Processing of Si_3N_4/SiC and Boron-Modified Nanocomposites Via Ceramic Precursor Route

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Consolidation of amorphous powders is emerging as a route for synthesis of high strength composite materials. Diffusion processes necessary for consolidation are expected to be more rapid in amorphous state(SRO) than in the crystalline state(LRO). A new synthesis technique of exploiting polymeric ceramic precursors(polysilazane and polyborosilazane) is derived for Si_3N_4/SiC and boron-modified nanocomposites for extremely high temperature applications, up to 2000°C. The characterization methods include thermal analysis of DTA, and XRD, NMR, TEM, after pyrolysis, as a function of time and temperature.

Key words : Ceramic precursor, Nanocomposite, Si_3N_4/SiC, BN

I. Introduction

Advanced ceramic materials that can withstand high temperatures (over 1200°C) without degradation and oxidation are needed for applications such as in advanced heat engines. Si_3N_4 and Si_3N_4 composites are good candidates for such high temperature applications due to their high strength, fracture toughness and corrosion resistance. Owing to the covalent nature of the Si-N bonds and, hence, the low diffusion coefficients in Si_3N_4, high sintering temperatures and the addition of sintering aids are normally used to enhance densification. During densification, the sintering additives form second phases located at the grain boundaries which commonly impair the mechanical and physical properties of the material especially at higher temperatures.

New processing routes for processing ceramic precursors to produce nanocrystalline silicon nitride have been conducted. Reference[1] is a composite of references for this earlier work. Significant work has been made in more recent years in the synthesis, processing and consolidation of amorphous powders produced by the polymer precursor method as a route for producing high strength Si_3N_4. More importantly, the incorporation of 6 wt% boron by using polyborosilazane precursor[2,3,5] to produce a nano-SiC dispersed in nano-Si_3N_4 matrix where both of the phases are

coated with a turbostratic layer of BN gives the microstructure remarkable elevated temperature stability.

The successful application of polymer-precursor derived silicon nitride coposites would require a detailed study of microstructure-property correlations. The mechanical properties of conventionally processed silicon nitride composites are known to have a strong microstructural dependence. For example, the mechanical behavior of submicron and nanocomposites are summarized in Table 1.

This paper presents a systematic experimental investigation for SiC/Si_3N_4 nanocomposite derived from the polymer precursors. Although the model material is a specific polymer precursor, polysilazane, the scientific knowledge will be gathered and applicable to a broad class of Si-N-C structural ceramics.

II. Cross-Linking and Ceramization of the Polymers

The transformation of linear polymer-precursor chains into branched structures prevents the loss of the lower molecular weight compounds during pyrolysis, and thus increases the ceramic yield.[6] Moreover, fragmentation and depolymerization reactions leading to the volatilization of cyclic or linear oligomers are avoided.[7] Therefore, the polymers have to be transformed into highly cross-linked prece-

Table 1. Comparison of Strength in Submicron β-Si_3N_4 vs. Nanocomposite Si_3N_4-SiC[4]

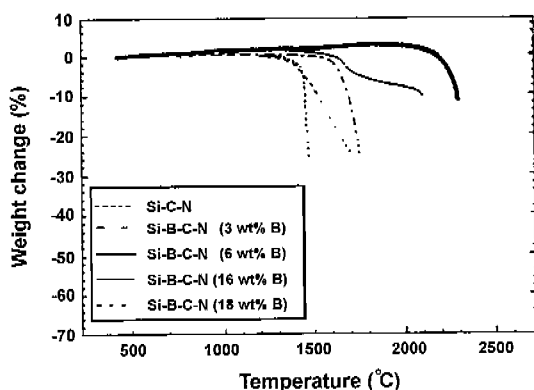| Toughness (MPa m$^{0.5}$)		Strength (MPa)		Max. Operating Temp. (°C)	
Submicron	Nanocomposite	Submicron	Nanocomposite	Submicron	Nanocomposite
4.5	7.5	850	1550	1200	1400

Fig. 1. Thermogravimetric analysis of the Si-N-C-(B) composites (Ref. 3).

ramic networks prior to pyrolysis. Furthermore, cross-linking provides a means to transform the precursors into infusible materials which do not lose their shape by melting during processing at elevated temperatures.

The subsequent ceramization step involves the thermolysis and the evaporation of organic groups and the transformation (organic-inorganic transition) of the preceramic compound via different intermediates into so-called amorphous covalent ceramics (ACC).[8]

Whereas pure silicon carbonitride decomposes around 1500°C, the ceramic with a boron content of 6 wt% exhibits an excellent high-temperature stability in argon up to temperatures around 2000°C in Fig. 1 after Riedel *et al.*[3].

