



## Preparation and properties of $\beta$ -SiAlON/ZrN nano-composites from ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder

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### Abstract

*In this study we report on the preparation and properties of  $\beta$ -SiAlON/ZrN electro-conductive nano-composites from ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder. The silicon nitride powder was coated with nano-sized zirconia particles by the precipitation of ZrO<sub>2</sub> from a zirconium acetate solution using urea as the precipitating agent. For the preparation of sintered  $\beta$ -SiAlON/ZrN composites two different approaches were used. In the first one the ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder was mixed with the appropriate sintering additives (Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub> and AlN) and reaction sintered, while in the second approach the coated powder was first calcined at 1600°C to prepare ZrN-coated Si<sub>3</sub>N<sub>4</sub> powder that was subsequently mixed with the sintering additives and sintered. For comparison, composites with the same composition were also prepared by mixing Si<sub>3</sub>N<sub>4</sub> and ZrO<sub>2</sub> powders with sintering additives and sintered. During the thermal treatment and/or sintering of the Si<sub>3</sub>N<sub>4</sub>/ZrO<sub>2</sub>/AlN powder mixtures zirconia reacts with silicon nitride and aluminium nitride to form zirconium nitride. However, during sintering the agglomeration and grain growth of small, nanometric ZrN particles occurs. Despite the fact that the samples were sintered at atmospheric pressure they are dense, have relatively good flexural strengths and are electrically conductive.*

*Keywords:*  $\beta$ -SiAlON/ZrN, reaction sintering, nanocomposites, mechanical/electrical properties

### 1. Introduction

SiAlON ceramics (silicon aluminium oxynitrides) have been developed during the last decade mainly because of their outstanding high-temperature mechanical and thermal properties [1]. Their high toughness and high wear resistance combined with good chemical stability offer the potential for many commercial and functional applications [2]. SiAlONs can be produced by the reaction sintering of a mixture including the appropriate amounts of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, AlN, Al<sub>2</sub>O<sub>3</sub> and a suitable sintering additive (i.e., Y<sub>2</sub>O<sub>3</sub>). To obtain the fully dense ceramic with a uniform microstructure, pressure sintering is essential. The reason for this is the low diffusion coefficient of these highly covalently bonded materials and because of the high partial pressure of Si<sub>(g)</sub>/SiO<sub>(g)</sub> at temperatures higher than 1500°C [3,4]. These composite materials are interesting because of their multifunctionality, in particular their variable elec-

trical conductivity, obtained by the addition of electrically conductive phases. Due to their good mechanical and electrical properties, and their good oxidation and corrosion resistance, these materials are attractive for cutting-tool applications, glow plugs for diesel engines, ceramic heaters, igniters, etc. [5].

Generally, most composite materials contain a dispersed second phase, which is formed as a result of the direct addition of secondary particles. The most commonly used second phases are nitrides (TiN, ZrN), borides (TiB<sub>2</sub>, ZrB<sub>2</sub>) and carbides (TiC), which have an electrical resistivity in the range  $1.4\text{--}5.3 \times 10^{-5} \Omega\cdot\text{cm}$ . This novel type of composite has two main advantages: the first is the possibility of using electrical discharge machining (EDM) [6] to produce complex shapes, the second is the availability of materials appropriate for high-temperature heaters and igniters. In general, the electrical conductivity of these materials is highly dependent on the size and a suitable amount of conductive particles. A preferable alternative is the in-situ composite method, which can result in a homogenous distribution of electrically conductive second phase [7].

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In this paper we report on the preparation of  $\beta$ -SiAlON/ZrN electro-conductive nano-composites from ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder by using the homogenous precipitation method. The idea was to obtain an electrically conductive network of ZrN nano-particles around the larger Si<sub>3</sub>N<sub>4</sub> grains. Two different experimental approaches were investigated: 1) the ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder (with sintering additives) was reaction sintered to  $\beta$ -SiAlON/ZrN and 2) the ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder was thermally treated to form ZrN-coated Si<sub>3</sub>N<sub>4</sub> powder that was subsequently mixed with the sintering additives and sintered to form a  $\beta$ -SiAlON/ZrN composite. For comparison particulate composites with the same composition were prepared by mixing Si<sub>3</sub>N<sub>4</sub> and ZrO<sub>2</sub> powders with sintering additives and sintered. The microstructure, mechanical properties and electrical conductivity of the composites were also analysed.

