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β-SiAlON/TiN nanocomposites prepared from TiO_2-coated Si_3N_4 powder

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Abstract

In this study the fabrication of β-SiAlON/TiN nanocomposites by sintering Si_3N_4 powder coated with nanosized titania or TiN particles was studied. The TiO_2 coating on the Si_3N_4 powder was prepared by the sol–gel method from tetra-butyl titanate. Two approaches were used for the preparation of the β-SiAlON/TiN composites: the first was the reaction sintering of TiO_2-coated Si_3N_4 powder, and the second was the calcination of the coated Si_3N_4 powder and subsequent sintering. The results show that during the thermal treatment and/or sintering of the coated Si_3N_4 powder the titania reacts with the Si_3N_4 to form TiN. However, during sintering the segregation and densification of small, nanometric TiN particles occurs. Despite the fact that the samples were prepared from relatively cheap starting materials and were sintered at atmospheric pressure they have high densities and relatively good bending strengths.

Keywords: β-SiAlON/TiN; Powders–solid state reaction; Nanocomposites; Mechanical properties

1. Introduction

In the past two decades much attention has been devoted to the production of particulate reinforced materials, because of their improved toughness and strength as well as their mechanical reliability.[1,2] Another potential advantage of such composite materials is their multifunctionality, in particular their variable electrical conductivity, obtained by the addition of electrically conductive phases. Due to their excellent mechanical properties and good oxidation and corrosion resistance, such materials are interesting for the applications where electrically conductive components are needed, for example, glow plugs, heaters, igniters, etc. Another advantage of electrically conductive materials is that they can be shaped using electrical discharge machining (EDM), not only by conventional tools; such tools can be problematic due to the materials' hardness and wear resistance.[3] Increased attention has been devoted to particulate additions for the production of structural Si_3N_4-based ceramics. The development of Si_3N_4 and SiAlON composites with an electrically conductive secondary phase, e.g., TiN, TiC or TiCN, has been considered for some specific applications.[4,5] TiN, in particular, exhibits a number of desirable properties, including high hardness, good chemical durability and high electrical conductivity, as well has good compatibility with Si_3N_4. Si_3N_4–TiN composites have also received a lot of attention due to their compatibility with EDM.[6]

Usually, ceramic composites are prepared by the addition of a second phase to the powder mixture, the homogenisation of the constituents, and densification. Composites prepared using this method sometimes have poor mechanical and electrical properties due to relatively large second-phase particles and/or their agglomeration. Also, to achieve a desirable electrical conductivity the percolation threshold, which when starting with large second-phase particles is around 25–30 vol.% of the conductive phase, must be reached. Such a relatively large amount of secondary phases can, however, lead to poor sinterability of the system. A good, alternative method is the in situ composite method, where the conductive phase is formed by reaction sintering, which can result in a homogenous distribution of the electrically conductive phase with a small particle size. This can also lead to a decrease in the percolation threshold for the electrical conductivity.[7–9]

In this work the preparation of electrically conductive SiAlON–TiN ceramic composites by in situ TiN formation was studied. The idea was that if the particles of TiN were

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small enough they would form an electrically conductive network around the larger Si_3N_4 particles, and so a much smaller amount of the TiN would be needed. Two different approaches were investigated: (a) the TiO_2-coated Si_3N_4 powder (with the appropriate sintering additives) was reaction sintered to β-SiAlON–TiN and (b) the TiO_2-coated Si_3N_4 powder was thermally treated to form TiN-coated Si_3N_4 powder, which was then sintered to form a β-SiAlON–TiN composite. The microstructures and mechanical properties of such composites were also investigated.