XRD investigations reveal that the amorphous state of Si-B-C-N materials can be maintained up to temperatures of 1800-1900°C, indicating boron's retarding effect on the atomic mobility of these materials. TEM investigations reveal that at these temperatures the amorphous state transforms into the nanocrystalline state containing crystallite sizes of SiC and Si_3N_4 below 50 nm. The crystallization into the nanocomposite structure is combined with segregation of BN layers at the grain boundaries of the nanocrystals. Obviously, these intergranular layers inhibit grain growth.

III. Experimental Procedure

Commercially available polysilazane precursor from Lanxide Corporation and polyborosilazane precursor from Max Plank Institute, Germany, were acquired, which are inorganic polymers. The polysilazane material contains repeat units in which Si atoms are bonded in alternating sequence to N atoms. It has an alternating backbone of Si and N using vinyl appendages for cross-linking reactions. Although the polysilazanes $[(Si_{1.0}N_{1.0}C_{1.4}H_{5.4})_2]$ contain no Si-C bonds, most polysilazanes of practical interest have organic groups attached to Si, as shown in Fig. 2 (a and b), which is a generalized polysilazane and a polyborosilazane structures. These may produce $Si_3N_4/SiC/(BN)$ composites upon pyrolysis.
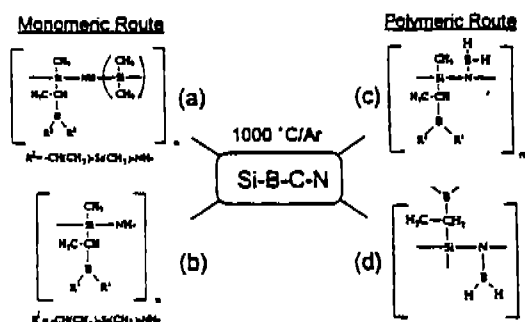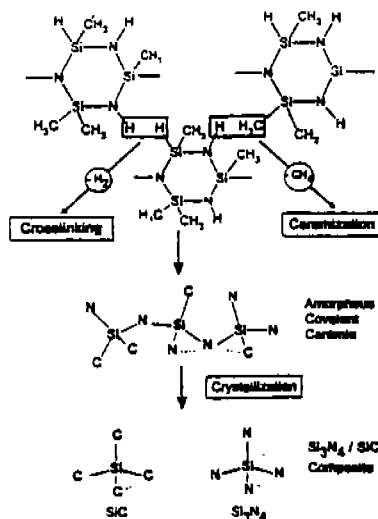

Fig. 2. Generalized polysilazane and polysilazane with boron structure (Ref. 8 and 7).
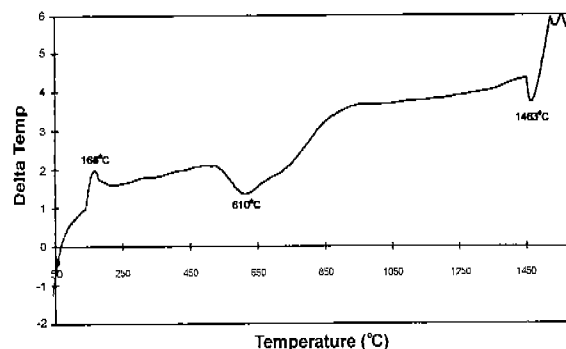

Fig. 3. DTA analysis of polymer precursor Si-N-C powder.

The low viscosity liquid polymer is thermoset (cured) to a solid through the addition of a free radical initiator such as an organic peroxide. The polysilazane, a yellow sluggish liquid polymer, was added with a room temperature stable organic peroxide by 0.5 wt%, and stirred gently for 1 min, and was heated up to 150°C for 1/2 hour on the hot plate for curing. In the process of the curing, it was very exothermic and reacted quickly. The fully cross-linked polymer after the curing was like "cracked ice" and "hard plastic material." The solid material was broken and ground in high purity alumina mortar and pestled for fine powders. The
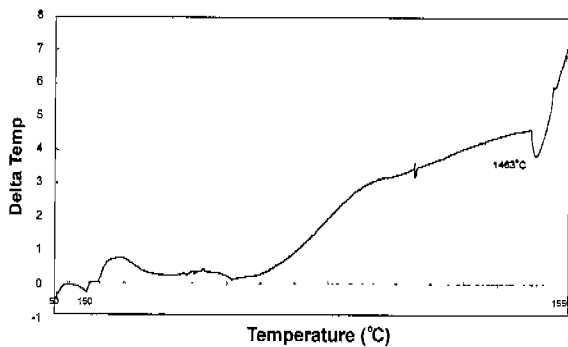
Fig. 4. DTA analysis of polymer precursor Si-N-C.B.

curing of polyborosilazane was done in glove box to prevent the drastic oxidation of the material. The two cured fine powders were run by DTA for thermal analysis.