## II. Experimental Details

For the preparation of zirconia-coated Si<sub>3</sub>N<sub>4</sub> powder (with 10 wt% of ZrO<sub>2</sub>, which roughly corresponds to 10 wt% of ZrN in the final sample) the following starting materials were used: Si<sub>3</sub>N<sub>4</sub> powder UBE SN-E10 (SKW, Germany), zirconium acetate solution – Zr (CH<sub>3</sub>COO)<sub>2</sub> (Swinton Manchester, Great Britain), urea – CH<sub>4</sub>N<sub>2</sub>O (Kemika, Croatia) and distilled water. The concentration of the zirconium acetate solution was 0.5 mol/l. Urea was used as the precipitating agent and the molar ratio of the zirconium acetate solution to the urea was 1: 2 [8]. The preparation process was as follows. First, the zirconium acetate and urea solution was prepared and mixed with the Si<sub>3</sub>N<sub>4</sub> powder. The mixture was then heated to 95°C for 20 minutes under a saturated vapour pressure. The obtained precipitate was filtered, washed with distilled water and dried at room temperature (25°C) for 24 h. The powder was subsequently thermally treated at 450°C for 2 h in air and finally zirconia-coated Si<sub>3</sub>N<sub>4</sub> powder was obtained.

The sintering additives to form the SiAlON matrix phase were: AlN powder Grade C (H.C. Starck, Germany), Al<sub>2</sub>O<sub>3</sub> powder A-16 (Alcoa, USA) and Y<sub>2</sub>O<sub>3</sub> powder Grade fine (H.C. Starck, Germany).

In the first approach (1) the ZrO<sub>2</sub>-coated Si<sub>3</sub>N<sub>4</sub> powder was mixed with the sintering additives (2.2 wt% AlN, 5.5 wt% Y<sub>2</sub>O<sub>3</sub> and 8.4 wt% Al<sub>2</sub>O<sub>3</sub> with respect to the Si<sub>3</sub>N<sub>4</sub> powder), homogenised and sintered at 1850°C for 2 h in flowing N<sub>2</sub>. This material was denoted as Sample A I. In the second approach (2) the coated Si<sub>3</sub>N<sub>4</sub> powder was first calcined at 1600°C for 2 hours in flowing nitrogen to prepare ZrN-coated Si<sub>3</sub>N<sub>4</sub> powder, which was subsequently mixed with the same sintering additives as above, homogenised and sintered at 1850°C for 2 h in flowing N<sub>2</sub>. This material was denoted as Sample A II. For comparison, particulate composites with the same composition were also prepared by mixing Si<sub>3</sub>N<sub>4</sub>, zirconia powder (TZ-O, Tosoh, Japan) and the same sinter-

ing additives, which are necessary to form the SiAlON matrix phase. This powder mixture was homogenized and reaction sintered at 1850°C for 2 h in flowing N<sub>2</sub>. This material was denoted as Sample B.

The ZrO<sub>2</sub>- and ZrN-coated Si<sub>3</sub>N<sub>4</sub> powders and  $\beta$ -SiAlON/ZrN composites were examined using X-ray powder diffraction (D4 Endeavor, Bruker-AXS, Germany). The morphology and composition of the coated Si<sub>3</sub>N<sub>4</sub> powders were observed with a transmission electron microscope (JEM-2010F and JEM-2100, Jeol, Japan). The microstructure of the dense  $\beta$ -SiAlON/ZrN composites was examined with a scanning electronic microscope (SEM, Jeol-5800, Japan). The densities of the sintered samples were determined with the Archimedes method. The bending 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 cross-head speed of 1 mm/min. The size of bodies for strength tests had the following dimensions 2.3 mm × 3.9 mm × 38.5 mm. The resistivity of the sintered materials with dimension of 2.3 mm × 3.9 mm × 19.2 mm was measured on Multimeter 3457A testing machine (HP, USA) using four-probe measurements at room temperature (25°C) with a direct current.

## III. Results and Discussion

Figure 1 shows the XRD spectra of the zirconia-coated Si<sub>3</sub>N<sub>4</sub> powder after calcination at 450°C for 2 h in air (sample A) and at 1600°C for 2 h in flowing nitrogen (sample B). The results indicate that in sample A some crystalline zirconia (orthorhombic) is present in the powder mixture together with  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>, while in sample B the crystalline ZrN (cubic) was observed in addition to the signals of  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>.