2. Experimental

For the preparation of titania-coated Si_3N_4 powder (with 10 wt.% of TiO_2, which roughly corresponds to 10 wt.% of TiN in the final sample) the following starting materials were used: SILZOT HQ Si_3N_4 powder (SKW, Germany), tetra-butyl titanate (Sigma–Aldrich Chemie, Germany), anhydrous ethanol (Carlo Erba Reagenti, Italy) and distilled water. The Si_3N_4 powder and tetra-butyl titanate were mixed in the appropriate ratio and homogenized by ball milling for 2 h using anhydrous ethanol as the liquid medium. After the homogenisation, distilled water was added to the stirred Si_3N_4/tetra-butyl titanate suspension. The final Ti/H_2O molar ratio was then adjusted to 1:150.[7] The tetra-butyl titanate was hydrolyzed to form titania gel on the surface of the Si_3N_4 powder, and the coated Si_3N_4 powder was separated from the mother liquor, and then washed with distilled water and anhydrous ethanol. The cake was dried at 120 °C and calcined at 680 °C for 2 h.

The sintering additives for the formation of the SiAlON matrix phase were as follows: Grade C AlN powder (H.C. Starck, Germany), A-16 Al_2O_3 powder (Alcoa, USA) and Grade fine Y_2O_3 powder (H.C. Starck). In the first approach the TiO_2-coated Si_3N_4 powder was mixed with the sintering additives (2.2 wt.% AlN, 5.5 wt.% Y_2O_3 and 8.4 wt.% Al_2O_3 with respect to the Si_3N_4 powder), homogenised and sintered at 1850 °C for 2 h in flowing N_2. This material is referred to as Sample A. In the second approach the TiO_2-coated Si_3N_4 powder was first calcined at 1200 °C in flowing nitrogen to form TiN-coated Si_3N_4 powder, which was subsequently mixed with the sintering additives (2.2 wt.% AlN, 5.5 wt.% Y_2O_3 and 8.4 wt.% Al_2O_3 with respect to the Si_3N_4 powder), homogenised and sintered at 1800 °C for 2 h in flowing N_2. This material is referred to as Sample B. For comparison, a sample with the same composition was prepared by mixing Si_3N_4, titania powder and the same sintering additives and reaction sintered at 1800 °C for 2 h in flowing N_2. This material is referred to as Sample 0.

The TiO_2- and TiN-coated Si_3N_4 powders were examined by X-ray powder diffraction (D4 Endeavor, Bruker-AXS, Germany) and transmission electron microscopy (JEM-2010F and JEM-2100, JEOL, Japan). The densities of the sintered samples were measured using 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 crosshead speed of 1 mm/min.

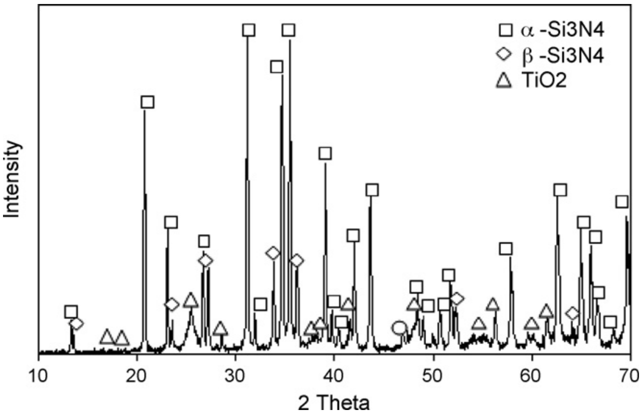

Fig. 1. X-ray diffraction pattern of titania-coated Si_3N_4 powder after calcinaton at 680 °C for 2 h in air.

3. Results and discussion

The XRD analysis of the TiO_2-coated Si_3N_4 powder after calcination at 680 °C for 2 h in air is shown in Fig. 1. The results show that crystalline titania (brookite phase) is present in the powder mixture. The morphology of the coated powder analysed by TEM is presented in Fig. 2. It is clear that the silicon nitride particles are completely covered with small, nanometric particles of titania. The TiO_2 particle size is relatively uniform and is around 10 nm. These results are in accordance with the results of Gao et al., who used the same method for the preparation of TiO_2-coated Si_3N_4 powders.[7]

The Si_3N_4 powder coated with TiO_2 particles was sintered to a reasonably dense β-SiAlON/TiN composite (Sample A) with the addition of sintering additives. AlN, yttria and alumina were chosen because we wanted to form a SiAlON matrix. The microstructure of this composite is presented in Fig. 3, at low and high magnifications. One can see elongated β-SiAlON grains, a brighter, transient liquid phase in between the β-SiAlON grains, and white TiN particles with a size of around 1 μm. The bright TiN particles were also analysed by EDXS, and the results, indicating the presence of Ti and N, are shown in Fig. 4. From

