

# ELECTROCONDUCTIVE $\beta$ -SiAlON/TiN COMPOSITES PREPARED BY REACTION SINTERING

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*An in situ formed electroconductive  $\beta$ -SiAlON/TiN ceramic composite was prepared by reactive sintering from Si + Al +  $Al_2O_3$  +  $TiO_2$  +  $Si_3N_4$  + AlN powder mixture. The heat treatment, nitrogen pressure and starting powder composition were optimized and homogeneous ceramic material was prepared. The reaction time was remarkably reduced by this method in comparison to the common liquid phase sintering route. The electrical resistivity of  $\beta$ -SiAlON + 17 vol.% TiN composite was  $2.7 \cdot 10^{-4} \Omega m$ , confirming the suitability of this material for electrical discharge machining.*

## INTRODUCTION

$\beta$ -SiAlON based materials are potential candidates for many special engineering applications, such as cutting tools, structural parts of combustion engines, etc. Although the commercial preparation of  $\beta$ -SiAlON ( $Si_z Al_{2-z} O_2 N_{8-z}$ , where  $0 < z < 4.2$  [1]) from  $Si_3N_4 + (SiO_2) + Al_2O_3 + AlN$  powder mixture by pressure-less sintering is relatively economic in comparison to other advanced ceramic materials with comparable properties, the final machining of high-strength and hard  $\beta$ -SiAlON materials by conventional diamond grinding is a rather complicated and expensive process. Electrical discharge machining (EDM) is an alternative to the conventional diamond machining technique, but it is remarkably cheaper and by this method mirror finish can be obtained on ceramics surfaces. EDM requires electrically conductive materials with an electrical resistivity of less than  $1 \Omega m$  [3].

Several studies have been carried out to increase the electrical conductivity of  $Si_3N_4$ -based materials, because  $Si_3N_4$  is in principle an insulator with extremely high electrical resistivity of  $10^{11} \Omega m$ . It has been shown that the addition of TiN with electrical resistivity of  $3.34 \cdot 10^{-7} \Omega m$  into  $Si_3N_4$  matrix can result in a good conductivity necessary for EDM [4-8].

$Si_3N_4$ /TiN electroconductive composites were fabricated by sintering or hot-pressing of TiN and  $Si_3N_4$  powder mixture with different sintering additives [4,5,8-11]. This type of composite was also prepared by nitridation of Si powder compacts (so called Reaction Bonded Silicon Nitride, RBSN) containing TiN particles [5]. This RBSN/TiN composite showed a low shrinkage after sintering ( $< 2\%$ ) due to the small dimensional change of RBSN during preparation. TiN particles were also added to SiAlON ceramics [12].  $Si_3N_4$ /TiN powder mixtures were also prepared by direct nitridation of silicon and titanium, using SHS process [13]. Promising

is the preparation of TiN by *in situ* reduction of  $TiO_2$  in the  $Si_3N_4$  matrix, as was shown in [14,15]. The electrical properties of this composite are better compared to materials with direct addition of the same amount of TiN particles due to the very good distribution of fine TiN particles. By direct nitridation of the Si +  $TiO_2$  powder mixture ( $1400^\circ C$ , 200h) and subsequent hot-pressing of the sample containing sintering additives also  $Si_3N_4$ /TiN composites have been prepared [7]. The most homogeneous distribution of TiN particles in  $Si_3N_4$  matrix has been achieved by the *in situ* preparation of TiN from organometallic  $(CH_3)_3SiNHTiCl_3$  precursor. The dried suspension of this soluble preceramic precursor and  $Si_3N_4$  powder was compacted into a green body and subsequently pyrolysed at  $600-800^\circ C$  under ammonia flow resulting in a homogeneous, however porous  $Si_3N_4$ /TiN composite [16].

The brief review confirms that high attention is devoted to the preparation of TiN reinforced electroconductive  $Si_3N_4$  based composites by different routes.

This paper describes the study on the *in situ* preparation of a bulk  $\beta$ -SiAlON/TiN composite from inexpensive Si, Al and  $TiO_2$  raw materials by SHS and RBSN methods.