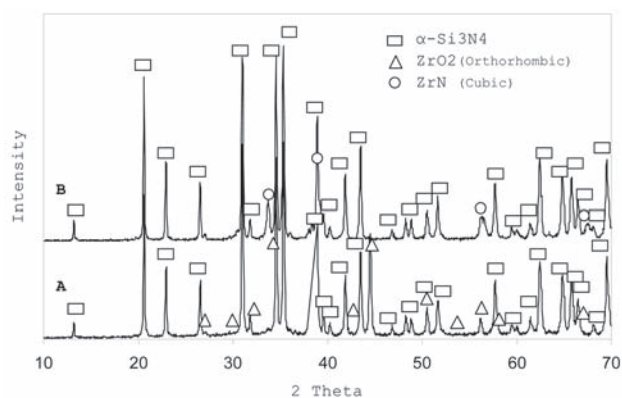


Figure 1. X-ray diffraction pattern of zirconia coated Si<sub>3</sub>N<sub>4</sub> powder after calcination at A) 450°C for 2 h in air and B) 1600°C for 2 h in flowing nitrogen

These results indicate that the zirconia reacted with Si<sub>3</sub>N<sub>4</sub> to form ZrN during the heat treatment at 1600°C for 2 h in flowing nitrogen. The reaction is as follows [9–11]:

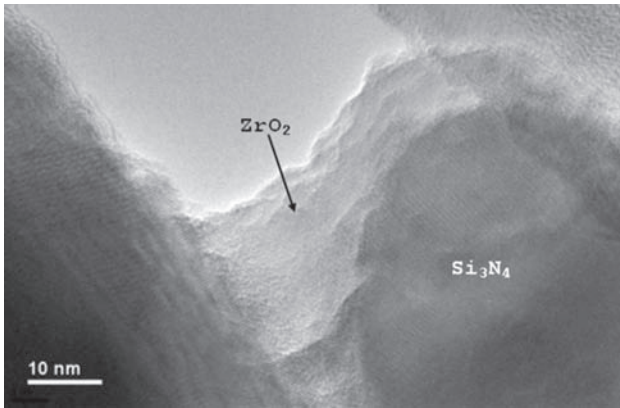


Figure 2. TEM micrograph of Si<sub>3</sub>N<sub>4</sub> particles coated by nano-sized zirconia after calcinations at 450°C for 2 h in air

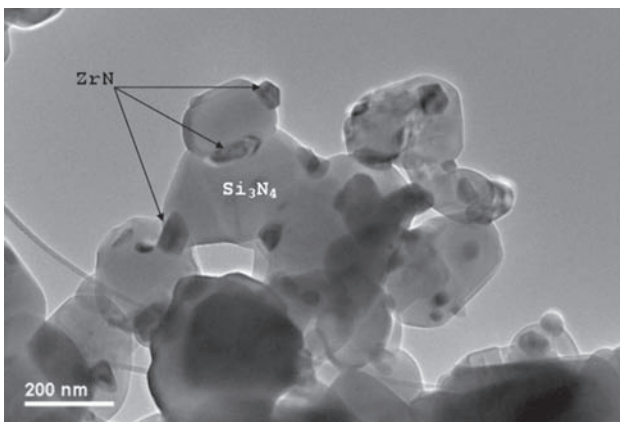
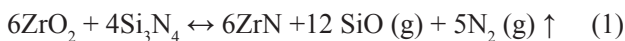
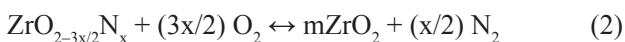


Figure 3. TEM micrograph of Si<sub>3</sub>N<sub>4</sub> particles coated by nano-sized ZrN particles after heat treatment or calcinations at 1600°C for 2 h in flowing N<sub>2</sub>



The thermodynamic compatibility of the zirconia/ $\beta$ -Si<sub>3</sub>N<sub>4</sub> couple has been investigated extensively and the reaction 1 has been proposed to occur under reducing conditions at temperatures above 1600°C [12]. In our case the Si<sub>3</sub>N<sub>4</sub> particles coated by nano-sized zirconia transformed to ZrN-coated Si<sub>3</sub>N<sub>4</sub> powder at 1600°C. According to the literature, ZrN or related ZrON can easily oxidize at temperatures between 600–800°C, to prepare monoclinic zirconia [12]. The oxidizing process takes place according to the following reaction:



The morphology and a small amount of grain boundary phase from the ZrO<sub>2</sub>- and ZrN-coated powders analysed with the TEM is presented in Figs. 2 and 3. From Fig. 2 it is clear that the silicon nitride particles are covered with small, nanometric particles of zirconia. It is difficult to determine whether the whole silicon nitride particle is completely covered with zirconia, but we did not observe the existence of microcracks along the orthorhombic zirconia/ $\alpha$ -Si<sub>3</sub>N<sub>4</sub> grain boundary.