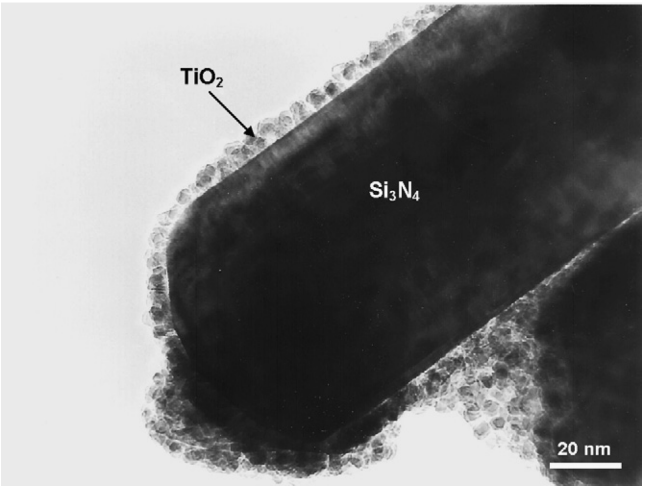

Fig. 2. TEM micrograph of Si_3N_4 particles coated by nano-sized titania powder after calcinaton at 680 °C for 2 h in air.

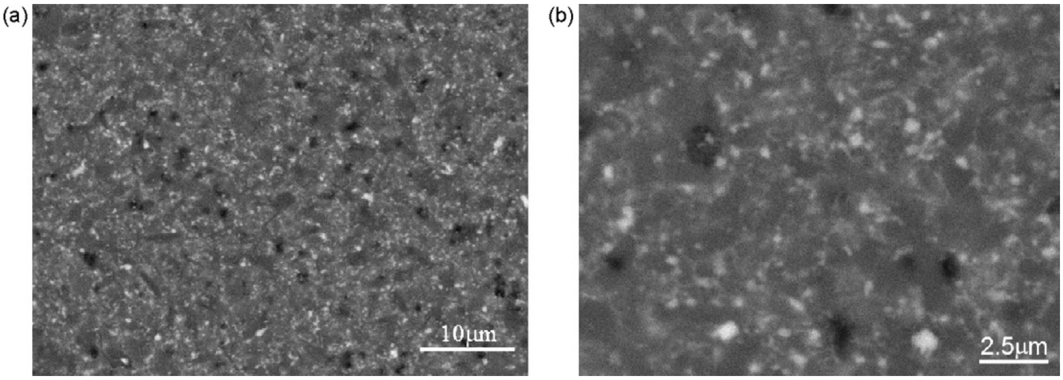

Fig. 3. Microstructure of SiAlON/TiN composite produced by reaction sintering from titania-coated Si_3N_4 powder at 1850 °C for 2 h in flowing N_2: (a) lower magnification; (b) higher magnification.

these results it can be concluded that during the reaction sintering the segregation and/or sintering of titania particles occurred. According to the literature, TiO_2 can take part in the formation of a low-viscosity liquid during the initial stage of sintering,[10] which can also be the reason for the increased particle size, although other authors claim that the conversion of TiO_2 to TiN is finished before the sintering of the Si_3N_4 matrix begins.[7] The electrical conductivity of this composite was relatively low, about $3.0 \times 10^{-4}\,\Omega^{-1}\,m^{-1}$, which is in the same range, i.e., $1.6 \times 10^{-4}\,\Omega^{-1}\,m^{-1}$, as the conductivity of the β-SiAlON/TiN composite with the same composition that was prepared by mixing the Si_3N_4 and titania powders (Sample 0). It is obvious that the reaction sintering of titania-coated Si_3N_4 powder did not result in a composite with very small, nanometric TiN particles arranged around the Si_3N_4 grains that would increase the electrical conductivity.

The flexural strength of Sample A was 420 MPa, which is significantly lower than the 620 MPa of Sample 0. The reason for this is the slightly lower density of Sample A (3.19 g/cm^3) compared to Sample 0 (3.22 g/cm^3).

