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Ceramics International 37 (2011) 2957–2961

CERAMICS
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Letter to the Editor

Enhanced sintering of SiC using infiltration of preceramic polymer

Abstract

The effects of infiltrated preceramic polymers on the formation and sintering of SiC ceramics were investigated. Polysilazane was chosen as SiC precursors. Partially sintered SiC specimens were infiltrated with preceramic polymer by vacuum infiltration and ultrasonic stirring. The specimens infiltrated with the preceramic polymers were cured at 200–250 °C. The specimens were then sintered at 2000–2100 °C in flowing Ar atmosphere. The preceramic polymers were converted to SiC during heating. After sintering, the densification behavior and microstructure of the specimens were analyzed. The bending strength and Vickers hardness were measured and discussed.

Keywords: A. Precursors: organic; A. Sintering; C. Mechanical properties; D. SiC

1. Introduction

Silicon carbide (SiC) is one of the key engineering ceramics for high temperature applications owing to its high oxidation resistance, high corrosion resistance and high mechanical strength. Despite its superior properties, it is difficult to obtain dense SiC because of its poor sinterbility resulting from strong covalent bonding. To obtain high-density SiC without high pressures, a powder with a high specific surface area or small amounts of additives are needed. Prochazka [1] developed a method where the addition of small amounts of boron and carbon resulted in a high density without the application of an external pressure. Later, it was reported that the addition of alumina and yttria could be used to obtain a high density due to the presence of a liquid phase [2–4]. Hurtado et al. reported that pressureless sintered SiC specimens could be obtained using polycarbosilanes as binding agents. In addition, silicon containing a preceramic polymer, such as –carbosilanes and –silazanes, were converted to SiC with a sufficient ceramic yield at 1600 °C [5]. A preceramic silicon containing polymer, such as –carbosilanes, –silazanes, were investigated due to their outstanding ceramic yield. They were used to produce ceramic matrix composites, such as turbine components (inner scroll support) with a complex shape, using the preceramic-polymer-impregnation method followed by several heat treatment steps [6,7] with binders for the sintering powder [8] utilizing the thermosetting property of the polymers. The polymer-derived amorphous silicon carbonitride exhibited oxidation and creep resistance at high temperatures [9–11]. The enhanced densification of ceramic like Si_3N_4 [12,13], ZrB_2–SiC [14] using preceramic polymer have been investigated also. It was reported that the SiC nano-particles from polymer derived ceramic increased nano/macro-hardness and fracture toughness in Si_3N_4/SiC micro/nano-composites [15].

This study examined the effect of pre-ceramic polymer on the sintering of SiC. The pre-ceramic polymer was infiltrated into the SiC specimens. The sintering properties and processing of the composites were examined and the mechanical properties were compared with or without infiltration.

2. Experimental procedure

Commercially available SiC spray dried granules (FCP 15RTP, Norton: containing carbon resin and boron carbide as sintering additives; the average particle size is 0.5 μm), polysilazane (Ceraset Polysilazane 20.KION) was used as the starting materials. With SiC granule, pellets were uniaxially pressed in a steel die (20 mm diameter) at 125 MPa pressure. The pellets were heated at 1200 °C or 1450 °C for 1 h to achieve the minimum strength that could sustain polymer infiltration impact. The polymer was infiltrated into the pellets through the use of a vacuum and agitated ultrasonically at 19,800 Hz to force the ceramic precursor to penetrate the inner pores of the pellets. The specimens were cured at 200 °C to 300 °C for 2 h in an Ar atmosphere. The infiltrated pellets were sintered at 1450–2100 °C for 1 h in an Ar atmosphere. In addition, PSZ was heated to 1600 °C in an Ar atmosphere to observe the characteristics of SiC, which were derived from the pre-ceramic polymer. X-ray diffraction (XRD) and micro-structural analysis were performed to examine the phase of the heat-treated polymer and powder morphology, respectively.

