

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, N₂ 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. © 2006 Elsevier Ltd. All rights reserved.

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, $\{\text{CH}_3(\text{CH}=\text{CH}_2)\text{SiO}\}_n$ ($n=3-7$, Shin-Etsu Chemical Co. Ltd., VC-4) and $(\text{CH}_3)_3\text{SiO}\{\text{CH}_3(\text{H})\text{SiO}\}_m\text{Si}(\text{CH}_3)_3$ ($m \approx 20$, 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 $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$ to $20 \text{ mm} \times 20 \text{ mm} \times 3 \text{ mm}$ 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



Here, $\equiv\text{Si}$ 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 $1000-1600^\circ\text{C}$ 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 $K\alpha$), 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

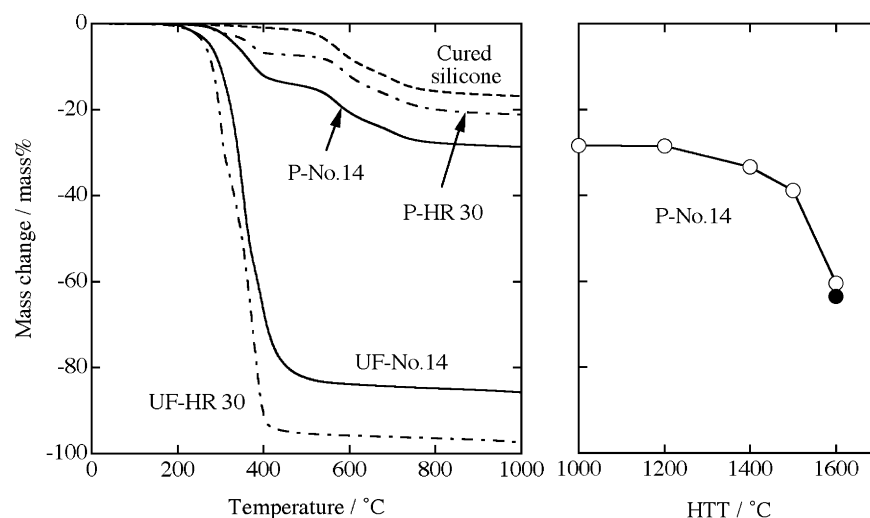


Fig. 1. (a) Mass changes of UF chips, the cured silicone without UF, and P-No. 14 and P-HR30 precursors measured at 300 K h^{-1} and (b) those of P-No. 14 by 1 h (\circ) or 5 h (\bullet) treatment at fixed temperatures, both in a flow of argon (cf. text and Table 1 for sample codes).

In UF-HR type chips, however, the silicone mostly clung onto the frames of the reticulated structure, leaving the inner space connected to the outside. The latter morphology is similar to that reported previously.⁴

The urethane foams start to decompose at about 200°C and very large mass loss emerges in a range of $300\text{--}400^\circ\text{C}$ as shown in Fig. 1(a). In Fig. 1(a), TG curves for representative materials are shown, and at 500°C a group of UF-No. 1–14 in Table 1 shows around 85 mass% loss, and UF-HP70 and a UF-HR type more than 95%, in argon. The difference is mainly due to the bulk density and additionally to morphological structure, but may also be caused by chemical structure of polyurethane and the forming processes. The detailed information on the latter, however, is not available from the original supplier. In contrast, substantial decomposition of the cured silicone (without UF) starts above 500°C . A moderate mass loss is observed for the cured silicone between 500 and 800°C and the steady value is attained between 800 and 1000°C . Consequently the precursors show two step decomposition behavior, affected by the character of two raw materials, UF and silicone, and the cured silicone is left at around 400°C in a form of aggregated hollow spheres or of reticulated structure (viz., three-dimensional network structure). The behavior shown in Fig. 1(a) is different from that reported by using polysilanes.⁴ The starting temperature of decomposition for the cured silicone used here is higher than those of polysilanes, and the mass loss of the present precursors up to 1000°C is much smaller. It should be noted here that the total mass is mainly determined by the amount of silicone in the precursor, so that in Fig. 1(a) P-No. 14 is lower than P-HR30, contrary to the curves for UF-No. 14 and UF-HR30. Above 800°C , large mass loss is not observed up to 1400°C even by holding the temperature for 1 h, as shown for P-No. 14 in Fig. 1(b). The yield after 1 h pyrolysis at 1600°C was 33–44 mass% depending on the precursor and the highest was P-HP70. The precursors shrank by 10–25% in size but the original shape was kept after the pyrolysis. Prolonged pyrolysis at 1600°C did not lead to large mass change as shown in Fig. 1(b); the differ-

