Paper

Fabrication of Diamond/SiC Composites Using HIP from Mixtures of Diamond and Si Powders

Ken HIROTA^{1*}, Motoyasu AOKI¹, Masaki KATO¹, Minoru UEDA² and Yoichi NAKAMORI²

¹Department of Molecular Chemistry & Biochemistry, Faculty of Science & Engineering, Doshisha University, Kyoto 610-0321, Japan.

²Metal Technology Co., Ltd., 1-32-2 Honcho, Nakano-ku, Tokyo 164-8721, Japan.

Received August 28, 2018; Revised November 14, 2018; Accepted November 26, 2018

ABSTRACT

Diamond/SiC = 75/25~50/50 vol% composites were fabricated utilizing liquid-phase reaction sintering during hot isostatic pressing (HIP) at 1723 K under 196 MPa for 7.2×10^3 s from mixtures of four kinds of diamond (average particle size P_s of 69, 60, 9.2, and 3.5 $\mu\text{m}\phi$) and Si (P_s : 0.6 $\mu\text{m}\phi$) powders. After the starting powders were mixed for 1.8×10^3 s in ethanol, the mixtures were dried and compacted uniaxially (50 MPa) and isostatically (245 MPa). They were preheated at 1223 K for 7.2×10^3 s in a vacuum (Process (I)) or solidified using pulsed electric-current pressure sintering (PECPS) at 1623 K and 50 MPa for 0.6×10^3 s under reduced pressure (Process (II)). The compacts prepared via Process (I) and Process (II) were densified by Pyrex glass capsule HIPing (1723 K/ 7.2×10^3 s/196 MPa/Ar). High relative density (around 93%) was achieved at the composition of diamond/SiC = 55/45 vol% using bimodal diamond powders, *i.e.*, an average P_s of around 50 $\mu\text{m}\phi$ and Process (II). In order to improve Vickers hardness (H_v), a small amount of B₄C (P_s : 0.5 $\mu\text{m}\phi$) powders was added to [diamond (69:3.5 $\mu\text{m}\phi$ = 7:3)]/SiC = 55/45 vol% composite using Process (II) at 1623 K followed by HIP. Both the relative density and H_v values increased substantially, from 89 to 95.0% and from 38.7 to 51.3 GPa at 10 vol% B₄C addition, respectively.

KEY WORDS

diamond, SiC, B₄C, liquid-phase reaction sintering, Vickers hardness

1 Introduction

To satisfy the continuously increasing need for novel materials and properties, hard inorganic materials have been attracting a lot of attention. Among them, diamond is the hardest material (Vickers hardness H_v : ~150 GPa), and it has high mechanical and thermal properties (Young's modulus E : 1050 GPa; thermal conductivity σ : 600~2000 W·m⁻¹·K⁻¹), as shown in Table 1. Since the invention of artificial diamond in 1955 by Bundy *et al.* of General Electric¹⁾, there have been many attempts to fabricate polycrystalline diamond (PCD)²⁾ under diamond's thermodynamically stable region, such as 5~6 GPa and 2073~2173 K³⁾. On the other hand, few experiments have been attempted in the metastable region⁴⁾. M. Shimono and S. Kume⁵⁾ studied the fabrication of diamond/SiC composites from diamond and Si powders utilizing liquid-phase reaction sintering: $2\text{C} + \text{Si} \rightarrow \text{C}(\text{diamond}) + \text{SiC}$, by a glass-capsule HIP at the higher temperature of the Si melting point (T_m : 1687 K). They reported a bulk density of 3.2~3.3 Mg·m⁻³, *i.e.*, a relative density ~ 90%, average H_v of 37 GPa, and bending strength σ_b of ~550 MPa for composites fabricated at 1723 K for 1.8×10^3 s at 50 MPa. This process has some good characteristics, such as near net shape and

very mild fabrication conditions. However, it is difficult to control the composition of the diamond-to-SiC ratio, which difficulty often resulted in lower H_v values than expected. For example, the microstructure of a HIPed diamond/SiC composite depends heavily on the starting diamond powder sizes, as shown in Fig. 1 and Table 2.

