

Process development for porous Si-based ceramics by a decarburization method

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Recently, there has been an increasing interest in the applications of porous SiC ceramics as functional materials. A number of manufacturing approaches have been applied to fabricate porous SiC including polymer pyrolysis, oxidation bonding, and reaction bonding. However, these processes are complicated and conventional porous SiC shows insufficient physical and chemical stability under a high temperature environment. Therefore, from the view point of safety and stability, it is necessary to develop an uncomplicated manufacturing method for high performance porous SiC ceramics. In this study, SiC nano-powder and carbon particles have been used as starting material and pore former, respectively. Mixed powders were hot-pressed under a pressure of 20 MPa at 1900 °C for 1 h. Carbon powder which was added to the sintered body was burned out by a decarburization process in air at 700 °C. The porosity was measured by the Archimedes method with an immersion medium of water and an image analysis method. The microstructure was examined by scanning electron microscopy. Mechanical properties were investigated using three-point bend test. It was established that the critical additive amount of carbon particles for porous SiC ceramics was about 20 vol.%, through the microstructure and thermogravimetric analysis during the decarburization process. The porosity of the porous SiC ceramics could be controlled with a high degree of accuracy, from the relationship between the added amount of carbon particles and porosity. The flexural strength of the porous SiC ceramics with 50% pores, where spherical pores were introduced, was about 170 MPa. These porous SiC ceramics exhibited a substantially high strength in comparison with other conventionally processed porous SiC ceramics, due to their robust microstructures consisting of spherical pores.

Key word: Porous SiC ceramics, SiC nano-powder, Carbon particle, Decarburization process, Spherical pore.

Introduction

Recently, there has been an increasing interest in the applications of porous SiC ceramics as hot-gas or molten-metal filters, catalyst supports, battery electrodes, heat insulators, ion exchangers, gas sensors, and water cleaners. In particular, porous SiC ceramics are considered as functional materials for advanced energy systems, such as for perforated containment walls or flow channel inserts (FCIs) for the blanket module of fusion reactors, and the inner/outer tube of coated particle type fuel comp-artments for the horizontal flow cooling concept with a direct cooling system in a gas-cooled fast reactor, because of their low thermal-expansion coefficient and thermal conductivity, good thermal-shock resistance as well as excellent physical and chemical stability at elevated temperature [1-3]. Additionally, the manufactures of diesel engine automobiles in many countries legally have to reduce the emissions of both NO_x and particulate matter. They are required to introduce a diesel particulate filter (DPF) and are intensively investigating materials for DPFs. DPFs actually used are made of porous SiC or cordierite. Porous SiC has the advantage of high-temperature performance, as SiC has a high thermal conductivity, chemical resistance and high thermal strength [4-7].

A number of manufacturing approaches have been applied to fabricate porous SiC including polymer pyrolysis [8], oxidation bonding [9], and reaction bonding [10-13]. However, these processes are complicated and conventional porous SiC shows insufficient physical and chemical stability under a high temperature environment. Therefore, from the view point of safety and stability, it is necessary to develop an uncomplicated manufacturing method for high performance porous SiC ceramics. Therefore, the primary purpose of this study is the development of a new manufacturing method for high performance porous SiC ceramics.

Experimental

SiC nano powder (β -SiC, purity > 99.0%, mean particle size 50 nm, HeFei, China) and carbon nano powder (mean particle size 80 nm, Cancarb, Canada) were used as the starting materials. For sintering additives, we used Al₂O₃ (purity > 99.99%, mean particle size 0.3 μ m, Kojundo Chemical Lab. Co., Ltd., Japan) and Y₂O₃ (purity > 99.99%, mean particle size 0.4 μ m, Kojundo Chemical Lab. Co., Ltd., Japan). Mixed powders were hot-pressed under a pressure of 20 MPa at 1900 °C for 1h with a heating rate of 10 °C/min. The sintering atmosphere was argon. Then, porous SiC ceramics could be fabricated by a decarburization process at 700 °C in air. The weight change of the carbon powder in the C_p/SiC ceramics was investigated by thermogravimetric analysis. The bulk

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density of C_p/SiC and porous SiC ceramics was measured by the Archimedes method with an immersion medium of water and an image analysis method. The porosity was calculated from the relative density and theoretical density, which were obtained by the rule of mixtures.

Flexural strength of porous SiC ceramics was measured using three-point bend tests. Rectangular bars $25.0\text{ mm} \times 4.0\text{ mm} \times 2.5\text{ mm}$ were prepared by grinding and cutting. The tensile faces of the bars were subsequently polished down to $1\text{ }\mu\text{m}$ diamond polish. The tensile edges were beveled to decrease the effect of edge cracks. All tests were conducted on a conventional screw-driven loading frame (Model 5581, Instron, U.K.), with a crosshead speed of 0.5 mm/minute , using a three-point bending jig with an 18 mm support span, at room temperature.

