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COMPOSITES THEORY AND PRACTICE

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FABRICATION OF Al_2O_3-Ni GRADED COMPOSITES BY CENTRIFUGAL CASTING IN AN ULTRACENTRIFUGE

The work explored the possibility of producing Al_2O_3-Ni gradient composites using non-absorbent molds in a high-speed centrifuge. As a result of the centrifugal force, the mass was compacted and the solvent was separated from the solid part. The influence of rotational speed and the change in the solid phase content in the slurry on the obtained microstructure of the composites was investigated. The produced composites were characterized on the basis of macroscopic observations of the obtained samples immediately after the casting process (green body) and after the sintering process. To determine the gradient of the metallic phase, the observations were made on cross sections of the samples. Densification of the sinters was determined by the Archimedes method. The obtained results showed that using an appropriate correlation of technological parameters, i.e. rotational speed and solid phase content in the slurry, enables the fabrication of Al_2O_3-Ni composites with a microstructure gradient by the centrifugal casting method using non-absorbent forms. It was found that with an increase in the solid phase content in the mass, a clear boundary is formed which separates the area containing only ceramic (Al_2O_3) and metallic (Ni) particles.

Keywords: ultracentrifuge, ceramic-metal composites, Functionally Graded Material (FGM), Al_2O_3-Ni

OTRZYMYWANIE KOMPOZYTÓW GRADIENTOWYCH Al_2O_3-Ni W WYNIKU ODLEWANIA ODŚRODKOWEGO W WIRÓWCE WYSOKOOBROTOWEJ

W ramach pracy zbadano możliwość wytwarzania kompozytów gradientowych Al_2O_3-Ni z zastosowaniem form nienasiąkliwych. W tym celu zastosowano wirówkę wysokoobrotową. W wyniku działania siły odśrodkowej nastąpiło zagęszczenie masy poprzez odseparowanie rozpuszczalnika od części stałej. Zbadano wpływ prędkości obrotowej oraz zmianę zawartości fazy stałej w masie lejnej na uzyskaną mikrostrukturę kompozytów. Wytworzone kompozyty scharakteryzowano na podstawie obserwacji makroskopowych uzyskanych próbek bezpośrednio po procesie odlewania, jak również po procesie spiekania. Przeprowadzono obserwacje wzdłuż przekroju poprzecznego próbek w celu określenia gradientu rozmieszczenia fazy metalicznej. Zagęszczenie spieków oceniono poprzez pomiar gęstości metodą Archimedesa. Uzyskane rezultaty pokazały, że zastosowanie odpowiedniej kombinacji parametrów technologicznych, tj. szybkości obrotowej oraz zawartości fazy stałej w masie lejnej, umożliwia wytworzenie metodą odlewania odśrodkowego, przy użyciu form nienasiąkliwych, kompozytów Al_2O_3-Ni z gradientem mikrostruktury. Stwierdzono, że wraz ze wzrostem zawartości fazy stałej w masie lejnej powstaje wyraźna granica rozdzielająca obszar zawierający cząstki ceramiczne (Al_2O_3) oraz metaliczne (Ni).

Słowa kluczowe: wirówka wysokoobrotowa, kompozyty ceramika metal, materiały z gradientem funkcjonalnym, Al_2O_3-Ni

