecules in a fluid, and it is responsible for the resistance to flow.^[42] Therefore, as the mean particle spacing increases, the number of potential interactions between the particles decreases, and thus the viscosity decreases. Consequently, as the average distance between the particles increases (in addition, the particles are stabilized and there is no

Fig. 10—Energy dispersive spectroscopy mapping analysis of selected areas in composites: (a) Series I (5 vol pct metal phase), (b) Series II (10 vol pct metal phase), and (c) Series III (15 vol pct metal phase).

Table I. Statement of the Width Dimensions of the Conventionally Accepted Zones Occurring in the Composites Al₂O₃-Cu-Mo

Series	Total Width of Zones (μm)	Width of Zone I (μm)	Width of Zone II (μm)	Width of Zone III (μm)
Series I (5 Vol. Pct of Metal Phase)	5020	1130	274	3620
Series II (10 Vol. Pct of Metal Phase)	5020	1050	410	3560
Series III (15 Vol. Pct of Metal Phase)	5020	1050	420	3250

Table II. Selected Properties of Composite Materials: Series I (5 Vol Pct Metal Phase), Series II (10 Vol Pct Metal Phase), and Series III (15 Vol Pct Metal Phase)

Property	Series I (5 Vol. Pct of Metal Phase)	Series II (10 Vol. Pct of Metal Phase)	Series III (15 Vol. Pct of Metal Phase)
Relative Density (Pct)	94.60 $\pm$ 0.92	92.55 $\pm$ 1.46	90.05 $\pm$ 1.26
Absorbability (Pct)	0.16 $\pm$ 0.03	0.03 $\pm$ 0.04	0.23 $\pm$ 0.10
Open Porosity (Pct)	0.64 $\pm$ 0.13	0.14 $\pm$ 0.19	1.01 $\pm$ 0.44
Linear Shrinkage (Samples Diameter) (Pct)	14.00 $\pm$ 0.4	15.68 $\pm$ 0.25	10.37 $\pm$ 0.05
Volumetric Shrinkage (Pct)	35.67 $\pm$ 0.15	33.29 $\pm$ 0.33	31.74 $\pm$ 0.56
(± SD).			

heterofloculation), the number of potential interactions between the particles decreases, and thus the viscosity decreases.

Based on the hysteresis loops presented in the results section, it was indicated that the suspensions reveal a slight thixotropic behavior.^[43] From the observations of flow curves, it can be concluded that the internal structures of all suspensions are damaged throughout the shear and rebuilds. These results demonstrated that all suspensions are characterized by a molecular structure that causes the viscosity to increase. This effect may be due to the presence of copper and molybdenum particles in the alumina slurries and the electrostatic interactions between them.

Interestingly, our previous investigation on Al₂O₃/Ni suspensions using the same alumina powder also showed thixotropic properties.^[29] Moreover, literature data show that Pietrzak *et al.* in their research using the same Al₂O₃ powder, but with the addition of in water systems, also noted the thixotropic properties of the suspensions. Nevertheless, their systems were also subsidized with a large amount (about 4 wt pct) of monomers, which resulted from the selected forming method—gel casting.^[44] Furthermore, it should be noted that the thixotropic properties of aqueous ceramic slurries may also be obtained when other modifiers like 6-O-acryloyl-d-galactose are used, which were described in the work by Wieceńska and partners.^[45]

B. Microstructure

Based on the macroscopic and SEM observation results, it was concluded that the surfaces of the samples with a higher content of metallic phase (Series II and III)

contained microcracks. This is probably due to the escape of liquid copper during the sintering process and poor wetting of the ceramic matrix by copper. Addition of molybdenum limits the escape of liquid copper during the sintering process but does not eliminate it completely. An increase in the content of the metallic phase in the casting slip used to produce the composites results in the formation of microcracks on the surface of the shapes. It has been established that in the case of Series II, about 2 to 3 wt pct of the metal flows from the sample after the sintering process. On the other hand, in the case of the sample from Series III, a loss of about 3 to 5 wt pct metallic phase was indicated. Previous work on the production of Al₂O₃-Cu-Ni composites by the centrifugal casting method showed that in samples containing 15 vol pct metallic phase about 1 pct of the mass of the metal flows out of the specimens after the sintering process.^[27] Therefore, it can be concluded that the addition of Mo in three-component composites with Al₂O₃ matrix is less effective in preventing the outflow of copper during sintering compared to three-component composites with Al₂O₃ matrix with the addition of Ni particles.

