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Preparation and properties of TiN–Si_3N_4 composites

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Abstract

TiN–Si_3N_4 nanocomposite powders were prepared by in situ direct nitridation of TiO_2–Si_3N_4 nanocomposite powders prepared by a heterogeneous precipitation method using tetra-butyl titanate and silicon nitride as raw materials. TiN–Si_3N_4 dense composites were obtained by hot-pressing at 1550–1800 °C and 30 MPa for 1 h. The morphology of TiN–Si_3N_4 nanocomposite powder was observed by transmission electron microscopy, which showed that the average size of TiN nano particles was about 40 nm, and the surfaces of Si_3N_4 particles were uniformly coated with TiN nano particles. The effects of nano TiN particles on the mechanical properties and electrical conductivity of TiN–Si_3N_4 composites were studied. The addition of 20 vol.% TiN could increase the bending strength of the composite to 1154 MPa. The resistivity of composites decreased with the increase in TiN content and reached a minimum of 0.11Ω cm with 25 vol.% addition of TiN.

Keywords: Electrical properties; Mechanical properties; Nitridation; Si_3N_4; Si_3N_4–TiN; TiN

1. Introduction

Silicon nitride (Si_3N_4) ceramics are regarded as one of the most important high temperature structural materials. Recently, high-strength and high-toughness Si_3N_4 matrix composites, such as whisker-reinforced or particulate-reinforced ceramics, have been developed to improve the mechanical reliability of Si_3N_4 ceramics.[1,2] However, these composites are extremely hard and machining using conventional tools is difficult, which limits the widespread application of these materials in many fields. If sintered Si_3N_4 bodies can be made electroconductive, electrical discharge machining (EDM) technique can be applied to manufacture complex components.[3] It has been reported that the introduction of electroconductive second phase can improve the mechanical properties and electroconductivity of silicon nitride ceramics.[4–6] Titanium nitride (TiN) exhibits a number of desirable properties, including high hardness, good chemical durability, and high electrical conductivity,[7] and is a popular second phase additive due to its good compatibility with Si_3N_4 when sintered in nitrogen.[8–12] Recently, Si_3N_4–TiN composites have received much attention because of the possibility for electrical discharge machining.[9]

In general, most of the ceramic composites containing a dispersed second phase result from a direct addition of the second phase. Such materials can sometimes exhibit poor characteristics, which result from an inadequate dispersion process and the lack of sinterability caused by the large volume fraction of inert dispersion required for conductivity. The electrical conductivity of ceramic materials is strongly affected by the distribution of the electrically conductive second phase. Many studies have been initiated to increase the electrical conductivity of ceramic materials. A preferable alternative is the in situ composite method that can result in homogenous distribution of electrically conductive second phase.

In this paper, we report the preparation of TiN–Si_3N_4 composites by using the in situ composite method. Microstructure, mechanical properties and electrical conductivity of the composites were studied. The results showed that the bending strength and electroconductivity of composites were greatly improved.

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2. Experimental

2.1. Preparation of $TiN–Si_3N_4$ nanocomposite powder

Chemicals such as α–Si_3N_4 (grade SN-E10, UBE, Japan), anhydrous ethanol and tetra-butyl titanate were used as starting materials. The Si_3N_4 powder and tetra-butyl titanate were mixed in calculated proportion and homogenized by ball milling for 8 h using anhydrous ethanol as the liquid medium. Distilled water was dripped into the vigorously stirred mixing suspension of Si_3N_4 and tetra-butyl titanate and the final Ti/H_2O molar ratio was adjusted to 1:150. The tetra-butyl titanate was hydrolyzed to form nano TiO_2 on the surface of Si_3N_4 powder. The precipitate was separated from the mother solution, washed with distilled water and anhydrous ethanol, respectively. After final filtration, the cake was dried at 120 °C and subsequently calcined at 450 °C for 2 h.

The as-prepared TiO_2–Si_3N_4 nanocomposite powders were nitrided at given temperatures in a tube furnace to obtain TiN–Si_3N_4 nanocomposite powders. NH_3 gas was employed as the nitrided media with a flow rate of 1000 ml/min. The nitridation temperature ranged from 700 to 900 °C, while the nitridation time varied from 2 to 5 h. The nitrided powders were taken out from the furnace after cooling down to the room temperature in the flow of NH_3 gas.

