PREPARATION OF Si₃N₄-TiN CERAMIC COMPOSITES

PRIPRAVA KERAMIČNIH KOMPOZITOV NA OSNOVI Si3N4-TiN

Aljoša Maglica, Kristoffer Krnel, Tomaž Kosmač

Engineering Ceramics Department, Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia aljosa.maglica@ijs.si

Prejem rokopisa – received: 2009-07-24; sprejem za objavo – accepted for publication: 2009-09-04

In this work we report on the preparation of particulate ceramic composites based on a Si_3N_4 or SiAlON matrix phase. The composites were prepared with reaction sintering of Si_3N_4/TiO_2 powder mixtures using Y_2O_3 , Al_2O_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 atmospere with chemical reaction of Si_3N_4 and TiO₂. A comparison of the materials sintered with addition of TiO₂ have higher densities and better flexural strength. The electrical conductivity of the sintered composites with addition of TiO₂ 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: Si₃N₄, TiN, electrically conductive ceramics, ceramic heater

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 prahu Si₃N₄ in TiO₂, kot dodatke za sintranje pa smo uporabili Y₂O₃ in Al₂O₃, v primeru SiAlON-ov pa še AlN. Rezultati rentgenske difrakcije so potrdili, da med sintranjem v dušikovi atmosferi pri reakciji TiO₂ s Si₃N₄ nastane TiN. Ko smo primerjali kompozite, pripravljenje z dodatom TiO₂ v začetni mešanici z materiali matrične faze (sintrani Si₃N₄ ali SiAlON), smo ugotovili, da dosežemo višjo gostoto in boljšo upogibno trdnost pri materialu z dodanim TiO₂. Raziskali smo tudi električno prevodnost kompozitov z dodanim TiO₂ v začetni mešanici in ugotovili, da je njihova električna prevodnost odvisna od dodane količine TiO₂ in od pogojev sintranja.

Ključne besede: Si₃N₄, TiN, električno prevodna keramika, keramični grelec

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, MoSi₂, TiN, TiC, TiCN, TiB₂ and ZrN^{2,3}. Electro-conductive composite ceramics with good thermal conductivities are interesting for the production of various heating elements, such as ceramic glow plugs, igniters, ceramic heaters, etc^{4,5}. Such materials have also received great attention due to their compatibility with electrical discharge machining^{6,7}. The electrical conductivity of ceramic materials is strongly affected by the distribution of the electrically conductive second phase, and so many studies have been performed to increase the electrical conductivity of ceramic materials^{8,9}.

Composites of silicon nitride and titanium nitride have been investigated in order to obtain a combination of high hardness, high strength, good fracture toughness, and low electrical resistivity^{10,11,12}. Some attempts were made to use a silicon nitride matrix with titanium nitride as the conductive phase. There are three main processing routes to fabricate the Si₃N₄-TiN composites¹³. The first is conventional liquid-phase sintering of Si₃N₄ and TiN powder mixtures with a small amount of sintering additives. The second one is the chemical vapour deposition (CVD) method using gas components of SiCl₄-TiCl₄-NH₃-H₂. The third method, where Si and Ti are used as the starting materials, is called an "in-situ synthesis" process. By contrast to the conventional powder processing route and the CVD process, the in-situ chemical reaction method enables the production of composites with the following advantages: low cost, desirable microstructures and enhanced sinterability.

The aim of the work was to prepare Si_3N_4 /TiN and SiAlON/TiN ceramic composites with sintering in a nitrogen atmosphere by the in-situ chemical reaction of Si_3N_4 and TiO_2 . The microstructure, mechanical properties and electrical conductivity of the composites were investigated. The results indicated that the flexoral strength improved and that electrically conductive materials can be prepared if the amount of added TiO_2 is sufficient.

$$w(\alpha)/w((\alpha + \beta) - \mathrm{Si}_3\mathrm{N}_4) = 0.8$$

2 EXPERIMENTAL

The starting powders used were Si₃N₄ SILZOT HQ (SKW, DE, $d_{50} = 1.7 \mu \text{m}$; *BET* = 3.2 m²/g, *w* (α) / *w*

 $(\alpha + \beta)$ -Si₃N₄) = 0.8, Al₂O₃ (Alcoa, USA, $d_{50} = 0.5 \mu m$; $BET = 3-7 \text{ m}^2/\text{g}$, Y_2O_3 grade fine (H. C. Starck, DE, d_{50} $(max) = 0.9 \ \mu m; BET = 10.0-16.0 \ m^2/g), AlN grade C$ (H. C. Starck, DE, $d_{50} = 1.2 \ \mu\text{m}$; $BET = 4.1 \ \text{m}^2/\text{g}$) and TiO₂ RC8 (Cinkarna Celje, SLO, rutil, $d_{50} = 0.35 \ \mu m$; $BET = 6.5 - 8.5 \text{ m}^2/\text{g}$). The nominal compositions for the preparation of Si₃N₄ and SiAlON with and without the addition of TiO_2 are listed in **Table 1**. The powders were mixed with Si₃N₄ 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 × 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 $2.3 \text{ mm} \times 3.9$ mm × 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/%)

