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Fabrication of porous SiC ceramics having pores shaped with Si grain templates

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Abstract

SiC porous ceramics were prepared by heating mixtures of Si powder and carbon black at 900 °C for 24 h in Na vapor. The grains of the Si powder were not only the source of Si for SiC but also served as templates for the pores in the SiC porous ceramics. Angular-shaped pores with sizes of 2–10, 10–150 and 50–150 μm were formed by angular Si grains with sizes of ≤10, ≤50 and ≤150 μm, respectively. The porosity of the SiC porous ceramics was around 55–59%. Spherical pores were also formed when spherical Si grains were used. A bending strength of 14 MPa was measured for the SiC porous ceramics prepared with the Si grains (≤50 μm).

Keywords: B. Porosity; C. Strength; D. SiC

1. Introduction

As introduced in many previous papers, because of their excellent chemical resistance, thermal conductivities, mechanical strength and thermal shock resistance, SiC porous ceramics are used in a wide range of applications, such as filters for molten metal, diesel particle filters and light-weight structural materials. Various methods have been studied for the fabrication of SiC porous bulk ceramics.[1] Sintering is a popular production process in which SiC powder is sintered at 1300–2000 °C with oxide additives.[2–6] Carbon foams or carbon porous structures were converted into SiC porous bulk by infiltration of Si melt or Si vapor above the melting point of Si (1414 °C) at 1450–1700 °C,[7–9] and by infiltration of silica sol and carbothermal reduction at 1400–1600 °C.[10–13] For a low temperature process of SiC porous ceramics fabrication, SiC particles were bonded with the material produced by pyrolysis of polycarbosilane at 1100 °C.[14] In the processes of sintering and pyrolysis, porosity, pore size and shape and degree of interconnectivity of the porous structure can be controlled by the grain size and packing density of SiC powder, and/or by the size, shape and volume of polymer micro-beads and sacrificial templates. In the infiltration process, porous structures were designed with the structures of carbon preforms.

Recently, we reported the preparation of SiC at around 700 °C using Na.[15–17] Nano-powder of β-SiC was prepared from a mixture of Si and fullerene powders in a Na melt.[15] Biomorphic cellular SiC ceramics were prepared by heating carbonized wood at 700 °C with a Na–Si melt.[16] A SiC porous granule, having a porosity of 21%, was synthesized at 700 °C from activated charcoal by using a Na–Si melt.[17] The porous granule exhibited a fracture stress of 47 MPa and a micro-Vickers hardness of 13 GPa. Morito et al. proposed a Na–Si binary phase diagram based on thermal analysis and morphology of the products in this system, and revealed the presence of a Na–Si melt phase above 680 °C with a maximum Si content of around 50 at%.[18] SiC was formed by reaction of Si in the Na–Si melt with carbonized wood or activated charcoal. We have previously reported another method of SiC porous ceramics fabrication by using Na vapor.[19] In this method, pelletized mixtures of Si and fullerene or Si and carbon black were heated at 727–927 °C in Na vapor. The fracture surface and the walls of pores in the samples prepared with

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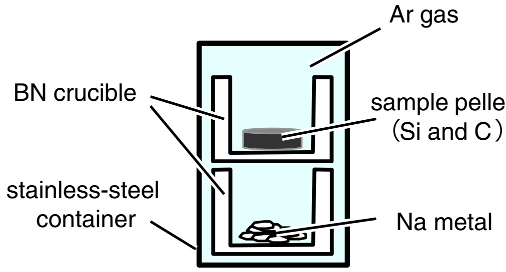

Fig. 1. Schematic illustration of the reaction container.

the mixture of Si and carbon black were dense and smooth. In the present study, Si grains of different sizes and shapes were used as the starting materials in order to control the size and shape of pores in the porous ceramics prepared by heating the mixture of Si and carbon black in Na vapor.

2. Experimental

Carbon black powder (Frontier Carbon, 99.9% purity; mean particle size 16 nm) and Si powder (High Purity Chemicals, 99.9%) were used as starting materials. The Si powder was crushed and sieved into grain sizes of ≤10, ≤50 and ≤150 μm. A mixture of the crushed Si powder (≤10 μm) and Si particles (∼200 μm) prepared by the pulsated orifice ejection method[20] was also used as a Si source.