Recently, a new sintering method called pulsed electric-current pressure sintering (PECPS) has been developed in Japan⁶⁾. This method can solidify poor sinterable powders for a shorter soaking time at lower sintering temperatures than those of conventional electric furnaces^{7,8)}. The present authors have been applying this

Table 1 Physical and mechanical properties of diamond, silicon carbide β -SiC, and B₄C.

	Symbol	Unit	diamond Cubic	β -SiC Cubic	B ₄ C Hexa
Theoretical density	D_x	Mg·m ⁻³	3.513	3.21	2.515
Vickers hardness	H_v	GPa	~150	28	33.5
Melting temperature	T_m	K	2723	3003	2723
Fracture toughness	K_{IC}	MPa·m ^{1/2}	2.0	4.0	3.1
Young's modulus	E	GPa	1050	430	385
Thermal expansion coefficient	α	10 ⁻⁶ K ⁻¹	0.8~1.2	4.5	2.3
Thermal conductivity	σ_T	W/(mK)	600~2000	270	37

* Corresponding author, E-mail: kirota@mail.doshisha.ac.jp

Fig. 1 SEM photographs of SiC-added diamond composites: P_s (diamond), (a) 69, (b) 9.2, and (c) 3.5 $\mu\text{m}\phi$.

Table 2 Densities of diamond-SiC composite fabricated by HIP.

P_s of diamond (μm)	Volume fraction of diamond	D_{obs} ($\text{Mg}\cdot\text{m}^{-3}$)	D_x ($\text{Mg}\cdot\text{m}^{-3}$)	D_{obs}/D_x (%)
69	45	3.27	3.35	97.6
9.2	65	3.22	3.41	94.4
3.5	70	3.24	3.42	94.7

sintering method to fabricate dense composite materials containing carbon nanofibers (CNF), such as $\text{Al}_2\text{O}_3/\text{CNF}^{(9)}$, $\text{SiC}/\text{CNF}^{(10)}$, $\text{SiAlON}/\text{CNF}^{(11)}$, $\text{B}_4\text{C}/\text{CNF}^{(12,13)}$, and (Fe-Ni) alloy/ferrite composites⁽¹⁴⁾, that could be fabricated just by utilizing short soaking times and lower sintering temperatures.

In the present study, we applied this method to fabricate diamond/SiC composites and compare them with those made by nearly the same

method as reported⁽⁵⁾. Furthermore, to improve the H_v value, we added particles of the third hardest material, B_4C (H_v : 33.5 GPa, Table 1), to diamond/SiC composites. This paper describes the properties of (PECPS + HIP)-sintered diamond/SiC composites and also reports on the effect of B_4C addition.

2 Experimental procedure

Fabrication of diamond/SiC composites with a small addition of B_4C particles

As shown in Fig. 2, the starting materials were four kinds of hydrogen-termination-processed (1073 K/ 7.2×10^3 s/ H_2) diamond powders^(15,16) (average particle size P_s of 69, 60, 9.2, and 3.5 $\mu\text{m}\phi$, IMS-OB 200/230, IMS-OB 230/270, IRM-OB 8-16, and IRM-OB 4-6, respectively; Tomei Diamond, Tokyo, Japan), Si (P_s of 5.0~6.0 $\mu\text{m}\phi$, High Purity Chemical Laboratories, Saitama, Japan),

Fig. 2 Flowchart for the fabrication of diamond/SiC.

