Microstructural control of macroporous silicon carbide

Manabu FUKUSHIMA*1

National Institute of Advanced Industrial Science and Technology (AIST),
2266–98 Shimo-Shidami, Moriyama-ku, Nagoya 463–8560, Japan

Wide range of porosity in 30–90 vol % could be created into silicon carbide by employing carefully selected manufacturing methods. Two fabrication methods have been proposed and reviewed in the present paper: (1) partial sintering of submicrometersized silicon carbide particle with a suitable amount of sintering additive, acting as an inhibition of grain growth during sintering; (2) the use of ice crystals, as sacrificial pore formers, formed by freezing a silicon carbide particle dispersed gel body, leading to highly porous silicon carbide after sublimating ice crystals by vacuum drying and subsequently sintering. Depending on the processing route adopted, average pore size could be modulated in the range from 0.03 to 0.70 μm and 30 to 150 μm by partial sintering and gelation freezing, respectively. All fabrication methods proposed are simple, economical and versatile to produce macroporous body with tailored pore architecture and engineering porosity.

Key-words : Macroporous, Pores, Porosities, Sintering, Gelation and Freeze cast

Corresponding author: M. Fukushima; E-mail: manabu-fukushima@aist.go.jp

1. Introduction

Macroporosities in brittle ceramic materials are usually considered as what they should be eliminated due to fracture origin and reduced mechanical reliability. On the other hand, macroporous ceramics have been widely utilized, where porosities are positively taken into account,11)13) in numerous industrial fields such as filtration, diffuser, catalyst support, fuel cell, bioimplant and thermal insulator as well as refractory.6)8)12) The macro-porous ceramics have attracted a great deal of attention, due to the synergy effects of intrinsic properties of ceramics themselves and properties of pores dispersed into ceramics, in which ceramics materials possess thermal and chemical stability, good biocompatibility and high specific strength, and the porosities can provide lowered thermal conductivity, enlarged specific surface area and controlled permeability as well as lowered dielectric constant. A great deal of studies has tried to tailor pore architecture like pore volume (porosity), pore size, its distribution, pore shape, pore location, pore interconnection, pore orientation and the surface morphology of pore.13)14)

In this paper, the main results concerning macroporous silicon carbide (SiC) ceramics will be discussed. Among ceramic materials, SiC possesses various desired engineering properties, such as good thermal shock resistance and thermal/chemical stability as well as superior mechanical properties due to the strong covalent bonding of silicon to carbon and a low self-diffusion coefficient, indicating that can be employed for high-temperature applications. Engineering applications of macroporous SiC, such as diesel particulate filter (DPF), molten metal filter, catalyst support, gas separation under elevated temperature and corrosion atmosphere, have been widely reported.15)19)22) In order to make macroporous ceramics with desired properties, various manufacturing processes have been proposed: partial sintering, replica templating, direct blowing and sacrificial fugitives.13)15)17)33) Porous materials with pore size more than 50 nm can be categorized as macroporous, according to IUPAC (Union of Pure and Applied Chemistry). In recent review paper about macroporous ceramics, pore size can be modulated by varied fabrication routes, in which pore size is reduced in the following order of processing routes: direct foaming > replica template > sacrificial fugitives > partial sintering.1) Numerous papers have been published dealing with the use of various pore formers to fabricate macroporous SiC ceramics with desired pores sizes: submicrometer around 0.1–0.5 μm by using nano-sized sacrificial beads,3)4)13)35) from submicrometer to micrometer around 0.1–10 μm by applying the partial sintering route,13)15)16)19)22)30)37) including morphological transformation from equiaxed to platelet SiC grains,30) in situ reaction bonding3)9)10) and oxidation bonding,4)12) subsequently micrometer size around 5–500 μm by using sacrificial fugitives, including typical polyethylmethacrylate (PMMA) beads,5)4)14) expandable microspheres,4)6) hollow microspheres,4)7) polymeric or graphite microspheres,5)8)10) the sublimation of camphene,5)5)13) 10–500 μm by templating of carbonized natural wood reacted with silicon vapor, molten silicon and silica,5)4)6)41) further larger size around 300–600 μm produced by direct foaming3)12)6)3) and millimeter range of ~3 mm by using replica sponge template6)4)3)6) All these proposed processing methods allow to produce macroporous SiC ceramics with engineering porosity affording varied and tailored characteristics, which is of significance for wide range of applications. The present article intends to focus on the processing of porous SiC with various porosities and wide ranged pore sizes from submicrometer to submillimeter by applying the following novel and versatile methods: (1) the use of partial sintering with systematically investigated sintering additives and (2) the use of sacrificial fugitives of ice crystals with controlled sizes by tailored freezing conditions.