The density of the sintered specimens was measured using the Archimedes method. XRD was used to analyze SiC phases of the final specimens with a Cu target (40 kV, 40 mA) after polishing the specimen surface with a diamond embedded plate. Cross sections of the sintered specimens were ground and polished to a 1 μm finish. The polished specimens were etched

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doi:10.1016/j.ceramint.2011.03.018

chemically in Murakami solution for 30 min at 100 °C to produce the contrast. The microstructure of the etched specimens was observed by scanning electron microscopy (SEM, S-2150, Hitachi). The flexural strength was measured at room temperature using a four point method with an inner and outer span of 10 mm and 30 mm, respectively. For strength measurement, bar shaped specimens were cut and polished to a size of 4 mm × 5 mm × 40 mm. The hardness was measured using a Vickers indenter with a load of 10 N.

3. Results and discussion

Table 1 shows the effects of pre-heat treatment on the amount of residual polysilazane in the infiltrated specimens after sintering at 2000 °C for 1 h. The yield of the residual polysilazane was believed to be the amount of SiC derived from the polysilazane. Therefore, the sintered density will improve with increasing residual polysilazane content. While it is well known that polysilazane converts into SiCN followed by adequate heat treatment generally, it was also reported SiC can be achieved at specific condition because pyrolysis composition was very dependant on process conditions [16,17]. As SiCN was formed at nitrogen atmosphere, SiC was done at argon atmosphere. Regarding the yield of the residual polysilazane, the yield is strongly dependent on the pre-heat treat temperature. The yield of the specimen treated at 1450 °C was approximately 50%, whereas most of the pre-ceramic polymer was vaporized in the specimen treated at 1200 °C. Treatment at 1200 °C did not increase the density or other properties after sintering. Polysilazane is quite sensitive to oxygen. Therefore, the infiltrated polysilazane reacted with the surface oxides on the SiC powder and formed SiO and CO, which is volatile, during sintering [18]. In case of 1200 °C, the surface oxide was not eliminated due to the insufficient carbo-thermal reduction. However, the surface oxide reacted with carbon in the SiC raw materials and was eliminated by carbo-thermal reduction at 1450 °C.

Ceraset, which was used as a preceramic polymer, has a ceramic yield up to 75% but was slightly lower in our case. Therefore, it will be necessary to increase the yield of the residual polysilazane to control the sufficient carbo-thermal reduction during pre-heat treatment [19]. Fig. 1 shows the microstructure of the fracture surfaces before and after polysilazane infiltration. The polysilazane was infiltrated well into the space between the SiC particles and cured, resulting in a higher green density. The porosity of green specimens before infiltration was 47%. Comparing the amount of void before infiltration and the weight gain after infiltration, it was estimated that 95% of void was filled by infiltrated polymer at one time.

Table 1
Effect of the pre-heat treatment of the green body on the residual polymer after sintering at 2000 °C.

Heat treatment temperature (°C)	Amount of polysilazane infiltrated (wt%)	Amount of residual polysilazane after sintering (wt%)	Yield of residual polysilazane (%)
1200	23.8	2.1	8.8
1450	27.1	13.6	50.2

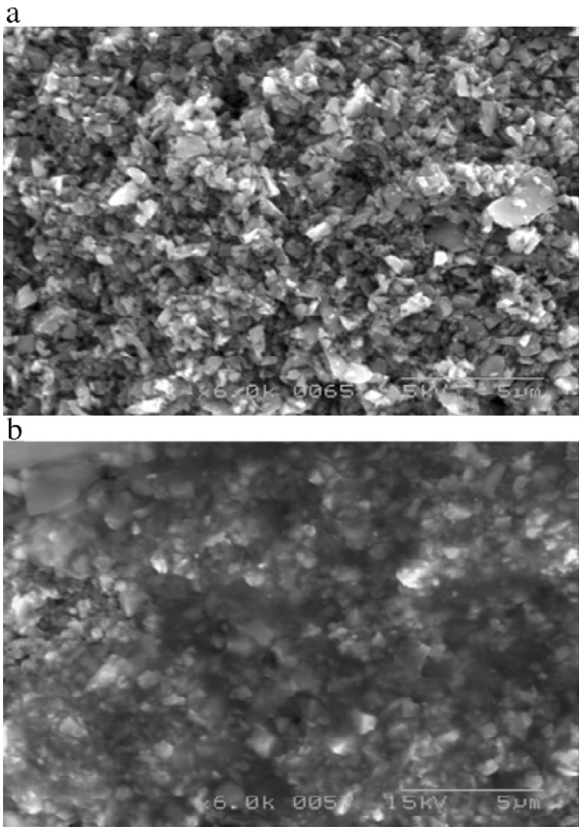

Fig. 1. Fracture surface of the SiC green body (a) without polysilazane infiltration and (b) with polysilazane infiltration.

