Journal of the Ceramic Society of Japan 116 [7] 812-814 2008 **Paper**

A novel approach for preparing electrically conductive α/β SiAlON–TiN composites by spark plasma sintering

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An effective approach for preparing electrically conductive SiAlON–TiN composites have been developed. Granules of a designed composition of α–β SiAlON were obtained by spray drying and coated with varying amounts of TiO_2 powder (0–10 vol%) homogenously by mechanical mixing. Fully dense composites were obtained by spark plasma sintering (SPS) under a pressure of 50 MPa at 1650°C for 5min. According to the scanning electron microscope (SEM) analysis, unique microstructures containing continuously segregated in-situ formed TiN phase in 3D were achieved. Additionally, X-ray diffraction (XRD) studies revealed that all TiO_2 was successfully converted to TiN. The resistivity of the α-β SiAlON (1×10^{11} Ω·m) was drastically reduced down to 2×10^{-4} Ω·m at 5 vol% TiO_2 addition.

Key-words : SiAlON, TiN, Electrical conductivity, SPS, Segregated network

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1. Introduction

Due to the intrinsic properties such as high wear resistance and thermo-mechanical properties, silicon nitride (Si_3N_4) based materials have received considerable amount of attention up to now. Nowadays, researches are also active in broadening the application of these materials. One of the important approaches is to improve the electrical conductivity of these materials in order to employ them as igniters, heating elements and glow plugs. In addition, as long as desired conductivity levels are achieved from Si_3N_4 based composites complex shapes can be produced by applying EDM techniques.[1] In order to achieve high electrical conductivity different methods can be used. The most common method is to introduce highly conductive secondary phases such as nitrides (TiN),[2] carbides (SiC),[3] carbonitrides (TiCN),[4] borides (TiB_2)[5] and silicides ($MoSi_2$)[6] by using composite approach. In order to obtain desired conductivity using this particular approach, high amount of secondary phases (~30 vol%) should be employed. However, densification of these composites with conventional techniques has been found very difficult due to the thermodynamic incompatibility of the incorporated phases. Apart from the densification problem the distribution of the phases was very important for the conductivity.

According to the basic electrical conduction theories such as effective media and percolation, it is possible to obtain low resistivity values by forming a continuous network of conductive particles around insulating matrix particles with very low volume fractions (~0.01 vol%) of conductive particles.[7] Considering these theories, another common approach to achieve electrical conductivity is coating the silicon nitride matrix particles with chemical precursors which promote in-situ formations of conductive particles such as TiN.[8),9] On the other hand, the complexity of the chemical methods and the application of additional heat treatment processes make the possible commercial use of these techniques difficult. Furthermore, the occurrence of gaseous reaction products and the grain growth of nano sized particles at the sintering temperature of Si_3N_4/SiAlON matrix material affects the densification and electrical conductivity, even different sintering methods were employed.[9),10] In this study, spherical α–β SiAlON based granules obtained by spray drying was used. Then the granules were coated with TiO_2 powder in an attempt to form of a segregated network of in-situ formed TiN particles.

2. Experimental procedure

SiAlON granules were supplied by MDA Advanced Ceramics Ltd. (Eskisehir / Turkey). The composition was designed to obtain 25% α-SiAlON / 75% β-SiAlON in the final composition. The investigated composition designated as SN was prepared through attrition milling with de-ionized water as liquid media for 2 h in a polyamide container and Si_3N_4 grinding balls. The slurries were then dried in a spray drier (Nubilosa, Germany) under suitable conditions in order to obtain spherical granules of around 100 μm in diameter. TiO_2 (~0.2–0.8 μm, Merck) powder was used as coating material. For the coating process, both SiAlON granules and TiO_2 powder (0–10 vol%) were put in a plastic container and mixed for 24 h without using any liquid and grinding media. Sintering of the samples was carried out by using a SPS furnace (FCT Systeme GmbH, Germany). Powders were placed in a graphite die of 20 mm in diameter. Sintering was achieved under vacuum with a heating and cooling rate of 100°C/min to the preselected peak temperatures of 1550, 1600 and 1650°C for a holding time of 5 min. A pressure of 50 MPa and pulse timing of 12:2 was applied during the overall sintering process. The temperature was monitored by an optical pyrometer. Relative densities of the samples were determined by the Archimedes method. Phase identification was performed using XRD (Rigaku Rint 2200-Japan) with Ni-filtered Cu Kα radiation. Both granule surfaces before and after coating and polished surfaces of the sintered samples were examined under SEM (FESEM, Supra 50 VP, Zeiss-Germany). Electrical resistivity measurements were carried out by using two probe DC method at room temperature on the disc shape samples. Au electrodes were deposited on the both sides of the samples. The volume

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resistivity of the composites was measured by using a Keithley 6517A Electrometer/High resistance meter.