This powder was subsequently heat treated at 1600°C for 2 h in nitrogen. The TEM analysis of the powder is presented in Fig. 3. The presence of small ZrN particles on the surface of the Si<sub>3</sub>N<sub>4</sub> was confirmed. During the nitriding of the ZrO<sub>2</sub> the particles coarsened due to the agglomeration and sintering, and their size varies from 40–60 nm.

The EDXS spectrum of the zirconia layer on the Si<sub>3</sub>N<sub>4</sub> particle is shown in Fig. 4. In this case the presence of Zr, O, N, and Si was detected, confirming that the particles are really ZrO<sub>2</sub> and not just silica, present due to the oxidation of Si<sub>3</sub>N<sub>4</sub> in air. In Fig. 5 the same analysis of the powder after the thermal treatment at 1600°C in nitrogen is presented. In this case only the signals of Zr, N and Si are detected, confirming the transformation of ZrO<sub>2</sub> to ZrN. In both cases the presence of Ni was also detected; this was due to the grid on which the powder was analysed.

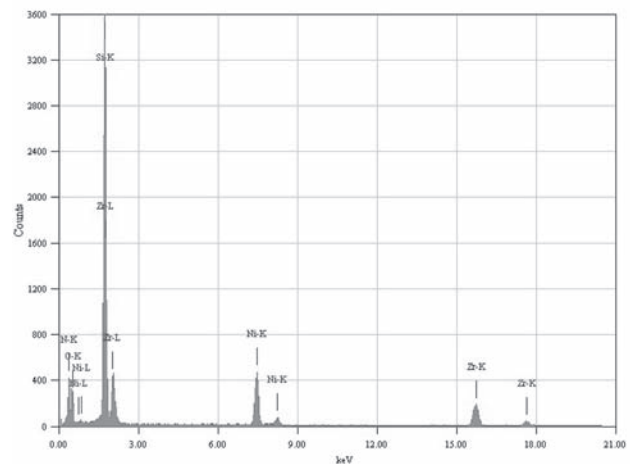


Figure 4. EDXS analysis of Si<sub>3</sub>N<sub>4</sub> particle coated by nano-sized zirconia after calcinations at 450°C for 2 h in air

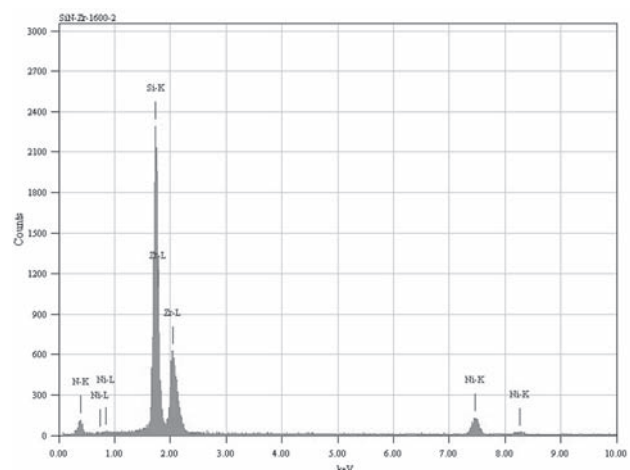


Figure 5. EDXS spectrum of nano-sized ZrN particle coated on the surface of Si<sub>3</sub>N<sub>4</sub> after heat treatment or calcinations at 1600°C for 2 h in flowing N<sub>2</sub>

The Si<sub>3</sub>N<sub>4</sub> powder coated with nano-sized zirconia particles was sintered to a relatively dense  $\beta$ -SiAlON/

ZrN composite (sample A I) with the addition of sintering additives. AlN, yttria and alumina were chosen because we wanted to form a SiAlON matrix, which has the general composition  $\text{Si}_{6-x}\text{Al}_x\text{O}_x\text{N}_{8-x}$ , with  $0 \leq x \leq 4.2$  [13]. This process is, in some ways, similar to the Kingery model of liquid-phase sintering. Due to the presence of aluminium as the oxide additive, more complex reactions occur, which partitioned the grain boundary from the amorphous matrix to produce the substituted form of  $\beta\text{-Si}_3\text{N}_4$ , named  $\beta\text{-SiAlON}$ .