2. Experimental

2.1 Partial sintering

β-SiC (Ibiden Co. Ltd., Japan) powder was used as a raw material, which had an average particle size of 0.30 μm. As the additive γ-Al2O3 (Taimei Chemicals Co. Ltd., Japan) with an average particle size of 0.20 μm was used. Mixtures with weight...
ratios (SiC/Al2O3) of 100/0, 99/1, 98/2 and 96/4 were blended in ethanol for 1 h using a planetary mill (compositions are referred as SCA0, SCA1, SCA2 and SCA4). After drying the slurry, disk shaped compacts were prepared by a steel mold and a cold isostatic press (CIP) at 100 or 400 MPa (hereafter denoted CIP100 or CIP400). The green bodies were sintered at various temperatures from 1500 to 1800°C for 2 h under Ar gas flow.

2.2 Sacrificial ice fugitives

α-SiC (Fujimi Incorporated, Aichi, Japan) with an average particle size of 0.40 μm was used as a starting powder. As sintering additives, Al2O3 (Taimei Chemicals Co. Ltd., Japan) and Y2O3 (Shin-etsu Chemical Co. Ltd., Japan) were used. Mixtures with weight ratios of additive of Al2O3/Y2O3 = 6/4 and additives/SiC = 4/96 were blended in ethanol by ball milling. After drying of the slurry, the dried powder was mixed with a gelatin solution (Wako pure chemical industries Ltd., Tokyo, Japan) in the volume ratio of (SiC an additives)/gelatin solution = 10/90. The slurry was casted into a plastic mold to obtain a SiC powder dispersed gel. The gel was subsequently immersed into a cooling medium of ethanol setting at −10 to −70°C. The frozen gel was dried under vacuum in a freeze drier with a heating plate around 35°C above 12 h (Tokyo Rikakikai Co, Ltd., Model FDU-2100, Tokyo, Japan), leading to the elimination of ice crystals in frozen gels by sublimating ice crystals. The green bodies were degreased at 600°C for 2 h and then sintered at 1800°C for 2 h under Ar gas flowing.

2.3 Characterizations

Open porosities of the obtained porous specimens were measured by the Archimedes method with water displacement. The microstructures of fractured or polished surfaces of porous specimens were observed using scanning electron microscopy (JEOL, Model JSM-5600 or JEOL-6330F, Tokyo, Japan). Pore size distributions of porous specimens were measured by mercury porosimetry (Quantachrome Instruments Co. Ltd., PoreMaster-GT, USA). The air permeability of specific specimens was characterized by the following Darcy’s law:

\[
\Delta P = \frac{\eta L Q}{\mu A}
\]

where ΔP, μ, η, A, L and Q indicate the pressure drop between the entrance and exit of the sample, air permeability, the dynamic viscosity of air, the cross-sectional area of the sample, the
thickness of the sample, and flow rate of air through the sample, respectively. Image analyses to quantify the average pore sizes, those distributions and porosity distributions of porous samples were done by using image analysis software (PhotoMeasure, KENIS, Osaka, Japan).

3. Results and discussion

3.1 Partially sintered SiC

Figure 1 shows FE-SEM micrographs of the fractured surfaces of the green compacts (a and d) and specimens sintered at 1500 (b and e) and 1800°C (c and f) for the SCA0 [Figs. 1(a)–1(c)] and SCA4 [Figs. 1(d)–1(f)]. In the SCA0, the appreciable grain growth and the formation of necking between grains as shown in the arrows [Fig. 1(c)] were observed, which was found to be promoted by elevated sintering temperature. Fine SiC particles less than 100 nm, observed in the green compacts, completely disappeared after sintering at 1500°C. However, fine SiC grains still remained in the SCA4 sample, indicating that the alumina addition did not cause morphological changes.

