FORMATION OF β-SiC BALLOONS AND POROUS BLOCKS USING URETHANE FOAM TEMPLATES

Hidetaka Konno, Ken'ichi Kimura, Hiroki Habazaki
Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Corresponding author e-mail address: ko@eng.hokudai.ac.jp

Introduction

Previously, we have reported a new process to synthesize submicrometer-sized β-SiC particles only by pyrolysis of the precursors that were prepared by sorption of silicone compounds into exfoliated graphite (EG) [1,2]. In the present work, urethane form (UF) was used instead of EG, which resulted in the formation of β-SiC balloons and porous blocks.

Experimental

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•20, Shin-Etsu Chemical Co. Ltd., KF-99B), and urethane foam chips (ca. 10x10x3 mm^3), UF No.14 (average pore size 420 μm) and UF HP70 (average pore size 200 μm) were used. A mixture of 43 g of VC-4, 31 g of KF-99B, and Pt catalyst (Shin-Etsu Chemical, PL-8, Pt•0.5 mass%) and catalyst regulator (Shin-Etsu Chemical, PLR-31), 0.5 g each, was impregnated into UF chips, and aged overnight at 50˚C followed by curing at 200˚C for 1 h in air. Formed block type precursors (*e.g.* Figure 1(a)) were heat-treated at 1600˚C for 1 or 5 h in Ar (heating rate 400 K h^{-1}). Thermal decomposition behavior of UF and the cured silicone was examined by thermo-gravimetry (TG) in Ar at 400 K h^{-1}. The products were examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA).

Results and Discussion

The urethane foams start to decompose around 200˚C and more than 95% disappears above 400˚C in Ar, while substantial decomposition of the cured silicone starts above 500˚C, as shown in Figure 2. Consequently, the cured silicone impregnated in the pores of UF is left as a spherical shape around 400˚C and decomposes slowly at higher temperatures. Mass loss by decomposition is about 20% up to 1300˚C but between 1300 and 1600˚C large mass loss of about 40% takes place due to the formation of β-SiC [2]. After the heat treatment at 1600˚C for 5 h, the precursor shrinks only slightly with keeping the original shape of UF chip, as shown in Figure 1(b). The SEM images of the surface shown in Figure 1(c) and (d) indicate that the formed blocks are

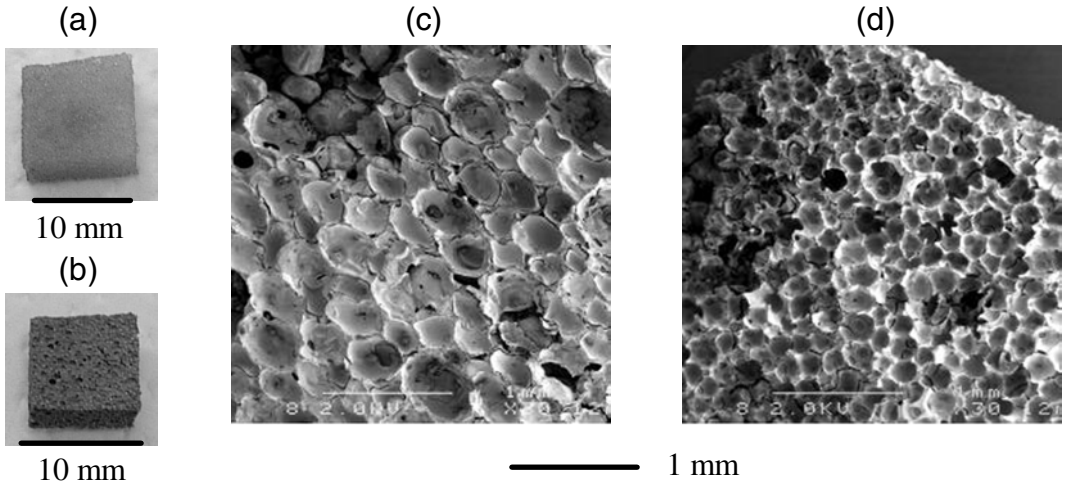

Figure 1. Photographs of (a) precursor (UF No.14) and (b) after heat treatment. SEM images of the surface of ß-SiC formed from (c) precursor (UF No. 14) and (d) precursor (UF HP70). All were heat- treated at 1600°C for 5 h in Ar, except (a).

