Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Ceramics International 35 (2009) 929–932
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Short communication

A novel method for preparation of dense silicon-based ceramics

Pei Yuchen [a], Luo Yongming [b], Li Shuqin [c,*], Li Jialu [a]

[a] *Composite Research Institute, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China*
[b] *Institute of Chemistry, The Chinese Academy of Science, Beijing 100080, People's Republic of China*
[c] *Institute 306th, China Aerospace Science and Industry Corporation, 7203#-21, Beijing 100074, People's Republic of China*

Received 14 November 2007; received in revised form 19 December 2007; accepted 10 March 2008
Available online 2 July 2008

Abstract

The dense ceramic part was prepared firstly using silazane with filler. The composition, structure and ceramic yield of silazane were characterized by elemental analysis, nuclear magnetic resonance (NMR), IR and thermogravimetric analysis (TGA). The ceramic yield was 63 wt% upon pyrolysis at 1000 °C under N_2 atmosphere. The fabrication of ceramic part involved cross-linking of the silazane with metallic fillers (Ti particles) followed by a polymer-to-ceramic transformation step. Near net shape manufacturing of polymer derived ceramics could be achieved. The strength of ceramic parts could achieve 450 ± 15 MPa and scanning electron microscopy (SEM) observation showed that there was very low porosity on the fracture surface of pyrolysed body.

Keywords: A. Precursors; B. X-ray methods; C. Mechanical properties

1. Introduction

Advanced structural ceramic materials are promising candidates for aerospace systems, engine components, machine tools, etc., due to their excellent high-temperature endurance, wear resistance and stability in corrosive environment. In recent years, novel ceramic materials made from Si-containing polymer $[R_{1\ldots2,}Si(C,N,B,O)_{0.1\ldots1.5}]$ where R is an organic functional group (for example, alkyl, aryl, etc., group) by the polymer-to-ceramic transformation process has attained particular interest. The ceramic materials can be prepared from high purity precursor in low temperature by using versatile plastic shaping technologies [1,2]. However, it is difficult to prepare the dense ceramics due to the large shrinkage and a lot of pores produced during the polymer-to-ceramic transformation process. The filler particles can form a stabilizing rigid network in the low viscous polymer phase, offer a large interface area for material transport during polymer decomposition, increase the ceramic yield of the polymer and decrease the shrinkage due to the reaction of filler particles with the gaseous decomposition products. Suitable active fillers are elements or compounds forming carbide, nitride, or oxide reaction products such as Al, B, Si, Ti, $CrSi_2$, $MoSi_2$, etc., which exhibit a high specific volume increase upon reaction. For adjusting elasticity, thermal expansion, electrical resistance, etc., inactive fillers offer an additional degree of freedom for tailoring the material properties [3–5].

The silicon-based ceramic was prepared by the polymer-to-ceramic transformation process. There were three main steps of the fabrication process described in the present article: the mixture of liquid polymer and fillers was poured into a mold, the liquid polymer polymerized into a rigid plastic material under uniaxis warm pressing, and followed by pyrolysis. The composition and structure of the synthesized silazane were analyzed by IR, TG and nuclear magnetic resonance (NMR). In order to overcome the brittleness and decrease the porosity of the green bodies, the precursors were compacted at the softening temperature under uniaxis warm pressing. The strengths were measured by 3-bending method and the microstructures were characterized by scanning electron microscopy (SEM).

2. Experimental procedure

The starting silazane was self-synthesized from coammonolysis of $MeViSiCl_2$ and $MeSiCl_3$ in molar ratio of 1:1.8

---

* Corresponding author. Tel.: +86 10 68190540; fax: +86 10 88534479.
E-mail address: lishuqin97@sina.com (L. Shuqin).

0272-8842/$34.00 © 2008 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2008.03.012

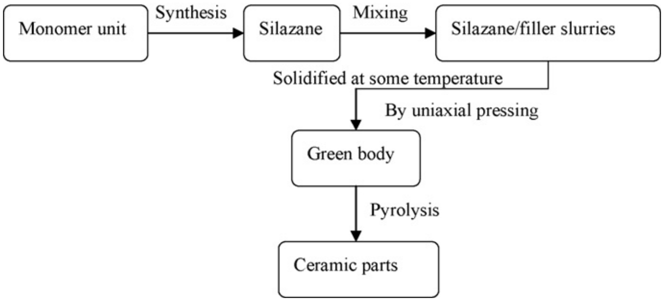

Fig. 1. Process pattern for the preparation of ceramic.