Results and Discussion

The open porosity of C_p/SiC ceramics was calculated by the Archimedes method and image analysis. Fig. 1 shows the dependence of open porosity on the amount of carbon powder added. The open porosity of C_p/SiC ceramics increased rapidly with the amount of carbon powder added beyond $20\text{ vol.}\%$. An increment of open porosity in C_p/SiC ceramics implies that carbon particles exist in an aggregated state.

The amount of residual carbon powder in C_p/SiC ceramics during the decarburization process is shown in Fig. 2. If $10\text{ vol.}\%$ of carbon powder was added to the SiC ceramics, the amount of residual carbon powder was not changed after 3 h . At that stage the amount of residual carbon powder in the C_p/SiC ceramics was about 98% . This means that the decarburization process was performed only at the surface of the specimen. Meanwhile, almost all carbon powder had been burned out when $V_{f(c)} = 20\text{ vol.}\%$, $30\text{ vol.}\%$, and $40\text{ vol.}\%$. The time required to complete the decarburization of C_p/SiC ceramics, which had $V_{f(c)} = 20\text{ vol.}\%$, $30\text{ vol.}\%$, and $40\text{ vol.}\%$, was about 110 h , 8 h , and 4 h , respectively. Then the amount of the residual carbon powder was less than 5% .

Fig. 3 shows cross-sections of C_p/SiC ceramics which had $V_{f(c)} = 10\text{ vol.}\%$ after a decarburization process for

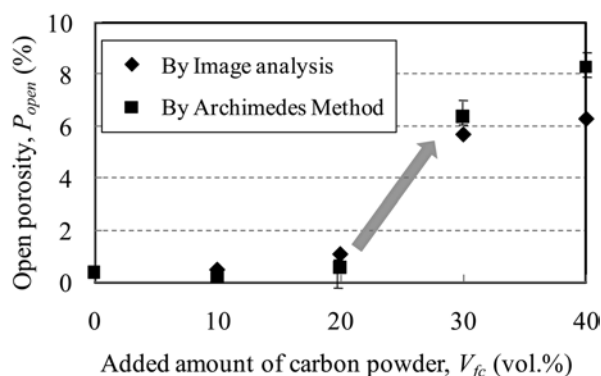


Fig. 1. dependence of open porosity on the amount of carbon powder added.

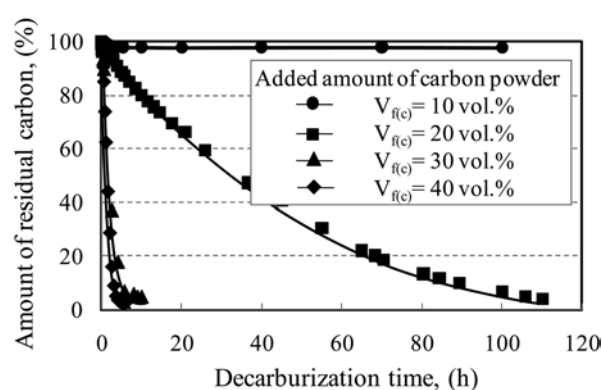


Fig. 2. Weight change of carbon powder in C_p/SiC ceramics during the decarburization process.

