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# Porous silicon carbide ceramics from silicon and carbon mixture

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Porous SiC ceramics were fabricated from a mixture of silicon (Si) and carbon (C). The Si and C mixture was treated first at 1500 °C for the formation of  $\beta$ -SiC and then heated further up to 2150 °C. When the  $\beta$ -SiC particles that were transformed into  $\beta$ -SiC at over 2100 °C, the rapid grain growth of  $\alpha$ -SiC consumed the  $\beta$ -matrix SiC particles and ultimately porous interconnected network structure with huge elongated plate-like grains was formed. The effect of the initial composition on the microstructure formation of the porous SiC ceramics was investigated. The mechanical properties of the porous SiC ceramics were examined and discussed.

Key words: Porous ceramics, Silicon, Carbon, SiC, Porosity, Strength.

## Introduction

Porous SiC is recognized as a leading candidate for porous filter applications related to the environmental and energy industry, owing to its excellent high temperature properties, good thermal resistance, good corrosion resistance and thermal shock resistance. These include diesel particulate filters, gas burner media, thermal insulators and catalyst supports. Sufficient strength and the associated requirements of porosity and pore size are needed for these applications. Various methods have been developed for preparing porous SiC ceramics [1-8]. However, some of these methods produce ceramics with insufficient strength, due to the partial and nonuniform bonding and high production costs. In addition, the additives for sintering or reaction bonding decrease the thermal strength and chemical stability.

In our previous work, a novel process for the fabrication of porous SiC ceramics with a unique microstructure was developed. These porous SiC ceramics were composed of an interconnected network structure with pure and large  $\alpha$ -SiC grains [9]. Therefore, high mechanical properties and chemical stability were expected. However, the high cost of the initial  $\beta$ -SiC powders has limited the application of these porous SiC ceramics.

In this work, porous SiC ceramics were fabricated using silicon and carbon powders as the starting materials. This method is simple and cost-effective for fabricating porous SiC ceramics. Microstructure and phase analysis were conducted with varying the process parameters, namely, the composition of the starting materials and the temperature.

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## **Experiments**

Commercially available Si (2-5 µm, Saint-gobain, Germany), C (5 µm, Kojundo chem. Co. Ltd., Japan) and B<sub>4</sub>C (0.5 µm, Kojundo chem. Co. Ltd., Japan) powders were used as the starting materials. The compositions of the Si and C mixtures are shown in Table 1. The corresponding amount of the mixture of Si, C and 1 wt% B<sub>4</sub>C were mixed by ball milling in methanol as a solvent for 3 h to obtain homogeneous slurries. After milling, the slurry was dried on a hot plate at 60-70 °C and sieved through a 100 mesh screen. The mixtures were moulded under a pressure of 250 MPa to form 20 mm diameter pellets. The specimens were fired at 1500 °C for 1 h in a vacuum and then sintered further at 2150 °C for 3 h in an Aratmosphere. The density and porosity of the sintered specimens were measured using the Archimedes method. The pore size distribution was measured by mercury porosimetry. X-ray diffraction (XRD) was used to analyse the SiC phases of the specimens with a Cu target (40 KV, 40 mA). The microstructures of the specimens were observed using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The bending strength was measured at room temperature by the 3-point bending method with a span length of 30 mm.

#### **Results and Discussion**

Fig. 1 shows the results of the XRD analysis of the specimens when they were heat treated at 1500 °C for 30 minutes under a vacuum atmosphere. After heat treatment at 1500 °C, the results showed that Si and C reacted to form  $\beta$ -SiC. Residual Si was present in the case of the S1 composition and a C peak was observed in the case of the S3 composition. This means that the

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Sample	Molar ratio of Si : C with phenolic resin	B <sub>4</sub> C (wt%)
S1	1:0.9	1
S2	1:1.0	1
<b>S</b> 3	1:1.1	1

Table 1. Molar composition of samples with Si and C.



