Synthesis of SiC via low-temperature heating of graphite and Si with Na flux

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SiC was prepared by heating a mixture of graphite and Si powders with sodium over the temperature range 1173–1273 K and was characterized via X-ray diffraction, electron microscopy, and electron diffraction. The sample prepared at 1273 K exhibited aggregates of truncated hexagonal pyramid-shaped SiC crystals that were a few hundreds nanometers in size, as evidenced by scanning electron microscopy. Transmission electron microscopy and electron diffraction revealed that the crystals contained stacking faults along [111] of the cubic lattice of β -type.

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Key-words : Silicon carbide, Sodium, Graphite, Powder, Stacking faults

[Received April 28, 2013; Accepted September 1, 2013]

1. Introduction

SiC ceramics are attractive materials for a wide range of applications such as abrasives, ceramic heaters and heat-resistant structural materials because of their high mechanical strength, high chemical resistance, high thermal conductivity, and low thermal expansion.¹⁾ These applications have inspired the preparation of SiC in various forms such as powder, porous bulk, sintered body, and single crystalline. SiC crystalizes in many structural forms such as β -type (3C) and α -type (e.g. 2H, 4H, 6H, 15R), depending on the stacking sequence of Si–C tetrahedral layers.¹⁾

SiC is industrially manufactured most widely by the Acheson process, which includes carbothermal reduction of quartz sand by coke at about 2500–2700 K.¹⁾ SiC prepared by this method has a large grain size, and its crystal structure is mainly of the α -type because of the high temperature adopted in the synthesis.

Lower-temperature synthesis methods such as chemical vapor deposition method using silane,^{2),3)} pyrolysis of organic Si polymer,¹⁾ and flux growth using metal melts^{4)–9)} have been investigated for the fabrication of SiC. Liquid phase epitaxial growth of a 4H or 6H SiC film in the range 1273–1473 K was achieved by using an Al–Si or Al–Zn solution as a starting material.^{4)–6)} 2H–SiC single crystals were prepared in the range 1073–1123 K using a Li flux.^{7),8)} Tanaka et al. synthesized β -SiC (3C–SiC) powder by the reaction between a Sn–Al–Si solution and C₃H₈ gas at 1223 K.⁹⁾

Recently, we reported the formation of nano-particulate and porous bulk samples of β -SiC from a mixture of Si powder and fullerenes or amorphous carbon (carbon black) powder, reacted at 1000 K by the Na flux method.^{10)–14)} While this procedure yielded SiC when fullerene and amorphous carbon were used as the carbon source, it did not afford SiC when graphite was used as the carbon source.^{10),11)} The purpose of the present study is to find conditions under which SiC is formed by the reaction of Si and graphite with Na, and to characterize the morphology and crystal structure of the resulting SiC samples.

2. Experimental

Graphite powder (Alfa Aesar, purity 99.995%, fragment size <75 μ m), Graphite fragments (Kojundo Chemical Laboratory, purity 99.95%, fragment size 2–5 mm), carbon black powder (Mitsubishi Chemical, 99.9%, mean particle size 16 nm), Si powder (Kojundo Chemical Laboratory, 5N, fragment size <75 μ m) and Na chunks (Nippon Soda, 99.95%) were used as starting materials. The Si and carbon source powders were combined at a Si:C molar ratio of 1.2:1.0, and mixed with an agate mortar and pestle under ambient air. In an Ar gas-filled glove box (O₂ and H₂O <1 ppm), about 0.1 g of the mixed powder and about 0.1 g of Na (molar ratio of Na:Si~2.0:1.2) were placed in a boron nitride crucible (Showa Denko, 99.5%, 6.5 mm inner diameter, 18 mm depth). The crucible was set in a stainless-steel tube (SUS316, 12.7 mm outer diameter, 80 mm height), and the tube was sealed with stainless-steel caps in an Ar atmosphere. Some samples were prepared by heating the tube at a predetermined temperature (1073–1273 K) for 24 h using an electric furnace. After heating, the samples were cooled in the furnaces by shutting off the electric power to the furnace. The SUS316 tube was cut, and the product in the crucible was taken out from the tube. Na and NaSi in the crucible were removed from the product by reaction with ethanol in air. The product was then washed with distilled water and dried.