and B_4C (P_s of 0.5 $\mu m\phi$, High Purity Chemical Laboratories). The diamond powders of P_s of (69 or 60 $\mu m\phi$) and (9.2 or 3.5 $\mu m\phi$) were mixed into 5:5, 7:3, and 9:1 ratios¹⁷⁾. The Si powder was pulverized into P_s of 0.6 $\mu m\phi$ using a bead mill (Easy Nano, AIMEX, Tokyo, Japan) at 2.67×10 rounds per second (1600 rpm) for 3.6×10^3 s using 2.0 mm ϕ zirconia balls (Nikkato, Osaka, Japan) in ethanol and Ar. The diamond and pulverized Si, along with B_4C powders with an inner proportion, were mixed homogeneously using an ultrasonic vibrating homogenizer (*US-300T*, Nihon-Seiki Ltd., Tokyo, Japan) with a power output of 300 W at 20 kHz for 1.8×10^3 s in ethanol. After drying, a small amount of 3% concentration acrylic binder was added to the mixture and compacted uniaxially and isostatically (245 MPa/6.0 $\times 10$ s). The compressed powder compacts were pre-heat-treated for 3.6×10^3 s at 1223 K under reduced pressure to eliminate the small amounts of water and oxygen adsorbed on the surfaces of diamond and Si fine powders without particle sintering^{12,13)} or transformation from diamond to graphite during heating³⁾.

On the basis of our preliminary experimental results, the compacts were pre-heated at 1223 K for 7.2×10^3 s Process (I) or solidified using pulsed electric-current pressure sintering (PECPS, *SPS-5104A*, SPS SYNTEX, Tokyo, Japan) Process (II). After elimination of adsorbed gas and wrapping with *h*-BN powder (P_s of $\sim 3 \mu m\phi$, >98% purity, GP, Denka, Tokyo, Japan), they were put into a cylindrical mold (20 mm ϕ -40 mm ϕ -40 mm ^{h} , high-density graphite carbon, Toyo-Tanso, Osaka, Japan) that was used for PECPS. Using this apparatus, sintering was performed at 1473~1723 K for 0.6×10^3 s under a uniaxial pressure of 50 MPa in a vacuum (~ 10 Pa) with a heating rate of $1.66 K \cdot s^{-1}$ and a cooling rate of $\sim 8.33 \times 10^{-1} K \cdot s^{-1}$, applying DC pulse electric current (on/off interval = 12:2). Heating above ~ 873 K was monitored at the center position of the outside wall of the carbon mold using a monochrome pyrometer.

The acrylic binder was removed by the calcination (1273 K/7.2 $\times 10^3$ s/vac.) in Process (I) and by PECPS in Process (II). Both of the compacts prepared via the two processes were densified by Pyrex glass capsule HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar) as shown in Fig. 2, using liquid-phase reaction sintering¹⁸⁾ between diamond and Si at temperatures above the melting point of Si (1687 K).

Characterization of samples

Crystalline phases were identified by X-ray diffraction (XRD) analysis (CuK α radiation, *Rint 22000*, Rigaku, Osaka, Japan). Microstructural observation by a field emission-type scanning electron microscope (Miniscope, TM3030Plus, Hitachi High Technologies, Tokyo, Japan) was performed on the fracture surfaces of the sintered materials. As the volume fractions of both diamond and SiC of HIP sintered composites could not be determined by conventional XRD (Rietveld) or chemical analysis such as ICP due to much difference in XRD scattering power for single crystal diamond and poly-crystal SiC, much difficulty for diamond and SiC to dissolve

into solutions, respectively., they were estimated using an image analysis softwear ("WinROOF 2015, Mitani corporation, Osaka, Japan) applied to the SEM (back scattered image: BEI) images on their polished surfaces. Also, a laser microscope (VK-x200, Keyence, Osaka, Japan) was used to observe the Vickers hardness indent in air. The bulk densities of the sintered samples were measured by the Archimedes method. Vickers hardness H_v was evaluated by applying a load of 9.81 N and a duration time of 15 s.