2.2. Preparation of sintered bodies

A 20 vol.% TiN–Si_3N_4 nanocomposite powder was used as the starting material. High purity Al_2O_3 (3 vol.%) and Y_2O_3 (5 vol.%) were used as sintering aids. The TiN–Si_3N_4 nanocomposite powder, Al_2O_3 and Y_2O_3 were mixed homogenously by ball milling in anhydrous ethanol for 24 h with silicon nitride balls as the grinding media. After the mixed slurry was dried, it was ball milled for another 8 h to crush the soft agglomerates. The mixed powders were sintered by hot-pressing at temperatures between 1550 and 1800 °C and with a pressure of 30 MPa for 60 min in N_2 atmosphere.

2.3. Characterization of nanocomposite powders and sintered bodies

The morphologies of prepared nanocomposite powders were observed by transimission electronic microscopy (TEM; model 2010CX, Jeol, Tokyo, Japan). The phase compositions of the nanocomposite powders were identified using X-ray diffractometry (XRD; model D/MAX 2550, Rigaku, Tokyo, Japan).

The densities of the sintered samples were measured using the Archimedes method. The theoretical density value of the samples was calculated according to the rule of mixtures using 3.184 g cm^{-3} for Si_3N_4, 5.44 g cm^{-3} for TiN, 3.98 g cm^{-3} for Al_2O_3 and 5.35 g cm^{-3} for Y_2O_3, assuming that no chemical reactions take place among the components. For mechanical testing, the hot pressed samples were cut and ground into rectangular bar specimens (4×3×35 mm). The bending strength was measured on an Instron-1195 testing machine, using the three point bending method with a span length of 30 mm and a crosshead speed of 0.5 mm/min. The hardness and the fracture toughness were measured by the Vickers indentation method with a load of 10 kg and dwell time of 10 s. The resistivities of the sintered samples were measured by the four-probe method.

3. Results and discussion

3.1. Morphology observation of nanocomposite powders by TEM

TEM micrograph of the TiO_2–Si_3N_4 nanocomposite powder was shown in Fig. 1 (a). It could be seen that TiO_2 nano particles with a particle size of ~20 nm were uniformly distributed on the surfaces of Si_3N_4 particles. When the Si_3N_4 powder and tetra-butyl titanate were

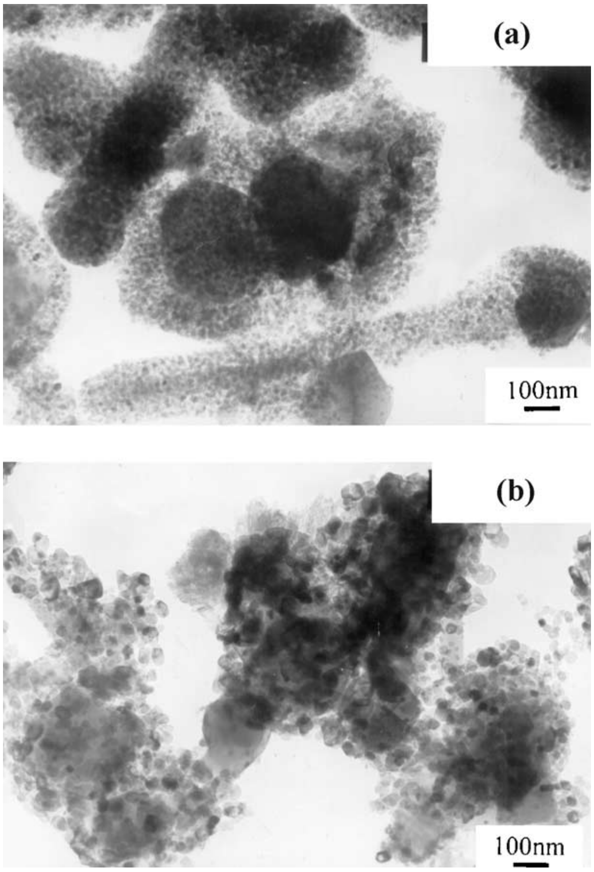

Fig. 1. TEM micrographs of (a) TiO_2–Si_3N_4 and (b) TiN–Si_3N_4 nanocomposite powders.

mixed and homogenized in anhydrous ethanol, the surfaces of Si_3N_4 particles were covered by tetra-butyl titanate on a molecular scale. As the distilled water was dripped into the mixture of Si_3N_4 and tetra-butyl titanate, tetra-butyl titanate was hydrolyzed on the surfaces of Si_3N_4 particles to form TiO_2 nano particles that coated simultaneously on the surface of Si_3N_4 particles.