INTRODUCTION

Rapid technical development, as well as ecological and economic aspects generate the demand for increasingly more advanced materials. Therefore, composite materials are becoming ever more popular and valued. The combination of components of different groups of materials gives the opportunity to create elements with unique properties. A special type of composites is materials with a gradient structure in which the physicochemical properties change smoothly along a specific direction [1, 2]. The production of such composites requires the development of new technological processes that would allow one to obtain a planned reinforcement distribution in the matrix. The challenge of material engineering is to determine the optimal microstructure of gradient materials for suitable applications and to develop technologies for the production of such complicated structures. Presently, various fabrication methods are applied to prepare composites [3, 4]. The current paper presents a method of obtaining gradient Al_2O_3-Ni composites by the centrifugal casting of composite slurries in an ultracentrifuge. Using centrifugal casting provides the opportunity to use various behaviours of ceramic and metallic slurry components due to the action of inertia forces. Higher density material particles move faster relative to lower density particles, which allows variable distribution of the components (structure gradient). The literature describes centrifugal casting processes using porous plaster forms (centrifugal slip casting CSC) [5-7]. In this case, the porous form absorbs the liquid from the slip which leads to mass consolidation and "fixation" of the sample structure. There are also studies of using slurries containing a polymerizing monomer during the process (gel--casting method) [8-14]. In this case, it is possible to use solid (non-absorbent) forms [2]. Other studies report on the production of ceramic materials using non-porous molds, however, they mostly concern monolithic ceramics [15-19]. The aim of the study is to determine the most beneficial conditions to form an Al_2O_3-Ni composite with a gradient arrangement of Ni particles using a high speed centrifuge - ultracentrifuge. Such devices allow powder compaction under the influence of centrifugal force. The work should show if it is possible to sufficiently and effectively thicken the powders (separate from the liquid) to avoid the necessity of using porous molds. The obtained results will allow the authors to determine the possibilities of controlling the gradient structure in the studied technological process. The influence of process parameters like a change in the solid phases in the slurry or rotation speed on the microstructure of composites with the gradient is widely recognized, though, still poorly understood. This is the reason why the process parameters such as the solid phase content in the composite slurry, and the rotational speed during centrifugation were changed during composite production. The scope of work included the production of test specimens, macroscopic observations, microscopic observations carried out using light microscopy, density measurement of the formed specimens as well as diffraction phase analysis.

MATERIALS AND METHODS

In the present study Al_2O_3-Ni composites were fabricated via centrifugal casting in a high-speed centrifuge. The composites were obtained from α-Al_2O_3 TM-DAR (Taimei Chemicals, Japan) with an average particle size of 0.16 μm, density 3.96 g/cm^3, purity 99.9%; Ni powder (Sigma Aldrich, Poland) with an average particle size > 50 μm, density 8.9 g/cm^3 and purity 99.9%. Diammonium hydrocitrate, DAC (puriss, POCh, Poland) and citrate acid, CA (puriss, POCh, Poland) were used as the dispersant. The suspensions were prepared in Milil-Q deionised water. The properties of the starting materials are shown in Table 1.

The samples were prepared according to the method shown in Figure 1. The dispersants were added to the water and then the alumina powder and nickel powder were added. The slurries were mixed and degassed in a planetary centrifugal mixer THINKY ARE-250. The aqueous suspensions were poured into a non-absorbable polypropylene mold with the dimensions φ 10.8 x 41.2 mm. Then the centrifugation process took place in an ultracentrifuge MPW-351RH. It is a laboratory centrifuge used for medical, biochemical and other analyses. This ultracentrifuge is used to separate mixtures, suspensions, and body fluids containing components of different densities under the influence of centrifugal force. In the study a hermetically sealed angle impeller (45°) was used in order to obtain a maximum rotational speed of 18000 rpm. Afterwards, the sample with the mold was dried in the vertical position in a vacuum chamber at 25°C for 24 hours. The sample, dried and shrunk, can be easily removed from the mold. Then, the samples were sintered at 1400°C in reducing atmosphere (H_2/N_2). The dwell time was 2 hours.

TABLE 1. **Properties of starting materials Al_2O_3 and Ni powder**

TABELA 1. **Właściwości wyjściowych materiałów: proszek Al_2O_3 i Ni**

Properties		Al_2O_3	Ni
Mean particle size from manufacturer data	[μm]	0.16	> 50
Mean particles size from SEM investigation	[μm]	0.11 ±0.03	33.80 ±14.13
Density	x 10^3 kg/m^3	3.96	8.9
Density from Pycnometer	x 10^3 kg/m^3	3.94	8.89
Melting point	[°C]	2050	1453