To convert the polymer to Si_3N_4/SiC ceramics upon pyrolysis at elevated temperature, the powdered polysilazane precursor was heated for pyrolysis from 1150°C to 1550°C in 100°C intervals in alumina crucibles under highly pure (99.998%) N_2 atmosphere. Samples were heated and cooled down at 10°C/min and dwelled 2, 4, 8 hrs each without any pressure on the loose powders in the furnace. The fired samples were analyzed by XRD for the degree of pyrolysis, depending on time and temperature. NMR was performed to identify both crystalline and amorphous phases, determine the structure of such phases and studying the chemistry of these phases at the atomic level. TEM was also performed to identify the microstructural developments of the sintered powders.

IV. Results and Discussion

1. Thermal Analysis of the Pyrolyzed Si-N-C and Si-N-C-B by DTA

The DTA result of the Si-N-C powder is shown in Fig. 3, which was run at heating/cooling rate, 10°C/min under N_2 atmosphere. Three peaks at 168°C, ~250°C, 610°C and 1506°C (not shown) are shown in the Fig. 3.

Polysilazanes of practical interest have organic groups

Table 2. Chemical Analysis of the Pyrolyzed Si-N-C

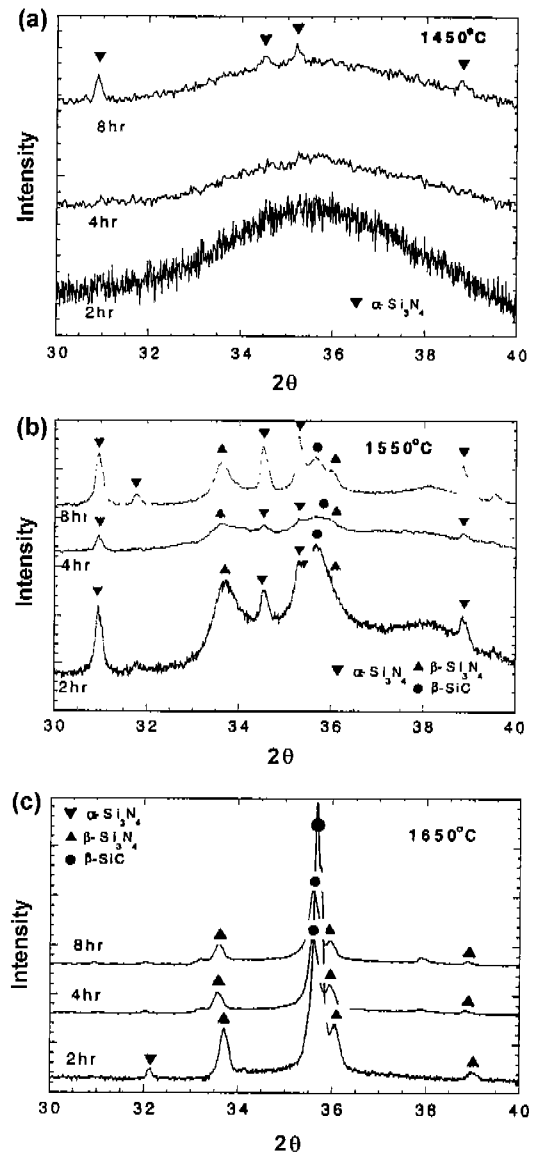| Element \ Sample	Si	C	N
1450°C, 2 hrs	59.4	13.9	26.7
1450°C, 4 hrs	65.1	14.2	20.7
1450°C, 8 hrs	57.1	10.6	32.3
1550°C, 2 hrs	70.3	14.8	14.9
1550°C, 4 hrs	66.3	16.0	17.7
1550°C, 8 hrs	69.8	13.0	17.2
1650°C, 2 hrs	-	18.0	-
1650°C, 4 hrs	76.0	14.4	9.6
1650°C, 8 hrs	-	19.8	-

-: not detectable.

Fig. 5. (a) X-ray patterns of Si-N-C at 1450°C. (b) X-ray patterns of Si-N-C at 1550°C. (c) X-ray patterns of Si-N-C at 1650°C.

attached to Si, as shown in Fig. 2 (a and b), which is a generalized polysilazane and a polyborosilazane structures. These may produce Si_3N_4/SiC (BN) composites upon pyrolysis.