## EXPERIMENTAL PART

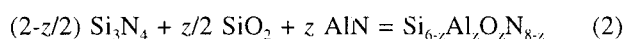
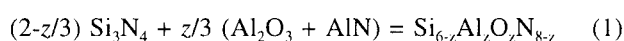
The silicon nitride powder was prepared from silicon powder by *in situ* nitridation during processing. The starting silicon powder was prepared by iron-ball milling of waste silicon plates for electronics (Tesla Rožnov, Czech Republic) and it contained 0.27 wt.% Fe to catalyze the nitridation reaction. The starting powder mixture contained also SiAlON forming additives:  $SiO_2$  (Aerosil OX-50, Degussa, Germany), Al (PAP I, Russia),  $Al_2O_3$  (Martoxide CS-400/M, Germany), AlN (Starck,

Table 1. Heat treatment schedule of the sintered samples.

Sample	Sintering *	Load (MPa)	N <sub>2</sub> press. (MPa)	TiN (vol%)	Heat. rate (°C min <sup>-1</sup> )	T (°C)	Dwell (min)
A	PLS	-	0.1	-	10 - 800	1800	6
B	HP	30	0.1	22	60 30	1370 1800	15 30
C	HP	30	0.1	12	10 2 10	1370 1500 1800	0 0 60
D	GPS	-	10	17	10 10	1370 1800	24 6

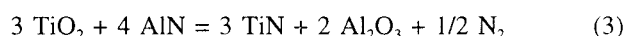
\*PLS: pressure-less sintering, HP: hot-pressing; GPS: gas-pressure sintering

Grade B, Germany) and Si<sub>3</sub>N<sub>4</sub> (Starck LC 12SX, Germany). The weight fractions were calculated according to the following equations



where the part or total amount of Si<sub>3</sub>N<sub>4</sub> and AlN was replaced by Si and Al powders as precursors for the respective nitrides. The *z* value in the Si<sub>6-z</sub>Al<sub>z</sub>O<sub>z</sub>N<sub>8-z</sub> formula varied from 0.5 to 4.0 with a step width of 0.5.

Two types of TiO<sub>2</sub> with different particle size (*D*<sub>50</sub> = 20 μm, TIONA, England, and *D*<sub>50</sub> = 3 μm, Wako Pure Chemical Ind., Japan) were used for the *in situ* preparation of TiN according to the reaction:



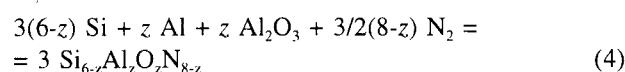
The starting powders were homogenized for 12 hours in dried acetone with Si<sub>3</sub>N<sub>4</sub> balls. In case when coarse-grained TiO<sub>2</sub> was added as a precursor for the preparation of TiN, the powder mix was crushed in an agate mortar before homogenization. From the dried and crushed powder mixture pellets were die-pressed with 100 MPa pressure. The samples were pressure-less sintered (diameter *d* = 7 mm, height *h* = 4 mm), hot pressed (*d* = 12 mm, *h* = 6 mm) or gas-pressure sintered (*d* = 20 mm, *h* = 10 mm) in different graphite resistance furnaces. The pressure-less sintered (PLS) samples are labeled as A, the hot pressed (HP) samples are labeled as B and C and the gas pressure sintered (GPS) sample as D. The heat treatments are summarized in table 1. The first annealing step in each case was the vacuum treatment at 200 °C for 20 minutes to remove the remaining moisture and organic oil, in which the fine aluminum powder was stored. Subsequent nitridation and sintering were done under various pressures of nitrogen and different heating rates. While for the small PLS samples the heating rate varied from 10 to 800 °C min<sup>-1</sup>, in the case of HP and GPS samples the heating rate was

limited to 100 and 20 °C min<sup>-1</sup>, respectively. The thermal analysis of exothermic reactions was carried out in a graphite resistance furnace. The bulk density of sintered samples was determined by the Archimedes immersion method in mercury and the phase composition by X-ray powder diffraction. The sample surfaces were analysed by X-ray photoelectron spectroscopy (XPS). The microstructures were examined with a scanning electron microscope (SEM) and the elemental analysis was done by a Kevex microanalyser. Electrical resistivity was measured by the Van der Pauw method on flat circular samples with uniform thickness. The wires for electrical resistivity measurements were attached to the samples with indium.