On the basis of nitridation of TiO_2 to TiN, the size and morphology of TiN nano particles were significantly influenced by those of TiO_2 nano particles.[13] Thus the morphology of TiN–Si_3N_4 nanocomposite powder was closely related to that of TiO_2–Si_3N_4 nanocomposite powder. TEM micrograph of TiN–Si_3N_4 nanocomposite powder was given in Fig. 1(b). It could be observed that the surfaces of Si_3N_4 particles were completely covered by TiN nano particles, similar to the case of TiO_2–Si_3N_4 nanocomposite powder shown in Fig. 1(a).

3.2. Identification of phase composition of nanocomposite powders by XRD

Fig. 2 showed X-ray diffraction patterns of TiN–Si_3N_4 nanocomposite powders prepared under different nitridation conditions in the flow of NH_3 gas. When TiO_2–Si_3N_4 nanocomposite powder was nitrided at 900 °C for 5 h, the distinct peaks assigned to TiN(cubic) and α–Si_3N_4 could be detected and no peaks of other substance appeared. This indicated that TiO_2 nano particle was completely converted to TiN at 900 °C for 5 h. When TiO_2–Si_3N_4 nanocomposite powder was nitrided at 900 °C for 2 h, the peak of TiO_2 (rutile) coexisted with those of TiN(cubic) and α–Si_3N_4. This indicated that the TiO_2 (anatase) nano particles had been converted to TiN, but the nitridation reaction was not complete. When the composite powder was nitrided at 700 °C for 5 h, the distinct peaks assigned to TiN(cubic), α–Si_3N_4 and TiO_2 (anatase) coexisted, which indicated that TiO_2 (anatase) nano particles were partially converted to TiN and the nitridation reaction was still not complete even though the nitridation time was prolonged to 5 h. Since the nitridation reaction is a gas-solid phase reaction with a relatively low reaction rate, it is important to keep enough holding time and temperature to make TiO_2 nitrided completely.

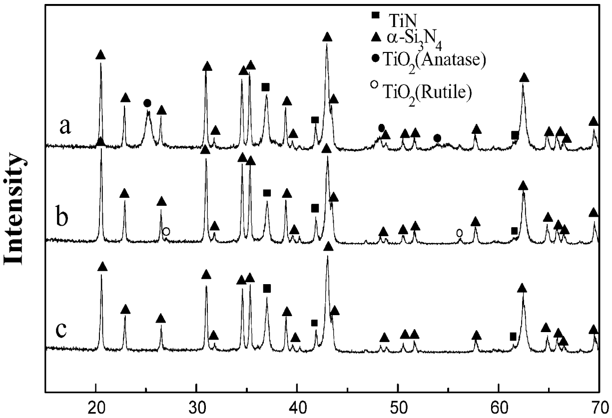

Fig. 2. XRD patterns of TiN–Si_3N_4 nanocomposite powders prepared under various nitridation conditions (a) 700 °C for 5 h, (b) 900 °C for 2 h and (c) 900 °C for 5 h, respectively.

3.3. Densification and microstructure

Prepared 20 vol.% TiN–Si_3N_4 nanocomposite powders were hot pressed at different temperatures, and the relative densities of the sintered samples were shown in Fig. 3. It could be seen that the sintered densities of all the samples hot-pressed between 1550 and 1800 °C were higher than 98% of the theoretical density. It suggests that TiN- Si_3N_4

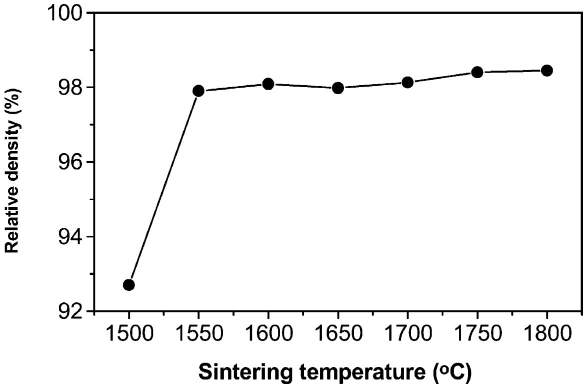

Fig. 3. Relative density of 20 vol.% TiN–Si_3N_4 composites vs. sintering temperature.

