

A New Method to Synthesize Polytitanosilazane as Ceramic Precursor

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Abstract: A new kind of polytitanosilazane precursor PTSZ for Si/C/N/Ti-based ceramic was synthesized from the condensation reaction of silazane lithium salt and titanium tetrachloride (TiCl₄). The results indicated that the ceramic yield of PTSZ was much higher than that of corresponding silazane oligomer.

Keywords: Polytitanosilazane, ceramic precursor, ceramic composite, pyrolysis.

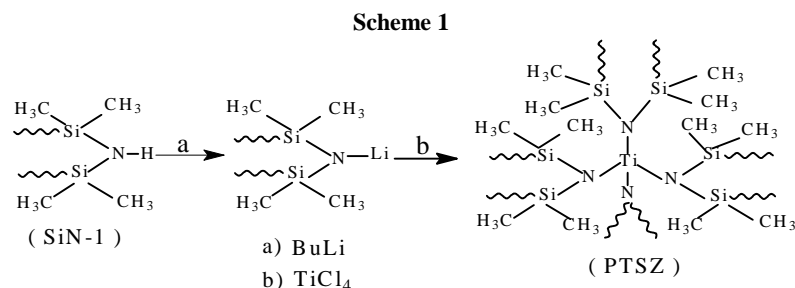
Multicomponent ceramic composites often exhibit improved properties compared with the single component ceramics¹. Therefore, researchers have paid much attention on the preparation of multicomponent ceramics. For example, TiN/Si₃N₄ composites have been suggested as structural materials because of their superior properties². Recently, increasing attention has been directed to the use of polymeric precursors for the manufacture of Si₃N₄-, SiC-, or Si/C/N-based ceramics³⁻⁷. In this process, desired elements for reinforcement can be introduced to the precursors and the chemical composition of the ceramic systems can be regulated at the molecular or atomic level to produce new types of high-performance silicon-based ceramic composites^{7,8}.

In this report, we have introduced titanium to silazane oligomer from the condensation reaction of silazane lithium salt and titanium tetrachloride (TiCl₄) to obtain polytitanosilazane PTSZ precursor for Si/C/N/Ti-based ceramics.

Experimental

Fourier-transform infrared (FT-IR) spectra were obtained with a PE 2000 IR spectrometer. ¹H and ²⁹Si nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ solution with a Bruker WM 300 spectrometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 1 TGA in 30 mL/min nitrogen flow up to 1000°C, at a heating rate of 10 °C/min. Elemental analyses for C and H in the

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polymeric precursor were determined with a Carlo Erba 1106 analyzer; N content in the precursor was obtained by Coulomb titration method⁹; analysis of Ti content in PTSZ was performed on inductively coupled plasma (ICP) spectroscopy. Pyrolysis of the precursors under N₂ was performed in a quartz tube furnace under flowing N₂ (40 mL/min). The temperature program used was as follows: ambient temperature to 200°C at 2°C/min, kept at 200°C for 1 h; 1°C/min to 350°C, kept at 350°C for 1 h; 5°C/min to 600°C, kept at 600°C for 1 h; then 1°C/min to 900°C, kept at 900°C for 2 h.

General Procedure

The polytitanosilazane precursor PTSZ was synthesized as described in **Scheme 1**.

Synthesis of silazane oligomer SiN-1

SiN-1 was synthesized from coammonolysis of Me₂SiCl₂ and MeSiCl₃. Into a 5000-mL three-necked flask equipped with a reflux condenser, a gas inlet tube and a mechanical stirrer under N₂ were added 3000 mL of toluene, 2 mol (263g) of Me₂SiCl₂ and 2 mol (298g) of MeSiCl₃. Ammonolysis was carried out at room temperature under high speed stirring until no NH₃ was absorbed. The reaction mixture was filtered, and 1000 mL toluene was added to wash the slurry for 2-3 times, ammonium chloride removed and transparent solution was obtained. The solution was concentrated and dried at 80°C under vacuum to constant weight. SiN-1 was obtained in 84% yield. The result of elemental analysis for SiN-1 was: C, 27.00; H, 8.34, N: 22.10 (Calcd: C, 25.99; H: 8.30, N: 23.27).

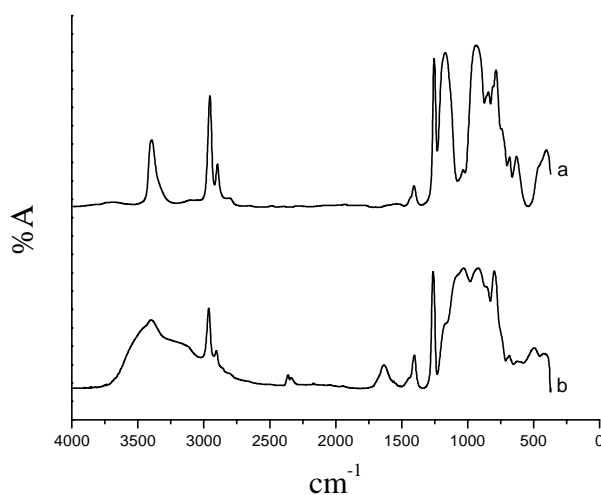
Synthesis of the silazane lithium salt and PTSZ

