Microstructural graded hollow cylinders were processed and characterized using the developed method called centrifugal slip casting (CSC). Water based slurries containing alumina and nickel powders were tested in this work. Two series were produced by the CSC technique at mould rotational speeds of 1000 rpm. The samples were prepared with a solid content of 50 vol.% with 10 and 20 vol.% nickel particles with respect to the total solid volume, respectively. The microstructure along the radial direction of a cross-sectional sample was presented. No new phases were observed after sintering. Microstructural observation and EDS analysis showed two zones with various concentrations of Ni particles in both series along the radial direction of the cylinders.

Keywords: composites Al₂O₃-Ni, centrifugal slip casting technique, microstructure
10 and 20 vol.% the metallic phase, respectively. Furthermore, ceramic and metallic powders of significantly different sizes were applied.

MATERIALS AND METHODS

CSC is a method that combines traditional slip casting with centrifugal casting. The advantage of the connected operation of the two processes - centrifugation casting and slip casting, is that the fluid removal process and particle orientation may occur at the same time [14, 25, 26]. Figure 1 shows the schematic diagram of centrifugal slip casting equipment for the functionally gradient composites used in our study.

![Diagram of CSC equipment for fabricating Al$_2$O$_3$/Ni composites](image)

Fig. 1. Diagram of CSC equipment for fabricating Al$_2$O$_3$/Ni composites

A commercially available α-Al$_2$O$_3$ powder (TM-DAR, Taimei Chemicals) of an average particle size of 133 nm and density of 3.96 g/cm$^3$, and Ni powder (Alfa Aesar) of an average particle size of 27 µm and density of 8.9 g/cm$^3$ were used as the starting materials. Particle size measurements were conducted by a Laser Particle Size Analyzer LA-960. The Al$_2$O$_3$ and Ni are highly pure powders (99.99%). In Figure 2, SEM micrographs of the starting powders are shown. The microstructure of the starting powders reveal that they have the tendency to agglomerate. Citric acid (≥ 99.5% Sigma-Aldrich) and diammonium hydrocitrate (puriss, POCh) were used as the dispersant in the composite slurries. Ceramic aqueous slurries were prepared with a solid content of 50 with 10 vol.% (Series I) or 20 vol.% (Series II) nickel particles with respect to the total solid volume. The sedimentation characteristics of the prepared suspensions were monitored in 20 ml tubes and the settling height in time was recorded up to 48 h. The scheme of the composite preparation process is shown in Fig. 3. The samples after sintering were 40 mm in length and the outer diameter was 20 mm with a wall thickness of ~16.5 mm. Figure 4 shows the schematic diagram of typical samples obtained by centrifugal slip casting.

![Scheme of Al$_2$O$_3$-Ni composite fabrication](image)

Fig. 3. Scheme of Al$_2$O$_3$-Ni composite fabrication

Rys. 1. Schemat urządzenia CSC do wytwarzania kompozytów Al$_2$O$_3$/Ni

Rys. 2. Morfologia proszków wyjściowych: a) niklu, b) tlenku glinu
The phase composition of the sintered samples was examined by X-ray diffraction. XRD analyses were conducted on composite cross-sections with a Rigaku MiniFlex II diffractometer using CuKα radiation (1.54178 Å), in the range 10° to 100° 2θ, with a step size of 1° 2θ and an acquisition time per step of 1 min.

The microstructure of the sample cross-sections after sintering was examined by SEM (HITACHI SU-70). The chemical compositions in microareas from the cross-sections were determined by EDS (HITACHI S-3500N).

RESULTS AND DISCUSSION

Sedimentation experiments were carried out to assess the effect of metal addition on the stability and settling of particles in the slurry. The results are presented in Figure 5.

For single spherical particles in a liquid, the sedimentation rate can be calculated using Stokes’ law. In the case of an Al2O3-Ni system, the density of alumina is much less than the density of nickel. As a result, Ni would likely segregate from the Al2O3 powder due to differential sedimentation rates driven by the difference in density. However, for slurries with a high solid content, the motion of the particles is hindered by interaction between the particles in the liquid medium. In our research, we are not dealing with the movement of individual particles but their agglomerates. For both slips, moving the metallic particles is accompanied by movement of ceramic particles. For that reason, after 48 hours the slurry with 10 vol.% Ni (Fig. 5a) is divided into two parts: composite (dark) and alumina (light). When increasing the amount of nickel in the slurry to 20 vol.%, sedimentation did not occur. Presumably, the entire ceramic phase has been linked to the nickel particle. In the slurry with the higher vol.% of Ni, the distance between the agglomerates was smaller, and the particles were intensively blocked by each other thus preventing their movement. The use of centrifugal force can significantly speed up the process of producing composites with gradients.

The XRD analysis of the Series I and Series II samples after sintering showed the presence of Ni and Al2O3 as the only crystalline phases. The presence of an alumina nickel spinel phase (NiAl2O4), sometimes observed in such materials [27], was not detected in our investigations. The application of a reductive atmosphere (H2/N2) during sintering prevented the formation of NiAl2O4.