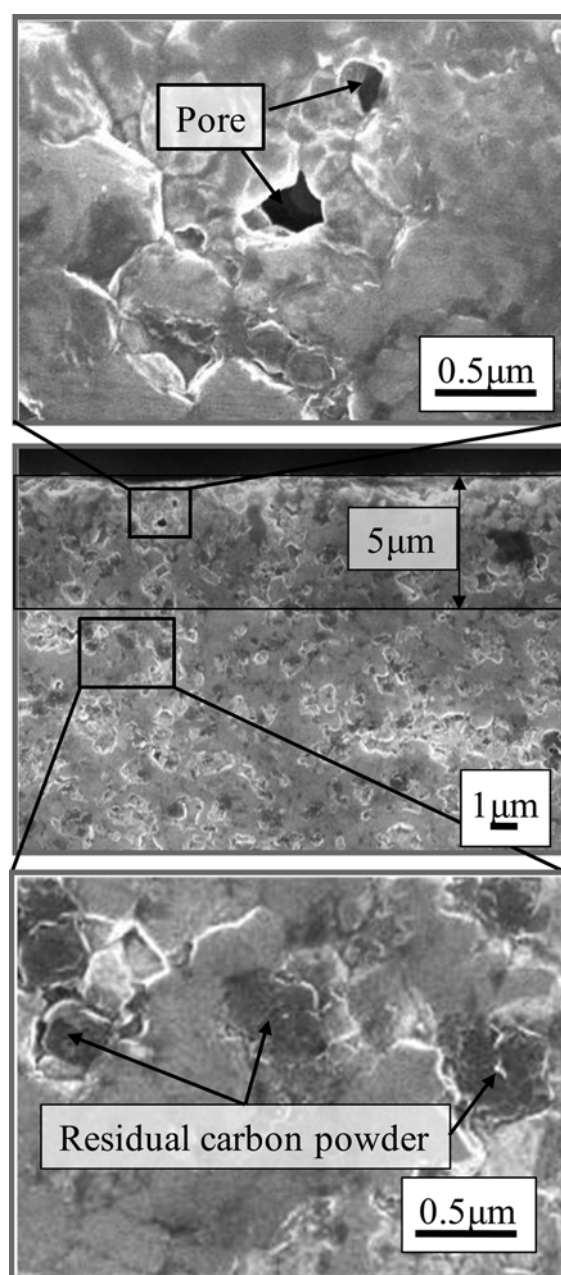


Fig. 3. Cross-sections of C_p/SiC ceramic specimens after the decarburization process ($V_{f(c)} = 10\text{ vol.}\%$).

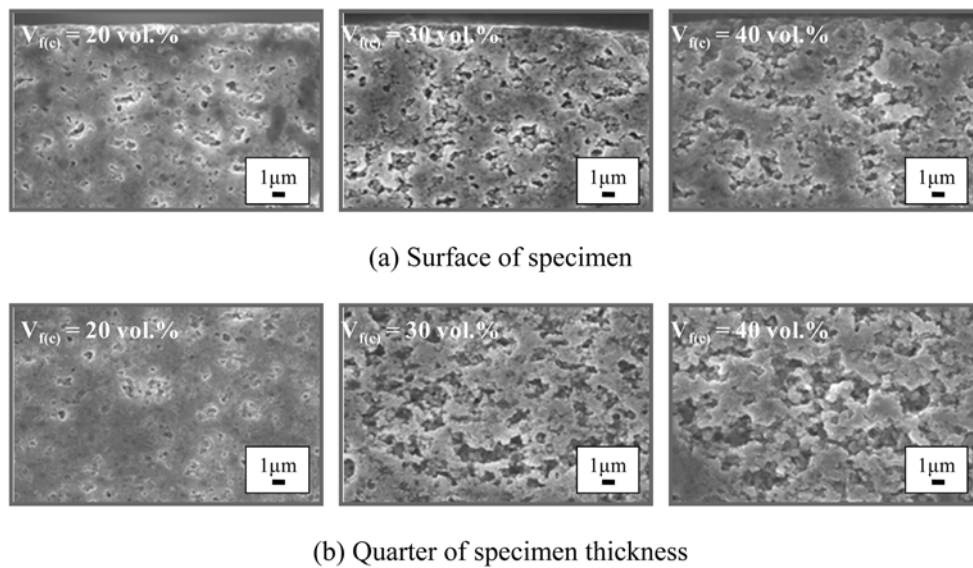


Fig. 4. Cross-sections of C_p/SiC ceramic specimens after the decarburization process ($V_{f(c)} = 20, 30, 40$ vol.%).

110 h. Pores formed by decarburization could be observed within $5\ \mu m$ from the surface. Meanwhile, residual carbon powder has been observed more than $5\ \mu m$ from the surface and surrounded by SiC ceramic particles. This means that oxygen was not able to infiltrate more than $5\ \mu m$ from the surface in the case of $V_{f(c)} = 10$ vol.%. Cross-sections of C_p/SiC ceramic specimens which have $V_{f(c)} = 20$ vol.%, 30 vol.%, and 40 vol.% after the decarburization process for 110 h are shown in Fig. 4. Residual carbon powders could not be observed in the surface of specimen (a) and at a quarter of the specimen thickness (b). In other words, porous SiC ceramics have been manufactured by decarburization of C_p/SiC ceramics. Also, it could be confirmed by microstructural observations that these materials have been constructed with open, spherical pores. The porosity of the porous SiC ceramics, which have $V_{f(c)} = 20$ vol.%, $V_{f(c)} = 30$ vol.%, and $V_{f(c)} = 40$ vol.%, was about 20%, 35%, and 45%, respectively. Additionally, as shown in Fig. 4, it was confirmed that the mean pore size was $0.5\ \mu m$. The mean pore size of these materials has been described elsewhere [14]. The mean pore size can be expected to be the size of the carbon particles added. In this study, the mean particle size of the carbon particles added was 80 nm. However, the mean pore size of the porous SiC ceramics became larger than the mean particle size of the carbon particles added, because the carbon particles existed in an agglomerated state.

