

Rapid consolidation of binderless nanocrystalline silicon carbide by pulsed current activated sintering

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Hard nanostructured SiC material was produced within 3 minutes from mechanically activated powder by the simultaneous application of a pressure of 500 MPa and a 2,800 A pulsed current. The pulsed current activated sintering was performed on SiC of various grain sizes. With a finer initial SiC powder size, the resulting density was higher and the SiC possessed improved mechanical properties. The fracture toughness, hardness, and grain size of the sintered SiC were investigated.

Key words: Rapid sintering, Nanostructured material, Silicon carbide, Hardness, Toughness.

Introduction

SiC has received much attention as a promising semiconductor with a high electric breakdown threshold and thus, SiC is attractive as an electronic material for high temperature, high frequency, and high power electronic devices [1]. In addition, SiC possesses the unusual combination of a low density, high hardness, chemical stability, low thermal expansion, and high strength at high temperatures.

Nanostructured materials have been widely investigated because they demonstrate wide functionality and exhibit enhanced or different properties compared to bulk materials [2, 3]. Particularly, in the case of nanostructured ceramics, the presence of a large fraction of grain boundaries can lead to unusual or better mechanical, electrical, optical, sensing, magnetic, and biomedical properties [4–10]. Recently, nanocrystalline powders have been developed by high energy milling [11]. The sintering temperature of high energy mechanically milled powder is lower than that of unmilled powder due to the increased reactivity, internal and surface energies, and surface area of the milled powder, which contribute to its so-called mechanical activation [12–14].

However, the grain size of sintered materials becomes much larger than that of pre-sintered powders due to the

rapid grain growth during conventional sintering processes. Therefore, controlling grain growth during sintering is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering method, which can make dense materials within 2 minutes, is effective in controlling grain growth [15].

In this study, we investigated the fabrication of nanopowder and the sintering of SiC by the pulsed current activated sintering (PCAS) method without the use of a binder. In addition, we also studied the effect of ball milling on the sintering behavior, grain size, and mechanical properties of binderless SiC.

Experimental procedure

The silicon carbide powder used in this study was supplied by the Alfa Company and had a purity of 99.8% with a grain size of $< 1 \mu\text{m}$. The powder was first milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for various periods of time (0, 1, 4, 10 h). Tungsten carbide balls (8.5 mm in diameter) were used for the milling in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of the balls : powder was 30 : 1. The milling resulted in a significant reduction of the grain size and the powder size of the SiC decreased with increasing milling time. The grain size of the SiC was calculated from the full width at half-maximum (FWHM) of the diffraction peak by applying Suryanarayana and Grant Norton's formula [16].

After milling, the powders were placed in a graphite

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die (outside diameter of 45 mm, inside diameter of 5 mm, and a height of 40 mm) and then introduced into the PCAS apparatus [15]. The PCAS apparatus used a 30 kW power supply which provided a pulsed current (on for 20 μ s and off for 10 μ s) through the sample and applied a uniaxial pressure of 50 kN. The system was first evacuated and a uniaxial pressure of 500 MPa was applied. The pulsed current was then activated up to 1,400 °C with a heating rate of 600 K·min⁻¹ and then turned off without a holding time. At the end of the process, the pulsed current was turned off and the sample was cooled to room temperature. The process was carried out under vacuum at a pressure of 4×10^{-2} Torr (5.3 Pa).

The relative density of the sintered sample was measured by the Archimedes method. Microstructural information was obtained from product samples which were polished and etched using Murakami's reagent (10 g potassium ferricyanide, 10 g NaOH, and 100 ml water) for 1 minute at room temperature. The compositional and microstructural analyses of the products were performed by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) in conjunction with energy dispersive X-ray spectroscopy (EDS), and transmission electron microscopy (TEM).

Results and Discussion

Fig. 1 shows SEM images of the SiC powders milled for various times. It can be seen that the powders are agglomerated and the particle boundaries are not clear. Therefore, the powders were observed by TEM and the images are shown in Fig. 2. The powder size decreased and the diffraction patterns changed from spot patterns to ring patterns with increasing milling time. The average grain sizes of the SiC powders milled for 1, 4, and 10 h were about 51 nm, 28 nm, and 26 nm, respectively, as determined by applying Suryanarayana and Grant Norton's formula.

