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COMPOSITES THEORY AND PRACTICE

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SURFACE LAYER STRUCTURE OF Al_2O_3-Ni GRADED COMPOSITES DEPENDING ON GYPSUM MOLD POROSITY

The paper presents the influence of gypsum mold porosity as one of the process parameters allowing change in the gradient microstructure of composites obtained by centrifugal slip casting (CSC). This method combines the effects of slip casting and centrifugation. Composites made by centrifugal slip casting have the shape of hollow cylinders. Three types of gypsum molds with different porosity were used in the experiment. Alumina matrix graded composites with nickel particles were investigated. Slurries with a 45 vol.% solid content were consolidated using centrifugation at 1700 rpm. The composite properties were characterized using X-ray diffraction and scanning electron microscopy. Selected physical properties of the sintered specimens were measured by the Archimedes method. Applying a reductive atmosphere (H_2/N_2) during sintering averted the formation of $NiAl_2O_4$. The research showed that the use of different gypsum molds has an influence on the microstructure of Al_2O_3-Ni composites. The presented results revealed that with an increase in gypsum mold porosity, the width of the zone with nickel particles in the composites increases. It was found that the maximum width of the zone with the metal particles was obtained by the composites produced using the gypsum mold with the highest porosity.

Keywords: **centrifugal slip casting, Al_2O_3-Ni, gypsum mold, microstructure**

BUDOWA WARSTWY WIERZCHNIEJ GRADIENTOWYCH KOMPOZYTÓW Al_2O_3-Ni W ZALEŻNOŚCI OD POROWATOŚCI FORM GIPSOWYCH

Przedstawiono wpływ porowatości formy gipsowej jako jeden z parametrów procesu umożliwiający zmianę mikrostruktury gradientowej kompozytów otrzymanych w wyniku odlewania odśrodkowego mas lejnych. Metoda ta łączy w sobie odlewanie mas lejnych z działaniem siły odśrodkowej. Kompozyty wytwarzane metodą odlewania odśrodkowego mas lejnych charakteryzują się cylindrycznym kształtem. W eksperymencie do wytworzenia kompozytów zastosowano trzy rodzaje form gipsowych, różniące się między sobą porowatością. Zostały zbadane kompozyty o osnowie Al_2O_3 z cząstkami Ni. Zawiesiny o zawartości 45% obj. fazy stałej zostały skonsolidowane w procesie odlewania odśrodkowego przy prędkości 1700 obrotów na minutę. Kompozyty scharakteryzowano za pomocą dyfrakcji rentgenowskiej oraz skaningowego mikroskopu elektronowego. Wybrane właściwości fizyczne spieków zostały wyznaczone za pomocą metody Archimedesa. Zastosowanie atmosfery redukującej (H_2/N_2) podczas procesu spiekania prowadzi do uniknięcia pojawienia się fazy $NiAl_2O_4$. Badania wykazały, że zastosowanie różnych form gipsowych ma wpływ na mikrostrukturę kompozytów Al_2O_3-Ni, a w szczególności na grubość warstwy wierzchniej. Przedstawione wyniki wskazują, że wraz ze wzrostem porowatości formy gipsowej zwiększa się szerokość strefy zawierającej cząstki niklu w kompozytach. Stwierdzono, że kompozyt charakteryzujący się maksymalną szerokość strefy zawierającej cząstki metalu wytworzono przy użyciu formy gipsowej o najwyższej porowatości.

Słowa kluczowe: **odlewanie odśrodkowe mas lejnych, Al_2O_3-Ni, forma gipsowa, mikrostruktura**

INTRODUCTION

Composites with a gradient distribution of phases are the subject of many studies due to the possibility of controlling the characteristics of this type of material depending on the content and distribution of a second phase [1, 2]. A material with a ceramic matrix with a gradient distribution of metal particles can be characterized by increased fracture toughness (in comparison to the matrix material) and variable hardness depending on the content of plastic phase [3, 4]. Composites of the ceramic-metal system with a gradient distribution of the metal phase have been produced by various methods such as tape casting [5] or magnetic assisted slip casting [6]. A new method - centrifugal slip casting (CSC) - was developed by the authors of the present manuscript. It is based on a combination of centrifugal force with classical slip casting using plaster molds [7]. Gypsum molds were selected because of their low cost, ease of forming and high availability. The CSC method allows the production of hollow cylinder samples with a gradient distribution of the metal phase. In the case of using this method for the alumina-nickel system, the authors obtained a composite with a variable distribution of nickel particles on the radius of the samples. The distribution of nickel particles is dependent on the properties of the slurries (viscosity, solid content) and rotation speed [8]. It was observed that the particle gradient is also affected by the kind of applied gypsum mold.

