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Structural characterization and mechanical properties of SiBONC ceramics derived from polymeric precursors

G. Wen [a,b], F. Li [a,*], L. Song [b]

[a] *Harbin Institute of Technology, Harbin 150001, China*
[b] *Harbin Institute of Technology at Weihai, Weihai 264209, China*

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Abstract

SiBONC ceramics with specific structural characteristics were designed. Nano-sized amorphous SiBONC ceramic powders were prepared by pyrolysis of polymeric precursors synthesized from chloro-polysiloxane [$(SiOCl_x)_n$], phenylamine ($PhNH_2$) and boron trichloride (BCl_3). Amorphous nano-sized powders were prepared through pyrolysis with designed compositions at Si/B molar ratios of 4:1. The density of the SiBONC ceramics is between 1.95 g/cm^3 and 2.15 g/cm^3, with the maximum bending strength of 150.50 MPa, Vickers-hardness of 3.78 GPa, fracture toughness of 2.10 MPa m$^{1/2}$. SiBONC ceramics can keep amorphous state up to 1700 °C, nano-sized β-SiC and bamboo like BN/C filaments can be precipitated from amorphous matrix, which indicates that adulteration of B, C, N can obviously increase crystallization temperature and mechanical property of the SiO_2-based ceramics.

Keywords: Precursor; Hot-pressing; Amorphous state; Mechanical properties; SiBONC

1. Introduction

In recent years, there has been increasing interest in preparing multi-component silicon-based ceramics in order to improve thermal, mechanical and electrical properties of the monolithic silicon based ceramics (SiO_2, SiC, Si_3N_4, etc.) [1–4]. In particular, the SiBCN system has been intensively studied, which made the onset of decomposition shift to as high as 2000 °C [5–8]. At the same time, SiBON system has also been studied by several researchers, which shows a combination of increased mechanical properties, thermal stability and electrical resistance [9–12]. However, the preparation of both SiBCN and SiBON need expensive raw materials, complex synthesis procedures and strict operation environments, which limited their applications in the actual engineering. Many researchers employed organosilicon compounds and organoboron compounds to synthesize the polymer precursors, however, these two kinds of organic compounds are expensive and moisture sensitive [7]. Therefore, new polymer precursor and synthesis methods are required for low cost fabrication purpose.

Here we reported a new multi-component silica-based ceramic SiBONC ceramic, named by its constituent elements. The design of the SiBONC was based on the hybridization of quartz glass or silica with B, N and C elements, by which an excellent enhancement on amorphous state maintain temperature, refractory and mechanical properties of the ceramic could be achieved. SiBONC ceramics can be produced far cheaper than SiBCN and SiBON ceramics because of the easy availability of raw materials, short preparation route and high ceramic yield.

2. Experiment instrument

Fourier transform infrared spectra (FT-IR) were obtained by a Bruker VECTOR 22 spectrometer as KBr pellets (solids) or as films in NaCl (liquids). The break experiment method was made in FT-IR analysis of the polymer precursor pyrolysis, selected 300 °C, 600 °C, and 1000 °C three temperatures as the reference points.

X-ray diffraction (XRD) was performed using a Philips instrument operating with Cu Kα radiation (λ = 1.54178 Å) at 40 kV/50 mA. Transmission electron microscopy (TEM) was

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[*] Corresponding author. Tel.: +86 45186418694; fax: +86 45186413922.
E-mail addresses: g.wen@hit.edu.cn (G. Wen), lifeng_02@hit.edu.cn (F. Li).

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carried out on a Philips TECNAI 20 microscope operating at 200 kV. TEM specimens were prepared by grinding and dimpling. The final thinning to electron transparency was performed by Ar ion beam bombardment in a JBL-1 at an angle of 15° and ion energy of 6 kV. Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDX) were performed using the Hitachi S4700 and Philips FEI Sirion microscope operating at 20 kV.

The samples were cut to various dimensions for mechanical property tests using a diamond saw. The bending strength and Young's modulus was evaluated by three point bending using an Instron instrument with a specimen size of 3 mm × 4 mm × 36 mm, and a crosshead speed of 0.5 mm/min. The tensile edges were beveled and the tensile surface was polished. With the same equipment as used for the fracture toughness (K_{IC}), which was measured by the single edge notched beam (SENB) method on notched specimens of 2 mm × 4 mm × 20 mm with a crosshead speed of 0.05 mm/min. Vickers-hardness was measured using Tukon microhardness tester from Wilson Instruments (Irvine, CA).