## RESULTS AND DISCUSSION

### Self-propagating high-temperature synthesis (SHS)

The *in situ* preparation of β-SiAlON from a Si + SiO<sub>2</sub> + Al powder mixture by reaction at 1800 °C for 6 minutes under 1.2 MPa nitrogen pressure resulted in the inhomogeneous sintered body with a high amount of oxynitride glassy phase. Although a high heating rate was used (500 °Cmin<sup>-1</sup>), the self-propagating high-temperature synthesis of β-SiAlON from Si, Al and SiO<sub>2</sub> was not initiated. From this reason in the following experiments only Al<sub>2</sub>O<sub>3</sub> was used as a source of oxygen for β-SiAlON formation:



The *z* value varied from 0.5 to 4. The influence of *z* value on the final density is shown in figure 1. According to the theoretical calculations, the density should decrease with increasing *z* value due to the linear increase of the unit cell dimensions [17]. The opposite slopes of density-versus-*z* dependence below and above *z* = 1.5 value can be explained by the different amount of transient liquid

phase and the above mentioned different unit cell dimensions for various  $z$ . For low  $z$  (where  $z < 1.5$ ) lower final densities were determined after sintering because small amount of transient liquid phase was present during the sintering. At higher  $z$  values a nearly linear decrease of bulk density was observed, which is in good agreement with the calculated theoretical densities of  $\beta$ -SiAlONs [17]. The lower final density in comparison to the theoretical one is due to the remaining porosity as a consequence of pressure-less sintering and the formation of rigid, but porous RBSN skeleton. Nearly the same slope of theoretical and experimental density suggests the same level of porosity in sintered samples with  $z > 1.5$ . The porosity remained on a relatively high level also due to the very short sintering time. Supposing the  $\beta$ -SiAlON formation is a faster process than the sintering, the liquid-solid phase conversion causes some additional porosity due to the negative volume change.

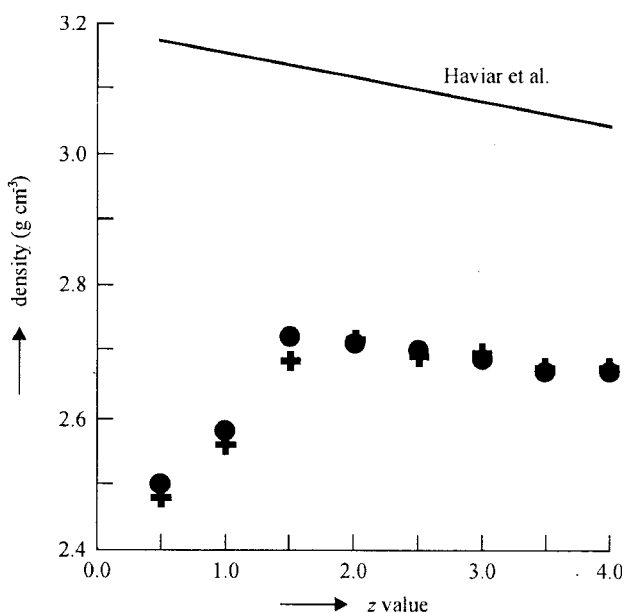


Figure 1. Influence of  $z$  value on the bulk density of pressure-less sintered  $\beta$ -SiAlON. The solid line shows the calculated theoretical densities as a function of composition [17]. Symbols ●, + represent parallel experiments which were performed according to the following heat treatment schedule: heating rate  $300\text{ }^{\circ}\text{C min}^{-1}$  up to  $1270\text{ }^{\circ}\text{C}$ ,  $30\text{ }^{\circ}\text{C min}^{-1}$  up to  $1370\text{ }^{\circ}\text{C}/10\text{ min}$  dwell,  $100\text{ }^{\circ}\text{C min}^{-1}$  up to  $1700\text{ }^{\circ}\text{C}$  without dwell.

