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Short communication

# In situ preparation of $Si_3N_4$–TiN composite by pyrolysis of polytitanosilazane (PTSZ)

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## Abstract

$Si_3N_4$–TiN composite powders were obtained by in situ pyrolysis of polytitanosilazane**.** Dense $Si_3N_4$–TiN composites were prepared by hot-pressing at 1800 °C under 20 MPa for 2 h without sintering additive. Crystallization of amorphous PTSZ powders occurred between 1400 and 1500 °C with major phases, $\alpha$-$Si_3N_4$, $\beta$-$Si_3N_4$, and small amount of phase TiN. Mechanical properties and microstructure of $Si_3N_4$–TiN composites were characterized. The results showed that the mechanical strength was 620 MPa, the fracture toughness was 7.8 MPa $m^{1/2}$ and the Vickers hardness was 8.5 GPa. SEM analysis indicated that $Si_3N_4$–TiN composite possessed excellent fracture toughness because TiN grains produced by in situ pyrolysis were well dispersed in $Si_3N_4$ matrix.

*Keywords:* A. Sintering; B. Composites; C. Mechanical properties; D. $Si_3N_4$

## 1. Introduction

Silicon nitride ($Si_3N_4$) ceramics are regarded as one of the most important high temperature structural materials. Recently, high-toughness $Si_3N_4$ matrix composites, such as SiC whisker-reinforced or SiC, $ZrO_2$ and TiN particulate-reinforced ceramics, have been developed to improve the mechanical reliability of $Si_3N_4$ ceramics [1–4].

Among these materials, TiN particles have been found to be particularly useful because of the microcracking mechanism when optimum amounts of TiN particles are dispersed in $Si_3N_4$ matrix [3,4]. However, such composite sometimes exhibits poor characteristics, which result from an inadequate dispersion process and lack of sinterability caused by the large volume fraction of inert dispersion. Recent years, the pyrolysis of precursors seems to be the most practical method for the synthesis of hybrid composites [5–8] because precursor pyrolysis can make the homogeneous distribution of different elements on a molecular or even atomic level.

In this work, $Si_3N_4$–TiN composites are obtained by in situ pyrolysis of polytitanosilazane (PTSZ). Dense $Si_3N_4$–TiN composites are prepared by hot-pressing at 1800 °C under 20 MPa for 2 h without sintering additive. The mechanical properties and microstructure of $Si_3N_4$–TiN composites are characterized.

## 2. Experimental

### *2.1. Fabrication of $Si_3N_4$–TiN composites*

The polytitanosilazane (PTSZ) was synthesized as described elsewhere [9]. The synthesized PTSZ powders were firstly pyrolyzed at 400 °C in $NH_3$ atmosphere, subsequently pyrolyzed PTSZ powders were balled for 4 h, and then powders were compacted at 20 MPa in a steel mould. The compacts were sintered by hot-pressing at temperature 1800 °C under pressure of 20 MPa for 2 h in $N_2$ atmosphere without sintering additives.

### *2.2. Characterization of polytitanosilazane and its pyrolytic products*

Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA in 30 mL/min $N_2$ flow up to 1200 °C, at a heating rate of 10 °C/min. Elemental analyses for C and H in precursors were determined with a Carlo Erba 1106 analyzer;

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N content in precursors was obtained by Coulomb titration method. Analysis of Ti content was performed on the polymeric samples by inductively coupled plasma (ICP) spectroscopy. Fourier-transform infrared (FTIR) spectra were obtained with a Perkin-Elmer 2000 IR spectrometer in the wave number range 4000–370 $cm^{-1}$ using standard procedures. The phase compositions of pyrolytic products at different temperatures were identified by X-ray diffraction (XRD) (Rigaku D/M4X 2500) using Cu Kα radiation.

### 2.3. Characterization of sintered bodies

For mechanical testing, the hot pressed samples were cut into rectangular bar specimens (4 mm × 3 mm × 36 mm). The bending strength was measured using the three-points 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 morphology of the fracture surface of the $Si_3N_4$–TiN composite was observed by SEM (S-4300).

