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Synthesis and characterization of balloons and porous blocks of β-SiC using silicone and urethane foam

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Abstract

A process to form different shapes of β-SiC was developed using precursors composed of silicone compounds and urethane foam. Two types of low molecular weight silicone, a Pt catalyst for curing, and a catalyst regulator were impregnated into urethane foam chips with different porosities and bulk densities, and cured at 200 °C for 1 h in air. Formed precursors were converted into β-SiC by pyrolysis at 1600 °C for 1–5 h in argon. Depending on the type of urethane foam, β-SiC balloons and β-SiC blocks with high porosities and low bulk densities were obtained. In addition, fine particles of β-SiC smaller than 100 nm were also obtained by crushing the blocks. For a disk formed by 5 h pyrolysis at 1500 °C, N_2 gas permeability, electric conductivity, and oxidation resistance at 900 °C in air were measured. The results indicated that the disk may be used as a gas permeable heater. The process is simple, and the materials for this process are not hazardous and commercially available at low cost.

Keywords: Electric conductivity; Oxidation resistance; Precursors-organic; Porosity; SiC

1. Introduction

Porous silicon carbide has a wide range of industrial applications, and recent years have seen rapid developments in the application of porous silicon carbide components as filters of exhaust gas from automobile engines. There may be variations but, in a broad way, three types of processes are practically useful to form porous silicon carbide components: (1) firing of the preformed components made of a slurry mixture of organic compounds, which disappear by pyrolysis, and fine SiC powder, (2) heat treatment of a porous preform, which disappears by pyrolysis, impregnated with slurry of fine SiC powder, and (3) siliciding porous carbon components with molten or vapor Si, or carbothermal reaction of porous carbon components with silicon compounds. The first one is known fairly early and still used generally. The second is a kind of replica method and also known as the polymeric sponge process,[1–3] since polymeric sponge or foam is often used as a replica. Recently, based on the third process, a large number of papers are published aiming at porous biomorphic SiC ceramics, by using carbon frames of biomass, such as wood, bamboo and paper. The references concerned with the processes (1) and (3) are too many and not cited here, since they are not the subject of the present paper.

As a modification of the process (2), a method using urethane foam and solutions of polysilanes has been reported.[4] Two steps are involved in this simple method; preparation of precursors by soaking urethane foam chips into the solutions and drying, and pyrolysis of the precursors to convert them into porous β-SiC blocks. This method, however, has two shortcomings: hazardous solvents must be used to dissolve polysilanes and evaporated to prepare the precursors, and sufficiently crystallized β-SiC is not obtained even by 2 h treatment at 1700 °C, which is probably due to a specific characteristic of the polysilanes synthesized by the authors.[5]

Previously, we have reported a new process to synthesize submicrometer-sized β-SiC particles only by pyrolysis of the precursors.[6,7] For the preparation of precursors, two types of low molecular weight silicone compounds, a cyclic type having vinyl groups and a chain-type having Si–H bonds, and trace amounts of Pt catalyst were mixed and impregnated into exfoliated graphite by sorption, then cured in air at 200–300 °C. Pyrolysis of these precursors in argon at 1500 °C for 5 h, or at 1600 °C for 1 h gave well crystallized β-SiC particles of several tens to a few hundreds nanometers in size.[7] Materials used

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for this process are not hazardous and commercially available at very low cost. In the present work, urethane foam (UF) was used instead of exfoliated graphite, which resulted in the formation of β-SiC balloons and porous blocks. Properties of formed β-SiC blocks, including bulk density, gas permeability, electric conductivity, and oxidation resistance were investigated.

2. Experimental procedure

2.1. Synthesis of β-SiC balloons and porous blocks

Two types of low molecular weight silicone, $\{CH_3(CH{=}CH_2)SiO\}_n$ ($n = 3$–7, Shin-Etsu Chemical Co. Ltd., VC-4) and $(CH_3)_3SiO\{CH_3(H)SiO\}_mSi(CH_3)_3$ ($m \approx 20$, Shin-Etsu Chemical Co. Ltd., KF-99B), a Pt catalyst for curing (Shin-Etsu Chemical, PL-8, Pt ≈ 0.5 mass%) and a catalyst regulator (Shin-Etsu Chemical, PLR-31) were used. The average pore diameter and bulk density of the urethane foam (UF) used are shown in Table 1. The average pore diameter was calculated from the number of cells (pores) in a unit area described in a catalogue. A group of relatively small pore diameter, UF-No. 1-14 and UF-HP70, are sponge-like structures and a UF-HR type having large pore diameter and low bulk density is a reticulated structure. UF-HR type is similar to those used by other investigators.[4] Most of them were manufactured by Bridgestone Corp. but some were unknown because the materials used were industrial wastes. UF chips of approximately 10 mm × 10 mm × 3 mm to 20 mm × 20 mm × 3 mm were soaked into a mixture of 43 g of VC-4, 31 g of KF-99B, 0.5 g of PL-8, and 0.5 g of PLR-31. The mixing ratio was determined to satisfy the following reaction by assuming $n = 4$ and $m = 20$[7]:

$$\equiv Si{-}CH{=}CH_2 + \equiv Si{-}H \rightarrow \equiv Si{-}CH_2{-}CH_2{-}Si\equiv \quad (1)$$

Here, ≡Si does not mean a triple bond but is an abbreviation for other bonds in the silicone compounds. After soaking, UF chips were dried overnight at 50 °C followed by curing at 200 °C for 1 h in air. Formed block type precursors were pyrolyzed in a flow of argon at different heat treatment temperatures (HTT) of 1000–1600 °C for 1–15 h. Heating rate was 300 K h^{-1}. Hereafter, the product is referred to as [precursor code]/[HTT in Celsius] − [pyrolysis time in hour], such as P-No. 14/1500-1.

For the measurements of gas permeability, electric conductivity, and oxidation resistance, disk shape β-SiC was synthesized. UF-HP70 (Table 1) disks of about 4 mm thick and 25–40 mm in diameter were used to prepare the precursors. Due to the size limitation of the high temperature furnace that can be used up to 1800 °C, the disks were formed at 1500 °C with other furnace.

2.2. Characterization of precursors and formed β-SiC blocks

Thermal decomposition behavior of UF chips, the cured silicone without UF, and typical precursors was examined in a flow of argon by thermo-gravimetry (TG; Seiko Instruments TG/DTA6300) at 300 K h^{-1}. The precursors and products were examined by optical microscopy (OM; KEYENCE digital microscope VH-700C), scanning electron microscopy (SEM; JEOL JSM-6300F or JSM-6500F, 5 kV), EPMA (JEOL JSM-5410 + Oxford WDX400, 20 kV), transmission electron microscopy (TEM; JEOL JEM2010FX, 200 kV), X-ray diffraction (XRD; Rigaku RAD-X RINT2000, Cu Kα), and magic angle spinning nuclear magnetic resonance (MAS-NMR; Varian Unity 300 plus or Bruker MSL 400) by the dipole decoupling mode (DD-MAS) and the cross-polarization mode (CP-MAS).

The bulk density of formed β-SiC blocks was calculated from the weight and the size of block, and the true density of representative product was determined by using a glass pycnometer and carbon tetrachloride at 20 °C after pulverizing. The fraction of open pore volume of a disk was estimated from the bulk density, the true density, and the density by Archimedes' method which was measured in water. Permeability of nitrogen at room temperature was measured for a disk of P-HP70/1500-5 (3.5 mm thick and 30 mm in diameter) by a differential pressure gauge (Okano DMP203N). Electric conductivity of the disk was measured by van der Pauw method.[8] Four copper leads were symmetrically connected to a disk, and a constant current in a range of 2–20 mA was applied to one pair of leads and the voltage between the other pair was measured.

Oxidation resistance was evaluated from mass change by repetitive heating at 900 °C for 1 h and cooling to an ambient temperature in air. The specimens used were disks of P-HP70/1500-1 and P-HP70/1500-5.

3. Results and discussion

3.1. Thermal decomposition behavior of raw materials and the precursors

The observation by OM revealed that the form of cured silicone impregnated in UF chips with relatively small pore diameter, UF-No. 1-14 and UF-HP70, the silicone was coating the inner wall of pores in the form of inscribed hollow sphere.

Table 1
Physical data of the urethane foam (UF) used and the β-SiC blocks formed by 1600 °C, 1 h treatment

Precursor code	P-No. 1	P-No. 3	P-No. 5	P-No. 9	P-No. 14	P-HP70	P-HR30	P-HR50
Urethane foam	UF-No. 1	UF-No. 3	UF-No. 5	UF-No. 9	UF-No. 14	UF-HP70	UF-HR30	UF-HR50
Average pore diameter (μm)	300	280	260	340	420	200	830	500
Bulk density (g cm^{-3})	0.16	0.13	0.13	0.16	0.15	0.06	0.03	0.03
β-SiC block								
Bulk density (g cm^{-3})	0.53	0.55	0.64	0.63	0.68	1.0	0.41	0.45
Porosity (%)	83	83	80	80	79	69	87	86