

Enhanced mechanical properties of nanostructured SiC– Graphene composites rapidly sintered by pulsed current activated heating

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SiC has a low density, high hardness, chemical stability, low thermal expansion, and high strength at high temperatures. However the low fracture toughness of SiC ceramic limits its widely industrial application. One of the most obvious methods to improve the mechanical properties has been to add a reinforcing agent to formulate a nanostructured composite materials. In this respect, graphene was evaluated as the reinforcing agent of SiC ceramics using pulsed current activated sintering (PCAS). SiC-graphene composites were obtained within short time by PCAS under a pressure of 80 MPa. The effect of graphene on hardness and microstructure of SiC-Graphene composite was evaluated using FE-SEM and Vickers hardness tester.

Key words: Nano-materials, Sintering, Hardness, Composite, Graphene.

Introduction

SiC has a low density, high hardness, chemical stability, low thermal expansion, and high strength at high temperatures. In addition, SiC is a wide gap semiconductor with a high electric breakdown threshold, and thus is attractive as an electronic material

for special applications [1]. However, the drawback of SiC for widely industrial applications is low fracture toughness below ductile-brittle transition temperature. To improve its mechanical properties, the approach commonly utilized has been the addition of a second phase to form composites and to make nanostructured materials.

Since the discovery of graphene using the simple scotch tape method [2], graphene has been considered as an ideal second phase to improve the mechanical, electrical and thermal properties of metals [3], ceramics [4] and polymers [5] due to its unique combination of electrical, thermal and mechanical properties [6-8]. Nanocrystalline materials have received much attention as advanced engineering materials with improved physical and mechanical properties [9, 10]. Since they possess a high strength and hardness as well as excellent ductility and toughness, they have garnered more attention recently [11, 12]. In recent days, nanocrystalline powders have been developed by the thermochemical and thermomechanical process named as the spray conversion process (SCP), co-precipitation

and high energy milling [13-15]. 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 [16-18]. However, the grain size in sintered materials becomes much larger than that in pre-sintered powders due to rapid grain growth during a conventional sintering process. So, controlling grain growth during the sintering process is one of the keys to the commercial success of nanostructured materials. In this regard, the pulsed current activated sintering (PCAS) technique has been shown to be effective in the sintering of nanostructured materials in very short times (within two minutes) [19-21].

The goal of this study was to produce nanostructured SiC-graphene composites within three minutes. The effect of graphene on the mechanical properties (hardness and fracture toughness) and grain size of SiC-graphene composites was also evaluated.

Experimental Procedure

SiC powder with a grain size of $< 1 \mu\text{m}$ and 99.7% purity was supplied by Alfa. Graphene (XG-Science, Graphene grade C-750) was used as the additive. Powders of four compositions corresponding to SiC, SiC-1vol.% graphene, SiC-3vol.% graphene, and SiC-5vol.% graphene, were prepared by weighting and milled in a high-energy ball mill (Pulverisette-5 planetary mill) at 250 rpm for 10 h. WC balls (9 mm in diameter) were used in a sealed cylindrical stainless steel vial under an argon atmosphere. The weight ratio of balls-to-powder was 30 : 1. The grain size of the

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powders was calculated from the full width at half-maximum (FWHM) of the diffraction peak by Suryanarayana and Grant Norton's formula [22].

The milled powders were placed in a graphite die (outside diameter, 35 mm; inside diameter, 20 mm; height, 40 mm) and then introduced into the pulsed current activated sintering (PCAS) system. A schematic diagram of this system is schematically shown in Ref. [23]. The PCAS apparatus includes a 30 kW power supply which provides a pulsed current through the sample, and a 50 kN uniaxial press. The system was first evacuated and a uniaxial pressure of 80 MPa was applied. A pulsed current was then activated and maintained until the densification rate was negligible, as indicated by the real-time output of the shrinkage of the sample. Sample shrinkage was measured in real time by a linear gauge measuring the vertical displacement. Temperature was measured by a pyrometer focused on the surface of the graphite die. A temperature gradient from the surface to the center of the sample is dependent on the heating rate, the electrical and thermal conductivities of the compact, and its relative density. The heating rates were approximately $1000\text{ }^{\circ}\text{K minute}^{-1}$ during the process. At the end of the process, the pulsed current was turned off and the sample was allowed to cool to room temperature. The entire process of densification using the PCAS technique consists of four major control stages: chamber evacuation, pressure application, power application, and cooling off. The process was carried out under a vacuum of 10.6 Pa.