3. Results and discussion

In order to understand the efficiency of coating process, surfaces of the uncoated and coated granules were observed under SEM (**Fig. 1**). Uncoated granules have a rough surface texture and the primary Si_3N_4 particles are visible (Fig. 1a). However, with the increasing amount of TiO_2 this texture disappears and a homogeneous layer of TiO_2 particles covers the surface of granules (Figs. 1b and 1c). This result was also confirmed by EDX analysis obtained from the coated granule surfaces (Fig. 1d).

A series of sintering trials were carried out with the SN composition in SPS to determine the optimum sintering temperatures of the investigated composites,. These trials showed that it was possible to fully densify the designed α–β SiAlON composition materials at 1600°C. In order to avoid the grain growth of the matrix and the in-situ formed TiN grains, 1650°C was selected as the maximum sintering temperature for the TiO_2 incorporated composites. Selected properties of the sintered composites were shown in **Table 1**.

Representative XRD spectra of the composites are given in **Fig. 2**. The composites mainly contain α-SiAlON, β-SiAlON, and TiN phases. In all the compositions, no evidence of residual TiO_2 was found indicating that TiO_2 phase was fully converted to TiN during sintering. When the TiO_2 amount was increased to 10 vol%, the formation of O-SiAlON phase was detected. The

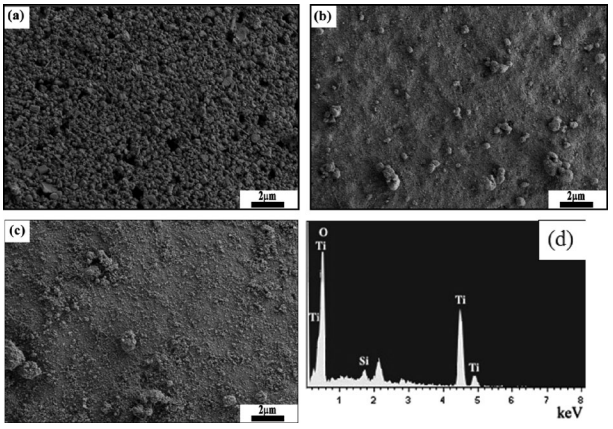

Fig. 1. SEM images of (**a**) uncoated SiAlON granule surface, (**b**) coated with 2.5 vol% TiO_2, (**c**) coated with 10 vol% TiO_2, (**d**) EDX analysis taken from the surface of coated granule.

Table 1. Properties of the Sintered Composites

Composition	Sintering Temperature (°C)	Density (g/cm^3)	Resistivity (Ω·m)
SN	1550	2.93	–
	1600	3.23	~10^{11}
	1650	3.23	~10^{11}
SN–2.5 vol% TiO_2	1650	3.25	9×10^{1}
SN–5 vol% TiO_2		3.26	2.1×10^{-4}
SN–7.5 vol% TiO_2		3.27	1.8×10^{-4}
SN–10 vol% TiO_2		3.27	1.7×10^{-4}

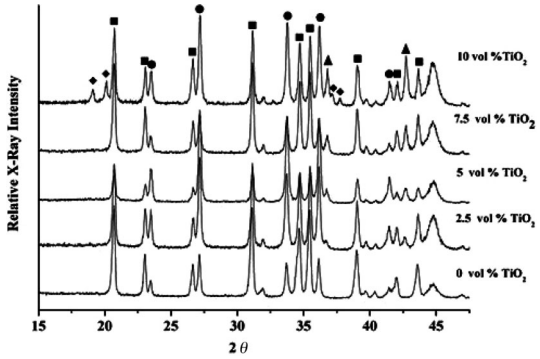

Fig. 2. Representative X-ray diffraction patterns of the sintered samples coated with 0–10 vol% TiO_2. (■: α-SiAlON, ●: β-SiAlON, ▲: TiN, ◆: O-SiAlON).

formation of this phase is thought to be occurred due to increase in the oxygen content of the liquid phase as a result of possible reactions between TiO_2–AlN and TiO_2–Si_3N_4 leading the formation of TiN. The possible reactions were given below.[11),13)]

$$6TiO_2 + 4Si_3N_4 \rightarrow 6TiN + 12SiO_{(g)} + 5N_{2(g)} \quad (1)$$

$$6TiO_2 + 2Si_3N_4 \rightarrow 6TiN + 6SiO_{2(l)} + N_{2(g)} \quad (2)$$

$$2TiO_2 + 3AlN + 5Si_3N_4 \rightarrow 3Si_5AlON_7 + 2TiN + 1/2O_{2(g)} \quad (3)$$

