Synthesis of β-SiC Powder using a Recycled Graphite Block as a Source

Minh Dat Nguyen*,**, Jung Won Bang*, Soo-Ryoung Kim*, Younghee Kim*, Eunjin Jung*, Kyu Hong Hwang** and Woo-Teck Kwon*

*Energy Materials Centre, Korea Institute of Ceramic Engineering and Technology, Jinju, 52851, Korea
**Department of Ceramic Engineering, Gyeongsang National Univ., Jinju, 660-701, Korea

Abstract

This paper relates to the synthesis of a source powder for SiC crystal growth. β-SiC powders are synthesized at high temperatures (>1400°C) by a reaction between silicon powder and carbon powder. The reaction is carried out in a graphite crucible operating in a vacuum ambient (or Ar gas) over a period of time sufficient to cause the Si+C mixture to react and form polycrystalline SiC powder. End-product characterizations are pursued with X-ray diffraction analysis, SEM/EDS, particle size analyzer and ICP-OES. The purity of the end-product was analyzed with the Korean Standard KS L 1612.

Key words : β-SiC powder, direct carbonization, recycled graphite, crystal growth

1. Introduction

Silicon carbide (SiC) single crystals own many excellent physical properties, which give promise to high-power, high-frequency, high-temperature electronic and optoelectronic device applications. Presently, SiC single crystals are mainly produced by physical vapor transport (PVT) technique[1-2]. In PVT growth process, the properties of SiC powder, used as a source material, will directly affect the quality and electrical properties of...
the obtained single crystals. Those skilled in SiC crystal growth technology recognize that the elimination of defects has been a major challenge of the technology development. Besides optimizing the growth temperature, pressure, and thermal gradient in a SiC crystal growth chamber, increasing the source purity has been a critical parameter for reducing defect formation during SiC crystal growth.

At the moment, many methods could be used to produce SiC powders, such as Acheson method, CVD, direct carbonization method, sol-gel methods, gas-phase reaction method, self-propagation high-temperature synthesis (SHS) and so on. Direct carbonization, among those methods, is the most promising method of synthesizing SiC powder because it requires lower amounts of energy while higher yields achieved and it is also simpler and more economic than other methods.

The electrodes used in furnaces are made almost exclusively of graphite. Manufacturers are recently concerned about graphite electrode recycling due to the cost of electrode replacement is very high. In this study, synthesis of β-SiC was studied using a recycled graphite block in the form of electrode rods in furnaces containing metallic impurities less than 5 mg/kg as a carbon source.

2. Experimental Procedure

The starting graphite powder (carbon powder) was recycled from graphite blocks used as electrode rods in furnaces. The graphite blocks were undergone several steps of breaking down into suitable small sizes by using some mechanical processes before being dry-ground in a laboratory-grade ball mill for 24h; 48h; 72h and 96h. The grinding vessel was made of SiC with the inner volume of 4537 cm³. SiC balls (including 15 mm; 10 mm; 5 mm and 1 mm with an amount of 450g; 645g; 1307g and 652g, respectively) were used as grinding medium. An additional 1% of diethylene glycol was added as aid medium. The raw ground graphite was characterized using scanning electron microscopy (SEM), particle-size analysis, and ICP chemical analysis. Silicon metal powder (99.999% Si, average particle size: 10 µm; SM-1565; Strategic Metal Investments Ltd) was used as a starting material (Table 1).

The SiC powder was synthesized using the silicon powder and carbon powder in a thermal reaction at 1400°C and then at 1800°C under the same condition of 6×10⁻² Torr vacuum, Ar gas environment and with the heating rate of 10°C/min and then natural cooling (Fig. 1). The molar ratio of carbon to silicon in the heat-treated sample was fixed at 1:2:1. The produced β-SiC powder were characterized using X-ray diffractometer (P/MAX 2200V/PC; Rigaku Corp.) with a Cu target (Kα=1.54 Å) to identify the crystalline phases of the powder. The shape and size of produced β-SiC powder were observed using SEM (JSM-6700F; JEOL) and the particle size distribution was measured with a Malvern particle size analyzer (Mastersizer S Ver. 2.15). The purity of β-SiC powders was measured based on Korean Industrial Standard (KS L 1612) by using inductively coupled plasma optical emission spectrometry (ICP-OES).