The low viscosity liquid polymer is thermoset (cured) to a solid through the addition of a free radical initiator such as an organic peroxide. The polysilazane, a yellow sluggish liquid polymer, was added with a room temperature stable organic peroxide by 0.5 wt%, and stirred gently for 1 min, and was heated up to 150°C for 1/2 hour on the hot plate for curing. In the process of the curing, it was very exothermic and reacted quickly. The fully cross-linked polymer after the curing was like "cracked ice" and "hard plastic material." The solid material was broken and ground in

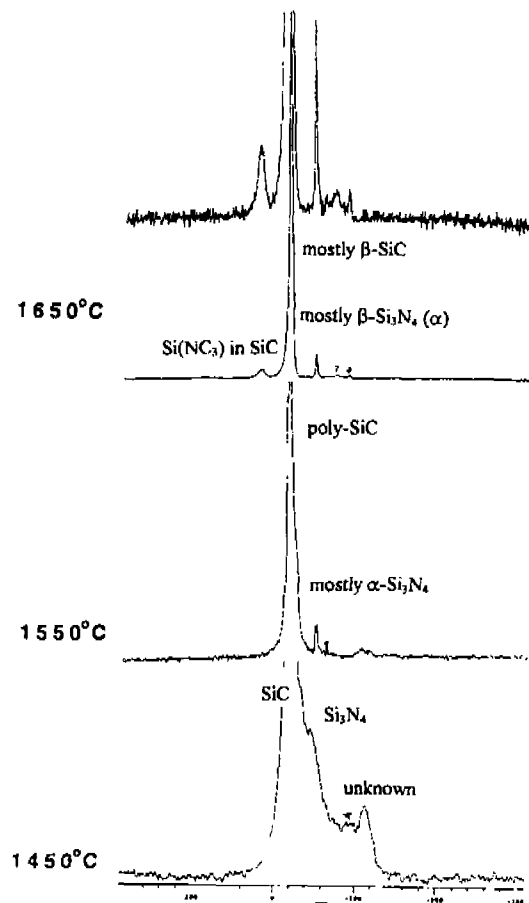The 168°C peak is due to further thermosetting, probably,

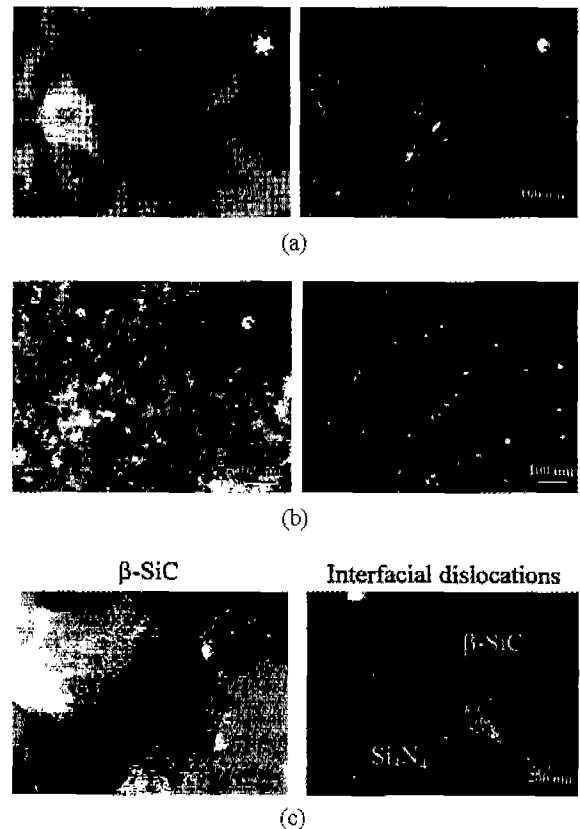**Fig. 6.** NMR analysis of the Si-N-C at 1450, 1550 and 1650°C for 2 hrs.

Fig. 7. (a) TEM analysis of Si-N-C at 1450°C for 2 hrs, (b) TEM analysis of Si-N-C at 1550°C for 4 hrs and (c) TEM analysis of Si-N-C at 1650°C for 2 hrs.

which is not fully cured. Cross-linking stage of the polymer at about ~250°C seems to have begun. At the 610°C peak may be the onset of the beginning of ceramization from the polymer. The 1463°C peak is definitely the temperature of crystallization to silicon nitride.