During the reaction sintering of such SiAlON/TiN composites the following reactions are taking place[9–11]:

$$6TiO_2 + 4Si_3N_4 \rightarrow 6TiN + 12SiO\,(g) + 5N_2\,(g) \tag{1}$$

$$6TiO_2 + 2Si_3N_4 \rightarrow 6TiN + 6SiO_2 + N_2\,(g) \tag{2}$$

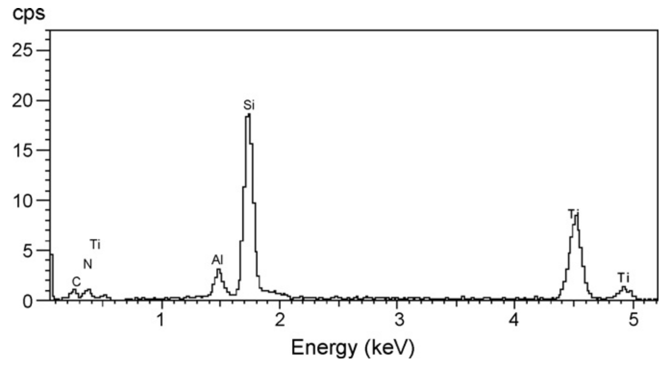

Fig. 4. EDXS analysis of a larger bright grain in the microstructure of SiAlON/TiN composite produced by reaction sintering from titania-coated Si_3N_4 powder.

$$2TiO_2 + 3AlN + 5Si_3N_4 \rightarrow 3Si_5AlON_7 + 2TiN + \tfrac{1}{2}O_2\,(g) \tag{3}$$

$$2TiO_2 + 2AlN \rightarrow 2TiN + Al_2O_3 + \tfrac{1}{2}O_2\,(g) \tag{4}$$

In all of the reactions gaseous species are formed; these can influence the density of the final sample. If the TiO_2 particles are smaller, as is the case in the starting mixture of Sample A, these reactions can occur faster and therefore decrease the density of the material.

In order to avoid the formation of gaseous species during the reaction sintering, and mainly to prevent the segregation and/or sintering of titania particles, the second approach was used. In this case the idea was to pre-react the TiO_2 nanoparticles with the Si_3N_4, to form Si_3N_4 powder coated by TiN particles, which would then sinter to a higher density, producing a composite with fine TiN particles distributed along the SiAlON grains. This was done by heat treatment of the TiO_2-coated Si_3N_4 powder at various temperatures. In Fig. 5, the XRD analyses of the coated powders calcined at 1100, 1200 and 1300 °C for 1 h in flowing N_2 are shown. The reaction of titania with Si_3N_4 starts already at 1100 °C, but at this temperature there is still some TiO_2 present. In the samples heat treated at temperatures of 1200 °C and above

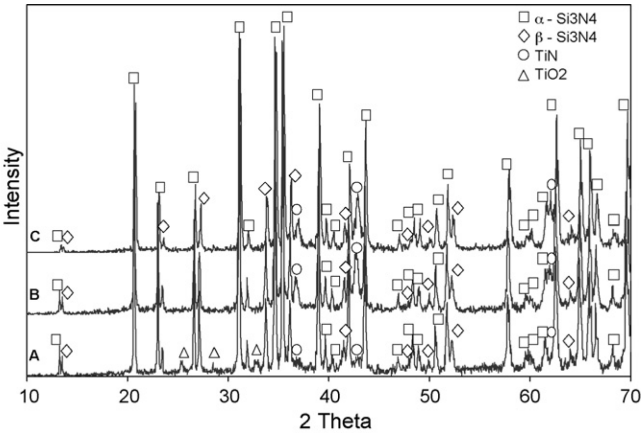

Fig. 5. X-ray diffraction pattern of titania-coated Si_3N_4 powder after calcinaton at 1200 °C for 1 h in flowing N_2.