#### Reaction sintering

Preparation of dense and silicon-free  $\beta$ -SiAlON by the SHS process was unsuccessful, although very high heating rates up to  $800\text{ }^{\circ}\text{C min}^{-1}$  were used. For this reason reaction sintering was applied for  $\beta$ -SiAlON preparation. The optimum conditions were studied by DTA measurements. The DTA results showed a broad exothermic peak at about  $650\text{ }^{\circ}\text{C}$  (formation of AlN) and

strong exothermic peak starting at  $1270\text{ }^{\circ}\text{C}$  (formation of RBSN). From this reason the heating rate was slowed down from  $300$  to  $10\text{ }^{\circ}\text{C min}^{-1}$  at  $1230\text{ }^{\circ}\text{C}$  for an easier control of the exothermic nitridation of silicon. Further improvement of the nitridation process was achieved by the addition of  $20\text{ wt.}\%$   $\text{Si}_3\text{N}_4$  as an effective seed for heterogeneous nucleation [18]. Moreover,  $\text{Si}_3\text{N}_4$  "diluted" the silicon powder compact and lowered the total heat evolved from exothermic reaction. In the samples with higher  $z$  values also the *in situ* formed AlN and added  $\text{Al}_2\text{O}_3$  diluted the silicon compact during the preparation of RBSN and reduced the exothermicity of the reaction. At higher temperatures ( $> 1500\text{ }^{\circ}\text{C}$ ) these phases acted as sintering and  $\beta$ -SiAlON forming additives.

The DTA of samples with higher  $z$  values (where  $z > 2.0$ ) and  $20\text{ wt.}\%$   $\text{Si}_3\text{N}_4$  addition showed a reaction with smooth exothermic peaks and provided  $\beta$ -SiAlON samples without melted silicon. The outer  $20\text{--}30\text{ }\mu\text{m}$  thick layer of the sample was white in colour. The XPS analysis showed the presence of Al, O and N, but Si was not detected. It was removed from the surface in the form of  $\text{SiO}(\text{g})$  during heat treatment. Using a powder bed of composition  $93\text{ wt.}\%$  ( $\text{Si}_3\text{N}_4 + \text{BN}$ ) +  $7\text{ wt.}\%$  ( $\text{Si} + \text{SiO}_2$ ) resulted in a homogeneous  $\beta$ -SiAlON sample because the  $\text{SiO}(\text{g})$  partial pressure was kept on a sufficiently high level and suppressed the loss of silicon from the sample. The final porosity was still relatively high after reactive pressure-less sintering,  $\sim 9\text{ vol.}\%$ . Therefore, hot pressing experiments and gas pressure sintering were carried out to prepare a material with lower porosity.

The microstructures of hot pressed B and C samples are shown in figures 2 and 3. These samples were prepared at similar sintering conditions, while the main difference was the particle size and the amount of  $\text{TiO}_2$ . The elemental analysis by the Kevex microanalyzer showed in both cases that the  $\text{TiO}_2$  particles had completely transformed to TiN. The agglomerates of TiN in sample B ( $22\text{ vol.}\%$  TiN) are present probably due to the crushing of coarse  $\text{TiO}_2$  particles during nitridation to TiN, which is accompanied with a considerable volume increase ( $48.9\%$ ) [19]. The TiN agglomerates are joining again into bigger grains at higher temperature and their shape is flat in the direction perpendicular to the applied hot pressing load. The measured electrical resistivity of sample B was  $4 \cdot 10^{-5}\ \Omega\text{m}$ , which corresponds with the relatively high  $22\text{ vol.}\%$  TiN content. Although, the distribution of TiN particles is the most homogeneous and the finest in sample C (Fig. 3), also the electrical resistivity is the highest ( $10^6\ \Omega\text{m}$ ) due to the low  $12\text{ vol.}\%$  TiN content. The high resistivity of sample C could be explained by the fine microstructure and large grain boundary surface of  $\beta$ -SiAlON matrix. The actual  $12\text{ vol.}\%$  of TiN is insufficient to create a conductive network. The critical volumetric fraction calculated on