Figure 2 shows typical examples of pore size distribution with sintering temperature and alumina additives. Pore size of CIP100 specimens was larger than that of the CIP400 specimens. Pore size in the SCA0 increased with increasing sintering temperatures. In contrast, pore size distribution in the SCA4 did not be changed significantly in all sintering temperatures, retaining the original small pore size. The pore size of sintered specimens was distributed in 0.20–0.70 and 0.03–0.20 μm for the SCA0 and SCA4, respectively. The porosity measured by the Archimedes principle or mercury intrusion showed all open in the range of 37–42 and 34–39% for CIP100 and CIP400 samples, respectively, decreasing with increasing alumina content, sintering temperature and CIP pressure, except the SCA0 and SCA1 samples without any changes at all sintering temperatures. The shrinkage of the samples during sintering increased up to 3.5% with increased sintering temperature, again except the SCA0 and SCA1 samples without any changes during sintering. In the initial sintering stage, mass transfer from the surface to the neck by surface diffusion or vapor route can occur without any dimensional and density changes. Because self-diffusion coefficient and vapor pressure of SiC are very low, it is reasonable to consider that surface diffusion is the main transport pass during sintering of SiC without additives. Seen in Figs. 1(a)–1(c), the disappearance of fine particles were observed, concurrently leading to the enlarged neck area, grain growth and pore growth. As fine particles possess less diffusion pass and high surface area, mass transfer from the surface to the neck must occur through surface diffusion of fine particles. In addition, a thin SiO2 layer naturally existing on the surface of SiC particle could react with free carbon of one of impurities of SiC powder to form SiO and CO gas species around 1400°C, consequently leading to the generation of fresh surfaces on the SiC particles, acting the promoted surface diffusion.

On the other hand, in the SCA4 sample, the finer microstructure seen in the green compact remained after sintering at 1800°C. Figure 3 shows TEM elemental mappings of the SCA4 sample sintered at 1800°C. It was found that Al and O existed at the grain boundary phase and especially free surface of SiC particles, suggesting that the SiC particles were well wetted and covered by SiO2–Al2O3 liquid formed by a reaction between the thin surface SiO2 layer on the SiC particles and the additive alumina during sintering. This result means that the observed liquid layer may prevent mass transfer, because the limited amount of alumina addition did not lead to the grain growth and the disappearance of fine particles during sintering. Thus, the mass transfer from the surface of particle to neck area was found to be interfered, and the resultant smaller pore size and finer particle size may be retained. Although a sufficient liquid phase promotes mass transfer, grain growth can always occur in the middle and/or final stage of liquid phase sintering. In the present results, the insufficient additive content and lower sin-
tering temperature to cause complete densification have been employed. It can be concluded that the sintering is still initial stage, implying that the mass transfer through surface diffusion could be inhibited by the covered liquid phase of SiC particles. By carefully employing additive and sintering temperature, submicrometer-sized pore could be modulated in the range of $0.03\mu m - 0.70\mu m$.

3.2 Use of sacrificial ice fugitives

In this section, gelation freezing route to create the pore size around micrometer will be discussed. Figure 4 shows typical SEM micrographs of the porous SiC with the open porosity around 86% in volume, which was prepared by gelation freezing method: frozen temperatures at (a–c) $-10^\circ C$ and (d–f) $-70^\circ C$, respectively. The micrographs were observed in parallel (a and d) to the freezing direction as indicated by the arrows, and perpendicular (b–c and e–f) to freezing direction. The unidirectional oriented pore morphology, parallel to the freezing direction, was found in (a) and (d). The cylindrical pore structures observed are found to be generated by the formation of growing ice crystals and its sublimation, because raw particles are rejected from the growing ice crystal during freezing and pushed aside. No dendritic structures which come from ice crystal grown were observed, though a dendritic or lamellar structure is well-known in the freeze casting route of water or camphene based slurries, suggesting gelation agent could prevent the dendritic growth of ice crystals. In addition, interconnected cells (indicated by circles) were also found due to the contacts among ice crystals each other during freezing. As you can see, perpendicular microstructure to freezing direction was clearly observed to be cellular structure like a honeycomb with micrometer-sized cells. The microstructure of this porous SiC was substantially different from those prepared by other fabrication methods like blowing, template, other freeze-casting routes and organic pore forming agents. The effect of freezing temperature on cell size was also monitored. When compared to Figs. 4(b) with 4(e), the cell size of porous SiC frozen at $-10^\circ C$ were much larger than those of SiC frozen at $-70^\circ C$. The average cell sizes were analyzed to be $147, 62, 54, 40$ and $34\mu m$ for the specimens frozen at $-10, -20, -30, -40,$ and $-70^\circ C$, respectively. The cell size decreased with the decrease in the freezing temperature. As the temperature range from 0 to $-7^\circ C$ is known as the temperature zone of maximum ice crystal formation, when the time required to pass this zone is short, namely low temperature of cooling medium, the size of ice crystals formed can be reduced.