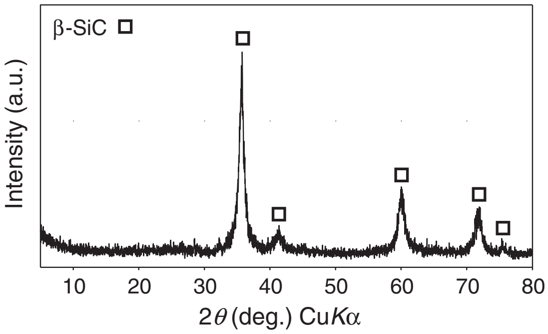

Fig. 2. Powder XRD pattern of the sample prepared with Si powder (grain size: ≤10 μm) and carbon black by heating at 900 °C in Na vapor.

The Si sources and carbon black powders were weighed with the stoichiometric molar ratio of Si:C = 1:1, and gently mixed in an agate mortar without grinding. The mixed powders were uniaxially pressed into pellets (15 mm in diameter, 4–5 mm in thickness) under a pressure of 120 MPa. For the flexural strength measurements, Si (≤50 μm) and carbon black powders were weighed with the Si:C = 1:1 molar ratio and mixed in a polyethylene bottle mixer. The mixed powder was pressed into bar-shaped compacts (3 mm × 6 mm × 14 mm) in a rectangular die under a pressure of 160 MPa.

In an Ar gas-filled glove box (O_2 and $H_2O < 1$ ppm), the pellets or compacts were placed in a boron nitride crucible (Showa Denko, 99.5%, 26 mm inner diameter, 18 mm depth),

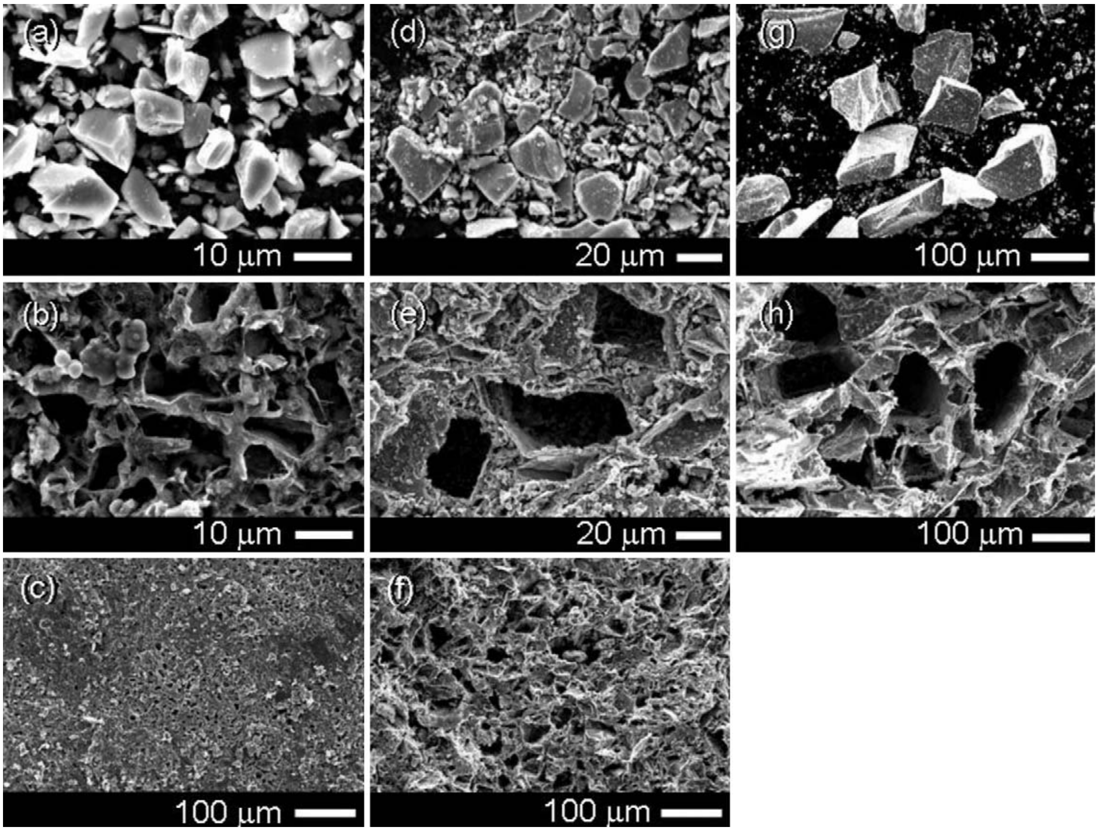

Fig. 3. SEM images of Si grains (≤10 (a), ≤50 (d) and ≤150 μm (g)), and the fracture surfaces of the samples prepared at 900 °C with Si grains (≤10 (b, c), ≤50 (e, f) and ≤150 μm (h)).