Fig. 3 shows SEM images of SiC sintered at 1,400 °C from the various milled powders. The pores decreased

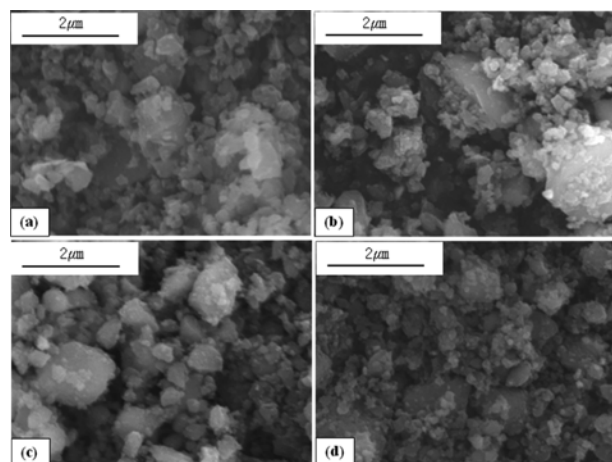


Fig. 1. SEM images of the SiC powder milled for (a) 0, (b) 1, (c) 4 and (d) 10 h.

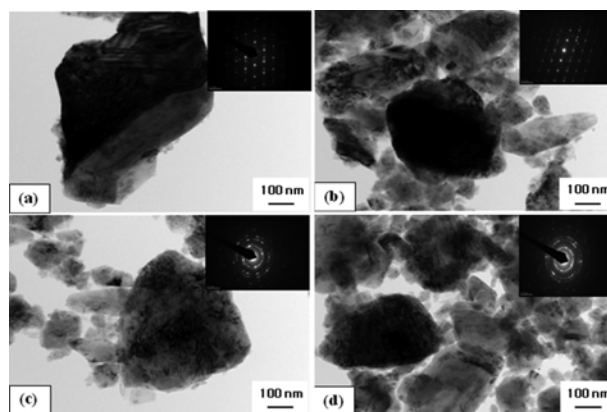


Fig. 2. TEM micrographs of the pure SiC powder milled for (a) 0, (b) 1, (c) 4 and (d) 10 h.

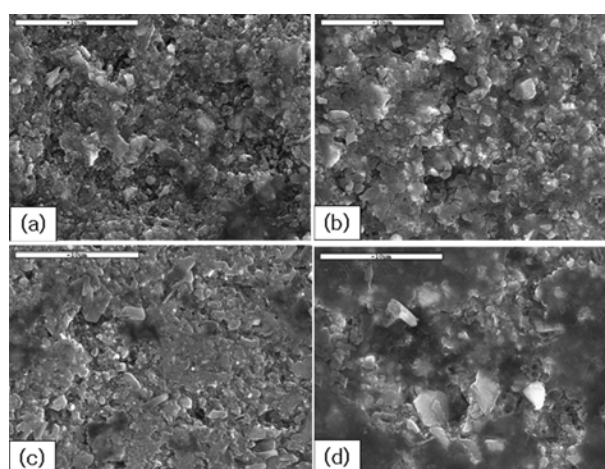


Fig. 3. SEM images of the sintered SiC powders milled for (a) 0, (b) 1, (c) 4 and (d) 10 h.

with increasing milling time and the corresponding relative densities of the SiC obtained from the powders milled for 0, 1, 4, and 10 hr were approximately 94, 90, 79, and 61% theoretical, respectively. The high energy ball milling affected the final density. The density of the high energy mechanically milled SiC is higher than that of the unmilled powder due to increases in the reactivity, internal and surface energies, and surface area of the powder, which all contribute to its so-called mechanical activation [17-19].