ence between P-No. 14/1600-5 and P-No. 14/1600-15 was only 1 mass%.

Particular diffraction peaks are not observed for the blocks pyrolyzed for 1 h at $\text{HTT} \leq 1300^\circ\text{C}$ and the peaks of $\beta\text{-SiC}$ become distinguishable at 1400°C , as shown for P-No. 14 in Fig. 2(a). A broad peak around $2\theta = 20^\circ$ is due to the adhesive tape used to support the block sample with a holder. The peaks of $\beta\text{-SiC}$ become sharp and strong with increasing HTT and low intensity peaks of 200 and 220 are clearly observed for the block of P-No. 14/1600-1. After pulverizing, the product is found to be single phase $\beta\text{-SiC}$ by XRD, as shown in Fig. 2(b). Thus, glass-like Si–C–O compounds are converted to $\beta\text{-SiC}$ by the pyrolysis in a HTT range of $1400\text{--}1600^\circ\text{C}$. A shoulder peak on the left-hand side of 111 peak is often observed for $\beta\text{-SiC}$ and considered to be due to stacking fault. As can be seen from the examples shown in Fig. 2(b), the products from the precursors in Table 1 by 1 h pyrolysis at 1600°C are more or less single phase by XRD, though there is a tendency for diffraction peaks to be sharper with P-HR type. Crystallinity of the products by XRD are much better than that of the products by pyrolysis of polysilanes at 1700°C for 2 h.⁴ The density of pulverized P-HP70/1600-1 measured with a glass pycnometer was 3.18 g cm^{-3} , which is very close to the value generally accepted for $\beta\text{-SiC}$, 3.210 g cm^{-3} . The ^{29}Si MAS-NMR spectra, however, revealed that the products contain small amounts of silicon compounds containing hydrogen and oxygen, and amorphous silica, as shown in Fig. 3 for example. For pure $\beta\text{-SiC}$, single and sharp peak appears at around -20 ppm of the DD-MAS spectrum and no peaks in the CP-MAS spectrum. In the CP-MAS spectrum peaks appear by interaction between ^{29}Si and the protons bonded in the vicinity of Si.⁷ In the DD-MAS spectra for P-HP70/1500-5 and P-HP70/1600-1 (Fig. 3(a) and (b)) shoulder peaks are distinguished at the right-hand side of $\beta\text{-SiC}$ peak and a small peak assigned to silica is present at -120 ppm . The shoulder peaks are due to the remnants of silicone compounds incompletely decomposed. In addition, two peaks in both CP-MAS spectra indicate the presence of bonding