3 Results and discussion

Difference between Processes I and II

Fig. 3 displays the XRD patterns of diamond (69:9.2 $\mu m\phi$ = 7:3)/SiC composites with various SiC intended contents from 35 to 50 vol% or 35 to 100 vol%, fabricated as follows: (a)~(d), calcined (1223 K/7.2 $\times 10^3$ s/vac.) through Process (I) and (e)~(h) sintered by PECPS (1723 K/0.6 $\times 10^3$ s/50 MPa/vac.) via Process (II), followed in either case by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar). The differences between Process (I) and Process (II) are as follows. First, when the content of SiC was increased from 35 to 50 vol%, the amount of graphite 2H-C in the HIPed composites decreased in (a) to (d) via Process (I). On the contrary, the amount of graphite increased in (e) and (f) via Process (II). Second, the remaining contents of Si in the composites were still high in XRD patterns of (b)~(d) via Process (I), whereas in Process (II) the amount of unreacted Si was not so high without the diamond/SiC = 30/70 vol% composition (in Fig. 3 (g)), suggesting that when a small amount of Si is added to the diamond powders and then PECPSed at 1723 K, unreacted diamond might transform into graphite. This might be explained by the fact that the dense microstructures of diamond/SiC after PECPS at 1723 K might block direct contact between diamond and remaining liquid Si, resulting in the suppression of their liquid-phase reaction during HIP. Here, the diffraction peaks of SiC phase in (h) shifted to the lower angles a little less than those for pure SiC, which might be explained by the bulk sample's inclination to the XRD measurement of the datum surface. Fig. 4 (i) to (iv)

Fig. 3 XRD patterns of diamond/SiC composites: (a)~(d), calcined (1223 K/7.2 $\times 10^3$ s/vac.) and (e)~(i) sintered by PECPS (1723 K/0.6 $\times 10^3$ s/50 MPa/vac.), followed by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar).

Fig. 4 Relative densities of diamond/SiC composites fabricated under various conditions as a function of SiC content.

display the relative densities D_r , i.e., $D_r = D_{\text{obs}}/D_x$, where D_{obs} and D_x are the bulk and theoretical densities, respectively. The D_r of diamond (69:9.2 $\mu\text{m}\phi = 7:3$)/SiC composites fabricated by two processes, i.e., via Process (I) and Process (II) before and after HIPing, are denoted as (i), (ii), and (iii), (iv), respectively, as a function of the intended content of SiC. In the D_r before HIP, the values of (i), only calcined materials, are much lower than those of PECPSed (iii). This might be due to activated pressing during PECPS heat treatment. Furthermore, a comparison of the D_r values of HIP composites, i.e., (ii) and (iv), showed that Process (II) could give a higher D_r than Process (I).

Then, the most appropriate PECPS temperature was investigated. Fig. 5 shows the dependence of D_r for the diamond/SiC = 75/25 vol% composites on the PECPS temperature from 1473 to 1673 K; the composites were fabricated using PECPS (0.6×10^3 s/50 MPa/vac.) followed by HIP (1723 K/ 7.2×10^3 s/196 MPa/Ar). The lower white circles represent D_r just after PECPS, and the upper black circles represent it after HIP. The most suitable PECPS temperature was considered to be around 1623 K. Then their

Fig. 5 Relative densities of diamond/SiC = 75/25 vol% composites: (a)~(d), PECPS (1473~1673 K/ 0.6×10^3 s/50 MPa/vac.) and (e)~(h) followed by HIP (1723 K/ 7.2×10^3 s/196 MPa/Ar).