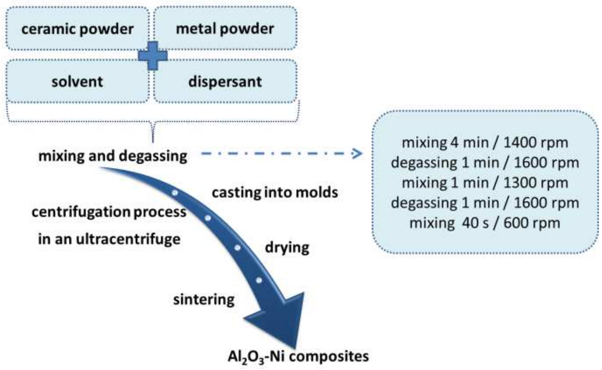

Fig. 1. Scheme of fabricating Al_2O_3-Ni composites

Rys. 1. Schemat wytwarzania kompozytów Al_2O_3-Ni

In accordance with the above assumptions, using an appropriate rotational speed during the centrifugal casting process in an ultracentrifuge should allow one to obtain the profiles shown in the diagram in Figure 2 (grey - Ni, white colour - Al_2O_3).

Two series of composites with different solid phases were obtained: Series I - contained 50 vol.% solid phase and Series II - contained 55 vol.% solid phase. Both series contained 10 vol.% nickel particles with respect to the total solid phases. The rotational speed in each series was also changed. An appropriately selected relation between the solid phase in the slurry (50 vol.% or 55 vol.%) and the rotation speed will most likely allow a composite to be obtained without using a plaster mold using an ultracentrifuge. Table 2 presents the parameters at which the samples were fabricated.

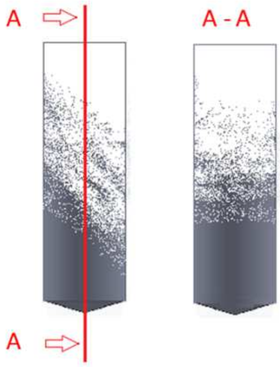

Fig. 2. Diagram of sample shapes obtained after centrifugal casting process via ultracentrifuge

Rys. 2. Schemat kształtki uzyskanej po procesie odlewania odśrodkowego w ultrawirówce

TABLE 2. **Process parameters used to obtain composites**

TABELA 2. **Parametry procesu używane do otrzymania kompozytów**

Rotation speed	Series I (50 vol.% solid phase)	Series II (55 vol.% solid phase)	Run time
1000 rpm	I-1	II-1	15 minutes
1500 rpm	I-2	II-2	
3000 rpm	I-3	II-3	
5000 rpm	I-4	II-4	
6000 rpm	I-5	II-5	
9000 rpm	I-6	II-6	
18000 rpm	I-7	II-7	

The selected physical properties of the sintered specimens were measured by the Archimedes method in water. Macroscopic and microscopic observation of the green and sintered bodies were used to characterize the microstructure of the obtained composites. Observation of sample cross sections was performed using the light microscope Nikon ECLIPSE LV150N and scanning electron microscope HITACHI S-3500N. XRD investigation was performed to determine the bulk crystalline phases of the composites. The XRD was conducted using a Rigaku MiniFlex II diffractometer with CuKα 1.54 ($\lambda = 1.54178$ Å). The results were obtained in the form of plots of the diffracted intensities as a function of 2θ.

RESULTS AND DISCUSSION

The results of macroscopic observations of the obtained samples immediately after the high speed centrifugal casting process are presented in Figure 3. Based on the macroscopic observations, it can be concluded that the applied process parameters allow the water to be separated from the other components of the slurry. Moreover also it was possible to obtain composites with a gradient of metal particle distribution.