$$2TiO_2 + 2AlN \rightarrow 2TiN + Al_2O_3 + 1/2O_{2(g)} \quad (4)$$

In all reactions above, oxide based products such as SiO_2 and Al_2O_3 form. These products might have an effect on both densification and the phase formation in terms of sintering temperature. SiO_2 may react with Si_3N_4 particles to form Si_2N_2O, and then Al^{+3} may cooperate in for the formation of O-SiAlON phase. Furthermore, low sintering temperatures promote the formation of O-SiAlON phase together with the β-SiAlON. Microstructural investigations revealed that elongated O-SiAlON particles were formed preferentially in the granule boundaries and the reaction zone for the oxygen incorporation can be seen on the SEM images (**Fig. 3**). In the images the bright phase represent the in-situ formed TiN and the gray phase indicates the α-β SiAlON granules. The dark elongated grains represent the O-SiAlON phase. In **Fig. 4** representative SEM images of all the investigated composites are given. It is obvious that in all cases a segregated network of TiN particles were formed successfully. However with the increasing amount of TiO_2 especially above 5 vol%, large clusters of TiN phases formed along the granule boundary which indicates that agglomeration of TiO_2 particles starts during the mixing process above this value. This can be prevented by adjusting the processing conditions.

Electrical resistivity values of the composites as a function of

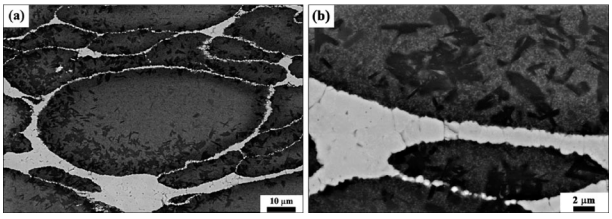

Fig. 3. Representative SEM images of the O-SiAlON grains formed along the granule boundaries (**a**) low magnification (**b**) high magnification.

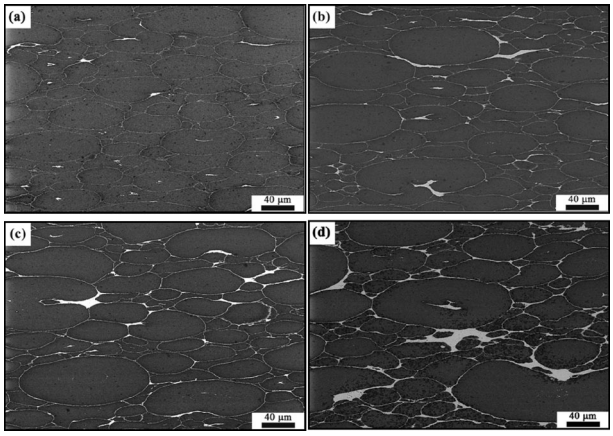

Fig. 4. Representative back scattered images of the investigated composites incorporated with (**a**) 2.5 vol% TiO_2, (**b**) 5 vol% TiO_2, (**c**) 7.5 vol% TiO_2, **(d)** 10 vol% TiO_2.

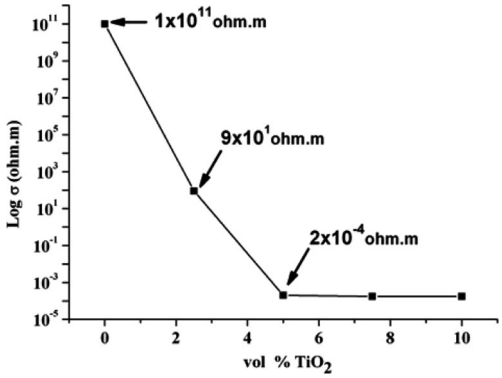

Fig. 5. Resistivity of the composites as a function of TiO_2 amount.

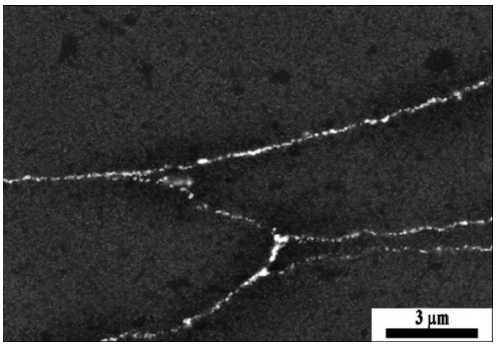

Fig. 6. SEM image representing the continuous network of in-situ formed TiN particles.

TiO_2 amount is given in **Fig. 5**. Even 2.5 vol% TiO_2 addition causes substantial decrease in resistivity, nearly ten orders of magnitude to a value of $9 \times 10^1\ \Omega$·m. Increasing the TiO_2 amount to 5 vol% the resistivity value further decreases values down to $2.1 \times 10^{-4}\ \Omega$·m. However increasing the TiO_2 amount over 5 vol% does not cause further decrease. This indicates that over 5 vol% TiO_2, conductivity is established due to the physical contact of in-situ formed TiN particles (**Fig. 6**).

4. Conclusions

Spark plasma sintered SiAlON–TiN composites with high electrical conductivity have been produced by coating spray dried granules mechanically with varying amounts of TiO_2 powder. After spark plasma sintering under selected conditions all TiO_2 was converted to TiN. O-SiAlON formation was also detected above 7.5 vol% TiO_2 due to the increasing amount of oxygen incorporation to the liquid phase. Formation of 3-D continuous TiN particles was observed at only 5 vol% TiO_2.

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