Figure 6 shows microstructures of this composite material (sample A I) at low and high magnifications. The darker elongated grains are the  $\beta\text{-SiAlON}$  matrix and the brighter-white grains are ZrN particles with a particle size of around 1.0–1.5  $\mu\text{m}$ . In between the  $\beta\text{-SiAlON}$  grains is the easily observable, brighter, transient liquid phase. The bright ZrN particles were also analysed by EDXS, and the results, indicating the pres-

ence of Zr and N. We found that during the reaction sintering the agglomeration and/or sintering of the zirconia and ZrN particles occurred.

The SiAlON grains surrounding the ZrN grains often appeared as prismatic and faceted, while the ZrN had a rounded irregular morphology. From these results it can be concluded that some zirconia grains participated in the formation of the transient liquid phase and actually represent a sintering aid [14].

The electrical resistivity of this composite material was also measured. Both dense  $\beta\text{-SiAlON/ZrN}$  composites (sample A I and A II) are electrically conductive. The material A I reached a relatively high electrical conductivity ( $0.017 \Omega^{-1}\text{cm}^{-1}$ ) in comparison with the composite A II ( $6.55 \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$ ). The reason why the material A II has a lower electrical conductivity is because of the conductive particles and the distances between them, the morphology, the particles distribution

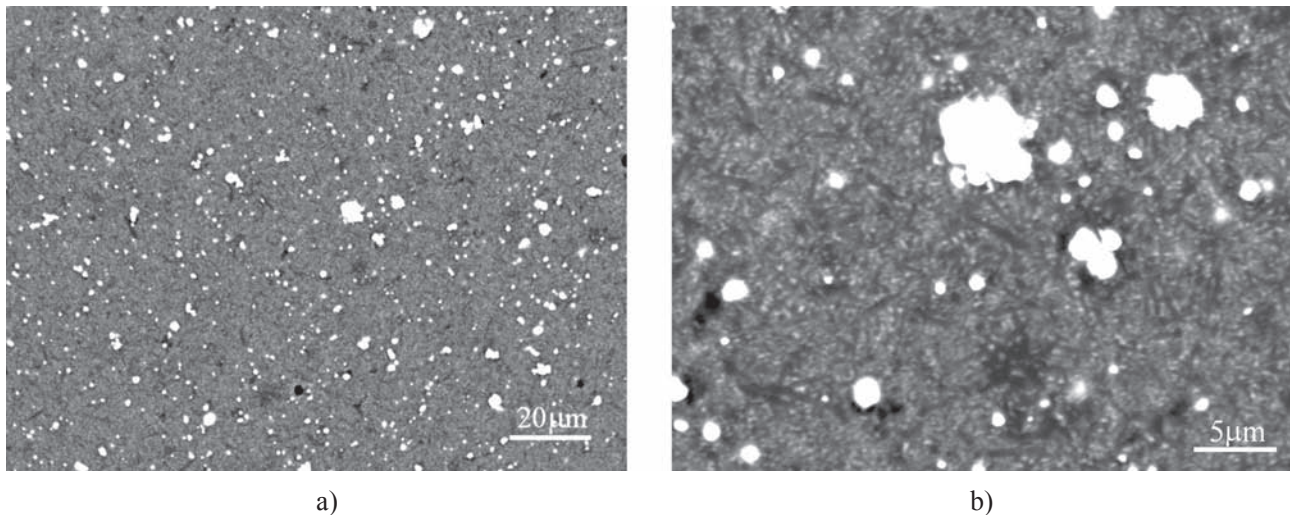


Figure 6. Backscattered electron micrograph of the  $\beta\text{-SiAlON/ZrN}$  composite reaction sintered from zirconia-coated  $\text{Si}_3\text{N}_4$  powder at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$ : a) lower magnification and b) higher magnification