Typical SEM microphotographs of FGM samples for Series I and Series II are shown in Figure 6. The light spots dispersed in the grey matrix were identified as Ni particles. In each series both zones were observed, with different metal particle contents. It can be clearly seen that zone A is composed almost entirely of alumina. The whole volume of the Ni particles was situated in the second as a result of the centrifugal process. It was found that the distribution of nickel particles in zone B in Series II was more homogeneous than in Series I. Furthermore, the width of the zones were different in both series. In the case of Series I, the width of zone A was 0.44 mm, while the width of zone B was 2.75 mm and Series II demonstrated a 0.14 mm width of zone A while zone B was 3.40 mm, respectively. No sedimentation of Ni particles in the slurry was probably responsible for the more homogeneous distribution of them and the narrower width of zone A. The use of centrifugal force during the casting of slurries with different amounts of nickel caused a similar movement of particles to that during gravitational sedimentation. The applied centrifugation speed was too low to increase the velocity of the particles in the suspension and prevented achieving a more pronounced gradient.

Furthermore, by using the EDS technique, successful property gradation was confirmed. The research consists in finding the chemical composition in several (four) regions along the grading direction. The areas used for making the EDS measurement are shown in Figure 7. As illustrated by Table 1, the chemical composition gradual changes from alumina with oxygen to nickel in each series. The lower nickel content in area 1 is due to the capillary force of the mold and deposition of a casting slip on the wall of mold before the process started.
Fig. 6. SEM micrograph of composite microstructures: a) Al$_2$O$_3$-Ni with 10 vol.% metallic phase, b) Al$_2$O$_3$-Ni with 20 vol.% metallic phase
Rys. 6. Zdjęcia SEM mikrostruktur kompozytów: a) Al$_2$O$_3$-Ni z 10% obj. zawartością fazy metalicznej, b) Al$_2$O$_3$-Ni z 20% obj. zawartością fazy metalicznej

Fig. 7. EDS for samples: a) Al$_2$O$_3$-Ni with 10 vol.% metallic phase b) Al$_2$O$_3$-Ni with 20 vol.% metallic phase
Rys. 7. Analiza EDS składu chemicznego próbek: a) Al$_2$O$_3$-Ni z 10% obj. zawartością fazy metalicznej b) Al$_2$O$_3$-Ni z 20% obj. zawartością fazy metalicznej

TABLE 1. Weight, atomic and volume [%] content of samples from different areas
TABELA 1. Zawartość masowa, atomowa i objętościowa [%] próbek w różnych obszarach

<table>
<thead>
<tr>
<th>Al$_2$O$_3$-Ni composites</th>
<th>Weight %</th>
<th>Atom %</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight</td>
<td>Atom</td>
<td>Volume</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>Al</td>
<td>Ni</td>
</tr>
<tr>
<td><strong>Series I with 10 vol.% Ni (Fig. 6a)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>area 1</td>
<td>26.61 ±0.87</td>
<td>52.60 ±0.77</td>
<td>20.79 ±2.86</td>
</tr>
<tr>
<td>area 2</td>
<td>25.22 ±0.76</td>
<td>50.47 ±0.70</td>
<td>24.31 ±2.67</td>
</tr>
<tr>
<td>area 3</td>
<td>23.67 ±0.73</td>
<td>50.07 ±0.67</td>
<td>26.26 ±2.53</td>
</tr>
<tr>
<td>area 4</td>
<td>36.63 ±0.98</td>
<td>63.37 ±0.80</td>
<td>0.00 ±0.00</td>
</tr>
<tr>
<td><strong>Series II with 20 vol.% Ni (Fig. 6b)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>area 1</td>
<td>18.67 ±0.76</td>
<td>45.99 ±0.73</td>
<td>35.34 ±3.07</td>
</tr>
<tr>
<td>area 2</td>
<td>18.62 ±0.69</td>
<td>41.93 ±0.65</td>
<td>39.46 ±3.14</td>
</tr>
<tr>
<td>area 3</td>
<td>18.56 ±0.66</td>
<td>42.22 ±0.62</td>
<td>39.22 ±2.95</td>
</tr>
<tr>
<td>area 4</td>
<td>34.59 ±0.99</td>
<td>62.77 ±0.83</td>
<td>2.64 ±0.95</td>
</tr>
</tbody>
</table>
SUMMARY AND CONCLUSIONS

$\text{Al}_2\text{O}_3$-$\text{Ni}$ graded hollow cylinders were effectively fabricated by the centrifugal slip casting technique. No additional phases were present when sintering was carried out in reducing atmosphere. SEM micrographs showed that there was a uniform gradient of Ni from the $\text{Al}_2\text{O}_3$ rich region in an outwards direction. In both series both zones were observed. The width of the zones and distribution of Ni particles inside the zone depend on the vol.% content of metal particles in the slurry. The higher content of Ni particles in the slurry resulted in no sedimentation which gave the narrow width of zone A where $\text{Al}_2\text{O}_3$ with a 2.64 wt.% of Ni was found. Moreover, in this case zone B was characterized by a more homogeneous distribution of Ni particles. For Series I where the Ni particles sedimented in the slurry and the region, only $\text{Al}_2\text{O}_3$ was distinguished in the composite and zone A with 100 wt.% alumina was obtained. All the Ni particles were distributed inside zone B.

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