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Oxidation bonding of porous silicon carbide ceramics with synergistic performance

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Abstract

Porous silicon carbide (SiC) ceramics were fabricated by an oxidation-bonding process, in which the powder compacts are heated in air so that SiC particles are bonded to each other by oxidation-derived SiO_2 glass. It has been shown that a high porosity can be obtained by adding a large amount of graphite into the SiC powder compacts and that the pore diameter can be controlled by the size of graphite particles and/or SiC powders. When a 0.3-μm SiC powder was used, a high strength up to 133 MPa was achieved at a porosity of 31.5%. Moreover, oxidation-bonded SiC (OBSC) ceramics were observed to exhibit an excellent resistance to oxidation and thermal shock.

Keywords: Mechanical properties; Oxidation bonding; Porosity; SiC

1. Introduction

Porous SiC ceramics have been widely used as catalyst supports[1–5] and hot-gas or molten-metal filters[6–10] because of their low thermal-expansion coefficient and good thermal-shock resistance as well as excellent mechanical and chemical stability at elevated temperatures. Conventionally, porous SiC ceramics are fabricated by heating the powder compacts in an inert atmosphere. Owing to the highly covalent character of the Si–C bonds in SiC,[11] however, high sintering temperatures are required to achieve sufficient neck growth between particles. This limits the practical applications of porous SiC ceramics.

Recently, we have successfully developed an unique oxidation-bonding technique for the fabrication of porous SiC ceramics at low temperatures.[12,13] In such a process, the powder compacts are heated in air instead of an inert atmosphere. Due to the occurrence of surface oxidation during heat-treatment, SiC particles are bonded to each other by the oxidation-derived SiO_2 glass. In the present work, the technical advantages of the OBSC process are further demonstrated.

2. Experiments

The fabrication process of porous OBSC ceramics has been described elsewhere.[12,13] Briefly, SiC powders with or without additives were dry-pressed into rectangular compacts, and then heat-treated in air at temperatures in the range of 1100–1500 °C using a one-step heating cycle with a heating and cooling rate of 5 °C/min. For strength measurements, the sintered compacts were machined into dimensions of 3.0 mm×4.0 mm×40 mm.

Bulk density and open porosity were determined by a water-displacement method. Phase compositions were identified by X-ray diffraction (XRD) analysis with CuK_α radiation. Pore size distribution and specific surface area were determined by mercury porosimetry (Autopore 9220, Shimadzu Corp., Kyoto, Japan). Flexural strength was measured by a three-point bending test with a support distance of 30 mm and a cross-head speed of 0.5 mm/min. Microstructures were observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Porous SiC with high surface area

As a catalyst support, a high surface area is required. In the porous OBSC ceramics, SiC particles are bonded at the contacting points by oxidation-derived SiO_2 glass.

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Thus, the surface area of the starting powders is expected to be retained to a large extent. To demonstrate this argument, a 0.3-μm SiC powder, which had a surface area of 20 m^2/g, was compacted under a 50-MPa pressure, and then oxidation-bonded at 1100 °C for 1 h. By mercury porosimetry, the surface area of the resultant SiC ceramics was measured to be 13.2 m^2/g. If a finer SiC powder is employed, a higher surface area should be attainable for porous OBSC ceramics.

3.2. Porous SiC with desired pore size

When a porous ceramic is used as a gas filter, a desired pore size is needed to achieve a high particulate filtration efficiency. This can be easily realized through the OBSC process with the incorporation of sawdust, starch, graphite or organic particulates. During heating in air, these particulates burn out, leaving pores in the OBSC ceramics. Hence, the pore size can be directly controlled by the size of the pore-forming agents. This is clearly demonstrated in Table 1. As can be seen, the average pore diameter increases with the increase in the graphite particle size. However, it should be noted in Table 1 that the measured pore sizes are much smaller than the graphite particle sizes. This is due to the fact that the measured pore sizes by mercury porosimetry are the diameters of pore channels rather than individual pores.[12,14]

On the other hand, the pore diameter of porous OBSC ceramics was found to be strongly dependent on the size of the starting powders. As shown in Fig. 1, coarser SiC powders result in larger pores. The mean pore diameters are 2.5, 3.5, 7.2 and 11.6 μm for the OBSC specimens prepared using 6-, 10-, 27- and 58-μm SiC powders.

3.3. Porous SiC with high porosity

In many applications of porous ceramics, high porosity is desirable. It is known that the amount of pores can be increased by increasing the volume fraction of the pore-forming agents.[15,16] However, the particle networks usually collapse when a large amount of the pore-forming agent is removed. In the current work, it is interesting to note that the burnout of 50 vol.% graphite does not destroy the structure of SiC particle networks. This is considered to result from the fact that some graphite particles can remain in the structure and support the SiC networks before SiC oxidation.[12] Thus, the OBSC process allows the preparation of porous SiC ceramics with a high porosity. Fig. 2 shows a typical microstructure of the OBSC specimen prepared with a 50 vol.% graphite addition. Such a highly porous structure cannot be achieved by a conventional process.