Fig. 4 shows the XRD patterns of the sintered SiC obtained from all four powders used in this study. Only a SiC phase is present in the XRD patterns. The full width at half-maximum (FWHM) of the diffraction peak in the sintered SiC increased with increasing milling time, due to grain refinement. Fig. 5 shows plots of $\text{Brcos}\theta$ versus $\sin\theta$, which were used to calculate the average grain sizes of the SiC using Suryanarayana and Grant Norton's formula. As a result, the grain sizes were about 313, 231, 96, and 60 nm for the samples produced with milling times of 0, 1, 4, and 10 h, respectively. An FE-SEM image of SiC sintered from the powder milled for 10 h is shown in Fig. 6, in which the SiC consists of a nanophase.

Ohyanagi *et al.* sintered SiC from milled SiC at 1,400 °C

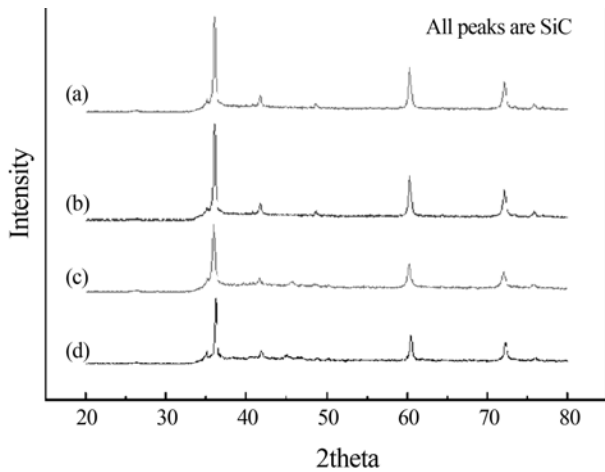


Fig. 4. XRD patterns of the binderless SiC obtained by sintering the powders milled for (a) 0, (b) 1, (c) 4 and (d) 10 h.

under a pressure of 40 MPa by spark plasma sintering (SPS) and the corresponding relative density was only 55% [20]. The relative density of the SiC in our study was higher than that obtained by Ohyanagi *et al.* using SPS at a pressure of 40 MPa at the same sintering temperature. The reasons for the higher SiC density obtained in our study are as follows. Firstly, the application of pressure during the initial stage of sintering adds another term to the surface energy driving force such that the total driving force, F_D , becomes [21] :

$$F_D = \gamma + (P_a r / \mu), \quad (1)$$

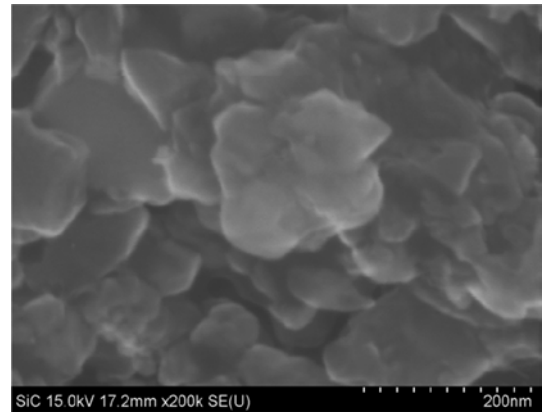


Fig. 6. FE-SEM micrograph of the pure SiC obtained by sintering the powder milled for 10 h.

where γ is the surface energy, P_a is the applied pressure, and r is the radius of the particle. The effect of pressure on the densification of nanometric, stabilized ZrO_2 during high frequency induction heated sintering was investigated by Kim *et al.* [21]. A significant increase in the relative density was observed as the pressure was increased from about 60 to 100 MPa during sintering at 1,000 °C. Secondly, the role of the current (resistive or inductive) in sintering and or synthesis has been the focus of several studies aimed at providing an explanation of the observed enhancement of sintering and the improved characteristics of the products. The role played by the current has been interpreted in a number of ways with the effect being