 Tabela 1: Začetna sestava mešanic prahov (masni delež, w/%)

Compositions	Si ₃ N ₄	Y_2O_3	Al ₂ O ₃	AlN	TiO ₂
SN	92	5	3	0	0
SN/TiO ₂	82.8	4.5	2.7	0	10
SiAlON	83.9	2.2	5.5	8.4	0
SiAlON/TiO ₂	75.5	2	4.9	7.6	10

3 RESULTS AND DISCUSSION

3.1 Ceramic materials based on Si_3N_4

The X-ray diffraction pattern of Si₃N₄ with and without the addition of TiO₂ in the starting mixture (denoted as SN and SN/TiO₂) after sintering at 1800 °C for 2 h in flowing N₂ is shown in **Figure 1**. In both samples we could observe the presence of the β -Si₃N₄ and YAG (Yittrium Aluminium Garnet) phases, while in the sample SN/TiO₂ we also observed TiN. The peaks of TiO₂ could not be detected, and it could be concluded that the transformation of TiO₂ into TiN was completed. During the sintering of such composites the following chemical reactions take place^{14,15,16}:

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

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



Figure 1: X-ray analysis of SN and SN/TiO2 after sintering at 1800 $^\circ\text{C}$ for 2 h in flowing N2

Slika 1: Rentgenska analiza materiala SN in SN/TiO₂, sintranega pri 1800 °C 2 h v pretoku N₂

The TiO₂ and Si₃N₄ 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



Figure 2: Microstructure of sintered silicon nitride ceramic at 1800 °C for 2 h in N_2 : a) SN and b) SN/TiO₂

Slika 2: Mikrostruktura sintrane silicijeve nitridne keramike pri 1800 °C, 2 h v N₂: a) SN in b)SN/TiO₂

Materiali in tehnologije / Materials and technology 44 (2010) 1, 31-35



Figure 3: The SEM micrographs of fracture surface of sintered silicon nitride samples: a) SN and b) SN/TiO $_2$

Slika 3: SEM-posnetki mikrostruktur prelomov sintranih vzorcev silicijevega nitrida: a) SN in b) SN/TiO $_2$

sample, especially in the samples with larger amounts of titania.

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 2 b**) 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 3 a**, the matrix β -Si₃N₄ grains are surrounded by the secondary bright phase, while in **Figure 3 b**, 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 ceramic^{17,18}.

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 Si_3N_4 samples

Tabela 2: Primerjava relativne gostote, upogibne trdnosti in električne prevodnosti sintranih vzorcev Si_3N_4

Material	$ ho_{ m rel.}$ /%	$\sigma_{\rm fl}$ /MPa	$\sigma_{\rm el.}$ /(Ω m) ⁻¹
SN	89.8	380	ND*
SN/TiO ₂	90.0	410	$7.1 \cdot 10^{-8}$

* 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-



Figure 4: XRD patterns of sintered SiAlON and SiAlON/TiO₂ materials at 1800 °C for 2 h in nitrogen atmosphere

Slika 4: Rentgenska difraktograma sintranega materiala SiAlON in SiAlON/TiO₂ pri 1800 °C 2 h v dušikovi atmosferi

A. MAGLICA ET AL.: THE PREPARATION OF Si₃N₄-Tin CERAMIC COMPOSITES



Figure 5: SEM microstructure of sintered SiAlON samples: a) SiAlON and b) SiAlON/TiO₂ at 1800 °C for 2 h in N₂. Slika 5: SEM-posnetki mikrostruktur sintranih vzorcev SiAlONa: a) SiAlON and b) SiAlON/TiO₂ pri 1800 °C, 2 h v N₂

mation of TiO_2 occurred during the sintering process, in accordance with the following chemical reactions^{16,19–21}.

$$2\text{TiO}_{2} + 3\text{AlN} + 5\text{Si}_{3}\text{N}_{4} \Rightarrow 3\text{Si}_{5}\text{AlON}_{7} + 2\text{TiN} + 12\text{O}_{2} \text{ (g)}$$
(3)

$$2\text{TiO}_2 + 2\text{AlN} \Rightarrow 2\text{TiN} + \text{Al}_2\text{O}_3 + 12\text{O}_2 \text{ (g)}$$
(4)

From equation 3 it is clear that TiO_2 reacts together with AlN and Si_3N_4 to form SiAlON, TiN and O_2 . The second chemical reaction (equation 4) leads to the formation of TiN, O_2 and Al_2O_3 . The formation of Al_2O_3 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 β -SiAlON 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



Figure 6: The SEM micrographs of fracture surface of sintered SiAlON samples: a) SiAlON and b) SiAlON/TiO₂. **Slika 6:** SEM-posnetki mikrostruktur prelomov sintranih vzorcev SiAlONa: a) SiAlON in b) SiAlON/TiO₂

 Table 3: Comparison of a relative density, a flexural strength and a electrical conductivity of sintered SiAION samples