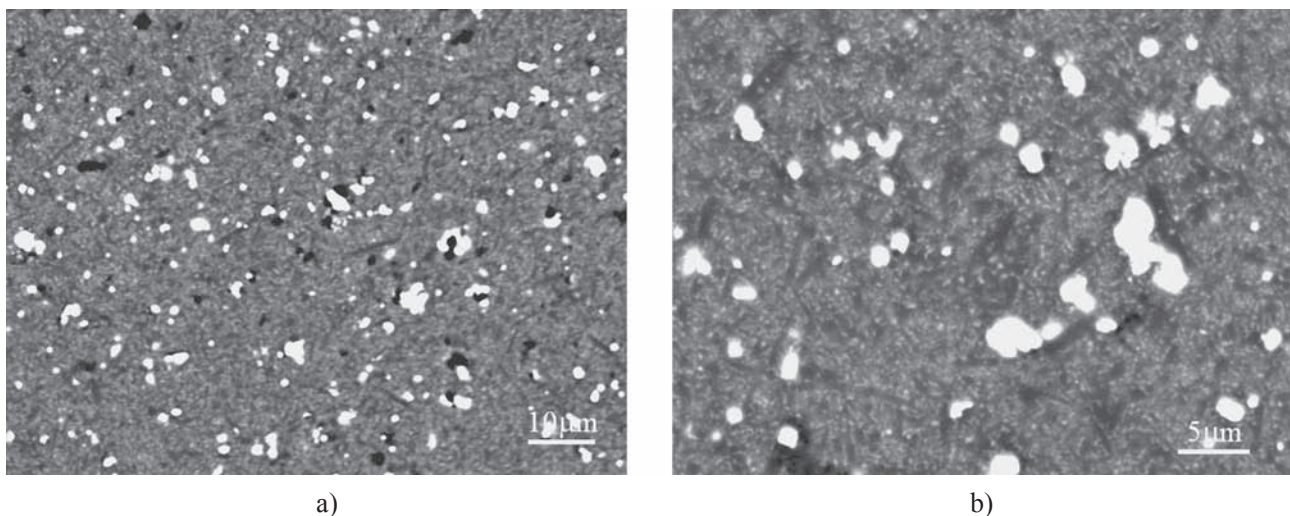


Figure 7. Backscattered electron micrographs of the  $\beta\text{-SiAlON/ZrN}$  composite produced by reaction sintering from ZrN-coated  $\text{Si}_3\text{N}_4$  powder at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$ : a) lower magnification and b) higher magnification

and their size. From these results it can be concluded that the lower electrical conductivity of material A II is a consequence of the grain growth, the sintering and the possible agglomeration of ZrN particles during the sintering process. Furthermore, we must also consider that these composites had only 10 wt% of conductive phase, which is not enough to exceed the percolation threshold if the particles are too big. It is obvious that the reaction sintering of zirconia-coated  $\text{Si}_3\text{N}_4$  powder did not result in a composite with very small, nanometric ZrN particles arranged around the  $\text{Si}_3\text{N}_4$  grains, which would increase the electrical conductivity.

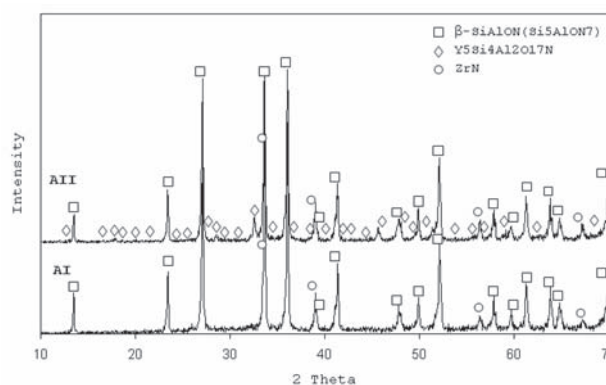
According to the reaction (equation 2) that occurs during the reaction sintering of such a  $\beta\text{-SiAlON/ZrN}$  composite, gaseous species were formed. Because of this the density of the final material can be lower. However, if the zirconia particles are smaller this reaction can occur faster in the initial stage of sintering and consequently the density of the material will decrease. This probably happened in the material denoted as Sample A I.

The reason why the second approach was introduced was to prevent the formation of gaseous species during the reaction sintering and to stop the grain growth and agglomeration and/or the sintering of the zirconia particles. In this approach the  $\text{ZrO}_2$ -coated powder was pre-reacted to form  $\text{Si}_3\text{N}_4$  powder coated with nano-sized ZrN particles, which was subsequently sintered with sintering additives to a higher density.

The backscattered electron micrographs of the  $\beta\text{-SiAlON/ZrN}$  composite produced by sintering from the ZrN-coated  $\text{Si}_3\text{N}_4$  powder at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$  are shown in Fig. 7. The large, brighter ZrN particles can be observed in between the elongated  $\beta\text{-SiAlON}$  particles. The ZrN particles had an irregular shape and were distributed inhomogeneously in the SiAlON matrix. It is clear that the transient liquid phase is in between the  $\beta\text{-SiAlON}$  particles. The particle size of the ZrN particles is the same as in the case of the sample A I. The brighter ZrN particles were analysed by EDXS, which revealed the presence of Zr and N.