The relative densities of the sintered samples were measured by the Archimedes method. Microstructural information was obtained from fracture surface of product samples. Compositional and microstructural analyses of the samples were carried out through X-ray diffraction (XRD), and field-emission scanning electron microscopy (FE-SEM). Vickers hardness was measured by performing indentations at a load of 20 kg_f with a dwell time of 15 s.

Results and Discussion

Fig. 1 shows X-ray diffraction patterns of raw powder of SiC and graphene. XRD patterns of the SiC- x vol.% graphene powders milled by high energy ball are shown in Fig. 2. The full width at half-maximum (FWHM) of the diffraction peak in Fig. 2 is more broad than that in Fig. 1 due to the refinement of powders and strains. Fig. 3 shows plot of B_r ($B_{\text{crystalline}} + B_{\text{strain}}$) $\cos\theta$ versus $\sin\theta$ in Suryanarayana and Grant Norton's formula [22] for particle size measurements. The average grain sizes of the SiC in the SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene powders were calculated as about 35, 30, 23 and 14 nm, respectively.

The shrinkage displacement-time (temperature) curve provides an useful information on the consolidation

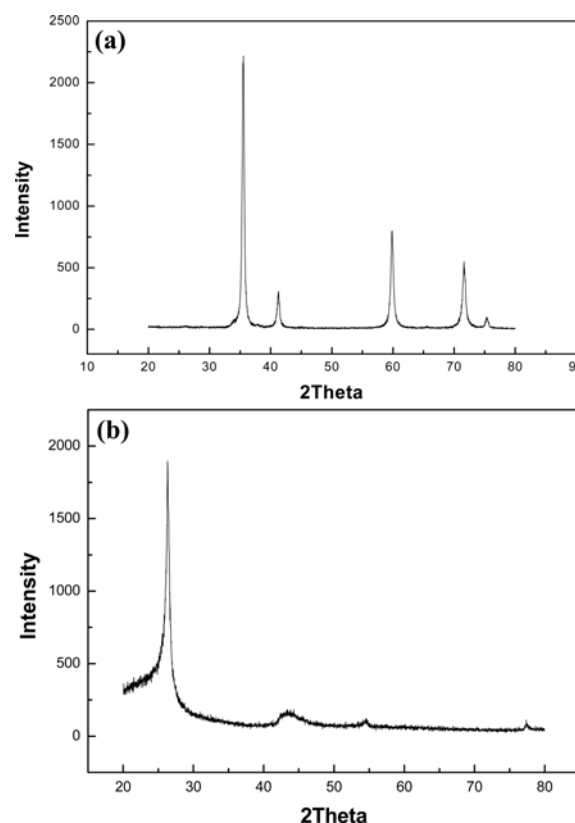


Fig. 1. XRD patterns of raw powders of SiC (a) and graphene (b).

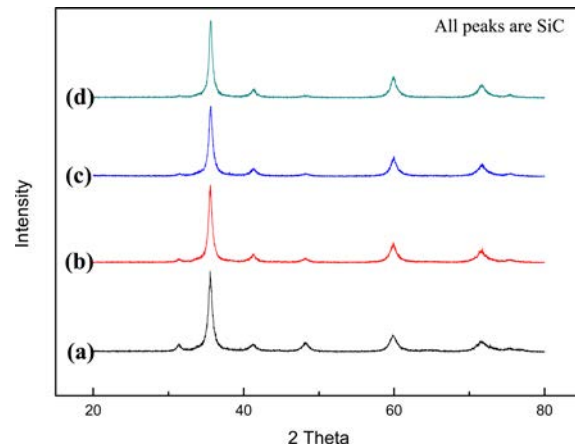


Fig. 2. XRD patterns of SiC + x vol.% graphene powders milled for 10 h: (a) $x = 0$, (b) $x = 1$, (c) $x = 3$, (d) $x = 5$.

behavior. Fig. 4 shows the shrinkage record of SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene compacts. In all cases, the thermal expansion of the compacts occurs up to heating time of 10 s and then the shrinkage displacement rapidly increases above the heating time. The shrinkage curve suggests that the consolidation terminates in three minutes.