Fig. 4. SEM micrographs of porous SiC. Frozen at (a–c) $-10^\circ C$ and (d–f) $-70^\circ C$, both parallel (a and d) and perpendicular (b–c and e–f) to the direction of freezing.
The connectivity among the cells in the obtained porous SiC was subsequently studied by air permeability based on Darcy’s law. Cell size, air permeability and theoretical permeability were plotted in Fig. 5, where airflow was parallel introduced to the freezing direction of the sample. The theoretical permeability ($\mu$) was computed according to the following capillary model:

$$\mu = d^2 \times P/32$$

(2)

where $d$ and $P$ means the diameter of capillary and porosity (volume ratio of capillary), respectively.\(^{65}\) When the porosity of 86% was kept (measured porosity by the Archimedes principle), the theoretical permeability could be calculated by the continuously varied diameter of capillary from 10 to 200 $\mu$m. The experimental permeabilities of the obtained specimens were well consistent with the calculated values, except that of the specimen frozen at $-10^\circ$C (cell size 147 $\mu$m). The orientation of cells was not always straight with curved morphology in the contact points among ice crystals. When frozen at $-10^\circ$C, the formation of connecting points among ice crystals is found to be more difficult due to thicker cell wall. Seen in Fig. 4(a), observed contact points among cells were actually less than that of Fig. 4(d). Compared to the permeabilities reported by the literatures with similar pore sizes,\(^{86,87}\) the present results showed higher values, and also higher than that required for a commercial diesel particulate filter ($10^{-11}$ to $10^{-12} m^2$).\(^{87}\) Then, compressive strength showed in the range from 5.2 to 16.6 MPa, depending on the cell size, where load was parallel to the cell (freezing direction). It has been shown that compressive strengths of porous SiC prepared by other methods exhibited $\sim$10 MPa with porosity around 70% and cell size of 20 $\mu$m\(^{77}\) and 16.7 MPa with porosity of 80% and cell size of 20–100 $\mu$m.\(^{56,39,39}\) The strength of the present porous SiC was similar or higher than those by other methods, regardless of higher porosity. It can be concluded that the microstructure of porous SiC fabricated by the gelation freezing method was comprised of unique honeycomb morphology with porosity around 90% and cell size around 30–150 $\mu$m with 3D interconnected pore network, affording very high gas permeability and compressive strength.

4. Conclusion

Porosity and pore size in silicon carbide ceramics can be tailored by employing processing methods of partial sintering and gelation freezing method. A high amount of porosity in the range of 30–90% can be created as well as a very wide range of pore size from submicrometer to submillimeter. The resultant porous silicon carbide has been studied with success in various pore morphologies with controlled pore size, size distribution and pore interconnection.

Acknowledgments The author gratefully acknowledges Doctors Yu-ichi YOSHIZAWA, Tatsuki OHJI, You ZHOU, Kiyoshi HIROTO, Hiroyuki MIYAZAKI, Hideki HYUGA and Norimitsu MURAYAMA of National Institute of Advanced Industrial Science and Technology (AIST) and Professor Paolo COLOMBO of University of Padova in Italy for their endless support, fruitful feedback and kind encouragements as well as their helpful suggestions. This study was partially funded by New Energy and Industrial Technology Development Organization (NEDO) program of highly efficient ceramic membranes for high-temperature separation of hydrogen, research foundation for the electrotechnology of Chubu, Japan Society for the Promotion of Science (JSPS) of Excellent Young Researchers Overseas Visit Program and TEPCO memorial foundation.

References
Manabu Fukushima is a senior research scientist in Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST). He received his PhD degree in Tokyo institute of technology in 2004. He has been working in AIST since 2004. In 2010, by an Excellent Young Researcher Overseas Visit Program in JSPS, he studied hierarchically porous SiC foams as a visiting research scientist at University of Padova in Italy. His main research topic is focused on the advanced manufacturing of engineering macroporous ceramics with tailored pore architecture. He is particularly involved in thermal management at high temperature for diverse and advanced engineering applications of macroporous ceramics.