XRD of the polysilazane derived SiC powder at 1600 °C revealed only the β-SiC phase (Fig. 2). Fig. 3 shows the polysilazane derived SiC powder at 1600 °C. Nanocrystalline particles <100 nm in size were observed. Fig. 4 shows the XRD patterns of the infiltrated specimen sintered at 1600, 2000 °C. The volume fraction of the α- and β-SiC polytypes was determined from the relative intensities of all peaks [20,21]. The fraction of the β-phase was approximately 12% in the

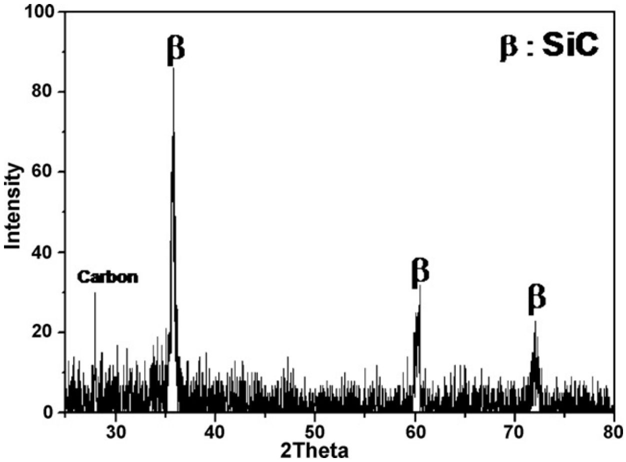

Fig. 2. XRD pattern of SiC power derived from polysilazane at 1600 °C.

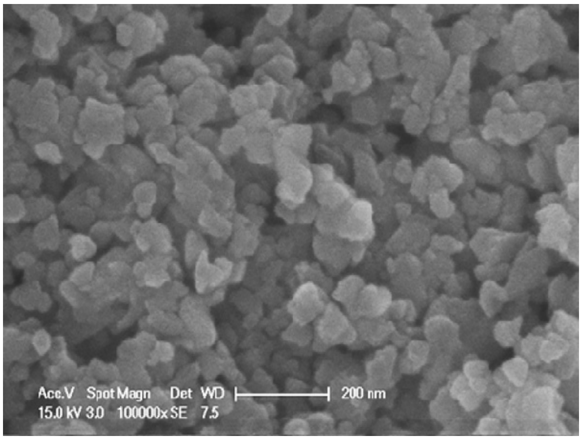

Fig. 3. Microstructure of powder derived from polysilazane at 1600 °C.

specimen sintered at 1600 °C and ~0% in the specimen sintered at 2000 °C. As the SiC raw material was composed of the α-phase only, it is certain that all the β-SiC in the specimen sintered at 1600 °C was derived from the polymer infiltrated, as shown in Fig. 2. The lack of a β-phase at 2000 °C means that the β-SiC derived from the polymer at 1600 °C had transformed to α-SiC at 2000 °C. Fig. 5 presents the change in density of the sintered body at various sintering temperatures. The sintered density of the specimen infiltrated with polysilazane was higher than that of the non-infiltrated specimen over the entire temperature range. It is considered that the high sintered density resulted from a higher starting green density. Moreover, the infiltrated specimen sintered at 2000 °C had a similar density (3.13 g/cm^3) to that of the non-infiltrated specimen sintered at 2100 °C. This shows that polysilazane infiltration increased the green density, resulting in a decrease in sintering temperature. Fig. 6 shows the level of shrinkage in the specimens. The 14.2% shrinkage in the specimen infiltrated with polysilazane was much lower than the 17.1% and 18.1% shrinkage in the non-infiltrated specimen sintered at 2000 °C and 2100 °C, respectively. The infiltrated polysilazane, with which the pores were filled, was converted to SiC during sintering resulting in a higher density with less shrinkage. Fig. 7 shows the microstructures of the specimens. The specimen with infiltration was sintered at 2000 °C (a) and the specimen without infiltration was sintered at 2100 °C (b), which have the same density. The grain size of the infiltrated specimen was slightly smaller than that of the non-infiltrated specimen because of the lower sintering temperature. The general microstructure shows little difference. The polysilazane derived nano SiC powders were mot observed in the infiltrated specimens. This means that the nano β-SiC particles derived from the polysilazane were completely transformed to α-SiC and grew at 2000 °C.