**Fig. 1.** XRD patterns of the porous SiC ceramics heated at 1500 °C under Ar atmosphere: (a) S1, (b) S2, (c) S3.



(b)

Fig. 2. SEM micrographs of fracture surface of S2: (a) green compact, (b) after heat treatment at 1500  $^{\circ}\mathrm{C}.$ 

formation of SiC was sensitive to the starting raw materials mixture.

Fig. 2 shows the fracture surfaces of the green compact and the specimen after heat treatment at 1500 °C. The size and morphology of the SiC powder were independent of the raw materials. Si and C particles remained in the raw powder form in Fig. 2(a).



**Fig. 3.** XRD patterns of the porous SiC ceramics heated at 2150 °C: (a) S1, (b) S2, (c) S3.







**Fig. 4.** SEM micrographs of the fracture surface of the samples with different molar compositions: (a) S1, (b) S2, (c) S3.

On the other hand, the particles were reduced in size after the heat treatment at  $1500 \text{ }^{\circ}\text{C}$  as shown in Fig. 2(b). This phenomenon was thought to be due to the



**Fig. 5.** EDS analysis of S3 sample: (a) SEM image of selected area EDS (b) circle area EDS pattern.

liquid-solid reaction as the Si melted. Shi et al. also synthesized submicron SiC powders by the liquid-solid reaction between liquid Si and C at 1500 °C [10].

Fig. 3 shows the results of the XRD analysis after heat treatment at 2150 °C for 3 h under an Ar atmosphere. It is observed that only the  $\alpha$ -phase was present in all of the specimens. It is generally accepted that the cubic  $\beta$ -SiC is the stable form of SiC at low temperatures of up to 2100 °C and that this  $\beta$ -SiC transforms into the hexagonal  $\alpha$ -phase at higher temperatures. Moreover, it has been reported that the addition of boron tends to stabilize the  $\alpha$ -phase [11]. Therefore, the addition of B<sub>4</sub>C accelerates the  $\beta$ - $\alpha$  phase transformation. No residual Si and C were found in any of the specimens after they were heat treated at a high temperature of 2150 °C, unlike after the treatment at 1500 °C.

Fig. 4 shows the results of the SEM observation of the porous SiC ceramics that were produced. The appearance of the product can be sensitively varied by adjusting the C content. In Fig. 4(a), SiC particles with a typical  $\alpha$ -type plate-like shape were observed to develop well and grow. As the C content increased, small grains around the particles were observed, as shown in Fig. 4(b). In Fig. 4(c), small clusters made of very small grains were observed. According to previous research [9], the dissociative evaporation of SiC occurs at high temperatures greater than 2000 °C, giving rise to Si(g), Si<sub>2</sub>C and SiC<sub>2</sub> vapor [12, 13]. According to the study of Singhal, the partial pressure of Si(g) and Si<sub>2</sub>C reduces the increase of the carbon potential [14]. Therefore, the dissociative evaporation of SiC is accelerated in the carbon deficient S1 composition. The total vapor

 Table 2. Shrinkage of the porous SiC samples at different temperatures.

Sample	Shrinkage (%)	
	1500 °C	2150 °C
S1	-5.51	-2.8
S2	-5.59	-1.9
S3	-5.69	-0.7



Fig. 6. Porosity and flexural strength of the specimens as a function of the carbon content.

pressure in  $\beta$ -SiC is higher than that in  $\alpha$ -SiC in this temperature range [15]. According to the difference in the vapor pressure, Si<sub>2</sub>C and SiC<sub>2</sub> evaporated from  $\beta$ -SiC, diffused into  $\alpha$ -SiC and condensed on the surface of  $\alpha$ -SiC. When the  $\alpha$ -seed is formed, it drastically grows during sintering and consumes the unstable  $\beta$ matrix. At the end of the process, the grains impinge on each other, resulting in an interconnected porous network structure. With increasing carbon content, such as in the case of the S2 and S3 compositions, the dissociative evaporation of SiC decreased and ultimately small grains around the particles were observed due to the decrease in the grain growth.

From the EDS analysis in Fig. 5, the small particle clusters in the S3 specimen were found to be mainly comprised of carbon, which was not detected by XRD.