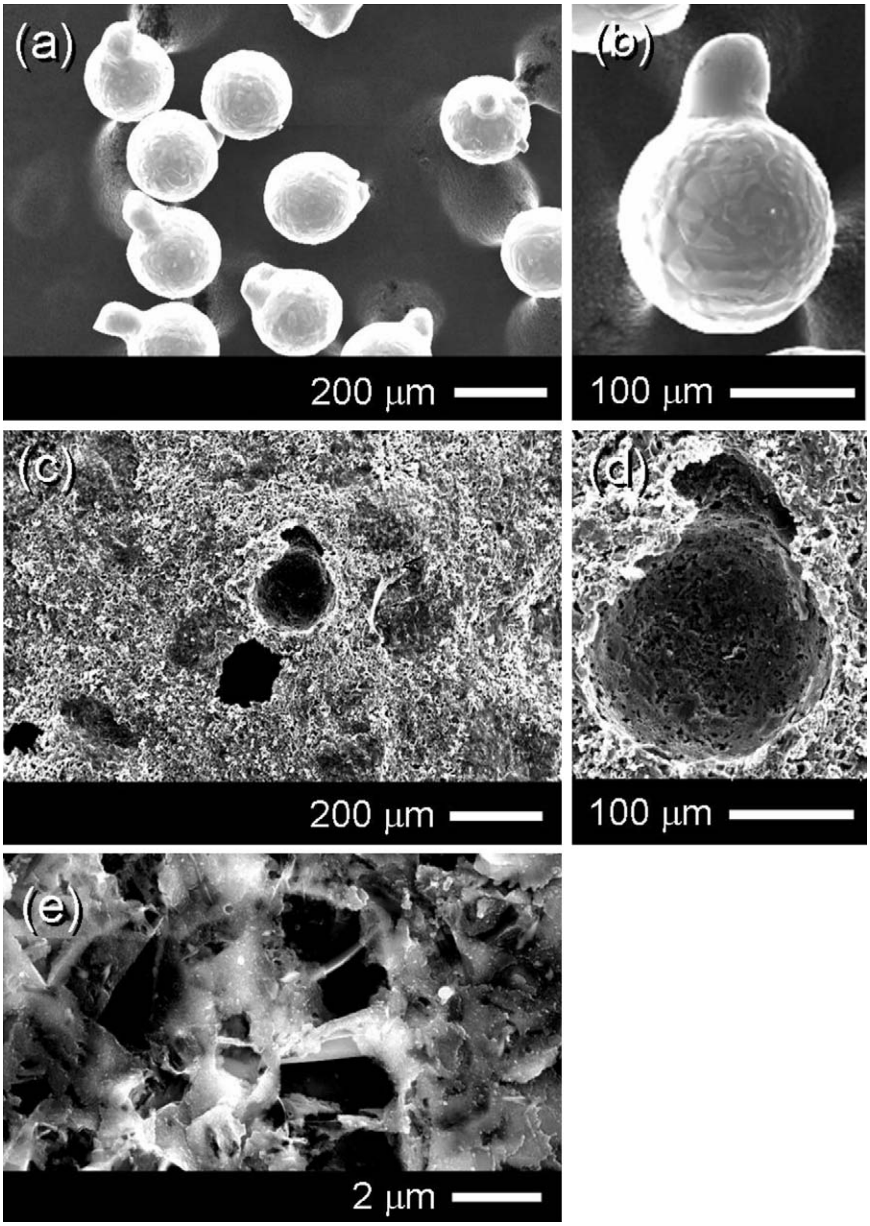

Fig. 4. SEM images of spherical Si grains (a, b), the fracture surfaces (c, d) and the wall of the spherical pore (e) of the samples prepared with spherical Si (~200 μm) and angular Si grains (≤10 μm) at 900 °C.