The present investigation was focused on the influence of the plaster mold on the microstructure of the Al_2O_3-Ni composite produced from a slurry with a 45 vol.% solid content. During the casting process molds made from three different types of gypsum were used. The resulting composites were characterized by X-ray diffraction and scanning electron microscopy.

MATERIALS AND METHODS

The present experiments were carried out with TM-DAR α-Al_2O_3 powder (Taimei Chemicals, Japan) of the average particle size D_{50} = 0.11 µm and density of 3.95 g/cm^3; Ni powder (Sigma Aldrich, Poland) with the average particle size D_{50} = 15 µm and density of 8.9 g/cm^3. The purity of the powders was 99.99%. The dispersants used in the ceramic slurries were diammonium hydrocitrate (puriss, POCh, Poland) and citric acid (≥ 99.5% Sigma-Aldrich). The ceramic suspensions were prepared in distilled water. The aqueous ceramic slurries contained 45 vol.% solid phase and 10 vol.% nickel particles (with respect to the total solid volume). At the beginning of the process, the dispersants were added to the water followed by addition of the alumina and nickel powders. Then the slurries were milled in a planetary ball mill at the rotation speed of 300 rpm for 60 minutes. The aqueous suspensions were afterwards poured into tubular gypsum molds. The three molds of varying porosity were used. Next the mold was centrifuged in the radial direction at the speed of 1700 rpm for 2 hours. After the centrifugation, the sample together with the gypsum mold was removed from the device and was dried in the vertical position in a dryer at 45°C for 24 hours. The dried sample could be easily removed from the gypsum mold due to the drying shrinkage. After that the samples were sintered at 1400°C in H_2/N_2 atmosphere. During the sintering, the heating and cooling rates were 5°C/min. This method allowed the authors to obtain composites in the shape of a hollow cylinder with a gradient concentration of the metal particles. The schematic diagram of the process to obtain composites by the centrifugal slip casting technique is shown in Figure 1.

This study was focused on the influence of the gypsum mold on the microstructure of the Al_2O_3-Ni composite fabricated from a slurry with a 45 vol.% solid content. In the experiment, three gypsum molds (STODENT) of different porosity were used. The gypsum molds were prepared in accordance with the manufacturer's recommendations. Certain selected physical properties of the gypsum mold were measured by the Archimedes method according to standard EN-623-2:1993. The results of the measurements of selected physical properties and the microstructure of gypsum are shown in Figure 2. The obtained selected physical properties reveal that the gypsum mold was characterized by different porosity and soaking. It was found that the gypsum molds had soaking in the range of 8.9÷16.58%, and open porosity in the range of 16.69÷29.55 % depending on the used gypsum.