3. Results and discussions

3.1. Synthesis and chemical structure

All reactions to prepare polymer precursors were carried out in a purified nitrogen (N_2) atmosphere. Chloro-polysiloxane [$(SiOCl_2)_n$] was prepared in our lab at room temperature in a translucent airtight container, through the reaction between $SiCl_4$ and PhCHO with a volume ratio of 1:1 by [13]. The $SiCl_4$, PhCHO, $PhCH_3$, BCl_3 and $PhNH_2$ are commercial analytically pure chemical reagents. All chemical reagents were purified by distillation before experiments. Chloro-polysiloxane [$(SiOCl_2)_n$], boron trichloride (BCl_3) and phenylamine ($PhNH_2$) were used as raw materials to synthesize the SiBONC polymeric precursor via following overall reactions:

$$[SiOCl_2]_n + naPhNH_2 \rightarrow [SiOCl_{2-a}(PhNH)_a]_n + naHCl \quad (1)$$

$$[SiOCl_{2-a}(PhNH)_a]_n + nbBCl_3 \rightarrow [SiOCl_{2-a}(PhN)_a H_{a-b}(BCl_2)_b]_n + nbHCl \quad (2)$$

where a and b represents the degree of the replacement between active groups in reactions (1) and (2), respectively. In the synthesis of the precursor, [$(SiOCl_x)_n$] was dissolved in toluene ($PhCH_3$) at a temperature near 80 °C. A specific amount of phenylamine was then added into the solution drop by drop. When the solution became turbid and hydrochloride (HCl) released, it indicated that reaction (1) had occurred between the phenylamine and the [$(SiOCl_x)_n$]. After completion of reaction (1), BCl_3 gas was slowly introduced into the above polymer solution to promote reaction (2), where HCl was also detected in the tail-gas absorber. Finally, residual solvent was removed by distillation at a temperature near 120 °C, and the end polymer precursor was synthesized. Precursor is a brown, hard glassy solid. Sample of polymer precursor turned more yellow and solidified on prolonged exposure in air.

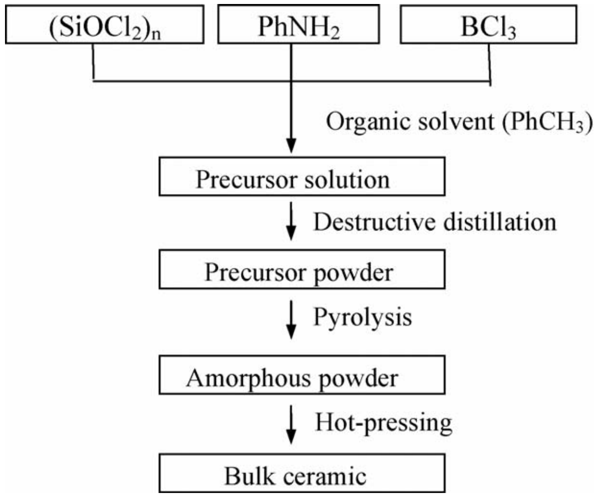

Fig. 1. Overall development plan.

The SiBONC ceramic powder was prepared by pyrolysis of polymer precursors at 1000 °C for 30 min in a silica tube furnace in flowing nitrogen (N_2), with a typical heating rate of 3 °C/min. The pyrolysis yield is about 57%. Ceramic powders are black in color, amorphous in structure and nano-sized in particle dimensions.

The as-obtained ceramic powders were hot-pressed using graphite column dies with 55 mm in diameter (heating rate $T < 1400\,°C$: 10 °C/min, $T > 1400\,°C$: 2 °C/min, dwell time at different temperature for 1 h) in an argon atmosphere under mechanical pressure of 25 MPa to fabricate the bulk ceramics. The overall flow chart of the experiment is shown in Fig. 1.

Fig. 2 shows the infrared spectra of the polymer pyrolysed at different temperatures. The characteristic Si–O–Si stretching band at 1050 cm^{-1}, B–N stretching band at 1450 cm^{-1}, and N–H stretching band at 3400 cm^{-1}, and C=C stretching bonds at 1610–1590 cm^{-1}, =CH_2 stretching band at 3010 cm^{-1} are confirmed [14]. The as-synthesized polymer from the reactants showed a broad absorption at 2500–3200 cm^{-1}, which corre-

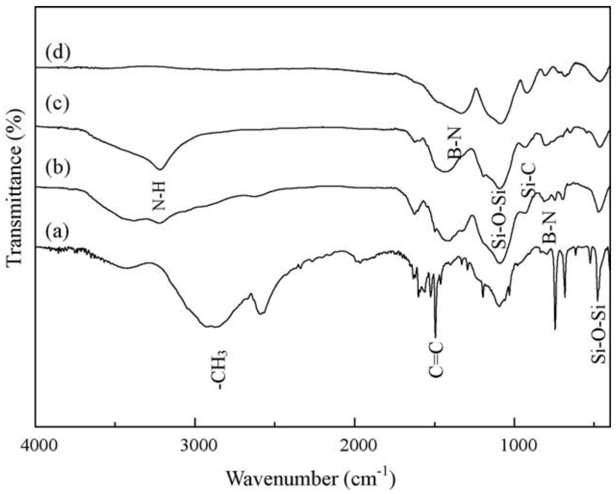

Fig. 2. FT-IR spectra of precursor pyrolyzed at different temperature: (a) room temperature; (b) 300 °C; (c) 600 °C; (d) 1000 °C.