microstructures were observed. Fig. 6 shows SEM photographs of the fracture surfaces of diamond/SiC composites with the 65/35 and 50/50 vol% compositions. The upper (a) and (b) images show the composites fabricated via Process (I), and the lower (c) and (d) via Process (II). Large diamond particles and small (gray, SiC; black, diamond) grains are observed, and their relative densities D_r are also shown on the right side of the photograph. In Process (I), a high D_r (93.3%) is achieved in diamond/SiC = 65/35 vol%, and in Process (II) a high D_r (90.7%) is achieved in diamond/SiC = 50/50 vol%, as shown in Fig. 4. It is clear that a dense grain boundary consisting of fine SiC and small diamond grains could bring a high D_r . In addition, good contact or good adhesiveness between large diamond particles and the grain boundary also significantly affects the densification. Based on these data, in the SiC-rich regions, Process (II) was expected to show higher D_r (Fig. 4). Then, the volume fractions of diamond and SiC of composites were estimated using an image analysis as mentioned before. Fig. 7 (a) and (b) show the representative SEM (BEI)

Fig. 6 SEM photographs of the fracture surfaces of diamond/SiC composites: (a)~(b), calcined (1223 K/ 7.2×10^3 s/vac.), and (c)~(d) sintered by PECPS (1623 K/ 0.6×10^3 s/50 MPa/vac.), followed by HIPing (1723 K/ 7.2×10^3 s/196 MPa/Ar).

Fig. 7 Representative SEM (BEI) and thresholding (binarized) images, respectively, of diamond/SiC = 55/45 vol% composite fabricated using Process II (PECPS: 1623 K/0.6 $\times 10^3$ s/50 MPa/vac.), followed by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa).

and thresholding (binarized) images, respectively, of diamond/SiC = 55/45 vol% composite fabricated using Process II (PECPS: 1623 K/0.6 $\times 10^3$ s/50 MPa/vac.), followed by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa). In Fig. 7 (a), black fine particles in the matrix, gray large and small particles, and the fine matrix were classified into three categories, area A green, area B blue and area C red in Fig. 7 (b), respectively. As both area A and B are corresponding to diamond, and area C to SiC, diamond and SiC occupy 56.2% and 43.8% area fractions, respectively as shown in Table below Fig. 7 (a) and (b). If we presume that law of similarity between two-dimension of area and three-dimension of volume, *i.e.*, 1: x^2 for 2 dimension shape, then similarity rate in a 3 dimension is 1: x^3 . For example, two circles with the radius ratio of 1: x , then their areas are 1: x^2 , furthermore, the volume ratio of spheres with the same radius ratio are 1: x^3 . When this law of similarity can be applied to this image analysis, the volume fraction of diamond to SiC is 59.2/40.8 vol%; these values are not so bad in light of a small amount of Si and graphite particles detected in the composites by XRD. Afterward, the calculation of theoretical density of composites has been performed under the presumption that composites consisted of basically diamond and SiC, or in the case of B₄C added composite, including the B₄C, small amounts of other chemical compounds have been ignored.

The dependence on diamond powder size was investigated next. Fig. 8 displays the D_r of diamond/SiC = 55/45 vol% composites, as shown by the lower white circles and squares just after PECPS (1623 K/0.6 $\times 10^3$ s/50 MPa/vac.), and by the upper black circles, triangles, and squares followed by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa). They were fabricated using pulverized Si and diamond powders of

Fig. 8 Relative density of diamond/SiC = 55/45 vol% composites fabricated from diamond powders of various particle sizes by PECPS (1623 K/50 MPa/0.6 $\times 10^3$ s/vac.), followed by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa).

various particle sizes. In Fig. 8, both the left and right sides, *i.e.*, the smaller and larger powders, consisted of diamonds with mono-modal particles. On the other hand, a few squares and triangles represent a bi-modal P_s distribution, and numerical numbers above the marks indicate the diamond content ratio of large vs. small powders. It is clear that the composites obtained from the smaller diamonds gave lower D_r , and that the larger diamond resulted in higher D_r of up to 90% after HIP. On the other hand, the bi-modal distribution with an average P_s of around 51 μm (69:9.2 μm ϕ = 7:3 ratio) brought a high D_r value of around 93%, although the D_r value just after PECPS (83%) is lower than that (85%) of other average P_s (40 μm).