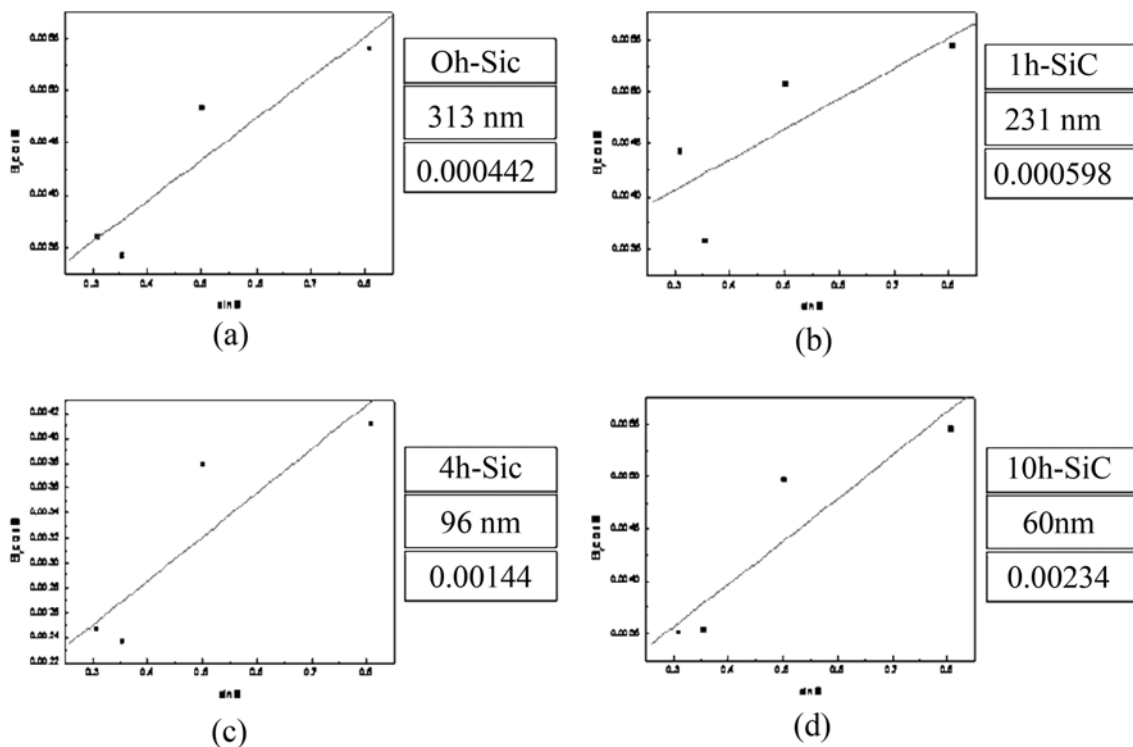


Fig. 5. Plot of $Brcos\theta$ versus $\sin\theta$ of the pure SiC obtained by sintering the powders milled for (a) 0, (b) 1, (c) 4 and (d) 10 h.

explained in terms of a fast heating rate due to Joule heating, the presence of plasma in the pores which separates the powder particles, and the intrinsic contribution of the current to mass transport [22-25].

Vickers hardness measurements were performed on polished sections of the SiC samples using a load of 10 kg_f and a dwell time of 15 s. Indentations with sufficiently large loads produced radial cracks emanating from the corners of the indent. The length of these cracks permits the fracture toughness of the material to be estimated using Anstis *et al.* expression [26]. The Vickers hardnesses of the SiC samples ball milled for 1, 4, and 10 h were 440 kg/mm², 1,040 kg/mm², and 1,420 kg/mm², respectively, and the fracture toughness for the SiC milled for 10 h was 2 MPa·m^{1/2}. The hardness of the SiC powders was remarkably increased by the refinement of the grain size and the increased density.

Summary

SiC nanopowder was fabricated by high energy ball milling. Dense nanostructured SiC was obtained from mechanically activated SiC powder by pulsed current activated sintering within 3 minutes. The relative densities of the SiC samples with milling times of 0, 1, 4, and 10 h were approximately 61, 79, 90, and 94% theoretical, respectively. The Vickers hardness and fracture toughness of the SiC obtained from the sintered powder milled for 10 h were 1,420 kg/mm² and 2 MPa·m^{1/2}, respectively.