Table 1
Average pore diameter of porous OBSC ceramics added with graphite of different particle sizes[a]

Graphite particle size (μm)	5	10	20
Average pore diameter (μm)	3.4	5.3	7.6

[a] 2.3-μm SiC powders were used and oxidation bonding was performed at 1450 °C for 1 h.

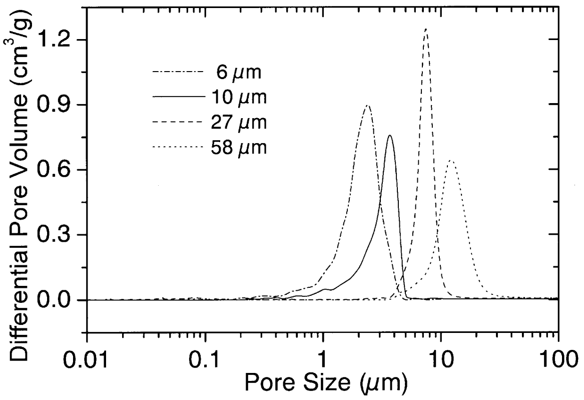

Fig. 1. Pore size distribution of porous OBSC specimens prepared using four SiC powders with different particle sizes, where oxidation bonding was conducted at 1500 °C for 5 h.

3.4. Porous SiC with high strength and reliability

The mechanical strength of porous ceramics is related not only to the volume fraction and geometrical nature of the pores but also to the size and type of the interparticle connections.[14,17] To achieve strong and reliable porous ceramics, a homogenous microstructure with fine grains and enhanced necks is expected. In the present work, a fracture strength up to ~40 MPa was obtained for a ~36% porous OBSC specimen by using a 2.3-μm SiC powder. As can be seen in Fig. 3, well-developed necks are formed between SiC particles in

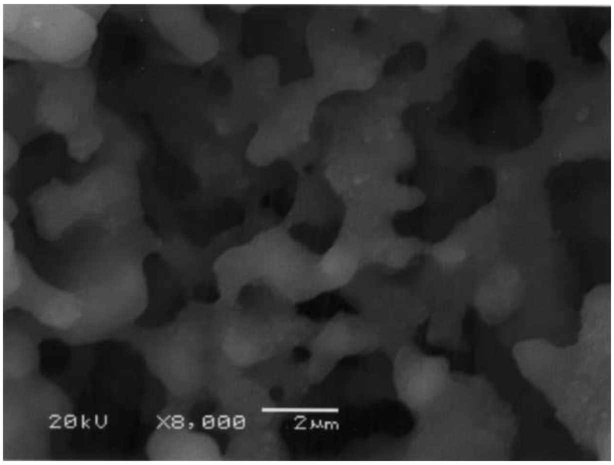

Fig. 2. SEM micrograph of an OBSC specimen, which was prepared by adding 50 vol.% of 5-μm-sized graphite particles into a 2.3-μm SiC powder. Oxidation bonding was carried out at 1450 °C for 1 h.

such a specimen. When a 0.3-μm SiC powder was used, a strength value as high as 133 MPa was achieved at a porosity of 31.5%.

Also, the mechanical reliability of porous ceramics should be considered in practice. Fig. 4 shows the strength distribution of a ~36% porous OBSC specimen. As shown, the strength values are in the range of 37–43 MPa. By fitting these data to the Weibull function, a high Weibull modulus of 22.6 was obtained. This indicates that the mechanical reliability of porous OBSC ceramics is sufficient for their practical applications.

3.5. Porous SiC with excellent oxidation resistance

As evidenced in Fig. 3, there is a layer of SiO_2 on the surface of every SiC particles in porous OBSC ceramics. Thus, an excellent oxidation resistance is expected. This was confirmed by using a ~36% porous OBSC specimen, which exhibited no weight increase after oxidizing in air at 1000 °C for 100 h. When oxidized at 1300 °C, however, the specimen had a ~4.5% increase in weight. Fig. 5 shows a typical microstructure of such an oxidized specimen. As can be seen, some cracks are formed in the surface SiO_2 layer. The reason for this phenomenon is not quite clear and requires a further investigation.