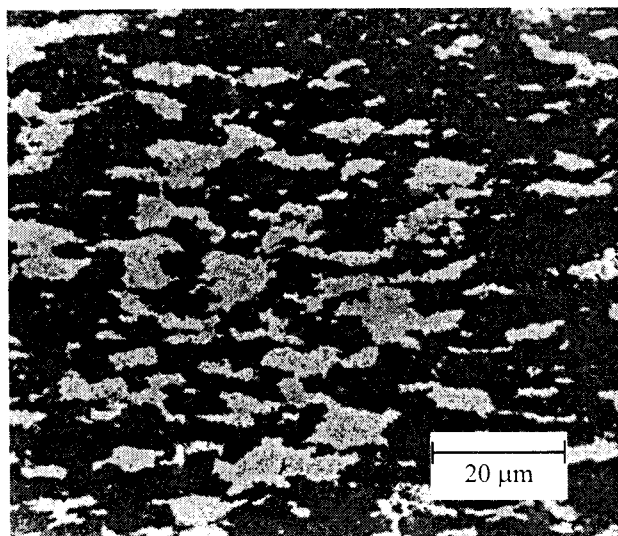


Figure 2. SEM micrograph of the hot pressed and polished surface of sample B. The white flat TiN agglomerates are aligned perpendicular to the hot-pressing direction.

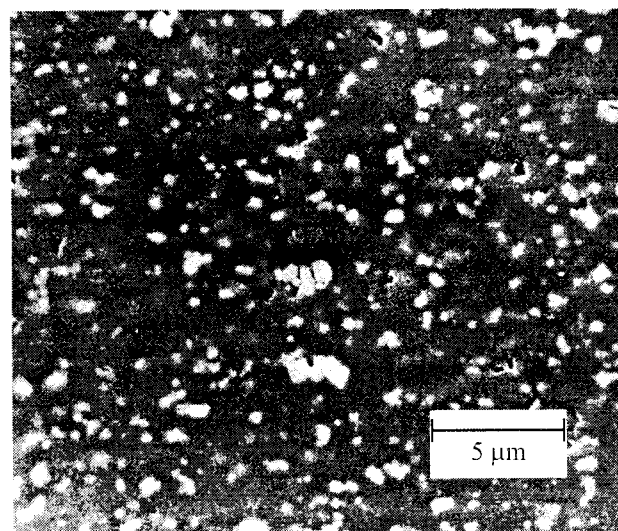


Figure 3. SEM micrograph of hot pressed and polished surface of sample C with very fine TiN particles.

the base of percolation theory for conductance is about 20.9 vol.% [20], if the particles dispersed in the insulating matrix are connected. In sample C the TiN content is considerably lower.

Bigger samples of  $\beta$ -SiAlON were nitrided in a gas pressure furnace (up to 10 MPa of  $N_2$ ), because higher pressure of  $N_2$  should increase the diffusion-controlled conversion of Si to  $Si_3N_4$ . It was confirmed with experiments carried out under 1, 3, 6 and 10 MPa nitrogen pressure. The higher the  $N_2$  pressure, the lower the amount of unreacted Si. Further decrease of free Si

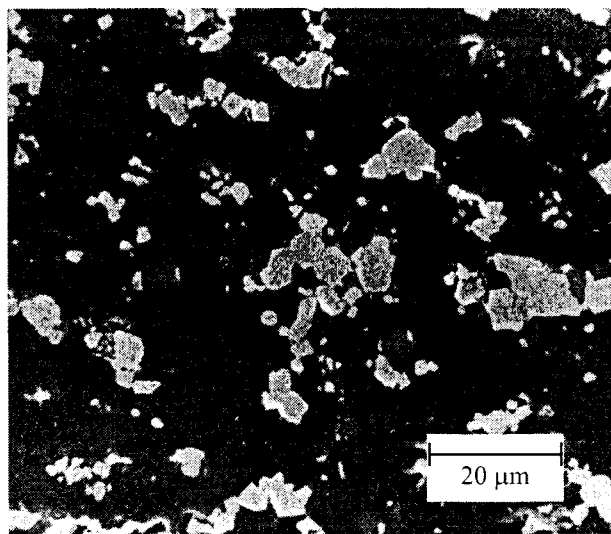


Figure 4. SEM micrograph of polished surface of gas-pressure sintered sample D. The TiN agglomerates are only partially joined into bigger grains.