(Me: methyl group CH_3–; Vi: vinyl group CH_2=CH–). Fourier transform infrared (FTIR) spectra of synthesized silazane oligomer was obtained with a PerkinElmer 2000 IR spectrometer in the wavenumber range 4000–370 cm^{-1} by using standard procedures. ^1H NMR and ^{29}Si NMR spectra of the samples were recorded in $CDCl_3$ solution with a Bruker WM 300 spectrometer. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Pyris 1 TGA in 30 mL/min nitrogen flow up to 1000 °C, at a heating rate of 10 °C/min.

Manufacturing of bulk components involved the formation of homogeneous polymer/filler particle mixtures or slurries, shaping, curing and finally pyrolysis. The adapted fillers were Ti and α-Si_3N_4 particles. The silazane was loaded with 20–60 vol% of various active filler Ti particles with mean size of 10–15 μm and inactive filler Si_3N_4 particle with mean size of 2–3 μm. The silazane/filler slurries were poured into a steel mold and solidified at some temperature by uniaxial pressing using warm-pressing equipment. The green part was sintered in active atmosphere. Fig. 1 shows the process pattern for the preparation of ceramic. The porosity of the pyrolysed ceramic materials was measured by mercury porosimery. Three-point bending tests were preformed to determine the strengths of the samples with size 3 mm × 4 mm × 36 mm and cross-head speed of 0.5 mm/min. The microstructures of the specimens were observed by SEM.

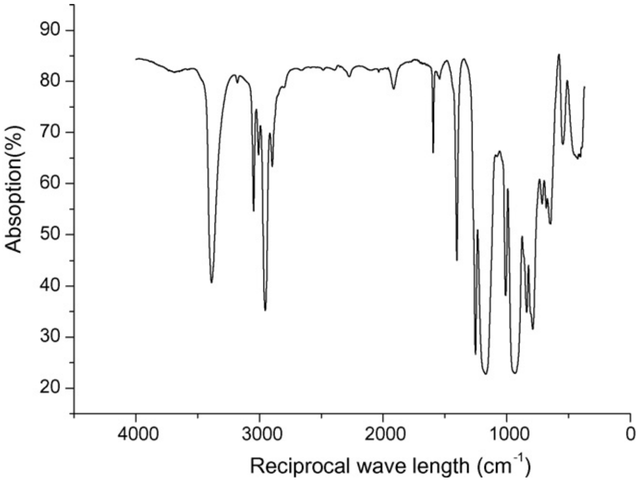

Fig. 2. The ^{29}Si NMR spectra of the synthesized silazane oligomer.

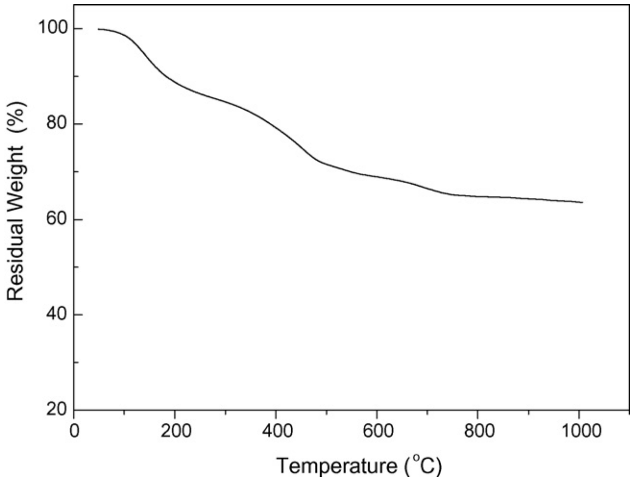

Fig. 3. TGA curve of silazane oligomer.