## 3. Results and discussion

### 3.1. Evolution from PTSZ precursor to the ceramic material

The FTIR spectra of the PTSZ precursor and its pyrolyzed products in nitrogen atmosphere at different temperatures were shown in Fig. 1. The detected signals are as follows: 2954–2960 $cm^{-1}$, 2897–2905 $cm^{-1}$ and 1403–1408 $cm^{-1}$ (C–H); 1253–1260 $cm^{-1}$, 790 $cm^{-1}$, 839 $cm^{-1}$ (Si–$CH_3$); 3390 $cm^{-1}$ and 1170–1180 $cm^{-1}$ (N–H). The strong peak at 940 $cm^{-1}$ is the typical asymmetric stretching vibration of Si–N–Si, which shifts to 925 $cm^{-1}$ in the PTSZ's spectra. And strong absorption peak at 1030 $cm^{-1}$ in the spectra of PTSZ's belongs to the Si–N–Ti bonds.

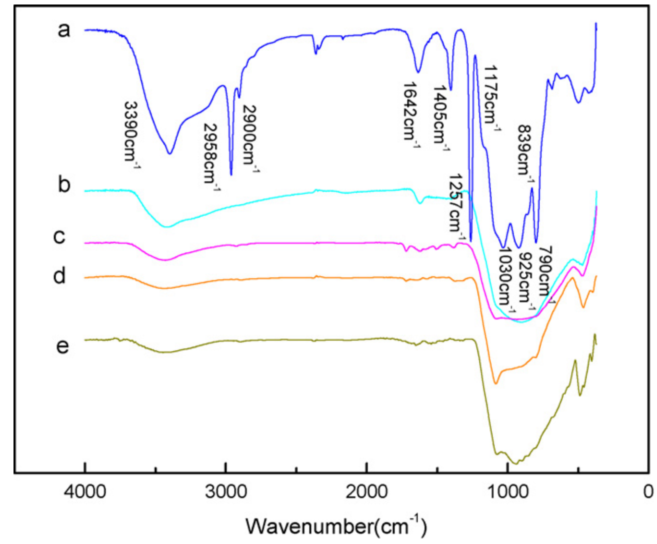

Fig. 1. IR spectrum of PTSZ precursor and its pyrolyzed products at different temperatures.

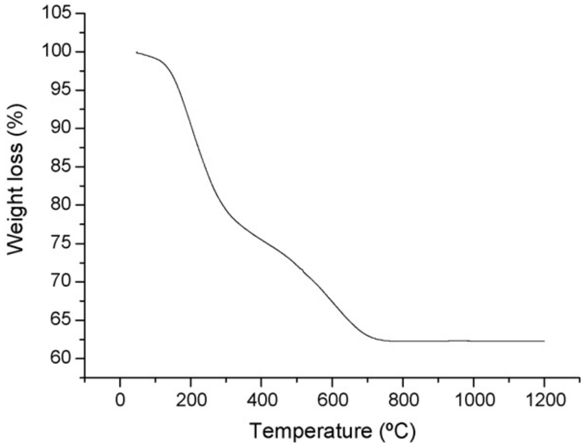

Fig. 2. TGA curve of the PTSZ powders in nitrogen atmosphere.

As the temperature increases, the major observed events via FTIR are that the intensity of the Si–H, C–H, Si–$CH_3$, and N–H peaks continuously decreased. This is due to the reaction of dehydrogenation and demethanation. When the pyrolysis temperature increased to 1500 °C, the Si–H band was completely eliminated and only shows two very broad absorptions belonging to peaks of the titanium–nitrogen and silicon–nitrogen stretching vibrations.

To prepare any kind of ceramics by pyrolysis process, a high yield of precursor was needed. The TGA curve of the PTSZ powder in nitrogen is shown in Fig. 2. A two-stage weight loss is observed from the PTSZ. The first weight loss occurs between 100 and 300 °C and is caused by the distillation of solvent and light oligomers. The second weight loss between 300 and 680 °C is associated with dehydrogenation and transamination by evolution of ammonia, methane and hydrogen gases. This is consistent with general pyrolysis behaviour for polysilazane. The PTSZ gave ceramic yield of 65 wt.% upon pyrolysis at 1200 °C under nitrogen.