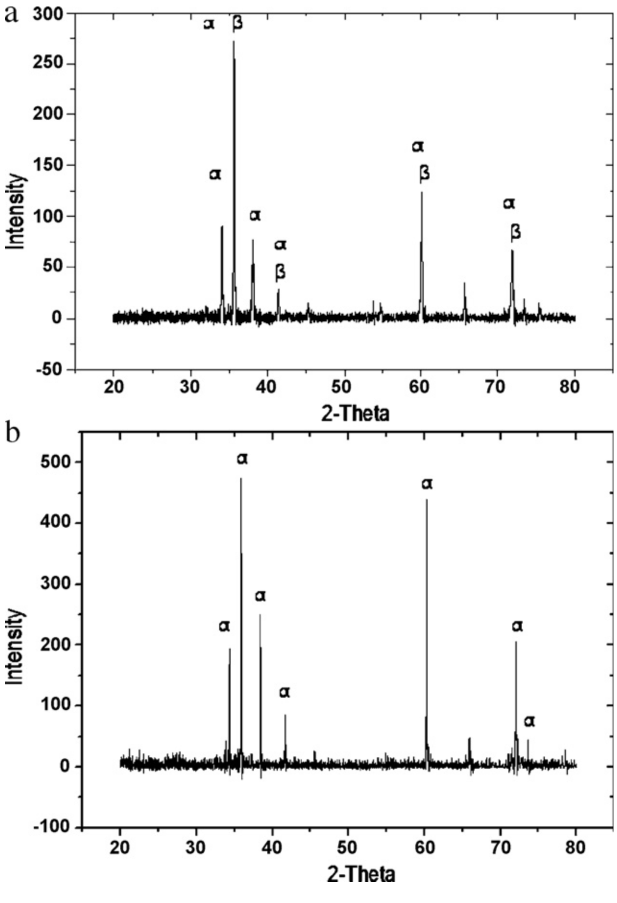

Fig. 4. XRD pattern of infiltrated SiC specimen sintered at (a) 1600 °C and (b) 2000 °C.

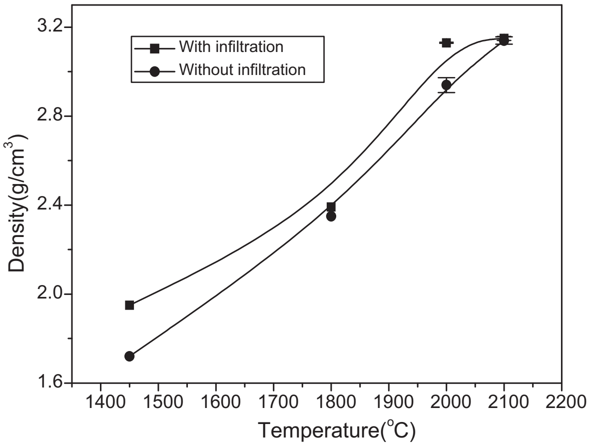

Fig. 5. Density as a function of sintering temperature.

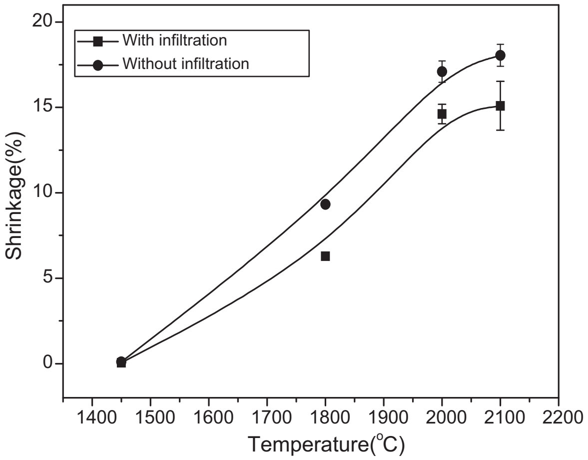

Fig. 6. Shrinkage as a function of sintering temperature.