This could be explained in terms of the re-arrangement of diamond particles in liquid Si during isostatic higher pressure (196 MPa) of HIP at 1723 K compared to the lower pressure (50 MPa) of uniaxial pressing of PECPS at 1623 K. It looks strange that even though the average P_s is nearly the same as 50 μm , the D_r values after HIP differ between the composite from bi-modal diamond (69:3.5 $\mu\text{m}\phi = 7:3$ ratio), black square, around 88%; and the composite from (69:9.2 $\mu\text{m}\phi = 7:3$ ratio), black triangle, around 93% from the theoretical expectation. The highest D_r of composites made from large and small sphere particles, *i.e.*, with bi-modal particle size distribution, can be given at a large:small sphere volume ratio of around 7:3. Also, a higher D_r value can be achieved at a higher ratio of $P_i:P_s$.

In order to improve the hardness of composites, we had already considered adding third component particles to the matrix. The criteria for such particles were i) they must be harder than SiC (H_v : 28 GPa in Table 1), and they must offer high chemical stability both ii) at a high temperature of 1723 K and iii) in the diamond/SiC matrix. One of the main reasons we selected B_4C was that it is carbide, the same as diamond and SiC. As shown in Table 1, H_v of B_4C is 33.5 GPa^{12,13} and its melting temperature is 2723 K. The other physical properties, such as Young's modulus E and thermal expansion coefficient α , are 385 GPa and $2.3 \times 10^{-6} \text{ K}^{-1}$, respectively¹⁹.

In the case of the addition of B_4C (0.5 $\mu\text{m}\phi$), a preliminary experiment was previously performed. Fig. 9 represents XRD patterns of the composites with diamond/SiC = 55/45 vol% with 7.0 vol% B_4C as an inner proportion, using the bi-modal diamonds a) (69:3.5 $\mu\text{m}\phi = 7:3$) and b) (69:9.2 $\mu\text{m}\phi = 7:3$); they were fabricated by PECPS (1623 K/0.6 $\times 10^3$ s/50 MPa/vac.) and HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar). From these data, it is easily

Fig. 9 XRD patterns of diamond/SiC = 55/45 vol% composites added with B_4C : (a)~(f) sintered by PECPS (1623 K/50 MPa/0.6 $\times 10^3$ s/vac.) and sintered by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar).

recognized that the former shows i) much smaller diffraction intensities of Si and carbon and ii) a much higher SiC phase. These results suggested that when we add a small amount of B_4C to the composite as the starting material of diamond, the mixed powders of (69:3.5 $\mu\text{m}\phi = 7:3$) would be better than those of (69:9.2 $\mu\text{m}\phi = 7:3$). This was proved by microstructural observation. Fig. 10 shows SEM (back-scattered electron image: BEI) photographs of the polished surfaces of [(diamond/SiC = 55/45 vol%)] + 7 vol% B_4C composites made from the diamond mixtures of (69:3.5 $\mu\text{m}\phi = 7:3$) (a)~(c) and (69:9.2 $\mu\text{m}\phi = 7:3$) (d)~(f) taken under low (0.5 $\times 10^3 = 0.5$ k), middle (1.0 k), and high (2.5 k) magnifications. By comparing (a) and (d), small black particles (diamonds) are scarcely present in the former, suggesting that small diamonds changed into SiC; (b) and (e), a larger number of small white particles (Si) are observed in the latter than in the former; (c)

Fig. 10 SEM (BEI) photographs of [(diamond/SiC = 55/45 vol%)] + 7 vol% B_4C composites fabricated by PECPS (1623 K/50 MPa/0.6 $\times 10^3$ s/vac.) and sintered by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar).

and (f), a dense grain boundary layer is seen in the former. These photographs also support the XRD results shown in Fig. 9.