The knowledge of phase evolution during the in situ crystallization of amorphous preceramic powders by pyrolysis

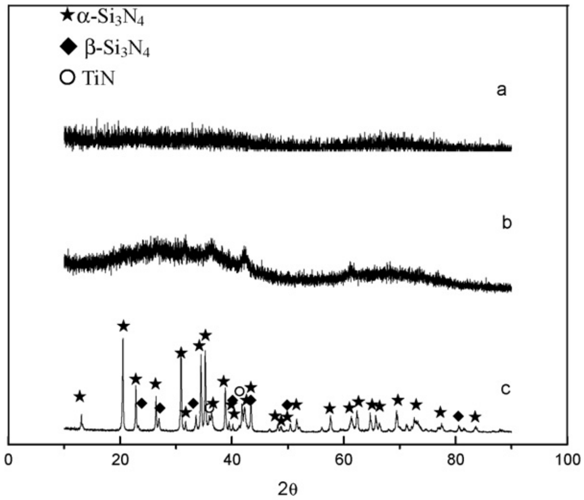

Fig. 3. XRD patterns of the PTSZ-derived ceramic at different temperatures: (a) 1300 °C; (b) 1400 °C; (c) 1500 °C.

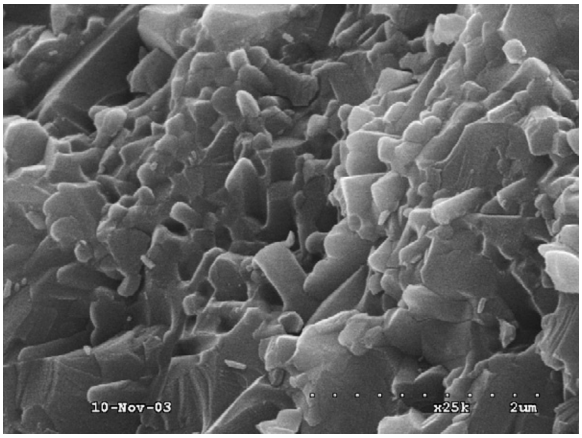

Fig. 4. SEM image of the fracture surface of the $Si_3N_4$–TiN composite.

of ceramic precursor is of special interest in the understanding of the sintering behavior. Fig. 3 shows the XRD patterns of the PTSZ-derived ceramic at different temperatures. The structure of pyrolytic products is completely amorphous up to 1400 °C as shown in Fig. 3(a and b). The crystallization of amorphous PTSZ powders occurs between 1400 °C and 1500 °C. $\alpha$-$Si_3N_4$ and $\beta$-$Si_3N_4$ are observed as major phases; yet there is a small amount of TiN phase in the pyrolytic products. No SiC and TiC phases could be detected.

### *3.2. The mechanical properties and microstructure of sintered bodies*

Some mechanical properties of bulk ceramics derived from the PTSZ have been characterized. The mechanical strength is 620 MPa, fracture toughness is 7.8 MPa $m^{1/2}$ and the Vickers hardness is 8.5 GPa. Their hardness value is lower than that of the $Si_3N_4$–TiN composites made by powder metallurgy method, which might be due to the presence of some fine pores in the ceramic bodies. The fracture toughness value is significantly improved. It is well known that even in the ceramic matrix composites, toughened by the addition of the second phase to ceramic matrix could get better mechanical properties and reliability, because residual stress existed due to the thermal expansion mismatch between matrix and reinforcement [4]. The TiN particulates with a higher thermal expansion coefficient than $Si_3N_4$ may create a complicated stress field around the TiN particles. These stresses could improve the fracture toughness, because of a longer crack path with a region of compressive residual stresses around the TiN grains and microcracking in the vicinity of the TiN particles. Furthermore, use of organometallic precursors in the preparation and the processing of composites might offer utility in the control of their microstructure because good and uniform mixing of the phases are possible.

SEM observation of the fracture surface of the $Si_3N_4$–TiN composite is shown in the Fig. 4. It can be seen that dense fracture surface was observed. It suggests that TiN–$Si_3N_4$ powders prepared by in situ formation using pyrolysis of PTSZ had a good sinterability. The fracture surface of the composite was characterized by a mixed mode of intergranular and transgranular fracture. Some pull-out of rod-like $\beta$-$Si_3N_4$ grains were observed on the fracture surface, which deflected the crack to travel through a more tortuous path and provided additional fracture energy consuming mechanism.

## 4. Conclusions

Dense $Si_3N_4$–TiN composites with excellent fracture toughness were successfully prepared by a novel method. Experimental results indicated that $Si_3N_4$–TiN powders by in situ pyrolysis of polytitanosilazane could be sintered by hot-pressing without sintering additive. The mechanical examination suggested that the addition of TiN particles greatly improved the fracture toughness of $Si_3N_4$–TiN composites.

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