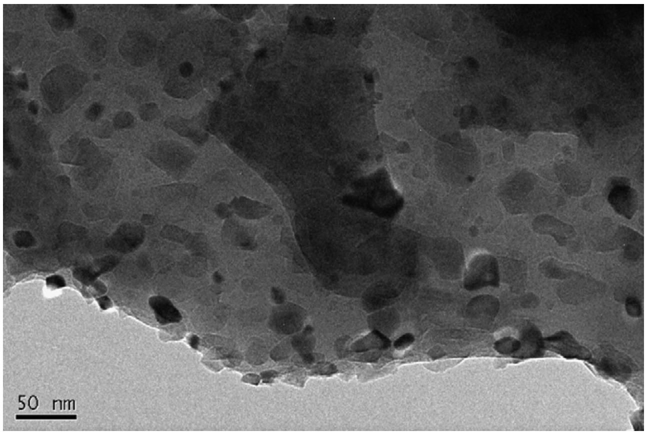

Fig. 6. TEM micrograph of Si_3N_4 particles coated by nano-sized titania powder after calcinaton at 1200 °C for 1 h in N_2.

no peaks of TiO_2 can be detected in the XRD pattern, and it can be concluded that the conversion to TiN is complete. A similar method was used by Gao et al., who calcined the coated powder in the presence of gaseous ammonia, and the conversion was achieved at lower temperatures (900 °C).[7]

The morphology of the powder heat treated at 1200 °C is presented in Fig. 6. Small TiN particles can be seen on the surface of the large Si_3N_4 grains. The size of the particles is from 10 to 30 nm. It appears as if the Si_3N_4 particles are not completely covered with the TiN, as is the case for the TiO_2-coated Si_3N_4 presented in Fig. 2. The reasons for this are twofold: one is the growth of the particles during the reaction, i.e., the TiN particles are larger than the TiO_2 particles, and the second is that the TiN has a higher density than the TiO_2, which results in a lower volume for the TiN phase.

After sintering the TiN-coated Si_3N_4 powder with the sintering additives, dense β-SiAlON/TiN composites were obtained (Sample B) with a nominal density of 3.25 g/cm^3, which is higher than that of Sample A, prepared by the reaction sintering of TiO_2-coated Si_3N_4 powder. The microstructure of Sample B is presented in Fig. 7. Again, large TiN particles can be observed in between the elongated β-SiAlON particles. The composition was analysed by EDXS, which revealed the presence of Ti and N (Fig. 8).

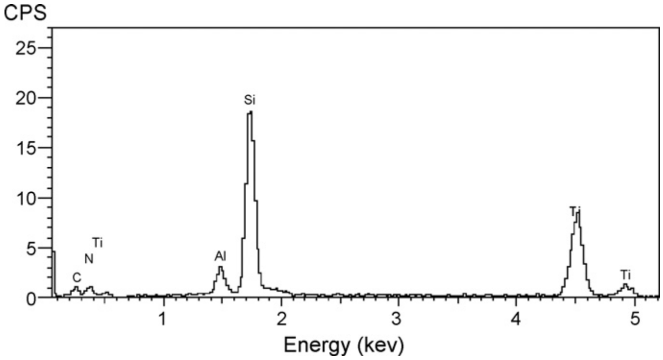

Fig. 8. EDXS analysis of a larger bright grain in the microstructure of SiAlON/TiN composite produced by sintering of TiN-coated Si_3N_4 powder.

Even with the pre-reacted, coated Si_3N_4 powders that already contain TiN particles on the surface, we were not able to obtain composites on the nanoscale, i.e., to get very small, nanometric TiN particles around the larger, Si_3N_4 grains, forming an electrically conductive network. The reason for such behaviour is not yet completely understood, but it is clear that TiN particles on their own are not easy to sinter, especially without the application of pressure. However, it has been reported that if the particles are very small, they have the potential for pressureless sintering.[12] Ueno et al. also described particle size growth during the in situ formation of TiN from TiO_2 at temperatures as high as 1850 °C. According to them, agglomerates of freshly formed TiN particles can grow to form one large TiN particle.[7]

In addition to this, on the surface of the TiN-coated Si_3N_4 powder prepared at 1200 °C some traces of liquid phases can be observed (Fig. 9). It was already confirmed that the formation of TiN from TiO_2 in such a system is not complete at 1400 °C.[7] This means that the liquid phase can consist of titania, silica and alumina formed during the reactions, and some other impurities present on the Si_3N_4 powder. After the addition of sintering aids for the formation of SiAlON (AlN, Al_2O_3 and Y_2O_3) these oxides may form a liquid phase that leads to the segregation of TiN particles and possibly also to their sintering to form the larger TiN grains visible in the microstructure of the sintered composite (Fig. 7).