Fig. 5 shows the XRD patterns of SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene after sintering. In all cases, only SiC peaks

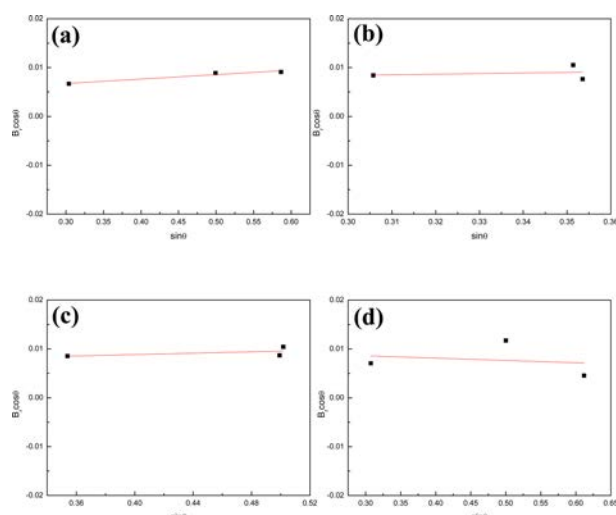


Fig. 3. Plot of $B_r (B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta$ versus $\sin\theta$ for SiC in SiC + x vol.% graphene powders milled for 10 h: (a) x = 0, (b) x = 1, (c) x = 3, (d) x = 5.

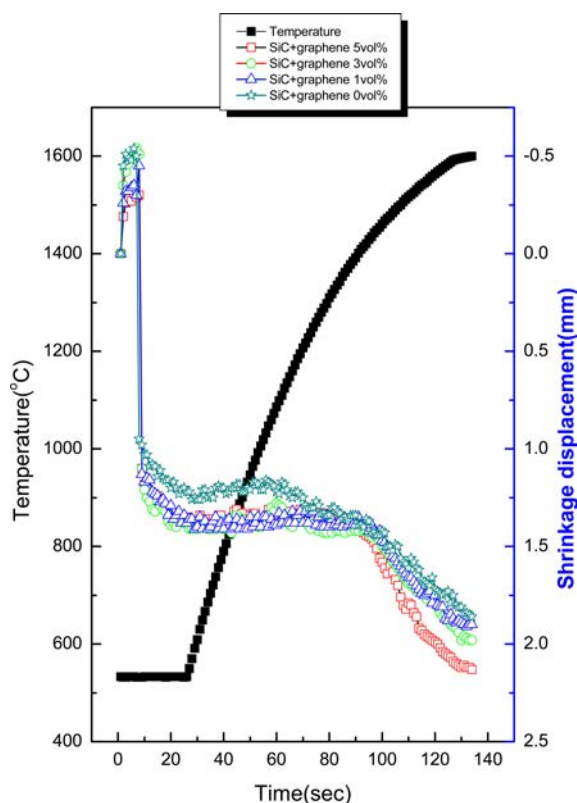


Fig. 4. Variations of temperature and shrinkage displacement with heating time during the sintering of SiC + x vol.% graphene samples by PCAS.

are detected. Again, their particle sizes were calculated by the plot of $B_r (B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta$ versus $\sin\theta$ in Suryanarayana and Grant Norton's formula [22] as shown in Fig. 6. The average grain sizes of SiC were about 143, 97, 43 and 17 nm for SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene, respectively. This means that the grain size of SiC decreases as the graphene content increases. It is believed that graphene

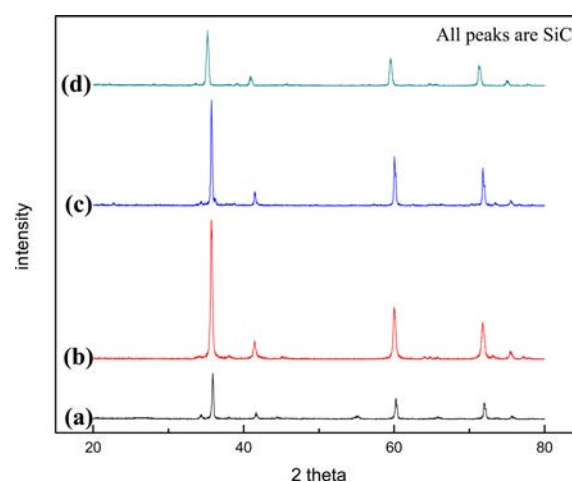


Fig. 5. XRD patterns of SiC + x vol.% graphene sintered by PCAS: (a) x = 0, (b) x = 1, (c) x = 3, (d) x = 5.