The X-ray diffraction (XRD) patterns of the samples were measured on an X-ray diffractometer (Rigaku, RINT2200) using CuK α radiation with a graphite monochromator. A scanning electron microscope with a field emission cathode (FE-SEM, Hitachi, S-4800) was used for observation of the sample morphologies. Specimens for transmission electron microscopy (TEM) were prepared with an ion slicer (JEOL, EM-09100IS). TEM images and electron diffraction (ED) patterns were taken with a 200 kV electron microscope (TOPCON, EM-002B).

3. Results and discussion

Figure 1 shows powder XRD patterns of the samples prepared by heating the Si–graphite mixture. Figure 1(a) corresponds to the sample prepared at 1273 K without Na flux. Figures 1(b)–1(d)

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correspond to the samples prepared by heating the Si-graphite mixture with Na flux at 1273, 1173, and 1073 K, respectively. Only unreacted Si and graphite were evident in the sample prepared without Na flux at 1273 K [Fig. 1(a)]. In contrast, the XRD reflection peaks for the samples prepared at 1273 and 1173 K [Figs. 1(b), and 1(c), respectively] were indexed with a cubic lattice parameter ($a = 4.36 \text{ \AA}$), which was identical to that of β -SiC.¹⁵⁾ Small shoulder peaks were observed at lower angles of the main 111 peak at $2\theta = 35^\circ$; these peaks are derived from stacking faults along the [111] of cubic β -SiC, as reported in previous studies,^{16)–19)} and are consistent with our data obtained via ED and TEM (Fig. 6).

In Fig. 1(d), graphite peaks were observed and SiC formation could not be confirmed. According to the Na–Si binary phase diagram, Si dissolves in molten Na, forming a Na–Si solution

Fig. 1. Powder XRD patterns of the samples prepared by heating a mixture of graphite and Si (a) without Na, and with Na flux at (b) 1273 K, (c) 1173 K, (d) 1073 K, and (e) the sample prepared by heating a mixture of carbon black and Si with Na flux at 1273 K.

at 1073 K.²⁰⁾ In the present study, a mixture of Na, NaSi and graphite was obtained by heating at 1073 K, followed by cooling to room temperature. Na and NaSi were removed by reaction with ethanol and subsequent washing with water. Therefore, the XRD peaks corresponding to Na and NaSi were not included in the pattern of the sample after washing. The broad peaks of the graphite indicated that its crystallinity was degraded during heating with Na and NaSi.

Figure 1(e) shows the XRD pattern of the sample prepared by heating a mixture of Si, carbon black, and Na at 1273 K. Carbon black was used as an alternative carbon source to compare with the results obtained for graphite in Figs. 1(b)–1(d). The XRD peaks were indexed with the cubic cell parameter of β -SiC. No shoulder peak was observed at lower 2θ angles of the 111 peak. The peak widths in the diffraction pattern were broader than those in the pattern corresponding to SiC prepared from graphite at 1273 K.

SEM images of the samples and starting materials are shown in Fig. 2. Figures 2(a)–2(c) correspond to the graphite powder used as the starting material. Figures 2(d)–2(f) and 2(g)–2(i) correspond to the SiC samples prepared with Na flux at 1173 and 1273 K, respectively. The graphite powder, comprised fragments ranging from a few dozen μm to 200 μm in size, with a flat smooth surface [Fig. 2(c)]. Fragments of a similar size were observed in the sample prepared at 1173 K; however, in this sample, the surface of the fragments was covered with grains of about 1 μm in size. High-magnification SEM image [Fig. 2(f)] revealed that these grains were composed of nano-crystals with hexagonal edges.

The SiC sample prepared at 1273 K [Fig. 2(g)] exhibited fragments smaller than those observed in the graphite sample, and consisted of approximately 5 μm -sized grains [Fig. 2(h)]. Truncated pyramidal hexagonal crystals were observed on the surface of the grains as shown in Fig. 2(i). The hexagonal plane corresponded to (111) of β -SiC or (0001) of hexagonal SiC, which probably related to the plane of the stacking faults. The hexagonal plane of cubic SiC (111) was observed in the powder and nanowire of β -SiC prepared by other methods such as direct reaction of Si and C in the range of 2173–2273 K,^{21),22)} thermal

Fig. 2. SEM images of (a)–(c) graphite powder, and the samples prepared by heating a mixture of graphite and Si with Na at (d)–(f) 1173 K and (g)–(i) 1273 K.

