PREPARATION OF $\text{Si}_3\text{N}_4$-TiN CERAMIC COMPOSITES

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1 INTRODUCTION

Recently, much attention has been devoted to the production of particulate-reinforced silicon nitride and SiAlON materials, not only because of their improved fracture toughness, strength and mechanical reliability, but also because of their potential multi-functionality, especially their electrical conductivity, which can be obtained with incorporation of electrically conductive particles into the matrix phase1. The most commonly used electroconductive particles are WC, MoSi$_2$, TiN, TiC, TiCN, TiB$_2$ and ZrN$_2$. Electro-conductive composites are prepared with reaction sintering of Si$_3$N$_4$/TiO$_2$ powder mixtures using Y$_2$O$_3$, Al$_2$O$_3$ and, in case of SiAlON, also AlN as sintering additives. The results of X-ray diffraction investigation confirmed that TiN was formed during sintering in a nitrogen atmosphere with chemical reaction of Si$_3$N$_4$ and TiO$_2$. A comparison of the materials sintered with addition of TiO$_2$ in the starting-powder mixture with the phase-matrix phase ceramics (Si$_3$N$_4$ or SiAlON) showed that materials with addition of TiO$_2$ have higher densities and better flexural strength. The electrical conductivity of the sintered composites with addition of TiO$_2$ in the starting powder mixture were also investigated. Their electrical conductivity was found to be highly dependent on the amount of added titania and on the sintering conditions.

Key words: Si$_3$N$_4$, TiN, electrically conductive ceramics, ceramic heater

In this work we report on the preparation of particulate ceramic composites based on a Si$_3$N$_4$ or SiAlON matrix phase. The composites were prepared with reaction sintering of Si$_3$N$_4$/TiO$_2$ powder mixtures using Y$_2$O$_3$, Al$_2$O$_3$ and, in case of SiAlON, also AlN as sintering additives. The results of X-ray diffraction investigation confirmed that TiN was formed during sintering in a nitrogen atmosphere with chemical reaction of Si$_3$N$_4$ and TiO$_2$. A comparison of the materials sintered with addition of TiO$_2$ in the starting-powder mixture with the matrix-phase ceramics (Si$_3$N$_4$ or SiAlON) showed that materials with addition of TiO$_2$ have higher densities and better flexural strength. The electrical conductivity of the sintered composites with addition of TiO$_2$ in the starting powder mixture were also investigated. Their electrical conductivity was found to be highly dependent on the amount of added titania and on the sintering conditions.

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V delu poročamo o pripravi delčnih keramičnih kompozitov na osnovi matrične faze iz silicijevega nitrida ali SiAlON-a. Kompozite smo pripravili z reakcijskim sintranjem mešanice prahov Si$_3$N$_4$ in TiO$_2$, kot dodatke za sintranje pa smo uporabili Y$_2$O$_3$ in Al$_2$O$_3$, v primeru SiAlON-ov pa še AlN. Rezultati rentgenske difrakcije so potrdili, da med sintranjem v dušikovi atmosferi pri reakciji TiO$_2$ s Si$_3$N$_4$ nastane TiN. Ko smo primerjali kompozite, pripravljene z dodatkom TiO$_2$ v začetni mešanici z materiali matrične faze (sintrani Si$_3$N$_4$ ali SiAlON), smo ugotovili, da dosežemo višjo gostoto in boljše upogibne trdnosti pri materialu z dodanim TiO$_2$. Raziskali smo tudi električno prevodnost kompozitov z dodanim TiO$_2$ v začetni mešanici in ugotovili, da je njihova električna prevodnost odvisna od dodane količine TiO$_2$ in od pogojev sintranja.