Into a 250 mL three-necked flask equipped with a dropping funnel and a gas inlet tube, 120 mL freshly distilled *n*-hexane and 15.4 g SiN-1 were added, and 37 mL 2.5 mol/L *n*-BuLi (0.093 mol) was charged into the dropping funnel by syringe after air was replaced by dry nitrogen. *n*-BuLi was added dropwise while stirring, and white precipitate formed. The reaction mixture was stirred for 8 h at room temperature, and then the solvent was removed by distillation at room temperature under reduced pressure to obtain white silazane lithium salt. Under the protection of nitrogen, 150 mL toluene was added into the flask while stirring. 2.6 mL (0.023 mol) TiCl₄ and 10 mL toluene were charged into the dropping funnel and then added dropwise into the silazane lithium salt/toluene system. The temperature was raised to 110°C and held for 24 hours and

then the mixture was cooled to room temperature. 50 mL THF was added into the mixture. Precipitated LiCl was removed by filtration, and the resulting solution distilled to give 16.2 g of PTSZ as yellow solid powders. The result of elemental analysis for SiN-1 was: C, 23.40; H, 7.25, N: 20.77, Ti: 6.80 (Calcd: C, 24.38; H: 7.22, N: 21.71, Ti: 6.76).

Results and Discussion

Figure 1 FTIR spectra of a) SiN-1; b) PTSZ



Elemental analysis showed that titanium could be introduced into silazane oligomer in the above-mentioned method to give PTSZ precursor for Si/C/N/Ti-based ceramics. The ^{29}Si NMR spectrum of the PTSZ was very similar to that of SiN-1, which indicated that the basic silazane skeleton changed little after introduction of Ti. The signals in the range δ -3.8 to -12 are assigned to N-SiMe₂-N, and δ -18 to -26 are assigned to N₃-SiMe. The FTIR spectra of SiN-1 and PTSZ were shown in **Figure 1**. The strong peak at 940 cm⁻¹ in the spectrum of SiN-1 is the typical asymmetric stretching vibration of Si-N-Si, which has shifted to 925 cm⁻¹ in PTSZ's spectrum. The intensity of N-H absorption peak has decreased in the PTSZ's spectrum compared with that in SiN-1's. And a new strong absorption peak at 1030 cm⁻¹ appeared in the spectrum of PTSZ. The reason is that Si-N-H bonds have been partially replaced by Si-N-Ti bonds.

To evaluate PTSZ as ceramic precursor, we performed pyrolysis in tube furnace and TGA experiments on SiN-1 and PTSZ. As shown in **Table 1**, the TGA ceramic yield of PTSZ (58.2%) is much higher than that of SiN-1 (15.9%), which indicated that there are more crosslinkage structure units in PTSZ. Pyrolytic ceramic yield in tube furnace even reached 67.1%, higher than in TGA experiment. This is because the heating rate in tube furnace pyrolysis is lower than in TGA, which is advantageous for the polymer to further crosslink at low temperature that retards the thermolytic degradation reaction frequently encountered in organosilicon compounds.

Table 1 Ceramic yield of SiN-1 and PTSZ

Precursors	Ceramic Yield (%)	
	Pyrolysis by TGA	Pyrolysis in tube furnace
SiN-1	15.9	19.8
PTSZ	58.2	67.1

Acknowledgments

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (No. 50072033) and the Chinese Academy of Sciences (CXJJ-10).

References

1. J. Bill, F. Aldinger, *Adv. Mater.*, **1995**, 7 (9), 775.
2. C. K. Narula, B. G. Demczyk, P. Czubarow, D. Seyferth, *J. Am. Ceram. Soc.*, **1995**, 78, 1247.
3. X. J. Bao, M. J. Edirisinghe, *J. Mater. Chem.*, **2000**, 10, 395.
4. R. Riedel, A.O. Gabriel, *Adv. Mater.*, **1999**, 11 (3), 207.
5. Y. L. Li, E. Kroke, A. Klönczynski, R. Riedel, *Adv. Mater.*, **2000**, 12 (13), 956.
6. M. Weinmann, J. Schuhmacher, H. Kummer, S. Prinz, et. al., *Chem. Mater.*, **2000**, 12, 623.
7. J. Hapke, G. Ziegler, *Adv. Mater.*, **1995**, 7 (4), 380.
8. F. Cheng, Y. Sugahara, K. Kuroda, *Appl. Organometall. Chem.*, **2001**, 15 (8), 710.
9. Z. M. Xie, Q. Z. Wang, *Chin. J. Anal. Chem.*, **1993**, 21 (2), 206.

Received November 25, 2003