3. Results and discussion

3.1. Characterization of synthesized silazane oligomer

The results of the element analysis of silazane oligomer are: C, 29.40 wt%; H, 7.42 wt%; N, 23.69 wt%; Cl < 0.30 wt%. The FTIR spectra of the silazane oligomer are shown in Fig. 2. The signals that are assignable to identify 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). As shown in Fig. 3, three regions were apparent in the TGA curve of silzane oligomer. The first region, below 220 °C, showed a weight loss of nearly 13 wt%, which resulted mainly from the evaporation of low molecular weight fraction and the loss of residual solvent; the second one between 220 °C and 500 °C were associated with dehydrogenation and transamination and the third one above 500 °C were caused mainly by evolution of methane and hydrogen gases.

3.2. Curing

The general requirements for a precursor suitable for bulk pyrolysis processing include (1) cross-linkablility to form infusible polymers; (2) compactability into dense green compacts. Cross-linking of the oligomeric silazane into large molecules with highly interlocked backbones is necessary to avoid the evaporation of oligomers during pyrolysis. The oligomeric silazane with vinyl units can be cross-linked either thermally or chemically using radical initiator like dicumylperoxide (DCP) as a radical initiator. The oligomeric silazane was examined using DSC equipment. There were obvious exothermal peaks between 140 °C and 210 °C, and the exothermal peak reached maximum value at 183 °C, which indicated that velocity of cross-liking was maximum.

3.3. Compaction

The silazane/filler slurry was cast into the steel mold, and then gas in the slurry was removed in vacuum oven, at last the slurry was hold at some temperature and was warm-pressed on the warm pressing equipment. The pressing temperature should be in the range of the softening point of the cross-linked polysilazane. The quality and density of the warm-pressed green bodies strongly depends on the cross-linking state of the polymer and the warm-pressing parameters, as well as the pressing technique. The porosities of green bodies, which were pressed at different temperatures under the pressure of 20 MPa, were measured by mercury porosimery.

When the slurry was pressed at 140 °C, it was extruded from the steel mold because the slurry was not cross-linked. When temperature was increased to 155 °C, the porosity was 8%. The porosity achieved the minimum value of 5% when forming temperature was 175 °C. If temperature reached 185 °C, the porosity increased to 15% due to its cross-linked state. So the suitable pressed temperature was 175 °C for half an hour.

3.4. Bulk pyrolysis

The bulk pyrolysis of polymer particle compacts to fabricate dense Si/C/N ceramics provides the opportunity to produce multi components materials. Instead of using a pure single source polysilazane precursor, active or passive particles (fillers) are added to precursor. The active fillers react with silazane, its decomposition products or active atmospheres during pyrolysis to form carbide, nitride, carbonitride, oxide phases, etc., which in turn can reduce the shrinkage and the amount of volatile side products.

From the TGA of the silazane, the relative weight loss appeared in the temperature interval between 150 °C and 700 °C. Therefore, the isothermal heat treatment at these intermediate temperatures was applied (1) to effectively influence the decomposition reactions by the furnace atmosphere as well as (2) to control outgassing of the volatile by pyrolysis caused by rapid gas evolution.

All pyrolysis experiments were performed in pure NH_3 up to 1100 °C, then continued in N_2 up to 1500 °C and held 2 h.

Fig. 4 showed the XRD spectrum of products, which were formed after pyrolysis of polysilazane with active filler Ti at 1500 °C. The results indicated that the Ti was turned into TiN completely, the silazane was converted into α-Si_3N_4 completely and the carbon was removed in the NH_3 atmosphere.

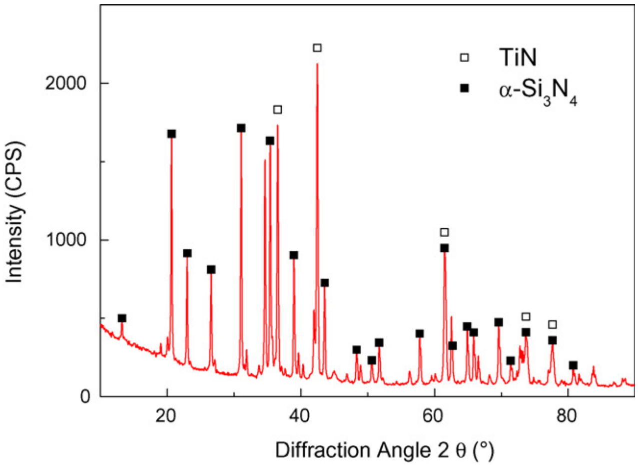

Fig. 4. The XRD spectrum of products.