Ključne besede: Si$_3$N$_4$, TiN, električno prevodna keramika, keramični grelec
\((\alpha + \beta) - \text{Si}_3\text{N}_4\) = 0.8, \(\text{Al}_2\text{O}_3\) (Alcoa, USA, \(d_{50} = 0.5 \, \mu m\); \(\text{BET} = 3–7 \, \text{m}^2/\text{g}\)), \(\text{Y}_2\text{O}_3\) grade fine (H. C. Starck, DE, \(d_{50} = 0.9 \, \mu m\); \(\text{BET} = 10.0–16.0 \, \text{m}^2/\text{g}\)), \(\text{AIN}\) grade C (H. C. Starck, DE, \(d_{50} = 1.2 \, \mu m\); \(\text{BET} = 4.1 \, \text{m}^2/\text{g}\)) and \(\text{TiO}_2\) RC8 (Cinkarna Celje, SLO, rutile, \(d_{50} = 0.35 \, \mu m\); \(\text{BET} = 6.5–8.5 \, \text{m}^2/\text{g}\)). The nominal compositions for the preparation of \(\text{Si}_3\text{N}_4\) and \(\text{SiAlON}\) with and without the addition of \(\text{TiO}_2\) are listed in **Table 1**. The powders were mixed with \(\text{Si}_3\text{N}_4\) ball milling in a planetary mill for 2 h in isopropanol. After evaporation of isopropanol using a rotating evaporator, the dry powder mixture was cold pressed at 100 MPa into bars with dimensions of 3 mm \(\times\) 5 mm \(\times\) 42 mm and subsequently cold isostatically pressed at 790 MPa. The pressed samples were then sintered at 1800 °C for 2 h in nitrogen atmosphere. The sintered samples were examined using X-ray powder diffraction (D4 Endeavor, Bruker-AXS, Germany) and a scanning electron microscope (SEM, Jeol–5800, Japan). The density of the sintered samples were determined using Archimedes’ method. The flexural strength was measured on an Instron–1362 testing machine (Instron, USA), using the four-point bending method with a lower-span length of 20 mm and an upper-span length of 10 mm, and a crosshead speed of 1 mm/min. The bodies for the strength tests had the following dimensions: 2.3 mm \(\times\) 3.9 mm \(\times\) 38.5 mm. The electrical resistivity of the sintered specimens with dimensions of 2.3 mm \(\times\) 3.9 mm \(\times\) 19.2 mm was measured on a Multimeter 3457A testing machine (HP, USA) using four-probe measurements at room temperature (25 °C) with a direct current.

**Table 1**: Compositions of the starting powder mixtures (mass fractions, \(w/\%\))

<table>
<thead>
<tr>
<th>Compositions</th>
<th>(\text{Si}_3\text{N}_4)</th>
<th>(\text{Y}_2\text{O}_3)</th>
<th>(\text{Al}_2\text{O}_3)</th>
<th>(\text{AIN})</th>
<th>(\text{TiO}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN</td>
<td>92</td>
<td>5</td>
<td>3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SN/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>82.8</td>
<td>4.5</td>
<td>2.7</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>SiAlON</td>
<td>83.9</td>
<td>2.2</td>
<td>5.5</td>
<td>8.4</td>
<td>0</td>
</tr>
<tr>
<td>SiAlON/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>75.5</td>
<td>2</td>
<td>4.9</td>
<td>7.6</td>
<td>10</td>
</tr>
</tbody>
</table>

**3 RESULTS AND DISCUSSION**

3.1 Ceramic materials based on \(\text{Si}_3\text{N}_4\)

The X-ray diffraction pattern of \(\text{Si}_3\text{N}_4\) with and without the addition of \(\text{TiO}_2\) in the starting mixture (denoted as SN and SN/TiO<sub>2</sub>) after sintering at 1800 °C for 2 h in flowing \(\text{N}_2\) is shown in **Figure 1**. In both samples we could observe the presence of the \(\beta\)-\(\text{Si}_3\text{N}_4\) and YAG (Yttrium Aluminium Garnet) phases, while in the sample SN/TiO<sub>2</sub> we also observed TiN. The peaks of TiO<sub>2</sub> could not be detected, and it could be concluded that the transformation of TiO<sub>2</sub> into TiN was completed. During the sintering of such composites the following chemical reactions take place:\(^{14,15,16}\)

\[
6\text{TiO}_2 + 4\text{Si}_3\text{N}_4 \rightarrow 6\text{TiN} + 12\text{SiO} (g) + 5\text{N}_2 (g) \quad (1)
\]

\[
6\text{TiO}_2 + 2\text{Si}_3\text{N}_4 \rightarrow 6\text{TiN} + 6\text{SiO}_2 + \text{N}_2 (g) \quad (2)
\]

The \(\text{TiO}_2\) and \(\text{Si}_3\text{N}_4\) react in the temperature range from 1150 °C to 1350 °C (equations 1 and 2) in a nitrogen atmosphere. In both reactions gaseous species are formed, which can influence the density of the final...
The microstructures of the SN and SN/TiO₂ composites are presented in Figure 2. In both SEM images (Figure 2a and 2b) we can see elongated β-Si₃N₄ grains (dark region), a brighter transient liquid phase based on Y₂O₃ and Al₂O₃, and some black pores. The material with the addition of TiO₂ in the starting–powder mixture (Figure 2b) also indicates white TiN particles with size around 0.5–1.0 µm. The bright TiN particles were analyzed with EDXS, and the results confirm the presence of Ti and N.

Figure 3 shows the fracture surfaces of sintered SN and SN/TiO₂ samples. As shown in Figure 3a, the matrix β-Si₃N₄ grains are surrounded by the secondary bright phase, while in Figure 3b, the white TiN particles are located in between the β-Si₃N₄ grains. From the SEM micrographs we can conclude that these materials have intergranular fracture, which is characteristic for this kind of ceramic¹⁷,¹⁸.