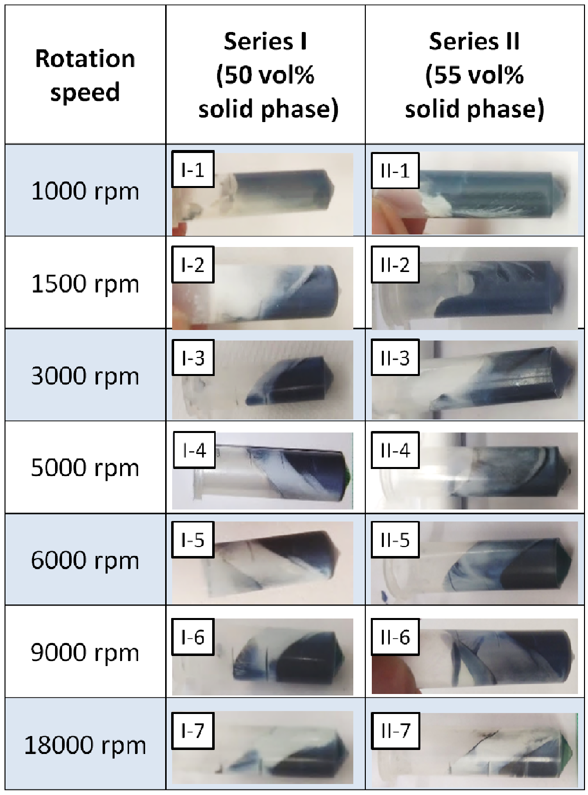

Fig. 3. Photographs of Series I and Series II samples after centrifugal casting process

Rys. 3. Zdjęcia próbek Serii I oraz Serii II po procesie odlewania odśrodkowego

It can be noticed based on macroscopic observation that using the rotation speed of 1000 rpm did not cause separation of water from the solid part of the slurry in the case of both slurries (Series I and Series II). In the case of Series I-1 and II-1, the distribution of nickel particles in the ceramic matrix is homogeneous. No apparent separation of the Al_2O_3 particles from the Ni particles was obtained. Applying the rotation speed of 1500 rpm enabled a greater degree of separation of both phases in the samples from Series I (I-2) than Series II (II-2) where this effect was not achieved. In both cases (I-2 and II-2) the solvent still remains in the sample volume, the suspension still has the properties of a viscous liquid. It was observed that after the casting process at 3000 rpm the gradient in the composites is clearly visible. It was found that a further increase in rotation speed did not cause any visible changes in the composites from Series I. On the other hand, in the case the Series II samples, it was observed that with an increase in the rotation speed the content of nickel particles in the outer part of the samples increases, which matched the direction of applied centrifugal force.

It was noticed that employing low rotational speeds did not allow effective separation of the solvent from the other components of the slurry. In contrast, using high rotational speeds creates an acute boundary between the zone containing the Ni particles and the zone with a higher content of Al_2O_3 particles.

The XRD patterns of all the composites after sintering at 1400°C show that the composites consist of two phases: Al_2O_3 and Ni. There is no reaction between the alumina and nickel. An example XRD diffraction obtained from the Al_2O_3-Ni composites (Series I-6) is shown in Figure 4.

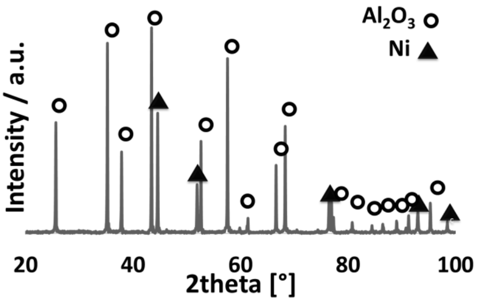

Fig. 4. XRD for Al_2O_3-Ni composites (Series I-6)

Rys. 4. XRD dla kompozytu Al_2O_3-Ni (Serie I-6)

Figure 5 shows photos of the obtained samples after sintering. In order to visualize the obtained results, a representative sample for each of the series was selected. The presence of defects on the surface of the samples from Series I-1 was observed. They are probably effects of the presence of water in the whole volume of the sample remaining after the centrifugation process. The appearance of visible grooves and holes in the surface of the samples presumably arose during the drying and sintering processes at the elevated temperature.

It was found that for higher velocities of 3000 rpm a visible gradient of the particle distribution was obtained.

It was also observed that the samples from Series II obtained at the rotation speed of 6000 rpm were cracked. The same situation was noticed for Series I but only at higher speeds of 18000 rpm. This effect occurred at the interface between the layers rich in Ni particles and Al_2O_3 particles. It can be assumed that at high rotation speeds there is permanent separation of the metallic particles from the ceramic particles. As a consequence, a sharp boundary between zones with different properties was formed, which results in cracking during the sintering process due to the large difference in the coefficients of thermal expansion of the components.

Selected physical properties of the composite materials are presented in Table 3. It was found that the obtained samples are characterized by a good relative density in Series I from 95.71 to 99.28%. Slightly lower values of relative density were obtained by Series II, which were characterized by a relative density from 86.94 to 99.28% depending on the employed rotation speed. The obtained values of open porosity and absorptivity may result from cracking of the samples and microcracking on the surface of the composites in which water accumulated during the Archimedes measurements.