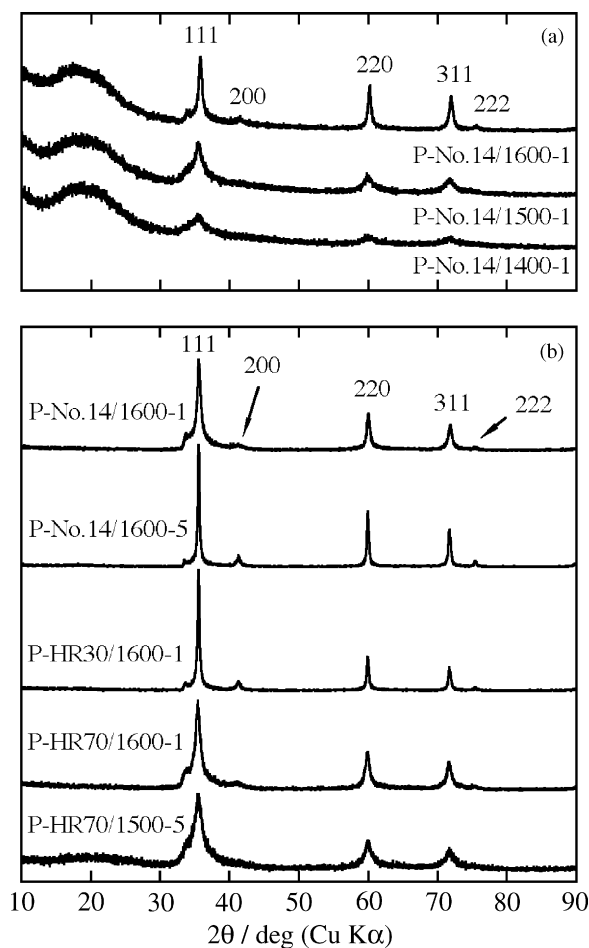


Fig. 2. XRD patterns of: (a) as formed blocks and (b) pulverized samples. Indices are of β -SiC (cf. Section 2.1 for sample codes).

protons in the silicone compounds and silica. Accurate estimation of impurities is difficult by MAS-NMR, but based on the previous studies⁷ the amount of oxygen may be far less than 10 mass%. The contamination peaks in the DD-MAS spectra disappear by 5 h pyrolysis at 1600 °C and only trace peaks are observed in the CP-MAS spectrum as shown in Fig. 3(c) for P-No. 14/1600-5, and XRD peaks also become sharper (Fig. 2(b)). Since the mass change by additional 4 h pyrolysis is less than a few percent (Fig. 1(b)), the contamination level is not very high. In the case of precursors composed of the same silicone and exfoliated graphite, pure β -SiC (by XRD and MAS-NMR) was obtained by 1 h pyrolysis at 1600 °C.⁷ This is probably ascribed to the availability of carbon: the exfoliated graphite functions as a reductant at the final stage of β -SiC formation,⁷ whereas UF mostly disappears at much lower temperature (Fig. 1(a)).

3.2. Morphology of formed β -SiC

Bulk density and porosity of blocks formed by 1 h pyrolysis at 1600 °C are summarized in Table 1. The porosities were calculated from the bulk densities on the basis of the true density of pulverized P-HP70/1600-1, 3.18 g cm⁻³. Since some blocks were very fragile and the size was not measured accurately, the values are limited to two digits. It is seen that precursors formed