Fig. 3. SEM images of (a) graphite fragment with a size of 2–5 mm, and (b)–(d) the samples prepared by heating a mixture of the graphite fragments and Si with Na at 1273 K.

decomposition of methyltrichlorosilane in the range of 1923–2023 K,²³⁾ and the metal flux method in the range of 1873–1973 K.²⁴⁾

SiC samples were also obtained from the graphite fragments with a few millimeters in size at 1273 K. **Figure 3** shows SEM images of (a) the graphite fragment and (b)–(d) the SiC prepared from the graphite fragment. Some graphite fragments were divided and changed into smaller SiC fragments by reaction as shown in Fig. 3(b). The SEM images of sample surfaces were shown in Figs. 3(c) and 3(d). The surfaces were covered with truncated pyramidal hexagonal crystals of a few μm -sized grains which were similar to the surface shown in Fig. 2(h). However, the unreacted graphite was slightly observed inside of the fragment. In this method, the reaction was progressed from the surface of graphite. The larger fragment size decreased the yield of SiC formation due to the heterogeneous reaction from the surface of the large graphite fragments.

Figure 4 shows SEM images of carbon black powder and the SiC powder prepared by heating Si and the carbon black with Na at 1273 K. The SiC sample comprised nano-crystals which had aggregated and formed secondary particles [Fig. 4(c)]. The size of the secondary particles (a few μm) was close to that of the secondary particles of carbon black. In previous studies, low-temperature formation of β -SiC was achieved by reaction of Si, dissolved in a Na melt, with carbon from fullerenes or amorphous carbon.^{10),11)} In the present study, the crystal size of SiC prepared from graphite is larger than that of SiC prepared from carbon black at the same temperature (1273 K). Owing to the stable structure of graphite, the dissolution rate of graphite into the Na–Si melt is probably smaller than the dissolution rate of carbon black, and that reduced the nucleation density of SiC and resulted in the growth of larger grains. According to the Na–Si binary phase diagram, Si completely dissolves in molten Na at a Na/Si molar ratio of 2.0/1.2 over 1073 K.²⁰⁾ Decreasing Si contents in the Na–Si solution by the SiC formation decreases the reaction rate of SiC at the late stage of the experiment. This was evidenced by the results shown in **Fig. 5**. The SiC formation from the mixture of Si and graphite (grain size $<75\mu\text{m}$) powders with a Si/C molar ratio of 1.2 was completed at 1273 K for 1 h and a Na/Si ratio of 1.0 [Fig. 5(a)], but not completed at the ratio of 10 [Fig. 5(b)].

Fig. 4. SEM images of (a) carbon black powder and (b, c) samples prepared by heating a mixture of carbon black and Si with Na at 1273 K.

Figure 6 shows the TEM image and the ED pattern corresponding to a SiC grain in the sample prepared by heating Si and graphite with Na at 1273 K. Streaks were observed along the [111] in the ED pattern, which was indexed with the cubic

Fig. 5. XRD patterns of the samples prepared by heating the mixture of Si and graphite (grain size $<75\mu\text{m}$) powders with a Si/C molar ratio of 1.2 at 1273 K for 1 h and Na/Si ratios of 1.0 (a) and 10 (b).

Fig. 6. TEM image of a SiC grain in the sample prepared by heating a mixture of graphite and Si with Na at 1273 K. The inset shows the electron diffraction pattern of the sample.

cell parameter of β -SiC. These streaks corresponded to stacking faults, formed along the $[111]$ of β -SiC, that were evident in the TEM image. Similar stacking faults were also observed by TEM along the $[111]$ of β -SiC prepared by carbothermal reduction of SiO_2 at 2023 K¹⁶⁾ and in a SiC whisker prepared by carbothermal reduction with $3\text{NaF}\cdot\text{AlF}_3$ at 1623 K.¹⁹⁾

4. Conclusions

SiC samples were synthesized by heating mixtures of Si and graphite with Na flux in the temperature range of 1173–1273 K. The sample prepared at 1273 K yielded fragments composed of SiC grains, a few hundred nm in size, with a hexagonal shape.

Stacking faults along the $[111]$ of β -SiC were observed in the grains.

Acknowledgement The authors would like to thank S. Ito for preparing a thin section of the sample and for TEM observation.

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