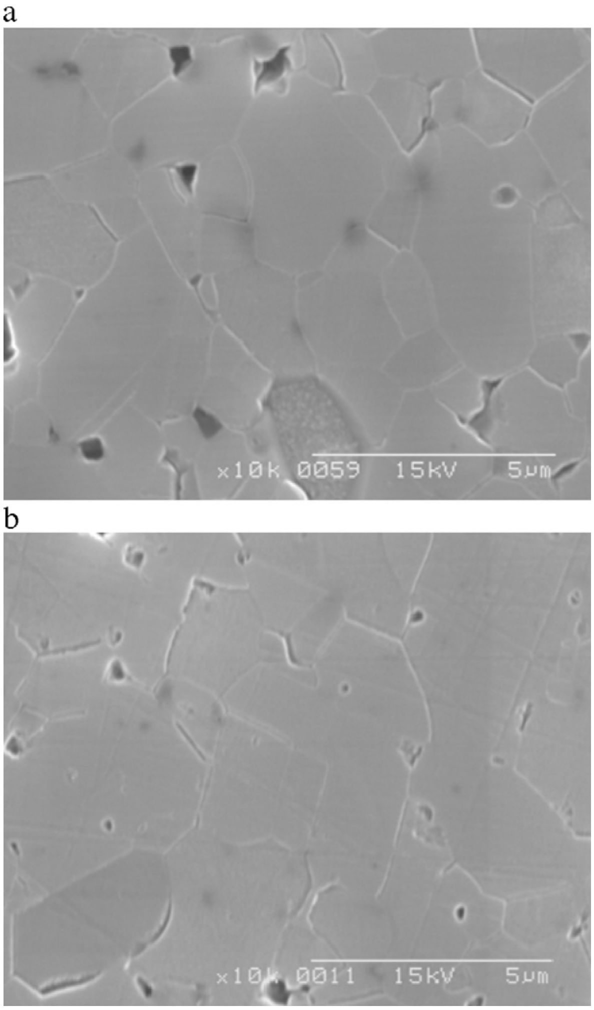

Fig. 7. Microstructure of the infiltrated specimen sintered at 2000 °C (a) and the non-infiltrated specimen sintered at 2100 °C (b).

Table 2
Vickers hardness and 4-point bending strength of SiC sintered at 2000 °C and 2100 °C.

Specimen	Vickers hardness (HV)	4-Point bending strength (MPa)
Infiltrated and sintered at 2000 °C	2784	313.5 ± 15.0
Non-infiltrated and sintered at 2100 °C	2596	297.9 ± 65.4

Table 2 lists the hardness and bending strength of the specimens with similar densities. Normally, the hardness is proportional to the reciprocal of the square root of the grain size. Decreasing the sintering temperature can restrain the increase in grain size, resulting in a higher hardness value. The hardness of the infiltrated specimen sintered at 2000 °C was higher than that of the non-infiltrated specimen sintered at 2100 °C. This was attributed mainly to the effect of the decreasing sintering temperature. A higher bending strength and lower deviation were observed in the specimen with infiltration, which means that the relatively large pores had been eliminated by pore filling through infiltration.

4. Conclusion

The mass loss of the polysilazane was decreased by eliminating the oxide layer on the SiC particle via carbothermal reduction. The infiltrated polysilazane filled the space between the particles, resulting in a higher green density. The density of the infiltrated specimen sintered at 2000 °C was similar to that of the non-infiltrated specimen sintered at 2100 °C. The shrinkage of the infiltrated specimen was also lower than that of the non-infiltrated specimen. The infiltration of polysilazane can lead to a decrease in sintering temperature and shrinkage, resulting in higher hardness, strength and reliability. The polymer derived SiC β-phase was fully transformed to the α-phase and grow during sintering. Therefore, the microstructure and XRD patterns were similar regardless whether is the specimen had been infiltrated.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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5 January 2011