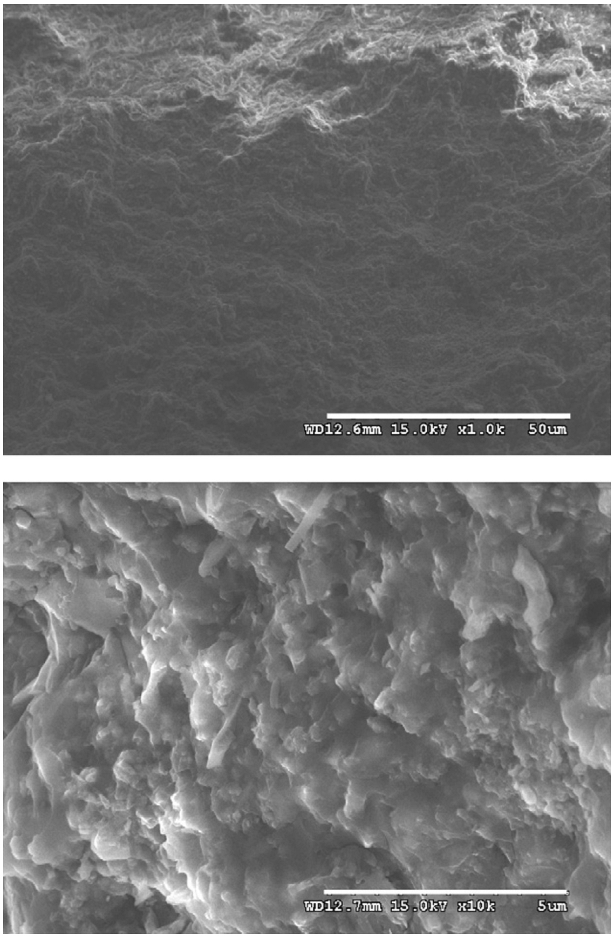

Fig. 5. SEM pictures of fracture surface of green body and pyrolysed body. (a) Green body and (b) pyrolysed body.

3.5. Mechanical properties and microstructure

The average bending strengths of green body and pyrolysed body at 1500 °C were 300 ± 22 MPa, 450 ± 15 MPa, respectively. And the Vickers hardness (Hv) of green body and pyrolysed body were 12.5 ± 0.8 GPa, 15.3 ± 1.6 GPa, respectively. Fig. 5 shows SEM micrographs of fracture surfaces of green body and pyrolysed green body. There was no porosity to be detected in the fracture surface of green body. During pyrolysis of green body, silazane was decomposed and produced some gases, which resulted in the appearance of pores, which, however, decreased by reacting of active filler with produced gas or atmosphere. SEM observation therefore shows very low porosity on the fracture surface of pyrolysed body.

4. Conclusion

A polymer-based process route for ceramic body manufacturing was developed. The structure and composition of the polysilazane with filler were characterized at different processing steps. Ceramic monoliths were obtained which contained less than 5% porosity. The flexural strength measured in 3-point bending was 450 ± 15 MPa and Vickers hardness 15.3 ± 1.6 GPa for pyrolytic body.

References

[1] E. Kroke, Y.L. Li, C. Konetschny, Silazane derived ceramics and related materials, Materials Science & Engineering R-Reports 26 (4–6) (2000) 97–199.

[2] R. Riedel, G. Passing, H. Schonfelder, Synthesis of dense silicon-based ceramics at low-temperatures, Nature 355 (6362) (1992) 714–717.

[3] P. Greil, Near net shape manufacturing of polymer derived ceramics, Journal of the European Ceramic Society 18 (13) (1998) 1905–1914.

[4] P. Greil, M. Seibold, Modeling of dimensional changes during polymer ceramic conversion for bulk component fabrication, Journal of Materials Science 27 (4) (1992) 1053–1060.

[5] P. Greil, Active-filler-controlled pyrolysis of preceramic polymers, Journal of the American Ceramic Society 78 (4) (1995) 835–848.