after nitridation was achieved by the replacement of 30 wt.% of commercial Si (grain size 2-20  $\mu m$ ) with fine Si (< 0.3  $\mu m$ ) powder prepared by the CVD method from  $SiH_4$  decomposition at 1230  $^{\circ}C$  in our lab. After sintering of this  $\beta$ -SiAlON sample (without TiN) at 1600  $^{\circ}C$  for 6 minutes about 3 wt.% of free Si has been still determined. Total elimination of free Si was achieved in the  $\beta$ -SiAlON/TiN composite by the additional reaction producing nitrogen (3), which reacted together and formed  $Si_3N_4$ . It was an effective route, because the diffusion of  $N_2$  to the unreacted Si from the furnace atmosphere is very slow at this stage of sintering due to the closed porosity. The above mentioned reaction is useful only for the elimination of small amounts of free Si, because it is desirable that the major part of reaction will be finished before sintering (<1500  $^{\circ}C$ ). The gas evolved can hinder sintering due to the formation of pores at higher temperatures. In optimum conditions all the products of reaction (3) should be incorporated into the composite:  $N_2$  into RBSN,  $Al_2O_3$  into the  $\beta$ -SiAlON and TiN remains as a chemically inert phase and improves the electrical conductivity of  $\beta$ -SiAlON. The microstructure of sample D prepared according to the above described procedure with 17 vol% *in situ* formed TiN is shown in figure 4. Near the larger TiN agglomerates pores are present. They were produced at the later stage of sintering, when the *in situ* formed  $N_2$  did not have a reaction partner (free Si). Moreover, some cracks around the TiN particles could be formed as a consequence of the considerably different thermal expansion coefficient of TiN ( $9.4 \times 10^{-6} K^{-1}$ ) in comparison with  $Si_3N_4$  ( $3.2 \times 10^{-6} K^{-1}$ ). Although, this sample still contained about 3-5 % remaining porosity,

the measured electrical resistivity was  $2.7 \times 10^{-4} \Omega\text{m}$ . Despite the above mentioned percolation theory, this excellent value for relatively low TiN content is probably due to the chain or network-like distribution of *in situ* prepared TiN. It should be pointed out that the electrical resistivity is lower compared with  $\text{Si}_3\text{N}_4/30 \text{ wt.}\%$  (app. 20 vol.%) TiN particulate composite with an electrical resistivity of  $9.4 \times 10^{-4} \Omega\text{m}$  [6]. The electrical resistivity of hot pressed pore free sample B with comparable TiN content (22 vol.%) is lower by one order of magnitude ( $4 \times 10^{-5} \Omega\text{m}$ ). In particulate composites formed by direct addition of TiN powder [6], the majority of conductive particles are isolated in the insulating  $\text{Si}_3\text{N}_4$  or SiAlON matrix. This might be the explanation for the better conductivity of samples B and D with *in situ* formed TiN. Both materials have high enough electrical conductivity for electrical discharge machining.

### CONCLUSION

In comparison to ceramic-ceramic composites in which the second phase is added directly prior to the sintering, an alternative reaction route has been demonstrated which produces electroconductive  $\beta$ -SiAlON/TiN ceramic composite from  $\text{Si} + \text{Si}_3\text{N}_4 + \text{Al} + \text{AlN} + \text{Al}_2\text{O}_3 + \text{TiO}_2$  powder mixture. Heat treatment schedule, nitrogen pressure, and starting composition were optimized resulting in a homogeneous ceramic material. The reaction time was remarkably shortened by this method in comparison with the common sintering route. The samples with 12 vol.% TiN and fine microstructure have insufficient electrical conductivity for EDM. The electrical resistivity of the composite with coarser  $\beta$ -SiAlON and with 17 or 22 vol.% TiN content was  $2.7 \times 10^{-4} \Omega\text{m}$  and  $4.0 \times 10^{-5} \Omega\text{m}$  respectively, confirming the suitability of this materials for EDM.