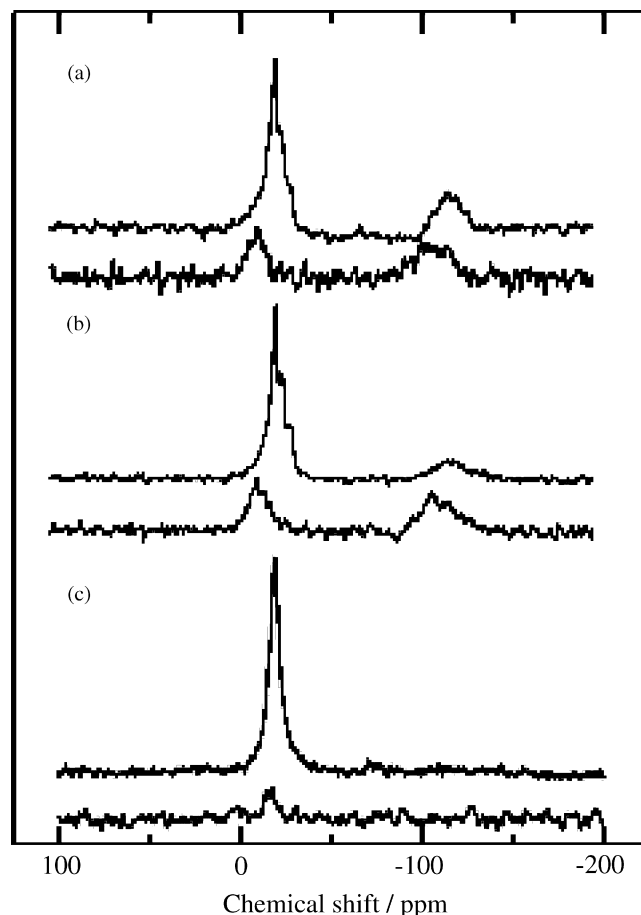


Fig. 3. MAS-NMR spectra by the dipole decoupling mode (upper) and the cross-polarization mode (lower) for: (a) P-HP70/1500-5, (b) P-HP70/1600-1, and (c) P-No. 14/1600-5.

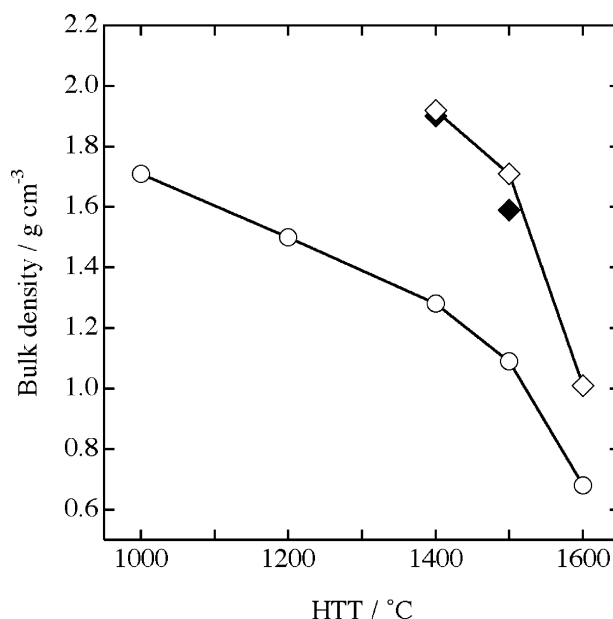


Fig. 4. Temperature dependence of bulk density for P-No. 14 (○: 1 h pyrolysis) and P-HP70 (○: 1 h pyrolysis; ◆: 5 h pyrolysis).

with UF of relatively large bulk density provide β -SiC blocks of nearly the same porosity, about 80%, and similar bulk density, $0.53\text{--}0.68\text{ g cm}^{-3}$. In contrast, precursors formed with UF of low bulk density provide β -SiC blocks of different porosities depending on the pore size of UF. P-HP70, which formed with the UF of the smallest pore size, produces β -SiC block of the lowest porosity and the highest bulk density. This is because of the sphere size and amount of silicone impregnated in UF. P-HR30 and P-HR50 form the β -SiC blocks of very low bulk density and high porosity, as expected from the morphology of precursors described in Section 3.1. Relationships between bulk density and HTT are shown for P-No. 14 and P-HP70 in Fig. 4. From a correlation between the mass loss in Fig. 1(b) and Fig. 4, it is evident that bulk density decreases steadily up to 1400°C without large mass loss, indicating that the silicone spheres are

expanding. From 1400 to 1600°C , at which glass-like Si–C–O compounds are converted into β -SiC by pyrolysis, the bulk density decreases proportionally to the mass change. This suggests that the shapes of blocks are roughly determined between 1400 and 1500°C . The bulk density of the products from HP70 is much larger than those from No. 14 and does not decrease very much by prolonged pyrolysis at lower temperatures.