The DTA result of the cured Si-N-C-B powder presents some different aspects in peak locations as shown in Fig. 4. It shows that the reaction process, presumably, with the three stages of cross-linking (~300°C), ceramization (~560°C) and crystallization (around ~1500°C, not shown) individually.

2. Chemical Analysis of the Pyrolyzed Si-N-C

The pyrolyzed samples were chemically analyzed by a gas adsorption analyzer in Table 2. At 1450 and 1550°C the content of the carbon was decreasing at 8 hrs, presumably, consuming amorphous carbon and N_2 for new bondings of Si-N and Si-C. On heating to 1650°C, the Si-N bonds are replaced with Si-C bonds as N_2 is expelled from the precursor.

3. X-Ray Diffraction Patterns of the Pyrolyzed Si-N-C

The evolution of crystallinity in the pyrolyzed polysila-zane is shown by XRD patterns at 1,450, 1550 and 1650°C for 2, 4, 8 hrs under N_2 in Fig. 5(a-c). At 1450°C, the materi-

Table 3. Summary of the Si-N-C TEM Results

Temperature (°C)	Time (hr)	α-Si_3N_4		β-SiC	
		Particle	Whiskers	Particle	Whiskers
1450	2	1-5 nm	Yes	Round (30 nm)	Yes
	4	1-5 nm	Straight Twin	Triangular	Stacked (irregular)
	8	1-5 nm	Straight	Triangular (150 nm)	Stacked (rounded)
1550	2	20-30 nm large	Yes		Yes
	4	20-30 nm large	Yes		Straight Cored Branched
1650	2	large	Yes	Equiaxed (1 μm)	Yes

als are mostly amorphous, initiating α-Si₃N₄ peaks for 4 and 8 hour firing.

By 1550°C, it has crystallized to β-Si₃N₄ and β-SiC with current β-Si₃N₄ phase, stronger in the relative intensities on further firing.

By 1650°C, however, mostly β-SiC has formed. The average sizes of the strongest peaks were determined to be below 150 nm by Scherrer analysis.

The real particle size of SiC might be larger than the average size calculated by Scherrer equation. SiC particles have stacking faults very often, so the observed particle size in Fig. 7 is much larger than the calculated one.

4. NMR Studies of the Pyrolyzed Si-N-C

NMR was performed on the 1450, 1550 and 1650°C for 2 hrs as shown in Fig. 6. All spectra were acquired using standard single-pulse or cross-polarization technique under magic angle spining (MAS) conditions.

At 1450°C, the shifts of SiC, Si₃N₄, unknown oxide were examined at -20, -50 and -110 ppm with the broad line width of peaks of less crystallinity. Some spinning side band was also detected around -100 ppm. At 1550°C, the peaks of SiC with crystalline mixed polytypes at -16.5, -19.7, -24.9 ppm, mostly α-Si₃N₄ at -46.8 and -48.8, and also unknown oxide at -100 ppm were detected with the narrow line width of peaks of more crystallinity. At 1650°C, it seems to be Si(NC₃) in SiC at +20 ppm, mostly β-SiC at -18 ppm, mostly β-Si₃N₄ and some α-Si₃N₄ at -46.8, -48.6 ppm, and oxynitride at -70 ppm, were detected with the narrower line width of peaks of the most crystallinity among three samples.

5. TEM Studies of the Pyrolyzed Si-N-C

TEM was also perormed on the 1450, 1550 and 1650°C for 2, 4, 8 hrs to investigate the microstructural developments, as shown in Fig. 7(a-c). At 1450°C for 2 hrs, crystallites of β-SiC, which were smaller than 100 nm, were nucleated on the amorphous phases.

By 1550°C for 4 hrs, nanocrystalline α-Si₃N₄ and β-SiC with whisker form was detected.

At 1650°C for 2 hrs, interfacial dislocation were found between β-SiC and a-Si₃N₄ phases.

The TEM analysis of microstructural development in the Si-N-C is summarized in Table 3.

V. Conclusion

Crystallization after pyrolysis of Si-N-C polymeric

ceramic precursor under N₂ atmosphere resulted in nanocrystalline Si₃N₄/SiC composites, and the pyrolyzed powders were examined by XRD, NMR, and TEM. Conversion of the Si-N-C precursor to β-SiC occurs because and β-Si₃N₄ is thermodynamically unstable in the presence of carbon in the range of 1550°C and 1650°C.

It is evident that by altering the processing, the microstructure can be changed to possibly improve bulk mechanical properties. In this aspect the polymer precursor route is very attractive because the ceramic can be consolidated in amorphous state and subsequently a wide range of microstructure can be developed by controlled heat treatment.

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