The materials SN and SN/TiO₂ (Table 2) exhibited around 90% relative density, and suitable flexural strengths. However, due to the cheaper submicron silicon nitride powder and the pressureless sintering process the relative density of materials could not be higher than 97%. Sample SN/TiO₂ had a higher flexural strength due to the presence of TiO₂ in the starting–powder mixture, which contributed to the larger amount of transient liquid phase. The electrical conductivity of this composite was relatively low, because it had the mass fraction only 10% of conductive phase, which is not enough to exceed the percolation threshold for particles of this size.

Table 2: Comparison of a relative density, a flexural strength and a electrical conductivity of sintered Si₃N₄ samples

<table>
<thead>
<tr>
<th>Material</th>
<th>ρrel./%</th>
<th>σf/MPa</th>
<th>σd/(Ω m)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SN</td>
<td>89.8</td>
<td>380</td>
<td>ND*</td>
</tr>
<tr>
<td>SN/TiO₂</td>
<td>90.0</td>
<td>410</td>
<td>7.1 · 10⁻⁸</td>
</tr>
</tbody>
</table>

* ND … the measured electrical resistivity is higher from the range of measurement / izmerjena električna upornost je večja od območja merljivosti

3.2 Ceramic materials based on a SiAlON matrix phase

For the formation of the SiAlON matrix the Si₃N₄ powder with the addition of sintering additives such as AlN, yttria and alumina was chosen (Table 1), together with and without the addition of TiO₂ in the starting–powder mixture. The phase analysis was conducted on the sintered specimens with and without the addition of the mass fraction of 10% of TiO₂ in the starting–powder mixture (denoted as SiAlON and SiAlON/TiO₂) using XRD analysis. The results of the XRD analysis, presented in Figure 4, revealed that in the case of sample without TiO₂ we could observe β-SiAlON and some signals from Y₂O₃, whereas in the SiAlON/TiO₂ material again β-SiAlON was formed together with TiN, implying that complete transfor-
formation of TiO₂ occurred during the sintering process, in accordance with the following chemical reactions₁₆,₁₉–₂₁:

\[
\begin{align*}
2\text{TiO}_2 + 3\text{AlN} + 5\text{Si}_3\text{N}_4 & \rightarrow 3\text{Si}_5\text{AlON}_7 + 2\text{TiN} + 12\text{O}_2 (\text{g}) \\
2\text{TiO}_2 + 2\text{AlN} & \rightarrow 2\text{TiN} + \text{Al}_2\text{O}_3 + 12\text{O}_2 (\text{g})
\end{align*}
\]

From equation 3 it is clear that TiO₂ reacts together with AlN and Si₃N₄ to form Si₅AlON₇, TiN and O₂. The second chemical reaction (equation 4) leads to the formation of TiN, O₂ and Al₂O₃. The formation of Al₂O₃ contributes to a larger amount of transient liquid phase and therefore could increase the densification of the material.

The microstructures of the sintered SiAlON and SiAlON/TiO₂ ceramics (Figure 5) contained as bright intergranular phase in a darker Si₅AlON matrix. In the SiAlON/TiO₂ ceramic, additional submicron (white) TiN particles with size around 0.8–1.2 µm are homogenously distributed around the elongated β-SiAlON grains. The presence of TiN was also confirmed by EDXS analysis, where signals of Ti and N were observed.

The fracture surfaces of these materials (Figure 6) show dark β-SiAlON grains, a brighter transient liquid phase and uniform white TiN particles.

The sintered SiAlON with and without the addition of TiO₂ in the starting–powder mixture reached a higher relative density, flexural strength and comparable electrical conductivity (Table 3) compared to the SN and SN/TiO₂ samples. The SiAlON/TiO₂ material had a
higher density compared to the SiAlON and consequently the flexural strength was higher by about 33%. The electrical conductivity of this composite is relatively low, and is in the same range as the conductivity of the SN/TiO₂ material. This could be explained by the grain growth of the TiN particles during sintering.

4 CONCLUSIONS

The results show that by sintering in nitrogen at atmospheric pressure we were able to sinter Si₃N₄ and SiAlON ceramic materials, with and without the addition of TiO₂ in the starting–powder mixture, to a relatively high density and with suitable mechanical properties. The SN and SN/TiO₂ materials exhibited 90% of relative density, while the SiAlON material reached 96% of relative density and consequently a higher flexural strength. The addition of AIN enhanced the densification of SiAlON under the same sintering conditions compared to the Si₃N₄. The composites with the addition of TiO₂ had a higher flexural strength, due to the larger amount of transient liquid phase. The SN/TiO₂ and SiAlON/TiO₂ composites were electrically conductive. However, their electrical conductivity is somewhat low and is not high enough to fulfill the requirements for the production of ceramic heaters. The reason for this is the amount of secondary conductive phase and the microstructure of the samples.

5 REFERENCES

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