SEM images and photographs of products from different precursors are shown in Fig. 5. In agreement with the above discussion, it is seen in Fig. 5(a)–(c) that with increasing HTT sphere size of No. 14 increases and sphere walls become thinner as indicated by arrows. A block of P-No. 14/1600-1 looks solid as shown in a inset of Fig. 5(c) but it is an aggregate of β -SiC spheres which are loosely fixed with socket-like structure between spheres (Fig. 5(c)). At resolution of EPMA, Si

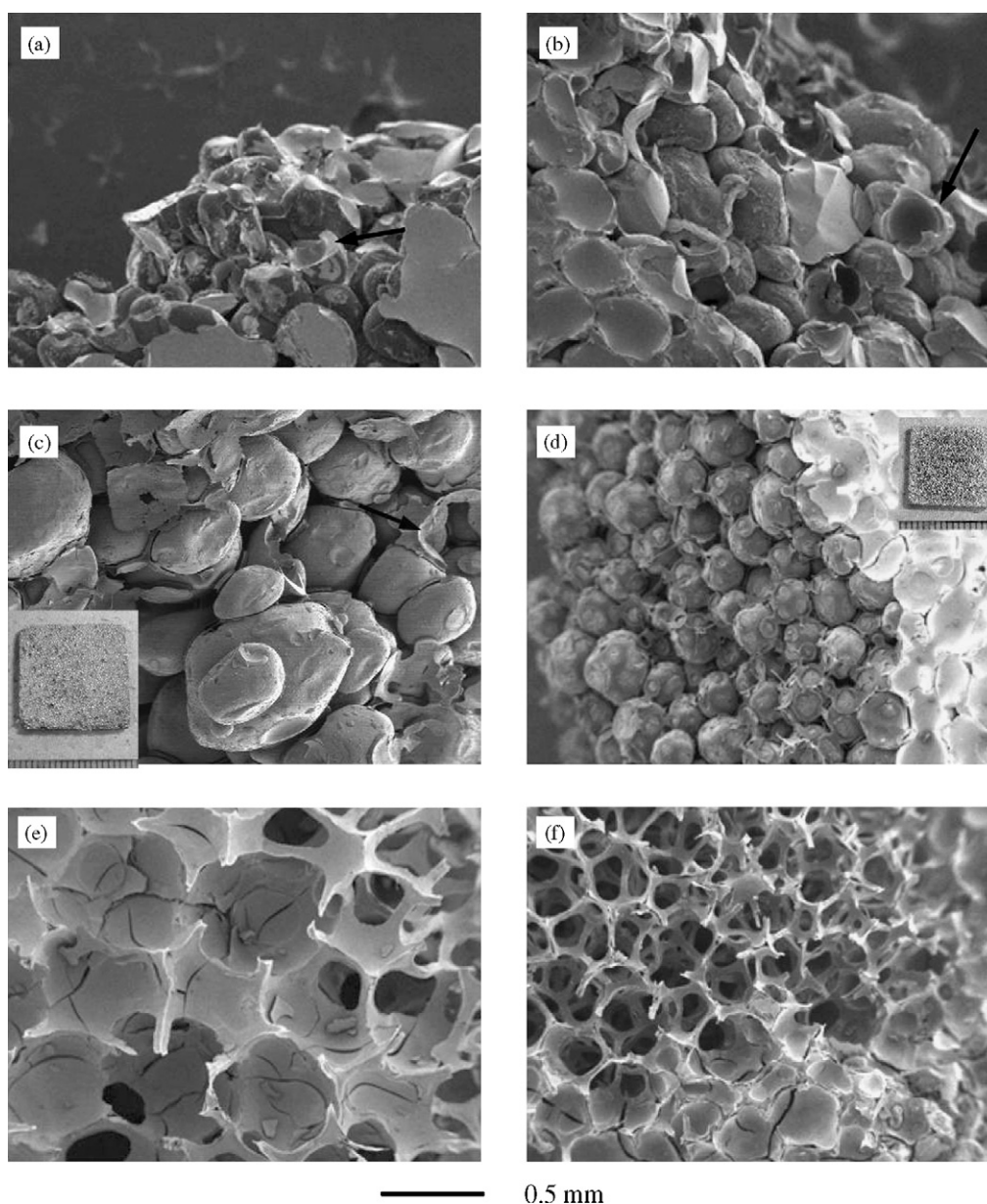


Fig. 5. SEM images of: (a) P-No. 14/1200-1, (b) P-No. 14/1400-1, (c) P-No. 14/1600-1, (d) P-HP70/1600-1, (e) P-HR30/1600-1, and (f) P-HR50/1600-1. Arrows indicate the cross-section of sphere wall. Insets are photographs of formed blocks and one division of scale is 1 mm.