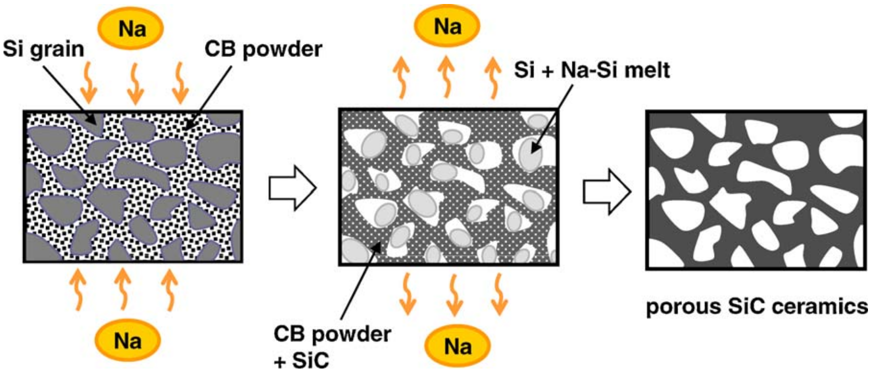

Fig. 5. Schematic illustration of the porous SiC ceramics formation process using Na vapor and Si grain templates.

Table 1
Synthesis temperature, porosity and flexural strength of porous SiC ceramics.

Synthesis method	Temperature (°C)	Porosity (%)	Flexural strength (MPa)	Reference
Sodium flux	900	61	14	This study
Sintering with Al_2O_3	1300	59–61	8–17	[6]
Sintering with cordierite	1350	54–61	5–10	[2]
Sintering with $Y_3Al_5O_{12}$	1950	57	5–30	[3]
Sintering with polysiloxane, Al_2O_3 and Y_2O_3	1800–2000	64	12–15	[4]
Sintering with SiOC, Al_2O_3, Y_2O_3, and MgO	1750	64	10	[5]
Reaction bonding (infiltration of Si)	1500	64	16	[10]

and 1.0–1.6 g of Na (Nippon Soda, 99.95% purity) was placed in another boron nitride crucible. The crucibles were set in a stainless-steel container (SUS316, 37 mm outer diameter, 45 mm height) as schematically illustrated in Fig. 1, and the container was filled with Ar gas and sealed by arc-welding.

The container was heated up to 900 °C within 2 h and the temperature was maintained for 24 h. After heating, the power to the furnace was shut off to allow cooling of the sample to room temperature. The container was cut open in air and Na metal deposited on the sample was removed by reaction with 2-propanol and ethanol. After the reaction, the sample was washed with distilled water and dried in air.

The morphology of the Si sources and the obtained samples was observed with a scanning electron microscope (SEM, Philips, E-SEM XL30). The X-ray diffraction (XRD) patterns of the powdered samples were taken using Cu$K\alpha$ radiation with a powder X-ray diffractometer (Rigaku, RINT2200). The bulk densities of the samples ρ_d were calculated from the weight-to-volume ratio. The porosity was determined from ρ_d and the theoretical density of β-SiC ($\rho_0 = 3.22\ g/cm^3$)[21]:

$$\text{Porosity}(\%) = 1 - \rho_d/\rho_0 \times 100$$

The obtained porous ceramics was characterized with a specific surface area analyzer (Micromeritics Instrument Corp., AutoPore III). Bend tests were carried out at room temperature with a materials testing machine (Shimadzu, AG-20KNG). The flexural strength was measured by three-point bending with a span of 10 mm and a cross-head speed of 0.5 mm/min on three specimens (6 mm × 3 mm × 14 mm).

3. Results and discussion

The sample pellet prepared by heating the mixture of the Si powder ($\leq$10 μm) and carbon black was powdered and the crystalline phase was identified by powder XRD. As shown in Fig. 2, all broad peaks observed in the XRD pattern of the powdered sample were indexed with a cubic lattice parameter ($a = 4.3581$ Å) of β-SiC.[21] The relative intensities of the reflections were also explained with the SiC structure. The powder XRD patterns taken for all other samples obtained in the present study were also similar to the pattern of Fig. 2, indicating that the samples were β-SiC.