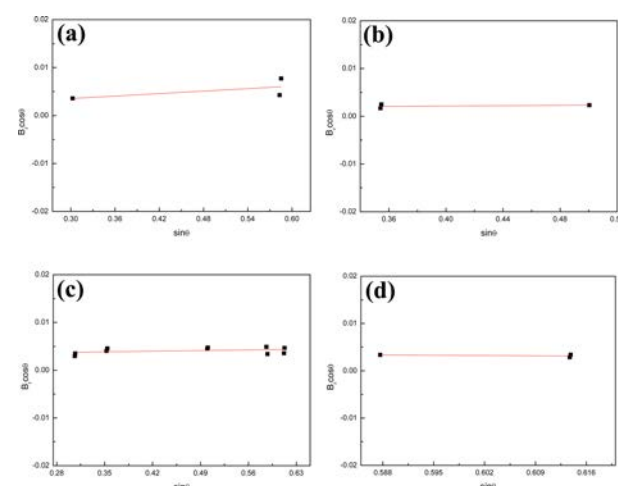


Fig. 6. Plot of $B_r (B_{\text{crystalline}} + B_{\text{strain}}) \cos\theta$ versus $\sin\theta$ for SiC in SiC + x vol.% graphene sintered by PCAS: (a) x = 0, (b) x = 1, (c) x = 3, (d) x = 5.

may block the grain growth of SiC during sintering. The grain refining effect of graphene can also be confirmed by the fracture surface. Fig. 7 shows the FE-SEM images of the fracture surfaces of the samples after sintering at about 1600 °C. The grain size of SiC remarkably decreased with increase of graphene. In any case, it should be mentioned that SiC ceramics having nano structure could be obtained by PCAS even for pure SiC without graphene. This retention of fine grain structure can be attributed to the high heating rate and the relatively short exposure to the high temperature. The relative densities of 92, 91, 90 and 93% were obtained for SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene, respectively.

Vickers hardness measurements were performed on polished sections of the SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene samples using a 20 kg_f load and 15 s dwell time. The Vickers hardness values of the SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene samples were

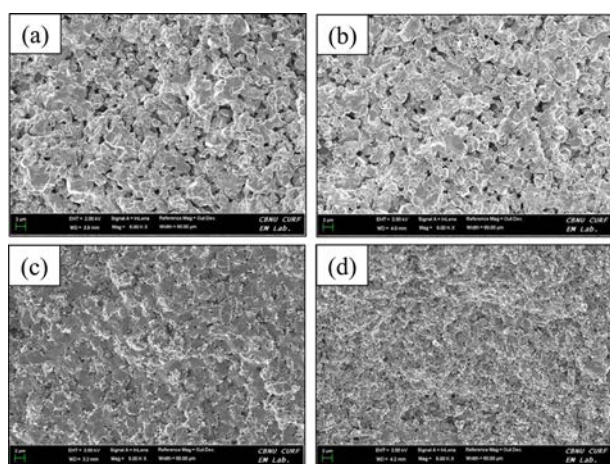


Fig. 7. FE-SEM images of fracture surface of (a) SiC, (b) SiC-1 vol.% graphene, (c) SiC-3 vol.% graphene and (d) SiC-5 vol.% graphene samples sintered by PCAS.

1600, 1640, 1750 and 1810 kg/mm², respectively. All values represent the average of five measurements. The results suggest that hardness of SiC-graphene composites increased in increase of graphene. To understand the effect of graphene on the hardness, two factors may be considered. One is the effect of grain refinement of SiC. The other would be the role of graphene to affect the hardness. It can be evaluated that the hardness of SiC-graphene composite is higher than that of monolithic SiC due to grain refinement of SiC and addition of hard graphene.