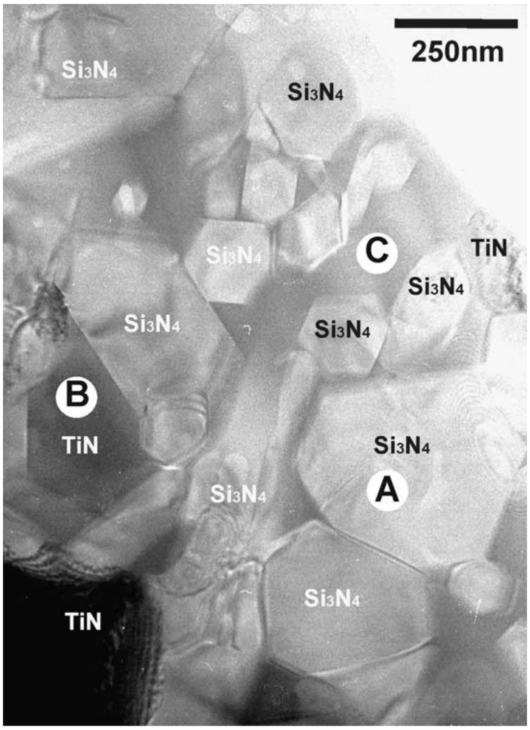

Fig. 4. TEM micrograph of 20 vol.% TiN–Si_3N_4 composite hot pressed at 1650 °C.

nanocomposite powders prepared by in situ formation of second phase (TiN) had a good sinterability.

Fig. 4 was a TEM micrograph of the 20 vol.% TiN–Si_3N_4 composite hot pressed at 1650 °C. This micrograph showed the fine-grained microstructure of the TiN–Si_3N_4 composite and TiN particles were distributed throughout Si_3N_4 matrices. The chemistry of regions A, B, C of composite, as shown in Fig. 4, was investigated with EDX analysis. It could be seen from Fig. 5 that the element detected in region A was only Si, while were Ti and N in region B. The elements detected in region C were Al, Y, O and Si. These four elements originated from the surface oxidation layer (SiO_2) on the starting powders and the sintering aids. Fig. 6(a) was a TEM micrograph showing a TiN particle inside a Si_3N_4 grain. The interface between the Si_3N_4 and the intragranular TiN was observed by HRTEM. As shown in Fig. 6(b), there was no amorphous glass phase at this boundary.

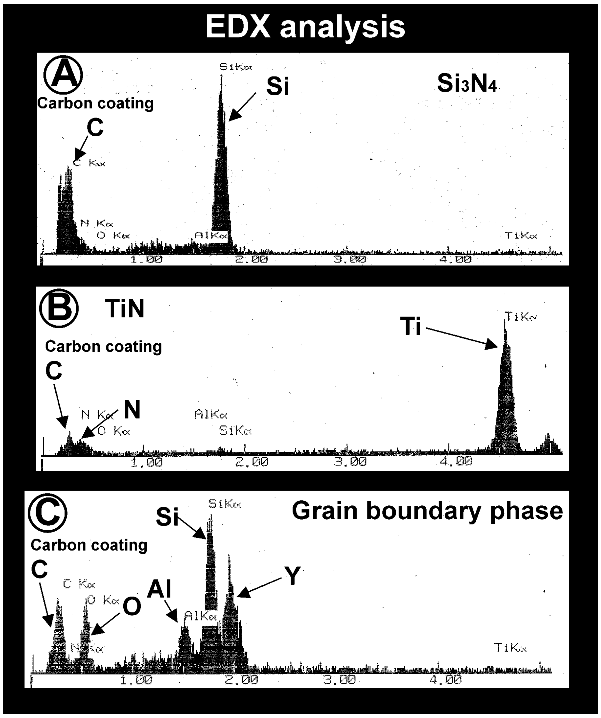

Fig. 5. EDX analysis of 20 vol.% TiN–Si_3N_4 composite hot pressed at 1650 °C.