The presence of three zones in the microstructure is dictated by the choice of the manufacturing method. During centrifugal casting, initially the capillary forces drain the liquid from the slurry, which is in direct contact with the plaster mold. As a result of this force, the particles become distributed around the outer periphery, and the centrifugal force acting on them is not intense enough to change their position. Previously, studies on the formation of composites by the centrifugal casting method showed that depending on the type of gypsum mold used for the production of composites,

Fig. 11—SEM images of fractures of manufactured composites in the Al_2O_3 -Cu-Mo system *via* centrifugal slip casting: (a) Series I (5 vol pct metal phase), (b) Series II (10 vol pct metal phase), and (c) Series III (15 vol pct metal phase).

the width of Zone I could be controlled.^[38] The width of Zone I along the outer edge depends mainly on the time between pouring the slurry and starting the centrifugal and the porosity of the plaster mold. Zone II is the area where the concentration of the metallic phase is greatest in all composites. From Zone II toward the inner edge of the sample, the concentration of metal particles is reduced. In Zone III, the presence of mainly fine and individual larger particles was observed.

Based on EDX results, it can be concluded that the Mo particles make spreading the copper in the pores of the ceramic matrix difficult. Based on the observations, it was found that the higher the content of the metallic phase in the composites is, the more numerous and larger the areas of the phase in the form of ultrafine Mo particles. The presence of ultrafine, submicron-sized

molybdenum particles was probably caused by mechanical collisions between the particles in the suspension. The starting molybdenum powder was characterized by an elongation shape and branched structure (Figure 3). Perhaps the narrower branches of Mo particles broke off during the slurry preparation and/or rotation during the forming process, and the Mo particles were crushed and became established in the form of fine particles in the Al_2O_3 matrix.

Moreover, during the analysis of EDS maps, particular attention was paid to the location of ultrafine molybdenum particles. They mainly arranged around the copper particles. This phenomenon can be explained by considering the wettability of the components of the composite. Literature data indicate that molybdenum is much better wetted by copper than Al_2O_3 .^[46–49] Therefore, it is possible that metallic particles are more likely to adhere to each other than to the ceramic matrix. Consequently, the increased concentration of fine molybdenum particles in the area around the Cu particles could reduce the flow of liquid copper during sintering. To confirm this theory, more detailed research should be carried out in this regard in the future.

XRD result analysis confirmed that the sintering process did not affect the phase composition of the analyzed samples.

C. Physical Properties

The relative density of the obtained shapes decreased with the increase of the metallic phase in the casting slip used to obtain the composites. It is likely that this dependence results from poor wetting of the matrix by copper; therefore, the more metal particles there were in the cast slip, the lower the relative density of the end product was. A correlation between the content of the metallic phase in the composites and their volumetric shrinkage was observed. The volume shrinkage decreased with increasing content of the metallic phase in the composites.

D. Fractography

SEM images revealed that a plastically fractured metallic phase that indicated no cracking initiated in the metallic particles. Observation of Al_2O_3 fracture allowed us to conclude that the matrix surface is characterized by the brittle fracture mechanism. Results of fractography analysis revealed that the bonds between the alumina matrix and metallic phase are the areas of main crack initiation. This was observed for all investigated samples. Fractography results revealed the brittle character of cracking.

E. Serological Analysis

The obtained results exhibited no influence of the change in the metal content in the slurry on the shape of the Al_2O_3 grains in the composite after the sintering process. The results obtained indicate that the higher the content of metallic phase in the casting slip, the lower the growth of matrix grains in the sintered composite.

Fig. 12—SEM images of: (a) Series I (5 vol pct metal phase), (b) Series II (10 vol pct metal phase), (c) Series III: (15 vol pct metal phase), illustrating the differences in Al_2O_3 grain size depending on the content of metallic phase in composites.

This may mean that the addition of metallic phase limits Al_2O_3 grain growth during the sintering process of Al_2O_3 -Cu-Mo composites.

F. XRD

Al_2O_3 matrix ternary composites with two different metals in the metallic phase are a relatively new segment of the ceramic matrix composite materials. Therefore, there are a limited number of publications regarding these materials in the scientific literature.

The results of the phase composition analysis remain consistent in both the current and previous work of the research team on materials from the Al_2O_3 -Cu-Mo system. Despite the high-temperature manufacturing process with liquid phase participation, the results do not indicate any reactions between the components or the formation of a metastable solid solution in the samples after the sintering process.^[25,28]

Analysis of the phase equilibrium system shows that the Cu-Mo system is practically completely insoluble at ambient temperature. For temperatures in the range of

Fig. 13—Histograms illustrate the differences in Al_2O_3 grain size depending on the content of metallic phases in samples from the Al_2O_3 -Cu-Mo system.