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References

1. M. Sheriff El-Eskandarany, K. Sumiyama and K. Suzuki, *J. Mater. Res.* 10 (1995) 659-665.
2. H. Gleiter, *Nanostructured Materials*. 6 (1995) 3-15.
3. J.R. Yoon, D.J. Choi, K.H. Lee, J.Y. Lee and Y.H. Kim, *Electron. Mater. Lett.* 4 (2008) 167-173.
4. J. Karch, R. Birringer and H. Gleiter, *Nature*. 330 (1987) 556-561.
5. A.M. George, J. Iniguez and L. Bellaiche, *Nature*. 413 (2001) 54-60.
6. D. Hreniak and W. Strek, *Journal of Alloys and Compounds*. 341 (2002) 183-189.
7. C. Xu, J. Tamaki, N. Miura and N. Yamazoe, *Sensors and Actuators B: Chemical*. 3 (1991) 147-152.
8. D.G. Lamas, A. Caneiro, D. Niebieskikwiat, R.D. Sanchez. D. Garcia and B. Alascio, *Journal of Magnetism and Magnetic Materials*. 241 (2002) 207-211.
9. C.W. Nahm, C.J. Kim, Y.J. Park, B.J. Lee and B.W. Park, *Electron. Mater. Lett.* 4 (2008) 5-9.
10. E.S. Ahn, N.J. Gleason, A. Nakahira and J.Y. Ying, *Nano Letters*. 1 (2001) 149-154.
11. D.M. Lee, K.M. Jo and I.J. Shon, *J. Kor. Inst. Met. & Mater.* 47 (2009) 344-348.
12. F. charlot, E. Gaffet, B. Zeghmami, F. Bernard and J.C. Liepce, *Mater. Sci. Eng. A262* (1999) 279-285.
13. V. Gauthier, C. Josse, F. Bernard, E. Gaffet and J.P. Larpin, *Mater. Sci. Eng. A262* (1999) 117-122.
14. M.K. Beyer and H. Clausen-Schaumann, *Chem. Rev.* 105 (2005) 2921-2926.
15. I.Y. Ko, B.R. Kim, K.S. Nam, B.M. M, B.S. Lee and I.J. Shon, *Met. Mater. Int.* 15 (2009) 399-405.
16. C. Suryanarayana and M. Grant Norton, *X-ray Diffraction A Practical Approach*, Plenum Press, New York, pp. 207 (1998).
17. F. charlot, E. Gaffet, B. Zeghmami, F. Bernard and J.C. Liepce, *Mater. Sci. Eng. A262* (1999) 279-285.
18. V. Gauthier, C. Josse, F. Bernard, E. Gaffet and J.P. Larpin, *Mater. Sci. Eng. A262* (1999) 117-122.
19. M.K. Beyer and H. Clausen-Schaumann, *Chem. Rev.* 105 (2005) 1921-2925.
20. M. Ohyanagi, T. Yamamoto, H. Kitaura, Y. Koderra, T. Ishii and Z.A. Munir, *Scripta Materialia* 50 (2004) 111-115.
21. H.-C. Kim, I.-J. Shon, I.-K. Jeong and I.-Y. Ko, *Metals and Materials International* 12 (2006) 393-398.
22. Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, *Spark Plasma Sintering of Alumina*, *J. Am. Ceram. Soc.* 85 (2002) 1921-2926.
23. J.E. Garay, U. Anselmi-Tamburini, Z.A. Munir, S.C. Glade and P. Asoka- Kumar, *Appl. Phys. Lett.* 85 (2004) 573-578.
24. J.R. Friedman and J.E. Garay. *U. Intermetallics* 12 (2004) 589-595.
25. J.E. Garay, J.E. Garay. U. Anselmi-Tamburini and Z.A. Munir, *Acta Mater.* 51 4487 (2003) 4487-4494.
26. G.R. Anstis, P. Chantikul, B.R. Lawn and D.B. Marshall, *J. Am. Ceram. Soc.* 64 (1981) 553-538.