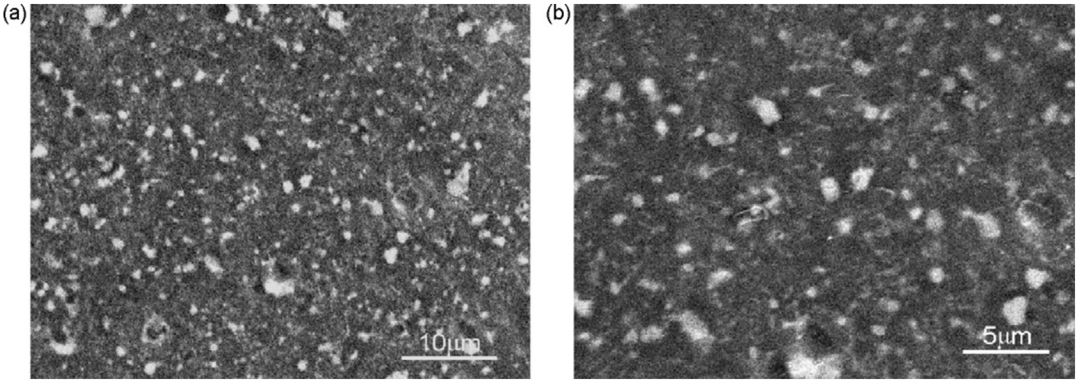

Fig. 7. Microstructure of SiAlON/TiN composite sintered from TiN-coated Si_3N_4 powder at 1850 °C for 2 h in flowing N_2: (a) lower magnification; (b) higher magnification.

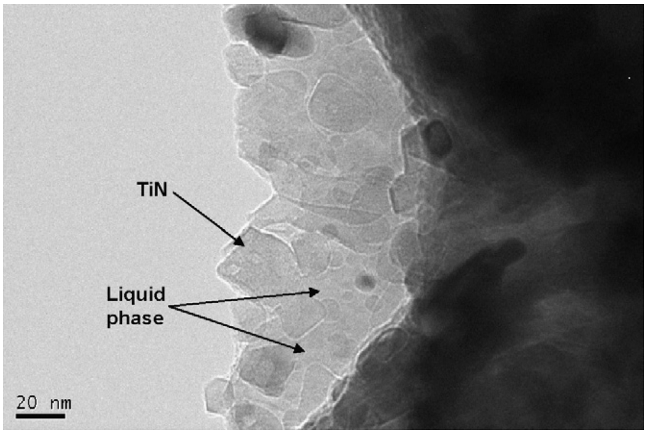

Fig. 9. TEM micrograph of Si_3N_4 particles coated by nano-sized titania powder after calcinaton at 1200 °C for 1 h in N_2, showing the presence of the liquid phase between the TiN particles on Si_3N_4 powder surface.

4. Conclusions

It has already been proved that Si_3N_4/TiN composites can readily be prepared by in situ reaction sintering by adding TiO_2 powder to the starting powder mixtures, especially if they also contain some AlN powder. Composites with a high TiN content are, however, often porous and have lower densities due to gaseous reaction products. To avoid this problem, a Si_3N_4 powder coated with nanometric TiO_2 particles was used in this study. This could lead to a homogenous distribution of the TiN phase with a small particle size, distributed around the larger Si_3N_4 particles. The results of our research show that using this approach it is possible to prepare dense β-SiAlON/TiN composites with good mechanical properties. However, the composites do not have the desired microstructures due to the segregation and sintering of small, nanometric TiN particles, which formed in situ on the Si_3N_4 powder surface. This is the case when the composites were prepared by reaction sintering from TiO_2-coated Si_3N_4 powders and also when the composites were sintered from pre-reacted TiN-coated Si_3N_4 powders.

Acknowledgement

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