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### References

- Jack K.H.: J. Mater. Sci. 11, 1135 (1976).
- Lis J., Majorowski S., Puszynski J.A., Hlavacek V.: Am. Ceram. Soc. Bull. 70, 1658 (1991).
- Gadalla A.G., Petrofes N.F.: Mater. Manuf. Process 5, 253 (1990).
- Yasutomi Y., Sobue M.: Ceram. Eng. Sci. Proc. 11, 857 (1990).
- Yasutomi Y., Chiba A., Sobue M.: J. Amer. Ceram. Soc. 74, 950 (1991).
- Bellosi A., Guicciardi S., Tampieri A.: J. Eur. Ceram. Soc. 9, 83 (1992).
- Lin W., Yang J.M., Ting S.J., Ezis A., Shih C.J.: J. Am. Ceram. Soc. 75, 2945 (1992).
- Gogotsi Yu.G.: J. Mater. Sci. 29, 2541 (1994).
- Nagaoka T., Yasuoka M., Hirao K., Kanzaki S.: J. Ceram. Soc. Japan Int. Ed., 100, 612 (1992).
- Sato Y., Ueki M.: J. Ceram. Soc. Japan, Int. Ed. 101, 354 (1993).
- Crampon J., Duclos R.: Acta Metall. Mater. 38, 805 (1990).
- Ekström T. in: *Proceedings of the International Conference on Silicon Nitride-Based Ceramics*, p. 327-332, editors M.J. Hoffmann, P.F. Becher and G. Petzow, Key Eng. Mater., vol. 89-91, Trans Tech Publications, Aedermannsdorf, 1994.
- Hillinger G., Hlavacek V.: J. Am. Ceram. Soc. 78, 495 (1995).
- Shih C.J., Yang J.M., Ezis A.: Scr. Metall. 24, 24119 (1990).
- Hong F., Lumby R.J., Lewis M.H.: J. Eur. Ceram. Soc. 11, 237 (1993).
- Narula C.K., Demczyk B.G., Cubarow P., Seyferth D.: J. Am. Ceram. Soc. 78, 1247 (1995).
- Haviar M., Johannesen O.: Adv. Ceram. Mater. 3, 405 (1988).
- Lenčoš Z.: Ceramics-Silikáty 38, 61 (1994).
- Ueno K., Inoue T., Sodeoka S., Suzuki M., Ishikawa H., Uchiyama K., Inui T.: J. Ceram. Soc. Japan Int. Ed. 105, 304 (1997).
- Dean P. and Bird N.F.: *Math Divisional Rep.*, May, National Physical Lab., Teddington, Middlesex, England, 1966.

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### IN SITU PRÍPRAVA $\beta$ -SiAlON/TiN KOMPOZITU

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Materiály na báze  $\beta$ -SiAlONu sú vhodné pre mnohé aplikácie najmä v strojárskom priemysle. Pre ich vysokú pevnosť a tvrdosť je však potrebné ich finálne opracovanie pomocou diamantových nástrojov čo bývajú často technicky aj finančne náročné operácie. Alternatívnym spôsobom obrábania môže byť obrábanie elektrickým výbojom (EDM- electrical discharge machining) za predpokladu, že obrábaný materiál má merný odpor menší ako  $1 \Omega\text{m}$ . Splniť túto podmienku možno prídavkom zložky s nízkou hodnotou merného odporu a dobrou chemickou stabilitou v sialonovej matrici. Medzi takéto zlúčeniny patrí TiN. Práca popisuje prípravu  $\beta$ -SiAlON/TiN keramického kompozitu reakčným spekaním.

Z práškovej zmesi obsahujúcej potrebné množstvá Si,  $\text{Si}_3\text{N}_4$ , Al, AlN,  $\text{Al}_2\text{O}_3$  a  $\text{TiO}_2$  sa pripravili reakčným žiarovým lisovaním a reakčným spekaním v pretlaku  $\text{N}_2$  do 10 MPa vzorky s obsahom 12, 17 a 22obj.% TiN. Vzorky s obsahom 12obj.% TiN a jemnozrnnou mikroštruktúrou nemali dostatočnú elektrickú vodivosť na rozdiel od vzoriek s hrubozrnnou mikroštruktúrou, ktorých merný odpor bol rádovo  $10^4 \Omega\text{m}$ .

Optimalizáciou zloženia východiskovej práškovej zmesi a procesu reakčného spekania možno pripraviť keramický kompozit  $\beta$ -SiAlON/TiN, ktorého merný odpor je vhodný pre jeho opracovanie metódou EDM.