Even with the second approach we were not able to prepare composites that have nanometric ZrN particles around the larger  $\beta\text{-SiAlON}$  grains to form an electrically conductive network. From these results we can conclude that the ZrN particles are also sintering during the sintering of the SiAlONs. One of the possible solutions to overcome this problem would be to sinter under a high pressure of nitrogen, where lower temperatures can be applied and the grain growth is reduced. However, in this case the reaction between the  $\text{ZrO}_2$  and  $\text{Si}_3\text{N}_4$ , which is associated with  $\text{N}_2$  gaseous evolution, will be diminished due to Le Chatelier's principle and the formation of ZrN will be prevented [12].

Figure 8 shows the XRD analysis of the reaction-sintered  $\text{ZrO}_2$  – (sample A I) and ZrN-coated (sample A II)  $\text{Si}_3\text{N}_4$  powder after  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$  to produce  $\beta\text{-SiAlON/ZrN}$  composites. The peaks of  $\text{ZrO}_2$  could not be found in any of the two samples (A I and A II), and it can be concluded that the transformation to ZrN is complete above  $1600^\circ\text{C}$  [15]. The results show that in sample A I we can observe the  $\beta\text{-SiAlON}$  matrix, which is also true for sample A II; however, another  $\beta\text{-SiAlON}$  phase was also detected in this sample.



**Figure 8.** X-ray diffraction pattern of  $\beta\text{-SiAlON/ZrN}$  composite produced by reaction sintering from  $\text{ZrO}_2$ -coated  $\text{Si}_3\text{N}_4$  powder (sample A I) and from ZrN-coated  $\text{Si}_3\text{N}_4$  powder (sample A II) at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$

The flexural strength of sample A I was 460 MPa, which is significantly higher than the 370 MPa of sample A II. The reason for this is the slightly higher density of sample A I ( $3.23 \text{ g/cm}^3$ , which roughly corresponds to a relative density of 93 % theoretical density (%TD)) compared to sample A II ( $3.15 \text{ g/cm}^3$ , which roughly corresponds to a relative density of 89 %TD).

In order to compare the grain growth, agglomeration and sintering of the  $\text{ZrO}_2$  and ZrN particles in the mixture, a  $\beta\text{-SiAlON/ZrN}$  composite with the same composition was fabricated by mixing  $\text{Si}_3\text{N}_4$  and zirconia powders (sample B). Large, brighter ZrN particles can be seen from the secondary-electron micrographs (Fig. 9) in between the elongated  $\beta\text{-SiAlON}$  grains. The composition was examined using XRD analysis, which revealed the presence of ZrN and  $\beta\text{-SiAlON}$  phases (Fig. 10). This was also confirmed by the EDXS analysis, which exhibited peaks of Zr, N, O, Si and Al. Dense  $\beta\text{-SiAlON/ZrN}$  composites were obtained (sample B) with an average density of  $3.32 \text{ g/cm}^3$  (which roughly corresponds to a relative density of 95 %TD), which is considerably higher than that of samples A I and A II, produced by the reaction sintering of zirconia- and ZrN-coated  $\text{Si}_3\text{N}_4$  powder. The reason for the higher density of this composite is however not yet completely clear. The flexural strength of such composites was 550 MPa, which is higher in comparison to samples A I and A II. The reason for the higher flexural strength of material B