and C were detected together on the spheres and the surrounding structure, and no large fragments of carbon were detected. Accordingly, they can be separated and balloon type β -SiC is available, though they are fragile. In contrast to P-No. 14-1600-1, P-HP70/1600-1 is made up of much more uniform spheres as shown in Fig. 3(d). The sphere size is nearly the same with the average pore size of UF-HP70 (Table 1), indicating that the porous structure having similar dimensions with the original UF can be formed in this case. A block of P-HP70/1600-1 shown in an inset of Fig. 5(d) is tougher than that of P-No. 14/1600-1 and easily handled. As can be seen from SEM images in Fig. 5(e) and (f), P-HR30/1600-1 and P-HR50/1600-1 resemble the morphologies of the products from polysilanes,⁴ closely. Because of too large pore sizes, the cured silicone was not able to form spherical shapes completely, leading to reticulated structure of β -SiC. Dimensions of space are much smaller than the average pore sizes of the original UF (Table 1). The structure of the precursors, however, favored the pyrolysis, resulted in the well-crystallized β -SiC comparable to the products by 5 h pyrolysis (Fig. 2(b)). At present, we do not have definite basis for the mechanical integrity of the blocks but it is possible to give one of the reasons why balloons or porous blocks were formed depending on the precursor. The experimental results indicated that the precursors with UF of small pore diameter and low bulk density (e. g. UF-HP70) formed blocks of better mechanical integrity, whereas those with UF of large pore diameter and higher bulk density (e. g. UF-No. 14) formed balloons. These imply that a template of small pore size and thin pore wall is preferable to form tougher porous blocks, suggesting that the silicone balloons in the pores of UF partly fuse each other by disappearing of pore wall during pyrolysis.

The blocks of low bulk densities are very fragile, and after crushing them with an agate mortar and pestle they were found to be composed of very fine particles. For crushed P-No. 14/1600-1, P-HP70/1600-1, and P-HR30/1600-1, particles larger than 100 nm were rarely observed by SEM and TEM. A TEM image of crushed P-No. 14/1600-1 is shown in Fig. 6 for example. Accordingly, the present process can be used to synthesize nano-

particles of β -SiC, though microscopic observation was not carried out for all the products.

3.3. Properties of β -SiC disk formed from HP70

As described above, the β -SiC blocks having large porosities of 80–90% (Table 1) are fragile and not easy to handle. Naturally they may be toughened by sintering at high temperatures, but as-formed blocks are not useful to evaluate various properties. Accordingly, β -SiC disks were prepared from HP70, though HTT was limited to 1500 °C due to the furnace used. A disk of 30 mm in diameter and 3.5 mm thick by 5 h pyrolysis at 1500 °C is shown in Fig. 7. The SEM image of the surface indicates that the disk is made of bonded spheres similar to P-HP70/1600-1 (Fig. 5(d)). From the XRD pattern (Fig. 1(b)) and the MAS-NMR spectra (Fig. 3(c)), the product is not well crystallized and contains other components than β -SiC, in comparison with the products by 1 h pyrolysis at 1600 °C, but it has acceptable properties as described below.