SEM micrographs of the Si grains with sizes of $\leq$10, $\leq$50 and $\leq$150 μm are shown in Fig. 3(a), (d), and (g), respectively. The angular shape of the source Si grains was achieved by crushing larger Si crystals. The fracture cross sections of the obtained samples are also shown in Fig. 3(b), (c), (e), (f) and (h). The pore sizes of the samples prepared with the Si powders of $\leq$10, $\leq$50 and $\leq$150 μm were 2–10, $\leq$50 and $\leq$150 μm, respectively. The pores observed in the porous SiC were also angular and the shapes were very close to the grain shapes of the Si powders. Fig. 4 shows an SEM image taken of the Si spherical grains with protrusions ((a) and (b)), the fracture cross-section of the sample prepared with the mixture of the spherical Si and the crushed Si powder ($\leq$10 μm) ((c)–(e)). Large cavities shaped by the spherical Si grains with the protrusions were clearly observed in the SiC porous ceramics (Fig. 4(d)). At the wall of the spherical pores, many angular pores of $\leq$10 μm were observed (Fig. 4(e)). These results clearly indicate that Si grains are not only the source of Si but also the templates of pores in the formation of the SiC porous ceramics. To the best of our knowledge, no previous paper has reported that silicon grains were used for the templates of pores as well as for the source of SiC porous ceramics fabrication.

Si and carbon black powders were mixed with the stoichiometric molar ratio of Si:C = 1:1. The densities of the starting pellets were 1.5–1.6 g/cm^3 and did not depend on the grain size of the Si powders. Therefore, the volume ratio of Si and carbon in the pellets was almost the same in the starting pellets. A volume change of <2% was observed after formation of SiC porous ceramics. The porosities of the SiC porous ceramics prepared with the Si powder grains of $\leq$10, $\leq$50 and $\leq$150 μm were 55.7, 58.5 and 54.6%, respectively, and did not depend so much on the grain size of Si. However, the specific surface of the sample prepared with the Si grains of $\leq$10 μm were 26.3 m^2/g, which was larger than the areas of other samples prepared with larger Si grains of $\leq$50 μm (4.2 m^2/g) and $\leq$150 μm (2.1 m^2/g). These results also suggest that most pores formed in the ceramics were from the Si grains.

The process of SiC porous ceramics formation by heating a starting mixture of Si and carbon black powders in Na vapor is schematically illustrated in Fig. 5. By pressing the mixture of Si grains and carbon black powder, the spacing between the Si grains is uniformly filled with carbon black powder due to the very fine particles of carbon black (16 nm). The Na vapor with a vapor pressure of 1.18 atm at 900 °C[22] permeates the pellet and reacts with Si grains, forming the Na–Si melt. The melt infiltrates into the compact wall of the carbon black powder around the Si grains, resulting in the formation of SiC. After SiC formation, Na vaporizes and leaves the pellet. The density of the carbon black is approximately 1.8 g/cm^3. The volume of SiC formed by the reaction of carbon black with Si was 1.8 times larger than the original carbon black. The relative packing density of the carbon black in the starting pellets was approximately 45–50% calculated with the density of the starting pellets. The volume change between the pellet and the obtained SiC porous ceramics was within 2%. Therefore, the relative density at the SiC wall and frame in the pellet samples was estimated to be 80–90% of the theoretical density of SiC.

A flexural strength of 14 (±2) MPa measured for the bar-shaped samples with a porosity of 61% is compared in Table 1 with the previous data reported for the samples with similar porosities. The strength of SiC porous ceramics prepared at 900 °C in the present study is close to the strengths of the SiC porous ceramics prepared at higher temperatures of 1300–2000 °C in the previous studies. This result may also suggest that a relatively dense SiC wall was formed in the porous ceramics by heating at 900 °C in Na vapor.

4. Conclusions

We studied the effect of grain size and grain shape of Si sources on the porous structure of SiC bulk samples prepared by heating mixtures of Si and carbon black at 900 °C in Na vapor. The carbon black powder compact around the Si grains was permeated by a Na–Si melt which was formed by reaction of the Si grains and Na vapor. The Si grains performed not only as the source materials but also as the templates of pores. The flexural strength of the SiC porous ceramics prepared in the present study was 14 MPa which was comparable with the strengths reported for the samples prepared at higher temperatures.

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