Conclusions

Using pulsed current activated sintering (PCAS), the rapid consolidation of the SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene samples was accomplished successfully. Nanostructured SiC-graphene composites could be obtained within short time. The grain size of SiC was reduced remarkably by the addition of graphene. The average grain sizes of SiC were about 143, 97, 43 and 17 nm for SiC, SiC-1 vol.% graphene, SiC-3 vol.% graphene, and SiC-5 vol.% graphene, respectively. The Vickers hardness of SiC-graphene composites increased in increase of graphene because of refinement of SiC and addition of hard graphene. This study demonstrates that the graphene can be an effective reinforcing agent for improved mechanical properties of SiC composites.

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References

1. M. Ohyanagi, T. Yamamoto, H. Kitaura, Y. Kodera, T. Ishii, Z. A. Munir, *Scripta Materialia* 50 (2004) 111-114.
2. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, Y. Zhang, S.V. Dubonos, *Science* 306(5696) (2004) 666-9.
3. M.C. Liu, C.L. Chen, J. Hu, X.L. Wu, X.K. Wang, *J. Phys. Chem. C* 115(51) (2011) 25234-40.
4. L. Zhang, W. Liu, C. Yue, T. Zhang, P. Li, Z. Xing, Y. Chen, *Carbon* 61 (2013) 105-115.
5. L.C. Tang, Y.J. Wan, D. Yan, Y.B. Pei, L. Zhao, Y.B. Li, L.B. Wu, J.X. Jiang, G.Q. Lai, *Carbon* 60 (2013) 16-27.
6. A.K. Geim, K.S. Novoselov, *Nat. Mater.* 6(3) (2007) 183-91.
7. C. Lee, X.D. Wei, J.W. Kysar, J. Hone, *Science* 321(5887) (2008) 385-8.
8. A.A. Balandin, S. Ghosh, W.Z. Bao, I. Calizo, D. Teweldebrhan, F. Miao, *Nano Lett.* 8(3) (2008) 902-7.
9. M. Sherif El-Eskandarany, *J. Alloys & Compounds* 305 (2000) 225-38.
10. L. Fu, L.H. Cao, Y.S. Fan, *Scripta Materialia* 44 (2001) 1061-1068.
11. I.J. Shon, H.G. Jo, H.J. Kwon, *Korean J. Met. Mater.* 52 (2014) 343-346.
12. S. Berger, R. Porat, R. Rosen, *Progress in Materials*, 42 (1997) 311-320.
13. Z. Fang, J.W. Eason, *Int. J. of Refractory Met. & Hard Mater.* 13 (1995) 297-303.
14. A.I.Y. Tok, L.H. Luo, F.Y.C. Boey, *Materials Science and Engineering A* 383 (2004) 229-234.
15. H.S. Kang, J.M. Doh, J.K. Yoon, and I.J. Shon, *Korean J. Met. Mater.* 52 (2014) 759-764.
16. F. Charlot, E. Gaffet, B. Zeghmami, F. Bernard, J. C. Liepce, *Mater. Sci. Eng. A262*, (1999) 279-288.
17. I.J. Shon, H.G. Jo, B.S. Kim, J.K. Yoon, and K.T. Hong, *Korean J. Met. Mater.* 53 (2015) 474-479.
18. M.K. Beyer, H. Clausen-Schaumann, *Chem. Rev.* 105 (2005) 2921-2944.
19. B.R. Kang and I.J. Shon, *Korean J. Met. Mater.* 53 (2015) 320-325.
20. S.M. Kwon, N.R. Park, J.W. Shin, S.H. Oh, B.S. Kim, and I.J. Shon, *Korean J. Met. Mater.* 53 (2015) 555-562.
21. I.J. Shon, H.S. Kang, J.M. Doh, and J.K. Yoon, *Met. Mater. Int.*, 21 (2015) 345-349.
22. C. Suryanarayana and M. Grant Norton, *X-ray Diffraction A Practical Approach*, Plenum Press, New York, 1998.
23. B.W. Kwak, B.S. Kim, J.K. Yoon, K.T. Hong and I.J. Shon, *Journal of Ceramic Processing Research*, Vol. 16, No. 3, (2015) 340-345.