Fig. 5 shows a schematic diagram of the decarburization process. When carbon powder particles are surrounded by SiC ceramic particles without micro-cracks (a), decarburization is performed only in the surface regions, because oxygen is not able to infiltrate into the inside of the specimen. During the decarburization process, carbon powder particles in the inside of the specimen cannot react with oxygen. This is similar to the case of $V_{f(c)} = 10$ vol.%. On the other hand, when carbon powder

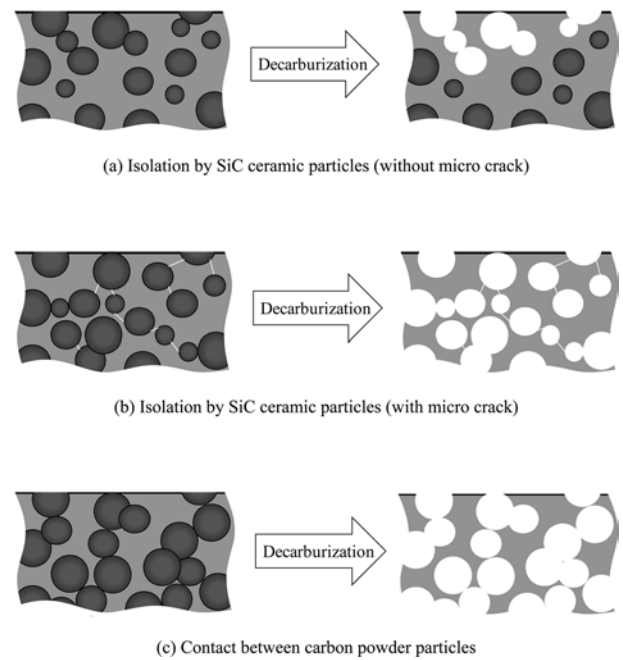


Fig. 5. Schematic diagrams of the decarburization process.

particles are surrounded by SiC ceramic particles with micro-cracks (b), a long time is necessary for the complete decarburization, because oxygen has to infiltrate through the micro cracks. This is similar to the case of $V_{f(c)} = 20$ vol.%. Meanwhile, in the case of contact between carbon powder particles, a short time is necessary for the complete decarburization, because oxygen infiltrates through micro cracks and pores. This applies when the amount of carbon powder added is 30 vol.% and 40 vol.%.

The flexural strength of porous SiC ceramics manufactured using the decarburization process and conventional methods is shown in Fig. 6. The flexural strength of the porous

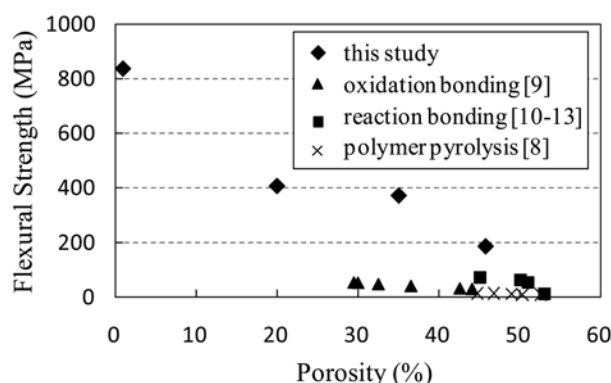


Fig. 6. Flexural strength of porous SiC ceramics.

SiC ceramics, which have $V_{f(c)} = 20, 30$, and 40 vol.%, was about 405, 370, and 185 MPa, respectively. These are substantially high strengths in comparison with other conventional porous SiC ceramics. Generally, the strength of the porous materials depends strongly on the porosity and the pore shape. Most conventional porous SiC ceramics have pores with a more irregular shape such as slit-shaped pores and wedge-shaped pores. However, porous SiC ceramics manufactured using the decarburization process has spherical pores, because carbon powders are used as precursor of pores. Therefore, porous SiC ceramics manufactured in this study exhibited a substantially high strength in comparison with other conventional porous SiC ceramics, due to their robust microstructures consisting of spherical pores.

Conclusions

A novel manufacturing method for high performance porous Si-based ceramics using a decarburization process has been proposed. The critical value of the amount of carbon powder added for the complete decarburization

was about 20 vol.%. Porous SiC ceramics manufactured using the decarburization process has been constructed with open, spherical pores. Furthermore, these materials exhibited a substantially higher strength in comparison with other conventional porous SiC ceramics, due to their robust microstructures consisting of spherical pores.

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