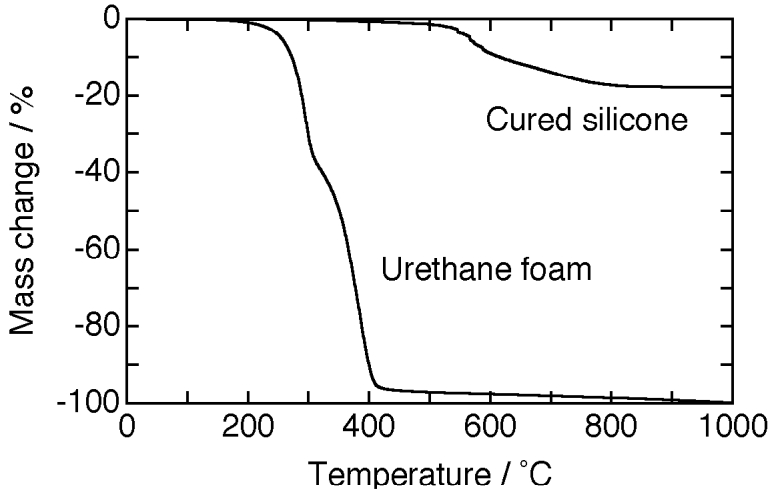

Figure 2. Thermal decomposition behavior of urethane form and cured silicone measured at 400 K h^{-1} in Ar.

aggregates of spheres. The sizes of these spheres are similar to the original pore sizes of UF and the spheres are not solid but hollow. This is due to the evolved gases by thermal decomposition of silicone, which is a reason that shrinkage of the precursor is not very large in spite of the large final mass loss. As the spheres are loosely fixed with socket-like structure between spheres as shown in Figure 3, they can be separated, that is, balloon type β-SiC is available. Thickness of the wall of larger spheres from UF No.14 (Figure 3, left), however, is only a few micrometers, so that they are very fragile compared with those from UF HP70 (Figure 3, right). With the resolution of EPMA, Si and C were detected together on the spheres and the surrounding structure and no

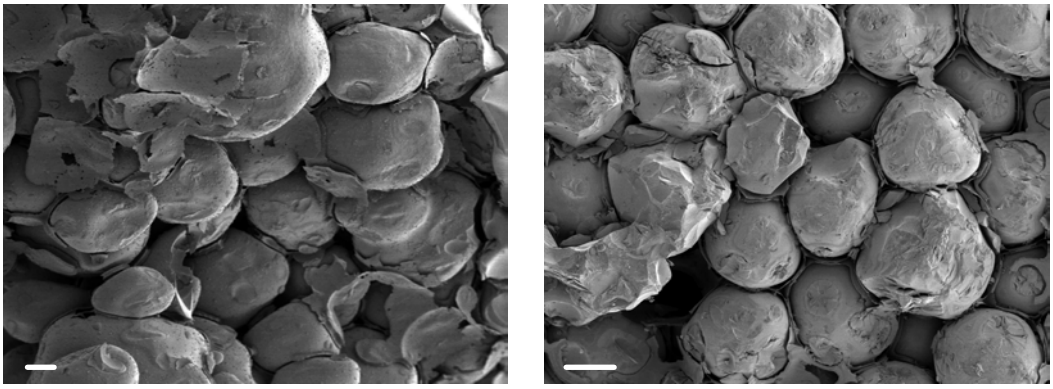

Figure 3. SEM images of 1600°C, 1 h products from precursor (UF No.14) (left) and precursor (UF HP70) (right). Bars are 100 μm.