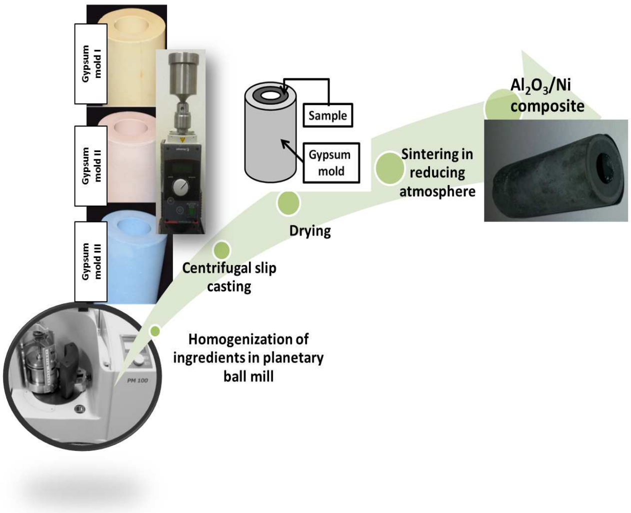

Fig. 1. Scheme of centrifugal slip casting process

Rys. 1. Schemat wytwarzania kompozytów metodą odlewania odśrodkowego mas lejnych

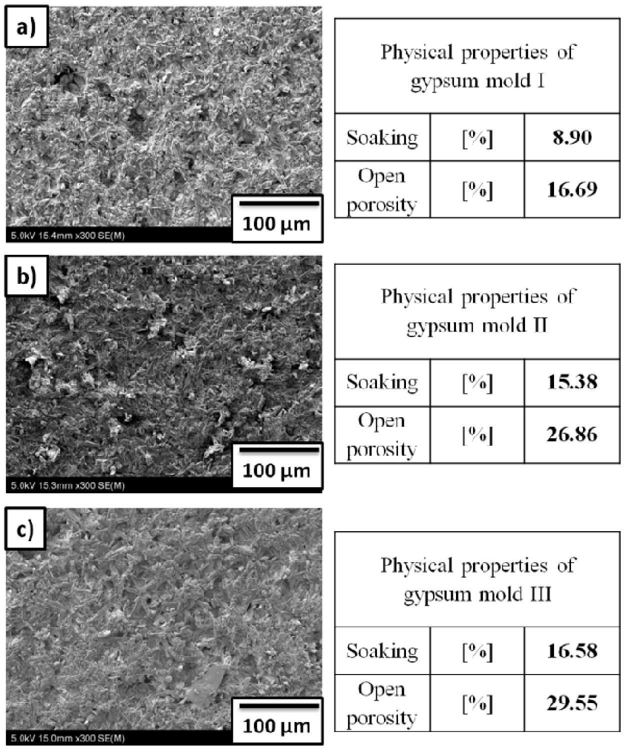

Fig. 2. Microstructure and physical properties of: a) gypsum mold I, b) gypsum mold II, c) gypsum mold III

Rys. 2. Mikrostruktura i właściwości fizyczne: a) formy gipsowej I, b) formy gipsowej II, c) formy gipsowej III

The X-ray diffraction measurements of the sintered composites were performed in a Rigaku MiniFlex II diffractometer with CuKα1.54 (λ = 1.54178 Å radiation). The results were obtained in the form of plots of the diffracted intensities as a function of 2θ on the surface of the samples.

The bulk density of the sintered specimens was measured by the Archimedes method in distilled water. The Archimedes method was conducted according to PN-76/6-06307. Measurements were made for 5 samples.

The microstructure of the sintered materials was observed on polished cross-sectioned surfaces by scanning electron microscopy using a HITACHI SU-70 microscope. The microstructure observations were performed using magnification 30x. Observations of the microstructure were carried out to characterize the area containing the metal particles. The average values of width of the metallic phase zones in each sample were calculated from measurements made on 5 images.

RESULTS AND DISCUSSION

The XRD patterns of the all the composites after sintering at 1400°C show that the composites consist of two phases: Al_2O_3 and Ni (Fig. 3). The reductive atmosphere (H_2/N_2) used during sintering averted formation of the $NiAl_2O_4$ spinel phase which frequently appears in such processes [9-11].

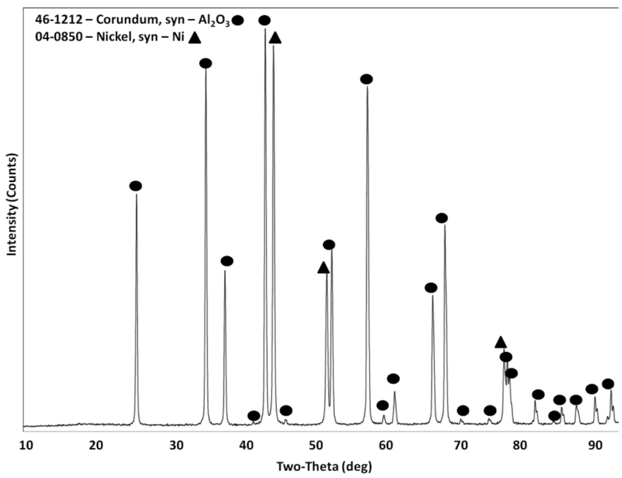

Fig. 3. X-ray diffraction pattern of Al_2O_3-Ni composite obtained using gypsum mold I

Rys. 3. Dyfraktogram uzyskany dla Al_2O_3-Ni kompozytu otrzymanego przy zastosowaniu formy gipsowej I

Selected physical properties of the sintered samples are presented in Table 1. The theoretical density was calculated according to the rule of mixtures. The following densities were used: 3.95 g/cm^3 for Al_2O_3 and 8.9 g/cm^3 for Ni. All the samples were characterized by similar values of bulk density (4.27÷4.33 g/cm^3), which is equal to more than 96% of the theoretical density. It can be noticed that the samples are characterized by an open porosity equal to 1%. Furthermore, Al_2O_3-Ni composites obtained with the use of different gypsum molds had soaking less than 0.28%. On the basis of the physical properties of the sintered samples, it was found that the use of the different gypsum molds to obtain the composites does not significantly influence the physical properties. The obtained values of the physical properties are close to each other and the difference between them is within the limits of standard deviation.