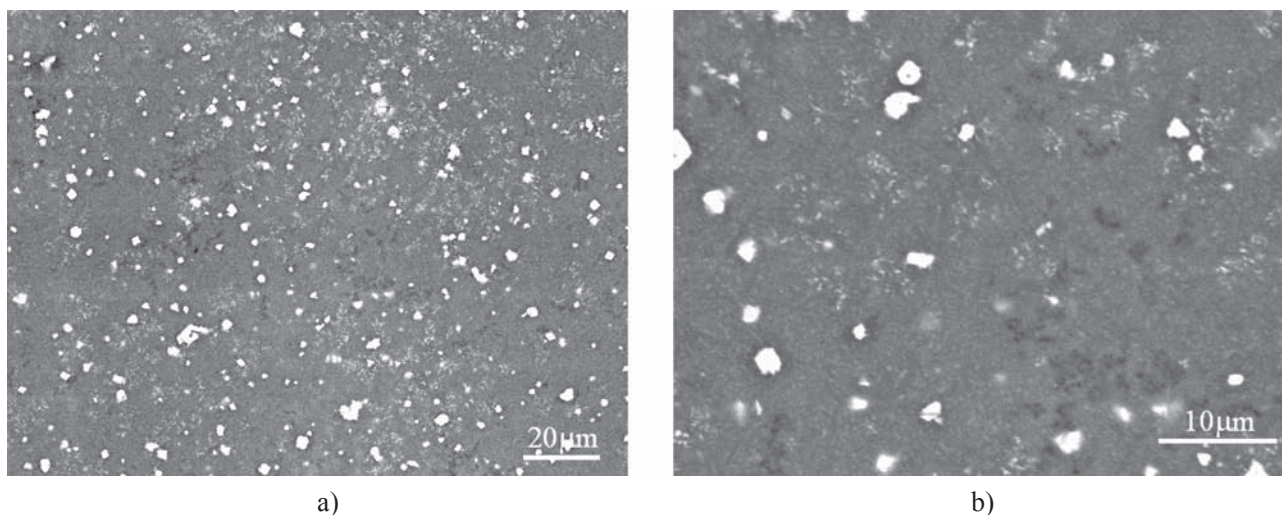


Figure 9. Secondary electron image of  $\beta$ -SiAlON/ZrN composite produced by reaction sintering from mixing of  $\text{Si}_3\text{N}_4$  and  $\text{ZrO}_2$  powders with sintering additives (to form the SiAlON matrix) at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$ : a) lower magnification and b) higher magnification

is the higher density ( $3.32 \text{ g/cm}^3$ ) compared to samples A I ( $3.23 \text{ g/cm}^3$ ) and A II ( $3.15 \text{ g/cm}^3$ ).

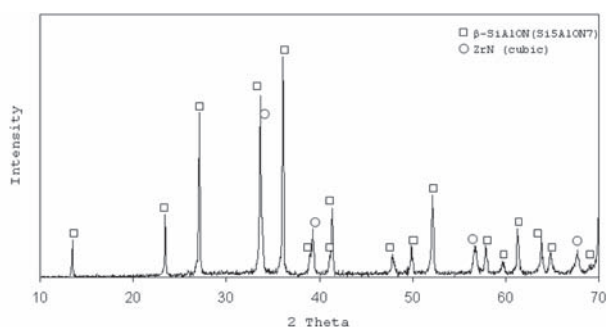


Figure 10. X-ray diffraction pattern of the  $\beta$ -SiAlON/ZrN composite (sample B) produced by reaction sintering at  $1850^\circ\text{C}$  for 2 h in flowing  $\text{N}_2$

The electrical conductivity of this composite (sample B) was relatively high, around  $0.6 \Omega^{-1}\text{cm}^{-1}$ . This result is comparable [16] to the  $\text{ZrN/Si}_3\text{N}_4$  composites reported in the literature, which reached an electrical conductivity in the range from  $10^{-1}$  to  $10^{-5} \Omega^{-1}\text{cm}^{-1}$ . These  $\text{ZrN/Si}_3\text{N}_4$  composites were obtained by the reaction of transition-metal silicides,  $\text{TiSi}_2$ ,  $\text{ZrSi}_2$  and  $\text{Ti}_5\text{Si}_3$ , with nitrogen gas in the temperature range between  $700$ – $1500^\circ\text{C}$ .

#### IV. Conclusions

The results of our investigation show that dense  $\beta$ -SiAlON/ZrN ceramic composites can be prepared by the in-situ reaction sintering of  $\text{ZrO}_2$  and  $\text{Si}_3\text{N}_4$  and/or AlN in the starting-powder mixtures either by the addition of zirconia powder to the starting powder mixture or by using the zirconia coated silicon nitride powder, prepared by the gel-precipitation method. The flexural strength of these composites is comparable to the

strength of similar ceramic composites not produced by the reaction sintering. All of the composites are also electrically conductive, however the conductivity of the materials prepared from the coated silicon nitride powder is lower than was expected. The reason for this is the amount of the secondary conductive phase and the microstructure of the samples. Namely, during the reaction sintering the agglomeration and grain growth of the zirconia and/or ZrN particles occurred. Due to this the conductive network of very small ZrN particles around larger  $\text{Si}_3\text{N}_4$  grains was lost. To preserve the ZrN conductive network hot pressing or gas pressure sintering at lower temperatures should be applied and investigated in more detail.

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