Table 2 presents the changes in the shrinkage of the specimen after the heat treatment. The results showed that the shrinkage was in the range from -5.51 to -5.69% when the specimen was heat treated at 1500 °C, while the final range was from -2.8 to -0.7% at 2150 °C. The expansion of the specimen at 1500 °C is considered to be due to the effects of the small volume expansion during the melting of Si within the green compact. There was no significant difference in the expansion rates of the specimens heat treated at 1500 °C. However, the shrinkage of the specimens sintered at 2150 °C increased with increasing carbon content. The lesser shrinkage of the S1 composition was thought to be a phenomenon that occurred due to the fast evaporation-condensation reaction. According to the classical sintering theory, a surface transport mechanism, such as evaporation-



Fig. 7. Pore size distribution of the porous SiC ceramics.



(b)



(c)

Fig. 8. SEM micrographs porous SiC ceramics of S1 with  $\beta$ -SiC : (a) 10 wt%, (b) 30 wt%, (c) 50 wt%.

condensation, does not cause shrinkage [16]. In the S3 composition, some of the sintering occurred due to the lesser evaporation.

Fig. 6 shows the porosity and flexural strength of the specimens that were produced. The porosity was 65.7%-



Fig. 9. Porosity and flexural strength of the  $\beta$ -SiC powder as a function of the  $\beta$ -SiC content.



Fig. 10. Pore size distribution of the porous SiC ceramics of S1 with  $\beta\text{-SiC}$  addition.

61.9% and the flexural strength was 6.4-12.1 MPa. It is known that the flexural strength of porous ceramics normally decreases as the porosity increases [17-19]. Our results show the same tendency. The reduction of the porosity and increase of the flexural strength are thought to be due to the increase in sintering as the C content increased, which caused slower evaporation-condensation.

Fig. 7 shows the poresize distribution of the samples. The median pore sizes of S1 and S2 showed no significant difference. However, the pore size of S3 decreased slightly to 22.7  $\mu$ m. It is considered that the low density of the porous SiC was due to the decreased volume during the synthesizing process of SiC from Si and C. Therefore, in order to control the porosity of the porous SiC,  $\beta$ -SiC powder was added to the raw material mixture.

Fig. 8 shows the fracture surfaces of the specimens to which 10-50 wt% of  $\beta$ -SiC powderwas added after heat treatment at 2150 °C for 3 h under an Ar atmosphere. As the  $\beta$ -SiC powder content increased, a more close grained structure and grown angular grains were observed.

Fig. 9 shows the porosity and flexural strength of the specimens as a function of the  $\beta$ -SiC content in the initial raw material mixture. The porosity decreased from 65.7% to 56.4% and the flexural strength increased from 6.4 MPa to 14.3 MPa as the  $\beta$ -SiC content increased to 50 wt%.

Fig. 10 shows the pore size distributions of the specimens to which  $\beta$ -SiC was added. As the  $\beta$ -SiC

powder content in the initial raw material mixture increased, the median pore size decreased from 36.9  $\mu$ m to 28.3  $\mu$ m, which is smaller than the pore sizes of the S1 specimen. It is thought that the increase of the  $\beta$ -SiC content in the initial raw material mixture reduced the volume loss that occurs during the synthesis of SiC and resulted in an increase in the density, improvement of the flexural strength and decrease in the pore size.

### Conclusions

Porous SiC ceramics were manufactured from a mixture of Si and C. The silicon and carbon were first converted into fine SiC particles at 1500 °C during heating. Finally, rapid grain growth with low shrinkage occurred accompanied by the transformation of the  $\beta$ - $\alpha$  SiC phase at 2150 °C, resulting in the formation of an interconnected porous network structure with huge plate-like grains. A low carbon composition was more favourable to build an interconnected porous network structure by rapid grain growth. The mechanism of this rapid grain growth is thought to be the evaporation-condensation reaction between the  $\beta$ - $\alpha$  SiC grains. The porosity and pore size were controllable by the addition of  $\beta$ -SiC powder.

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