1100 °C to 1500 °C, there are reports indicating that molybdenum is fully soluble in copper in amounts of 0.5 to 1.3 wt pct Mo.^[50–52]

The existence of Mo solubility in Cu supports the densification process during sintering for this type of material. This is particularly observed when Mo particles not exceeding 2 μm are used. In the literature, a positive result for increasing the range of Mo solubility in liquid copper is the use of a mechanical alloying process as a stage in the manufacturing procedure.^[53,54]

It should be considered, however, that most of the literature reports relate directly to Cu-Mo alloys. For the analyzed composites, the molybdenum content in the metallic phase was 53.4 wt pct, indicating that liquid copper and molybdenum are present in the material at the sintering temperature, according to the phase equilibrium system. However, it is worth noting that the fabricated composites are characterized by a gradient distribution of the metallic phase in the structure; hence, the ratio of molybdenum and copper contents to each other can change from zone to zone. Measurements of the phase composition were carried out for the entire

volume of the sample, which makes it impossible to specify diffractograms for each areas. Nevertheless, no shifts of peaks or presence of broadening that could indicate the occurrence of copper solid solutions with insoluble molybdenum was found in the XRD analysis results.^[55]

G. Mechanical Properties

Microhardness results show correlation between the volume of metal phase and the hardness of samples. Due to the metal phase's low hardness compared to the ceramic matrix, it is obvious that higher content of copper and molybdenum results in lower hardness of the whole samples. Even though the correlation of hardness and volume of the metal phase was observed, there was no dependence of hardness results and the presence of three zones in the microstructure. Hardness results indicated a significant difference between minimal and maximal values of hardness across the samples but with no correlation with the zones. The hardness reaches a maximum at 760 HV1 for Series I (5 vol pct metal phase) while the minimum hardness value was 175 HV1 for Series III (15 vol pct metal phase). Correlation between hardness and microstructure was observed in previous authors' research results. Previously published research on ceramic-metal gradient composites with single metal phase Al_2O_3 -Mo and Al_2O_3 -Cu indicated that Zone II, with the higher content of metallic phase, reaches the lowest hardness in composites: 364 HV1 for the Al_2O_3 -Mo system and 129 HV1 for the Al_2O_3 -Cu system.^[56] Maximum value reached for Al_2O_3 -Mo composites was 2075 HV1 and 2020 HV1 for Al_2O_3 -Cu. This means that in the composites with the single metal phase the decrease of the hardness was observed only in Zone II, while in composites with two metal phases, like Al_2O_3 -Cu-Mo, a lowering of the hardness was observed throughout the whole sample.

V. CONCLUSIONS

The innovation of the study is that it combines the two existing concepts of microstructure formation of composites and of formation by slip centrifugal casting and sintering with varying proportions of liquid phase. Combination of these methods gives ternary gradient composites. This study demonstrated the usefulness of the centrifugal slip casting method for producing Al_2O_3 -Cu-Mo shapes containing a metallic phase distribution gradient in the ceramic matrix. The gradient microstructure was formed by the simultaneous action of capillary centrifugal forces and sintering with varying proportions of liquid phase in the form of copper in the composite. The method made it possible to obtain a sleeve-shaped product. Investigations have shown that adding a third component in the form of molybdenum reduces the liquid copper flow onto the surface of the composites during the sintering process. Unfortunately, it does not eliminate it completely in the case of composites containing > 10 vol pct metallic phase in the total solid content. Observations of casting slip

Table III. Parameters Describing the Shape Factors of Alumina Grains in Al₂O₃-Cu-Mo Graded Composites

Series	Curvature of Grain Boundary	Elongation	Convexity
Series I (5 Vol Pct Metal Phase)	1.96 ± 0.42	1.42 ± 0.27	1.09 ± 0.04
Series II (10 Vol Pct Metal Phase)	1.71 ± 0.10	1.45 ± 0.27	1.11 ± 0.05
Series III (15 Vol Pct Metal Phase)	1.93 ± 0.42	1.39 ± 0.21	1.09 ± 0.04

(± SD).

Fig. 14—Diffractograms of composites of (a) before and (b) after the sintering process. **Fig. 15—**Hardness as a function of radial distance of samples.

stability showed that the suspensions used to form the composites did not tend to settle. Macroscopic and microscopic observations confirmed that a metallic phase distribution gradient in the ceramic matrix was obtained. It was found that the addition of molybdenum reduced the undesired process of liquid copper outflow during sintering; however, it did not eliminate it completely. Three zones in the microstructure were distinguished. Examination of the selected physical properties showed a relative density of 90.0 to 94.6 pct in the products obtained. The results showed that an increase in the content of the metallic phase in the casting slip used to make the composites resulted in a decrease in product density. It was also discovered that an addition of metallic phase > 10 vol pct impedes the densification of the shapes. The fractographic observations and quantitative image analysis showed that the increase in metallic phase content in the composites limits the growth of matrix grains during the sintering process.

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CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the works reported in this paper.

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