The mass and volume of the disk in Fig. 7 were 3.843 g and 2.47 cm³, and so the bulk density of the disk was 1.56 g cm⁻³ (Fig. 4). From this, apparent porosity is estimated to be 51%, assuming the true density to be 3.18 g cm⁻³. As the disk buoyancy in water was 1.565 g at 25 °C, the open pore volume of disk is 0.90 cm³ which is 36.4% of the total volume, leading to the closed pore volume of 14.6%. Permeability of nitrogen at room temperature measured by a differential pressure gauge

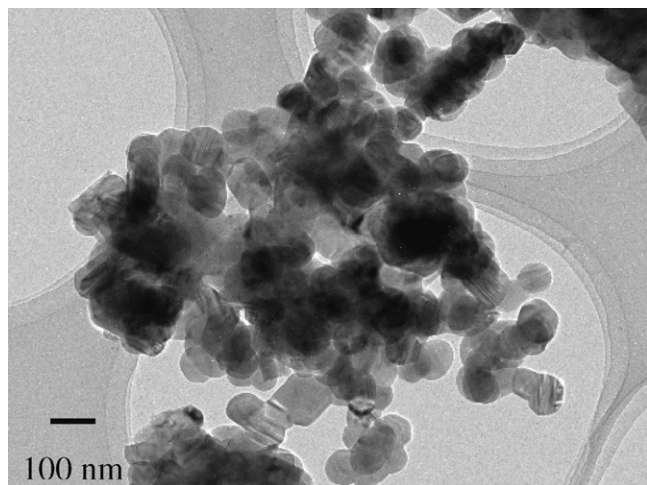


Fig. 6. A TEM image of P-No. 14/1600-1 particles after crushing with an agate mortar and pestle.

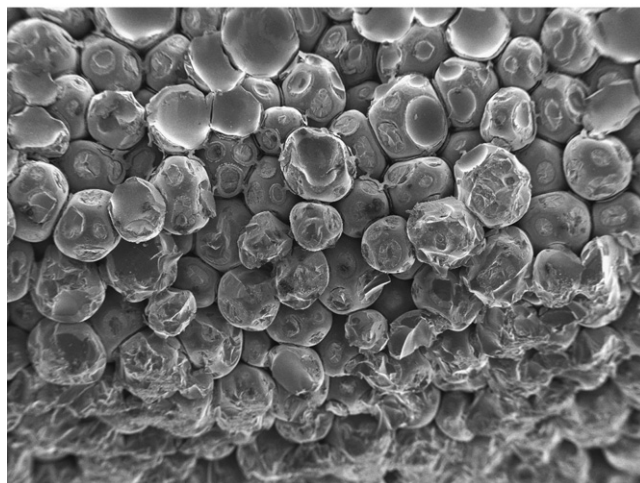
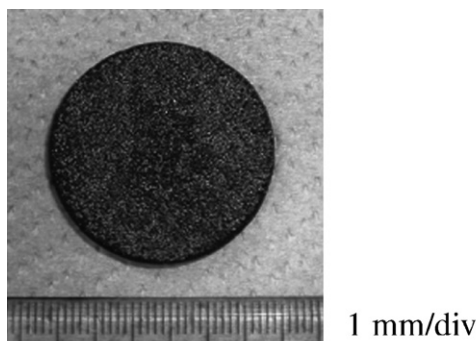


Fig. 7. A photograph of P-HP70/1500-5 disk and a SEM image of the disk surface.

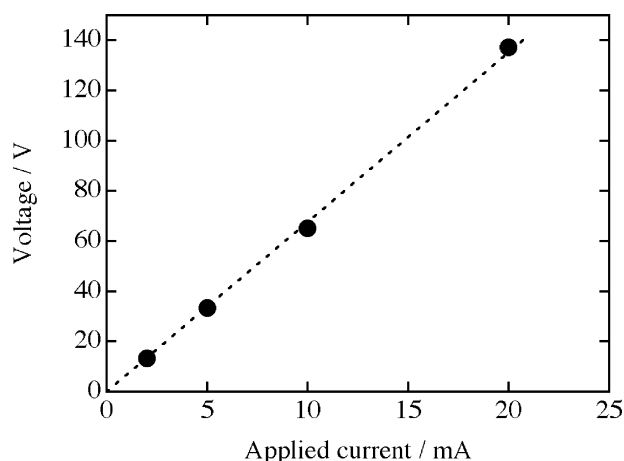


Fig. 8. Current–voltage characteristics of the disk in Fig. 7 measured by van der Pauw method. Note that the slope does not directly show the electric resistance of the disk.