3.4. Mechanical properties

The effect of sintering temperature on the mechanical properties of the 20 vol.% TiN–Si_3N_4 composites was studied. Fig. 7 showed the bending strength of 20 vol.% TiN–Si_3N_4 composites sintered at different temperatures by hot-pressing. It could be seen that with the exception of sample sintered at 1600 °C, bending strength data fell in a range of 919–1154 MPa and the highest value attained was 1154 MPa for the composite sintered at 1650 °C. This indicated that the optimum temperature for sintering was 1650 °C. In TiN–Si_3N_4 composites, the microhardness generally decreases with the addition of TiN since TiN is softer than the Si_3N_4 matrix.[10] As shown in Fig. 8, Vickers hardness

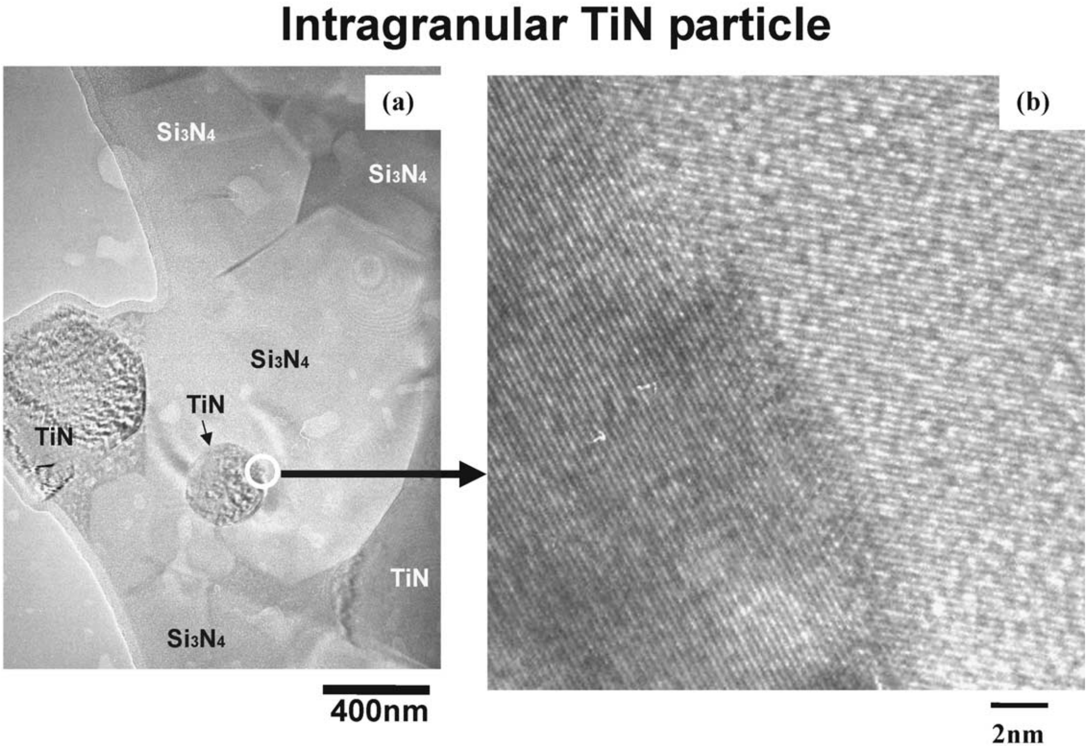

Fig. 6. (a) TEM micrograph, (b) HRTEM micrograph of 20 vol.% TiN–Si_3N_4 composite hot pressed at 1650 °C.

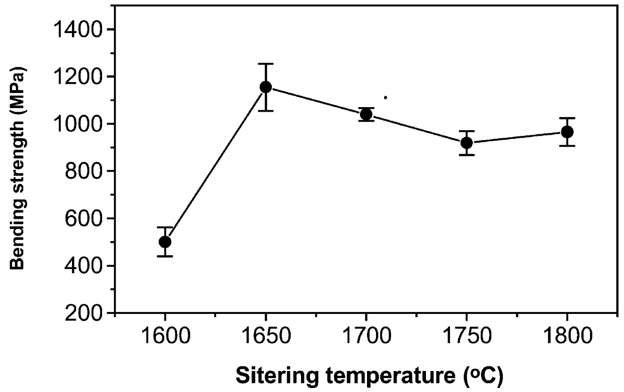

Fig. 7. Bending strength of 20 vol.% TiN–Si_3N_4 composites vs. sintering temperature.