It can therefore be concluded that centrifugal casting in an ultracentrifuge in non-absorbent molds allows high densification to be obtained as with other techniques like the centrifugal slip casting method where porous gypsum molds were used.

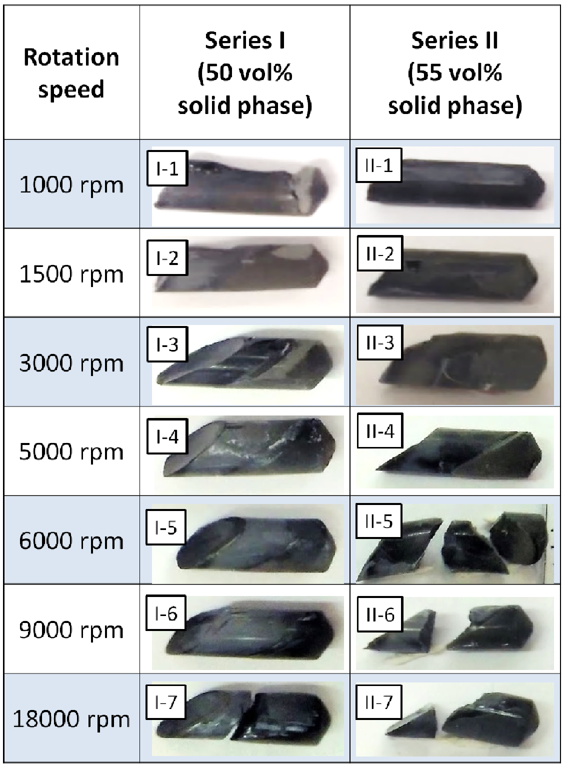

Fig. 5. Photographs of Series I and Series II samples after sintering

Rys. 5. Zdjęcia próbek Serii I oraz Serii II po procesie spiekania

TABLE 3. **Selected physical properties of composites after sintering process**

TABELA 3. **Wybrane właściwości fizyczne kompozytów po procesie spiekania**

Series		Rotation speed [rpm]	Physical properties		
			Relative density [%]	Open porosity [%]	Absorptivity [%]
Series I (50 vol.% of the solid phase)	I-1	1000	96.87	0.25	0.06
	I-2	1500	96.95	1.47	0.33
	I-3	3000	99.28	0.99	0.94
	I-4	5000	96.89	0.59	0.14
	I-5	6000	96.34	1.39	0.32
	I-6	9000	95.71	0.93	0.21
	I-7	18000	98.76	0.37	0.07
Series II (55 vol.% of the solid phase)	II-1	1000	96.89	0.40	0.09
	II-2	1500	94.97	2.01	0.49
	II-3	3000	99.28	0.58	0.32
	II-4	5000	98.41	0.53	0.11
	II-5	6000	95.92	0.15	0.03
	II-6	9000	92.80	0.93	0.32
	II-7	18000	86.94	2.76	0.93

Figure 6 presents examples of micrographs of the composites. Due to the strong differentiation of the microstructure along the length of the sample, it was decided that it is best represented by complex panoramic images which were taken at relatively low magnifications. Only selected microphotographs of the composites were published in this work. The light spots dispersed in the grey matrix (alumina) were identified as nickel particles. Microscopic observations carried out by means of light microscopy confirmed that an applied rotation speed higher than 1000 rpm allows composites with a clear boundary between the metallic and ceramic phases in fabricated materials to be obtained. It was observed that in the case of the samples from Series II (55 vol.%) the zone containing the metallic phase is wider than the same zone in Series I (50 vol.%) for composites obtained at rotation speeds of 3000 rpm or higher rotational speeds. However, observation of the microstructure revealed the presence of small microcracks (black lines) in part of the volume of the ceramic phases in the case of Series I-4 and Series II-4. The microcracks were created during the preparation of composite cross sections as a result cutting with a diamond saw.