TABLE 1. **Selected properties of Al_2O_3/Ni composite material**
TABELA 1. **Wybrane właściwości kompozytu Al_2O_3/Ni**

Property	**Al_2O_3/Ni obtained using gypsum mold I**	**Al_2O_3/Ni obtained using gypsum mold II**	**Al_2O_3/Ni obtained using gypsum mold III**
Theoretical density [g/cm^3]	4.45	4.45	4.45
Bulk density [g/cm^3]	4.27 ±0.04	4.33 ±0.06	4.30 ±0.05
Relative density [%]	96.08 ±0.35	97.43 ±0.40	96.88 ±0.38
Soaking [%]	0.27 ±0.02	0.15 ±0.01	0.25 ±0.01
Open porosity [%]	1.16 ±0.03	0.65 ±0.02	1.08 ±0.01

± standard deviation

The microstructures of three functionally graded materials obtained using the various gypsum molds are show in Figure 4. The values of the width of the metallic phase zones in each the samples are presented in Table 2. In these micrographs the grey area is Al_2O_3 and the bright area is Ni. Observation of the graded hollow cylinders reveals that each composite obtained using the various gypsum molds have a zonal construction: three zones with different contents of Ni particles and one zone composed of alumina oxide. It was observed that with increasing soaking of the gypsum mold, the width of the first zones with a metallic phase increased in each sample. In the case of using a gypsum mold with the lowest porosity (equal to about 9%), it was found that the width of the first zone of the metallic phase constitutes 0.26 ±0.01 mm (Fig. 4a). In the case of a gypsum mold with a porosity of 16% to produce a composite, the width of the first zone in a composite containing a metallic phase was 0.33 ±0.02 mm (Fig. 4b). However, in the case of a sample obtained using a mold having a porosity of about 17%, the width of the outer zone containing metal particles constituted 0.46 ±0.02 mm (Fig. 4c). In addition, it was observed that the zone containing the maximum content of metallic phase in each case has the same width, regardless of the kind of gypsum mold used to manufacturing the sample. The width of the zone containing the maximum content of metallic phase is shown in Table 2. This observation confirmed that the change in the width of the metal zones in the composites can be controlled by the porosity of the gypsum molds.

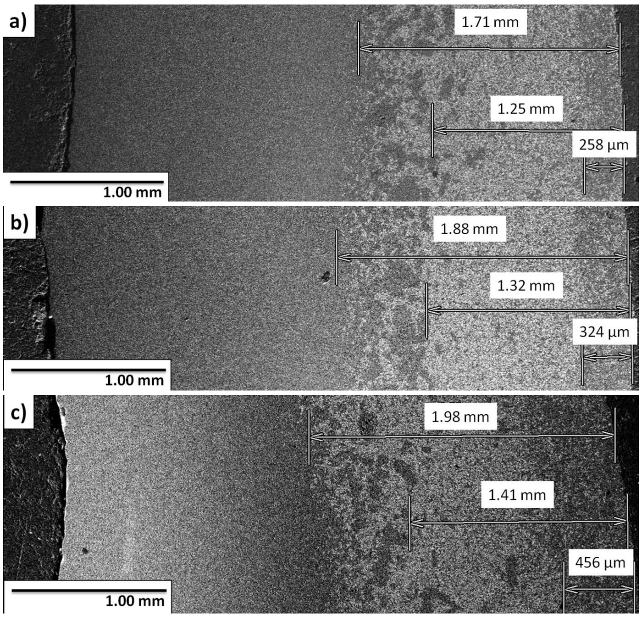

Fig. 5. SEM microphotographs of FGM samples produced using various molds: a) gypsum mold I, b) gypsum mold II, c) gypsum mold III

Rys. 5 Mikrofotografie SEM próbek otrzymane z użyciem różnych form gipsowych: a) formy gipsowej I, b) formy gipsowej II, c) formy gipsowej III

TABLE 2. **Width of metallic phase zones in each composite**

TABELA 2. **Szerokości stref zawierające fazę metaliczną w wytworzonych kompozytach**

Sample	Total width of zones containing metal particles	Width of central zone containing metal particles	Width of outer zone containing metal particles
	[mm]	[mm]	[mm]
Al_2O_3/Ni obtained used gypsum mold I	1.71 ±0.02	0.99 ±0.01	0.26 ±0.01
Al_2O_3/Ni obtained used gypsum mold II	1.88 ±0.02	0.99 ±0.02	0.33 ±0.02
Al_2O_3/Ni obtained used gypsum mold III	1.98 ±0.01	0.96 ±0.02	0.46 ±0.02

SUMMARY AND CONCLUSIONS

This investigation confirmed that the width of the surface layer in FGM composites can be controlled by the porosity of gypsum molds. The presented results revealed that with an increase in porosity of the gypsum mold, the width of the zone with the metal particles increases. The maximum width of the zone with the metal particles was obtained for the samples produced using the gypsum mold with the highest porosity.

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