3.6. Porous SiC with high thermal-shock resistance

Porous ceramics are usually subjected to transient thermal stresses and consequently susceptible to crack or damage in many of their applications such as catalyst supports and hot-gas or molten-metal filters. In this work, the thermal shock behavior of a ~36% porous OBSC specimen was evaluated by a water-quenching method,[18] and compared with that of a 35.5% porous Schumalith© SiC. It can be seen in Fig. 6 that the strength behavior after thermal shock is essentially the same for both specimens. However, the OBSC specimen is much stronger than Schumalith© SiC in all the

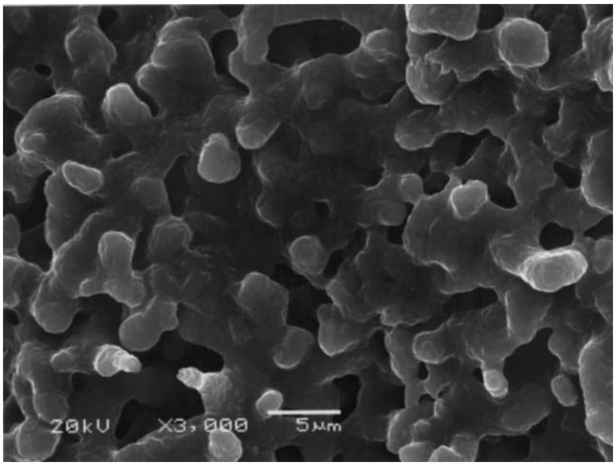

Fig. 3. Microstructure of an OBSC specimen prepared using a 2.3-μm SiC powder, where oxidation bonding was performed at 1450 °C for 1 h.

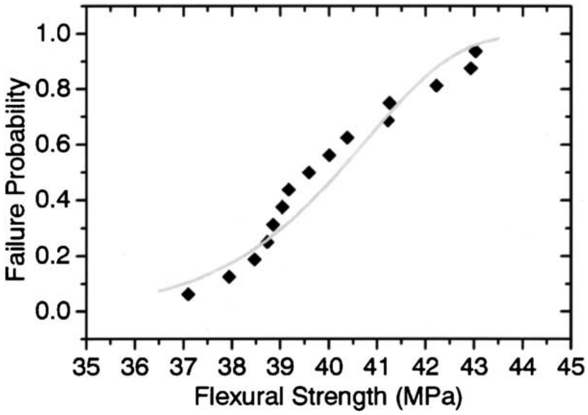

Fig. 4. Strength distribution of 36% porous OBSC specimens prepared by using a 2.3-μm SiC powder. The curve is a fit to the Weibull function.

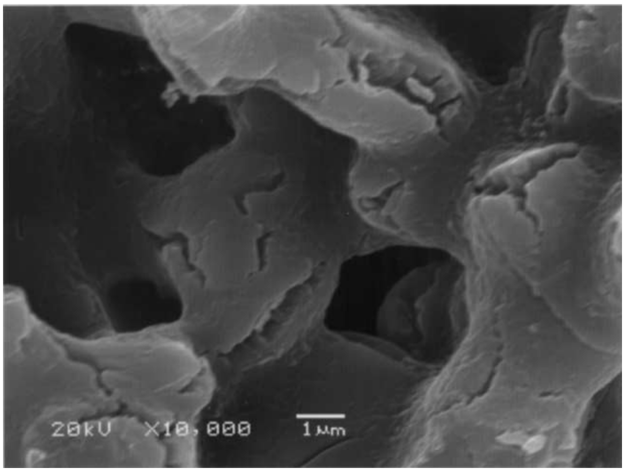

Fig. 5. Microstructure of a ~36% porous OBSC specimen after oxidizing in air at 1300 °C for 100 h.

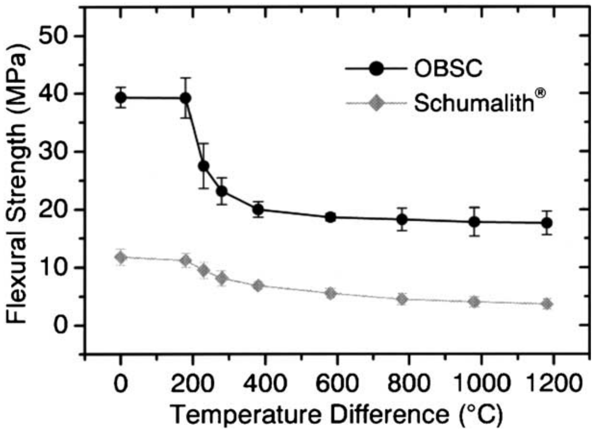

Fig. 6. Residual strength as a function of quenching-temperature difference for porous SiC specimens.

quenching-temperature range. This suggests that porous OBSC ceramics might have great potentialities for some applications under thermal-shock conditions.

4. Conclusions

A recently developed OBSC technology was used to fabricate porous SiC ceramics with synergistic performance. In the OBSC process, SiC particles are bonded to each other by oxidation-derived SiO_2 glass. This allows the low-temperature production of porous SiC ceramics with high surface area and excellent oxidation resistance. When a 0.3-μm SiC powder was used, a strength value up to 133 MPa was achieved at a porosity of 31.5%. Moreover, it has been shown that a high porosity can be obtained by adding a large amount of graphite into the SiC powder compacts and that the pore diameter can be controlled by the size of graphite particles and/or SiC powders. In addition, porous OBSC ceramics were observed to have a good thermal-shock resistance.

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