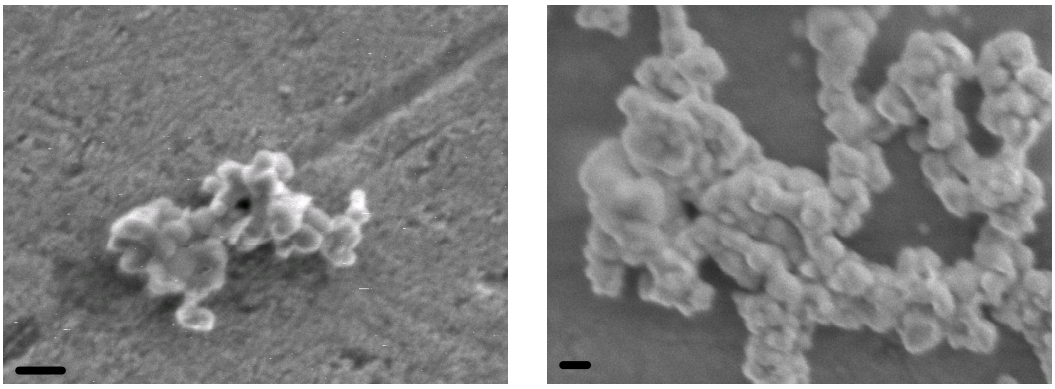

Figure 4. SEM images of 1600°C, 5 h products from precursor (UF No.14) (left) and precursor (UF HP70) (right) after crushing. Bars are 200 nm.

large fragments of carbon detected. After crushing these blocks with an agate mortar and pestle, they were found to be composed of very fine particles, as shown in Figure 4. Particle sizes are a few hundreds nanometers for the products from the precursor (UF HP70) (Figure 4, right) and those from the precursor (UF No.14) are much smaller (Figure 4, left). Accordingly, the present process can be used to synthesize nano-particles of β-SiC. In Figure 5, XRD patterns for 1600˚C products from the precursor (UF No.14) are shown, and the results were the same with the precursor (UF HP70). The results show that the precursor using UF requires longer heat treatment time at 1600˚C to form well crystallized β-SiC than the precursors using EG [1,2]. This is probably due to the fact that EG functions as a reductant at the final stage of β-SiC formation [2], whereas UF disappears at much lower temperature (Figure 2). Broad peaks in Figure 5 (left) are from tapes used to support a block sample in a frame of holder.

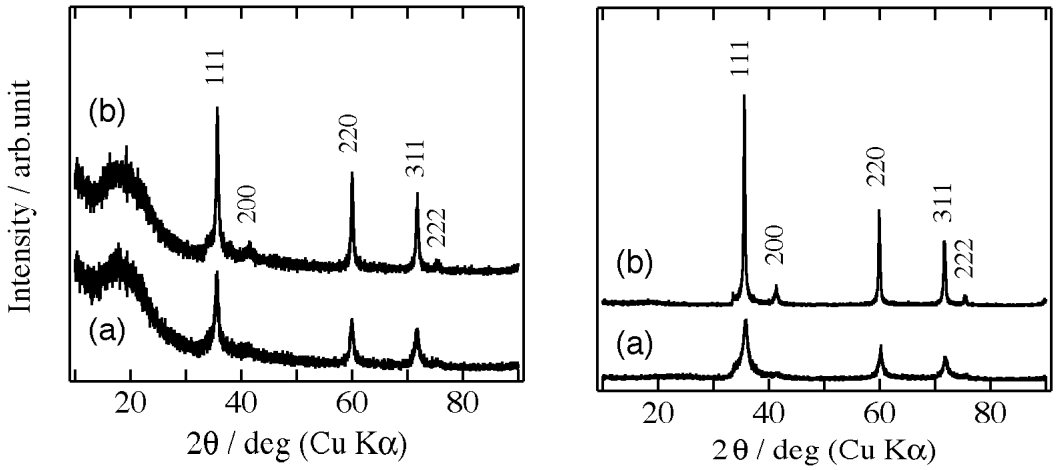

Figure 5. XRD patterns of the products from the precursor (UF No.14) by heat treatment at 1600°C for (a) 1 h and (b) 5 h in A. The left figure is for as formed blocks and the right after crushing.

Conclusions

By the present process, two types of β-SiC material were obtained: one was balloons of a few hundreds micrometers and the other porous blocks having macropores of a few hundreds micrometers in diameter. In addition, nano-sized β-SiC particles were also obtained only by crushing the blocks.

References

[1] Konno H, Kinomura T, Aramata M, Formation of β-SiC from exfoliated graphite and silicone, Carbon 2001;39: 2381-2383.
[2] Konno H, Kinomura T, Habazaki H, Aramata M, Synthesis of submicrometer-sized β-SiC particles from the precursors composed of exfoliated graphite and silicone, Carbon 2004;42. (in press).