3. Results and Discussion

Graphite particles were dry-ground in the SiC ball mill from 24 to 96h to decrease the size of them. Particle-size analysis was carried out to determine the particle size and particle distribution of C powder (Fig. 2). SEM was used to characterize the size variation and morphology of the particles (Fig. 3) and to compare with the size distribution shown in Fig. 2. The particle size gradually decreased when increasing the length of grinding time. Graphite powder with flaky shapes (Fig. 3) and the average grain size of 6.7 µm after 96hr grinding was selected for further chemical composition evaluation. However, the content of impurities in used graphite...
powder, measured by using ICP-OES Perkin Elmer OPTIMA 8300, such as metal elements (e.g. Fe...) is relative high. To improve the quality of synthesized SiC, the ground graphite powder should be purified by immersing in 0.2 M HCl solution for 24hr. The impurities of graphite before and after purifying were listed in Table 2. As a result, the purified graphite was chosen as a starting material.

After heat-treatment, X-ray diffraction was firstly conducted to determine the crystalline quality of the product (Fig. 4). Fig. 4a and Fig. 4b show the X-ray diffraction pattern of heat-treated samples at 1400$^\circ$C and 1800$^\circ$C, respectively. This result indicates that $\beta$-SiC can be formed below 1400$^\circ$C with low quality. Meanwhile, at 1800$^\circ$C the X-ray diffraction result shows larger and clearer sharpness peaks than 1400$^\circ$C heat-treated sample. From the results, it was confirmed that $\beta$-SiC powders without

### Table 1. Si powder content (wt.%)

| Element | Si  |
|---------|-----|
| Al      | 99.999 |
| B       | 0.0008 |
| Ca      | 0.0001 |
| Fe      | 0.0003 |
| P       | 0.0001 |

### Table 2. The content of impurities in used graphite block before and after purifying (mg/kg)

| Element | Al | Ca | Cr | Cu | Fe | Mg | Mn | Si | Ti | Zr |
|---------|----|----|----|----|----|----|----|----|----|----|
| Ground Graphite | 1.8 | 5.7 | 0.1 | 0.2 | 4.8 | 0.03 | 0.09 | 5.2 | 1.6 | 2.6 | <0.02 |
| Purified Graphite | 0.03 | 0.05 | 0.12 | 0.02 | 0.04 | 0.02 | 0.08 | <0.01 | 0.11 | 0.08 | <0.02 |

### Table 3. The chemical composition of synthesized SiC (wt. %)

| Sample | Si | Free SiO$_2$ | Free Si | Others |
|--------|----|--------------|--------|--------|
| SiC    | 99.53 | 0.02 | 0.03 | Bal.  |
extra phases were well developed with increasing temperature. The synthesized product with SiC content was then investigated by ICP-OES (Table 3). The remain impurities of end-product SiC originated from metallic impurities of C powder.

Secondly, SEM was used to analyze the configuration and crystallinity of the synthesized SiC particles (Fig. 5). Based on the Si-C phase diagram, the direct reaction of a powdered mixture of silicon and graphite under normal pressure begins slowly around 1150°C at the solid-solid contact areas according to reaction Si(s) + C(s) → SiC(s). When the temperature is increased beyond the melting point of Si (>1400°C), the reaction of molten silicon Si(l) with C(s) follows basically mechanism Si(l) + C(s) → SiC(s). At this state, the liquid silicon will penetrate or the Si atoms will diffuse through pores and other paths of least resistance into the C(s), where reaction then occurs to form SiC. In the course of the reaction, therefore, microstructural features of the formed SiC, such as the porosity, crystallite size and shape, will be markedly affected by those of given carbon. Fig. 5 shows that the overall SiC particles have the same flaky shapes with given carbon power’s shapes (Fig. 3), but they were enlarged while the clustered structure was obtained. In other words, reaction of a powdered mixture of silicon and carbon was progressing in which carbon particles were encroached on the neighboring Si particles to form a larger clustered structure β-SiC particles. As a result, the particle size of the synthesized SiC was partly agglomerated and was coarsened with mean size value, measured by Malvern particle size analyzer, was around 17 µm (Fig. 6).