 Tabela 3: Primerjava relativne gostote, upogibne trdnosti in električne prevodnosti sintranih vzorcev SiAlONa

Material	$\rho_{\rm rel.}$ /%	$\sigma_{\rm fl}$ /MPa	$\sigma_{\rm el.}/(\Omega {\rm m})^{-1}$
SiAlON	95	406	ND*
SiAlON/TiO ₂	96.5	610	$1.1 \cdot 10^{-8}$

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

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 TiO_2 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

Materiali in tehnologije / Materials and technology 44 (2010) 1, 31-35

higher density compared to the SiAION 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 AlN 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

- ¹S. De Bondt, L. Froyen, A. Deruyttere, Electrical conductivity of composites: a percolation approach, J. Mater. Sci, 27 (1992), 1983–1988
- ² A. Bellosi, S. Guicciardi, A. Tampieri, Development and characterization of electroconductive Si3N4-TiN composite, J. Am. Ceram. Soc., 9 (**1992**), 83–93
- ³M. Ade, J. Haußelt, Electroconductive ceramic composites with low-to-zero shrinkage during sintering, J. Eu. Ceram. Soc., 23 (2003), 1979–1986
- ⁴ B. Bitterlich, S. Bitsch, K. Friederich, SiAlON based ceramic cutting tools, J. Eu. Ceram. Soc., 28 (2008), 989–994
- ⁵M. Bracisiewicz, V. Medri and A. Bellosi, Factors inducing degradation of properties after long term oxidation of Si3N4-TiN electro-

conductive composites, Applied Surface Science, 202 (2002), 139–149

- ⁶ Lj. Zivkovic, Z. Nikolic, S. Boskovic, M. Miljkovic, Microstructural characterization and computer simulation of conductivity in Si3N4-TiN composites, Journal of Alloys and Compounds, 373 (2004), 231–236
- ⁷ Martin, C., Cales, B., Vivier, P., Mathieu, P., Electrical discharge machinable ceramic composites. Mater. Sci. Eng., A, 109 (1989), 351–356
- ⁸ R.-G. Duan, G. Roebben, O. Van der Biest, TiO2 additives for in situ formation of toughened silicon nitride-based composites, Materials Letters, 57 (2003), 4156–4161
- 9 R.-G. Duan, G. Roebben, J. Vleugels, Effect of TiX(X = C, N, O) additives on microstructure and properties of silicon nitride based ceramics, Scripta Materiallia, 53 (**2005**), 669–673
- ¹⁰ T. Hirai, S. Hayashi, Density and deposition rate of chemically vapour-deposited Si3N4-TiN composites, Journal of Materials Science, 18 (**1983**), 2401–2406
- ¹¹ M. Herrmann, B. Balzer, Densification, microstructure and properties of Si3N4-Ti(C,N) composites, Journal of the European Ceramic Society, 12 (**1993**), 287–296
- ¹² Huang QiLiang, Cai Juan, Pan Wei, In situ processing of TiN/Si3N4 composites by Ti-Si3N4 solid state reaction, Materials Letters, 31 (1997), 221–225
- ¹³ R.-G. Duan, G. Roebben, J. Vleugels, In situ formation of Si2N2O and TiN in Si3N4-based ceramic composites, Acta Materialia, (2005), 1547–2554
- ¹⁴ Yu. G. Gogotsi, Review-Particulate silicon nitride-based composites, Journal of Materials Science, 29 (1994), 2541–2556
- ¹⁵ H. X. Li, J. K. Yu, K. Hiragushi, Y. Mizota, Phase Composition of TiO2-Coated ZrO2/Si3N4 Composite, J. Eu. Ceram. Soc., 19 (1999), 299–303
- ¹⁶ M. B. Trigg, E. R. Mccartn, Comparison of the Reaction Systems ZrO2-Si3N4 and TiO2-Si3N4, Journal of the American Ceramic Society, (**1981**), C151–C152
- ¹⁷ L. J. Bowen, T. G. Carruthers, Development of mechanical strength in hot-pressed silicon nitride, 13 (1977), 684–687
- ¹⁸ B. Yuan, J-X. Liu, G-J. Zhang, Y-M. Kan et. al, Silicon nitride/boron nitride ceramic composites fabricated by reactive pressureless sintering, Ceramic International, In Press, Available online 13 January 2009
- ¹⁹ S. Zheng, L. Gao, H. Watanabe, T. Meguro, Improving the microstructure of Si3N4-TiN composites using various PEIs to disperse raw TiO2 powder, Ceramics International, 33 (2007), 355–359
- ²⁰Z. Lences, Z. Panek, Electroconductive β-SiAION/TiN composites prepared by reaction sintering, Ceramics-Silikaty, 43 (**1999**) 3, 81–85
- ²¹ K. Krnel, A. Maglica, T. Kosmač, β-SiAION/TiN nanocomposites prepared from TiO₂-coated Si₃N₄ powder, J. En. Ceram. Soc., 28 (2008), 953–957