was $16.4 \text{ cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$ in average, which enables a N_2 flux of about 1 L s^{-1} with a back pressure of 1 atm with a filter of 9 cm in diameter and 1 cm thick. To determine electric conductivity of the disk current–voltage characteristics were measured. As shown in Fig. 8, a linear relationship is observed between the applied current and the measured voltage, suggesting that the disk is electrically uniform. Using a slope of the line and an equation for specific resistance by van der Pauw,⁸ the conductivity is calculated to be $9.4 \times 10^{-2} \text{ S cm}^{-1}$. Theoretically cubic SiC (β -SiC) is a semiconductor having a band gap of 2.20 eV at 300 K but usually shows electric conduction, and the value is in a range described in handbooks.

The results of repetitive oxidation test at 900°C in air are shown for disks of P-HP70/1500-1 and P-HP70/1500-5 in Fig. 9. Both show mass gains mainly by the first cycle but practically no mass change is observed after the third cycle, showing good oxidation resistance. The mass gain is due to the formation of SiO_2 on the surface.⁹ The lower mass gain of P-HP70/1500-1 is probably owing to remaining Si–O bonds in the product.

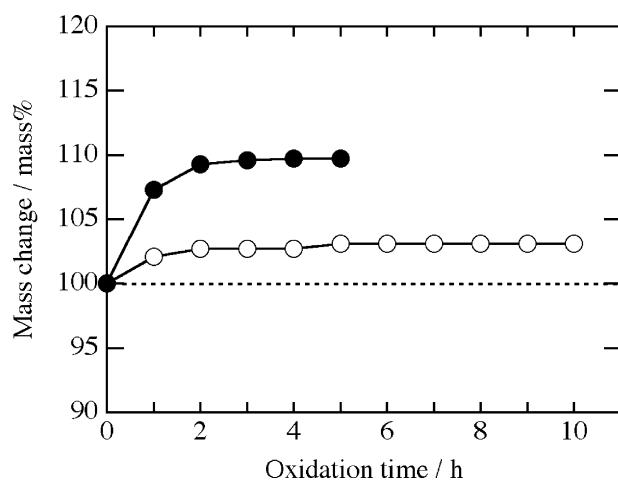


Fig. 9. Mass change by repetitive heating at 900°C for 1 h and cooling to an ambient temperature in air for disks of P-HP70/1500-1 (○) and P-HP70/1500-5 (●).

Actually, the products at lower HTT showed good oxidation resistance as reported previously.⁹

4. Conclusions

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 cyclic type having vinyl groups and a chain-type having Si–H bonds, 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. By heating in a flow of argon, most of urethane foam structure disappeared below 400°C , and the cured silicone was left in a form of aggregated hollow spheres or of reticulated structure, depending on the porosity and bulk density of urethane foam. On further pyrolysis in argon, the precursors were converted into β -SiC at 1600°C for 1–5 h, though they shrank by 10–25% in size. Depending on the type of urethane foam, β -SiC balloons and β -SiC blocks with high porosities and low bulk densities were obtained. The precursors of reticulated structure gave similar types of porous β -SiC blocks to the ones reported previously,⁴ but they were very fragile. Only by crushing the blocks, fine particles of β -SiC smaller than 100 nm were obtained, indicating that the present process can be used to synthesize nano-particles. Due to the limitation of high temperature furnace used, large blocks were not synthesized at 1600°C , but a disk of 30 mm in diameter and 3.5 mm thick formed from HP70 by 5 h pyrolysis at 1500°C showed acceptable properties; N_2 gas permeability at ambient temperature $16.4 \text{ cm}^2 \text{ s}^{-1} \text{ atm}^{-1}$, electric conductivity $9.4 \times 10^{-2} \text{ S cm}^{-1}$, and good oxidation resistance at 900°C in air. The results indicated that the disk may be used as a gas permeable heater. The process is simple, and above all the materials for this process are not hazardous and commercially available at low cost.

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