4. Summary

In this study, the β-SiC powder was successfully synthesized by using recycled graphite as starting material, in which the recycled graphite was purified by removing the metal impurities such as iron. It was confirmed that β-SiC powders without extra phases were well developed with increasing temperature. β-SiC phase can be formed at lower temperature below 1400°C. By increasing temperature up to 1800°C, the X-ray diffraction result
shows larger and clearer sharpness peaks than 1400°C heat-treated sample. End-product SiC powder with further purification process can be used as starting material for SiC single crystal growth.

Acknowledgment

This research was supported by Korea Institute of Energy Technology Evaluation and Planning (20163030013440) and the strategic core materials development program (10050661) funded by Ministry of Trade, Industry and Energy (MOTIE), Korea.

References

1. Wang, H., Yan, C. F., Kong, H. K., Chen, J. J., Xin, J., and Shi, E. W., 2012 : Synthesis of Source Powder for SiC Crystal Growth Using High Purity Silicon and Carbon Powder, Advanced Materials Research, Vol. 529, pp. 64-68.
2. Sakwe, S. A., Stockmeier, M., Hens, P., Mueller, R., Queren, D., Kuncke, U., Konias, K., Hock, R., Magerl, A., Pons, M., Winnacker, A., and Wellmann, P., 2008 : Bulk Growth of SiC-Review on Advances of SiC Vapor Growth for Improved Doping and Systematic Study on Dislocation Evolution, Phys. Status. Solidi. B, Vol. 245, pp. 1239-1256.
3. Barrett, D. L., Chen, J., Hopkins, R. H., and Johnson, C. J., 2009 : Method for Synthesizing Ultrahigh-purity Silicon Carbide, PCT/US2006/046673.
4. Yang, Y., Lin, Z. M., and Li, J. T., 2009 : Synthesis of SiC by silicon and carbon combustion in air, J. Eur. Ceram. Soc., 29, 175-180.
5. Kwon, W. T., Kim, S. R., Kim, Y. H., Lee, Y. J., Won, J. Y., and Oh, S. C., 2014 : Effect of Silicon Particle Size on Synthesis and Crystallinity of β-Silicon Carbide Particles, Defect and Diffusion Forum, Vol. 353, pp. 239-243.
6. Lefort, A., Parizet, M. J., El-Fassi, S. E., and Abbaoui, M., 1993 : Erosion of graphite electrodes, J. Phys. D: Appl. Phys., Vol. 26, pp. 1239-1243.
7. Kurzeja, R., 1976 : Protective Coating for Graphite Electrodes, US596,021.
8. Haase, V., Kirschstein, G. et al., 1986 : Gmelin Handbook of Inorganic Chemistry, 8th Edition (Springer-Verlag Berlin Heidelberg GmbH 1986), pp. 1-3.
9. Taylor, A. and Laidler, D. S., 1950 : The Formation and Crystal Structure of Silicon Carbide, Brit. J. Appl. Phys., 1(7), pp. 174-181.
### 정 은 진
- 연세대학교 신소재공학 석사
- 연세대학교 신소재공학 박사과정
- 현재 한국세라믹기술원 학연 박사과정

### 황 규 홍
- 서울대학교 무기재료공학과 학사, 석사, 박사
- ㈜알디케이 이사
- 현재 경상대학교 세라믹공학과 교수

### 권 우 택
- 한양대학교 화학공학 박사
- 현재 한국세라믹기술원 에너지소재센터 수석연구원

---

### 학회지 投稿 安內

| 종 체 | 내용 |
|------|------|
| 논 論 說 | 提案, 意見, 批判, 時評 |
| 展望, 解説 | 現況과 未來의 信息, 研究 技術의 綜合解説, Review |
| 技 術 報 告 | 實際的인 試驗, 調査의 報告 |
| 技術, 行政情報 | 價値있는 技術, 行政情報を 連结히 解説하고, comment를 붙인다. |
| 見 聞 記 | 國際會議的 報告, 國内外의 研究 幾開의 見學記 등 |
| 書 評 | 企業, 研究幾開, 大學 等의 評價 |
| 談 話 室 | 會員相互의 情報交換, 會員 自由스터로운 講, 階層 등 |
| Group 紹介 | 企業, 研究幾開, 大學 等의 紹介 |
| 研究論文 | Original 研究論文으로 本 學會의 會誌에 掲載하는 것이 適當하다고 보여지는 것 |

수시로 원고를 접수하오니 많은 투고를 바랍니다.