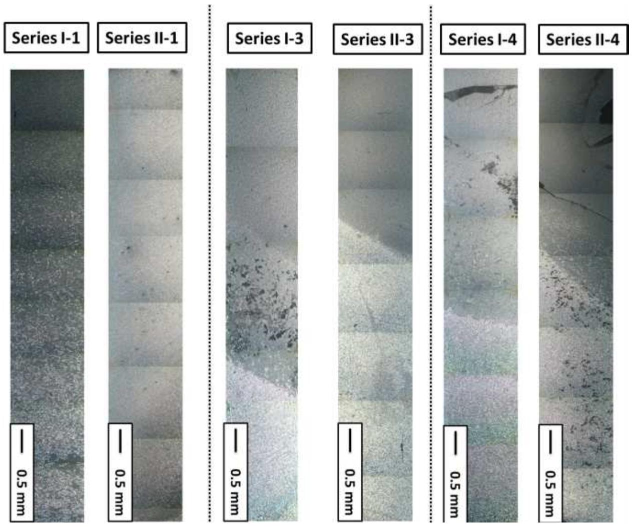

Fig. 6. Examples microstructure of cross sections of obtained composites

Rys. 6. Przykładowa mikrostruktura przekrojów poprzecznych wytworzonych kompozytów

In order to confirm the presence of a microstructure gradient in composites obtained by implementing a rotation speed of 3000 rpm or higher, SEM observations were carried out. The microstructure of the sintered materials is presented in Figure 7. The results of the SEM observation of the microstructure for Series I-3 and II-3 revealed that the fabricated samples are characterized by a gradient distribution of the metallic phase throughout the cross section of the composites.

It has been proved that it is possible to obtain consistent and well densified Al_2O_3-Ni composites with a gradient concentration by high speed centrifugal casting using non-absorbent molds. The aim of the work has been achieved. It has been observed that the microstructure of the composites changed with an increase in the rotational speed. It has been found that employing a rotational speed higher than 1000 rpm, results in a more visible gradient between the phases. It is possible that at this stage of the study, not all the factors affecting the structure of the material were controlled. There is also the possibility of accidental errors. To explain these differences, more research would need to be conducted. The research team plans to carry out other studies involving this type of composites in the future.

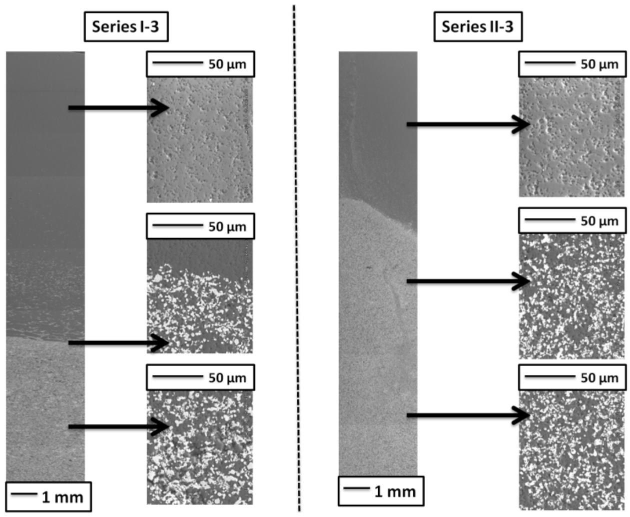

Fig. 7. SEM micrographs of Al_2O_3-Ni composites (Series I-3, Series II-3)

Rys. 7. Zdjęcia SEM dla kompozytów Al_2O_3-Ni (Seria I-3, Seria II-3)

CONCLUSIONS

Based on the conducted research, the following conclusions were formulated:

1. Centrifugal casting of slurries containing Al_2O_3 and Ni powders in a non-absorbent mold via high-speed centrifugation allows one to obtain materials characterized by good densification.
2. In the gradient composites obtained by centrifugal casting in a non-absorbent mold, we can distinguish three zones with different distribution of the Ni particles:
   a) a zone containing only the matrix material (Al_2O_3),
   b) a zone with a decreasing proportion of Ni particles,
   c) a zone with a higher Ni content.
3. It was found that with an increase in the rotational speed, the zone with the variable distribution of Ni particles (gradient) is narrowed.
4. It was also found that together with increasing the proportion of solid phase in the slurry, the range of the gradient zone decreases. Moreover, it was noticed that the gradient zone disappears at lower rotational speeds.

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