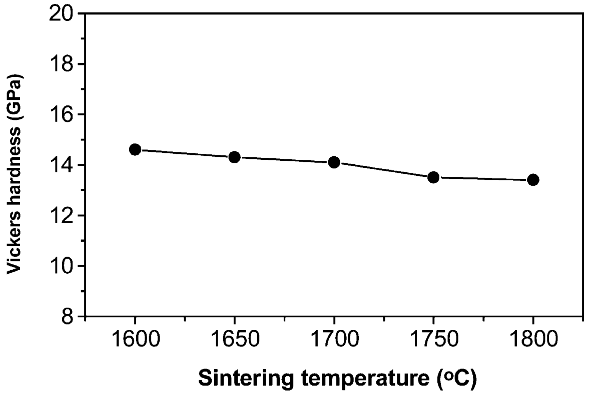

Fig. 8. Vickers hardness of 20 vol.% TiN–Si_3N_4 composites vs. sintering temperature.

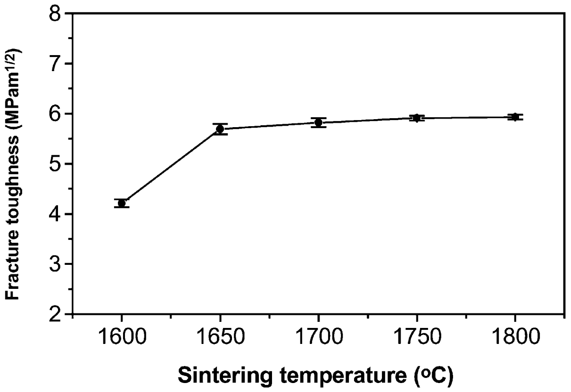

Fig. 9. Fracture toughness of 20 vol.% TiN–Si_3N_4 composites vs. sintering temperature.

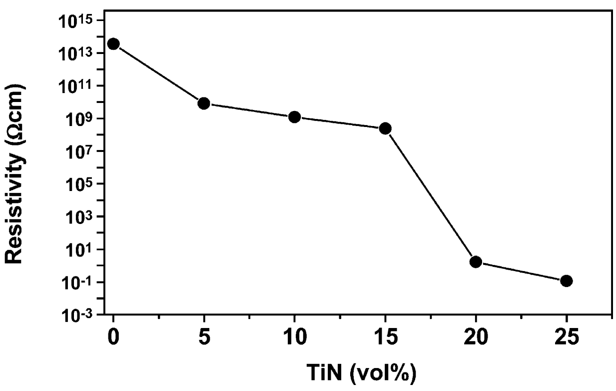

Fig. 10. Resistivity of TiN–Si_3N_4 composites hot pressed at 1650 °C vs TiN content.

of 20 vol.% TiN–Si_3N_4 composites was all about 14GPa for samples sintered at various temperatures. This hardness value was lower than that of monolithic Si_3N_4. Fig. 9 showed the fracture toughness of 20 vol.% TiN–Si_3N_4 composites sintered at different temperatures by hot-pressing. It could be seen that with the exception of sample sintered at 1600 °C, the fracture toughness of composites sintered at various temperatures was almost same and was stabilized at a level of 5.9 $MPam^{1/2}$. As compared with that of the Si_3N_4 matrix, the fracture toughness values of the composites were significantly improved.

3.5. Electrical properties

Fig. 10 showed the relationship between the TiN content and the electrical resistivity of the composites sintered at 1650 °C with a pressure of 30 MPa for 1 h. The electrical resistivity decreased with the increasing TiN content and reached a minimum (0.11 Ω cm) for the composite with 25 vol.% TiN. The experimental results showed that the as-prepared TiN–Si_3N_4 composites had good electroconductivities.

Because the mechanism of the electrical conduction for TiN–Si_3N_4 composite materials is the formation of a network of the TiN electrically conductive phase within the Si_3N_4 matrix, the distribution of TiN particles is one of the most important factors influencing the electroconductivity. Therefore, composites prepared by in situ formation of second phase (TiN) are expected to have a high electroconductivity, which is confirmed by the results of electrical resistivity measurement.

4. Conclusions

Dense TiN–Si_3N_4 composites with a high bending strength and good electrical conductivity were successfully prepared by a novel method. Experimental results indicated that TiN–Si_3N_4 nanocomposite powder prepared by in situ direct nitridation of nano TiO_2–Si_3N_4 powder could be sintered to a high density at a relatively low temperature by the hot pressing method. The addition of TiN particles greatly improved the bending strength and reduced the resistivity of TiN–Si_3N_4 composites. The experimental results suggested that the proposed method was effective for improving both the mechanical properties and electrical properties of TiN–Si_3N_4 composites.

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