Then B₄C-added diamond (69:3.5 $\mu\text{m}\phi = 7:3$)/SiC = 55/45 vol% composites were fabricated in the same manner as described above. The B₄C contents were increased by 10 vol% with an inner proportion. Fig. 11 shows the XRD patterns of these B₄C-added composites sintered by PECPS (1623 K/0.6 $\times 10^3$ s/50 MPa/vac.) and HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar). As the amount of B₄C increased, both Si (PDF: #27-1402) and B₄C (PDF: #35-0798) diffraction peaks occurred around $2\theta = 28.4^\circ$ and $2\theta = 37.4^\circ$, respectively, although without B₄C addition a small diffraction peak of Si at 28.4° is recognized. Furthermore, it should be noted that the B₄C addition enhanced the formation of both cubic (PDF: #29-1129) and hexagonal (PDF: #29-1126) SiC. After HIPing at 1723 K, B₄C, SiC, and graphite were recognized in the composites up to 5 vol% addition. Then, the values of D_{obs} and D_x of the composites were measured and calculated. In the calculation of D_x , a small amount of graphite was ignored and D_x of cubic α -SiC was assumed to be the same as that of hexagonal β -SiC.

Fig. 12 represents the D_r values of the composites before and after HIP, shown as round white and black circles, respectively, as a function of B₄C content. The D_r value decreased once at 1.0 vol% B₄C and then gradually increased up to about 95.0% with 10.0 vol% addition. In this figure, the D_r values of composites made from the mixture of (69:9.2 $\mu\text{m}\phi = 7:3$) diamonds are also plotted as black triangles, with 0 and 7 vol% B₄C addition as a reference. Though there is little difference in D_r values between (69:3.5 $\mu\text{m}\phi = 7:3$) and (69:9.2 $\mu\text{m}\phi = 7:3$) diamonds derived composites at 0 vol%, at 7 vol% B₄C addition, nearly the same values are observed in the HIP-sintered samples, as expected. This D_r increase by B₄C addition can be explained partially as follows. B₄C particles acted as sintering aids in the same manner as a small amount of the combined addition of Al₄C₃-B₄C-C for SiC⁽²⁰⁾ and suppressed the reduction in volume change $\Delta V/V_0 = -19.5\%$, followed by the formation of β -SiC from the mixture of diamond and Si, *i.e.*, C (diamond) + Si $\rightarrow$ β -SiC. Here in this calculation the values of (diamond C: atomic weight *a.t.*: 12.01, theoretical density D_x : 3.515 Mg·m⁻³, PDF: #06-0675), (Si: *a.t.*: 28.09, D_x : 2.329, PDF: #27-1402), (SiC: *a.t.*: 40.1, D_x : 3.211, PDF: #29-1129) were used. For example, when 1, 3, 5, 7, and 10 vol% B₄C are added to the diamond/SiC = 55/45 vol% composite, $\Delta V/V_0$ values decrease gradually with increasing B₄C addition; -9.70% (0 vol%), -9.61% (1 vol%), -9.43% (3 vol%), -9.26% (5 vol%), -9.08% (7 vol%), and -8.81% (10 vol% B₄C). Thus, it is clear that even a 10 vol% B₄C addition brings about the suppression of the reduction in volume change to around 0.89%. Therefore, B₄C might act as a sintering aid for SiC.

The composites' microstructures were then observed. Fig. 13 shows SEM photographs of the composites with the compositions of [diamond(69:3.5 $\mu\text{m}\phi = 7:3$)/SiC = 55/45 vol%]/B₄C =

Fig. 11 XRD patterns of diamond/SiC = 55/45 vol% composites with B₄C added: (a)~(f) sintered by PECPS (1623 K/0.6 $\times 10^3$ s/50 MPa/vac.) and sintered by HIP (1723 K/7.2 $\times 10^3$ s/196 MPa/Ar).

Fig. 12 Relative densities of [diamond (69:3.5 $\mu\text{m}\phi = 7:3$)/SiC = 55/45 vol%]/B₄C composites as a function of B₄C content.

100/0~90/10 vol%, fabricated by PECPS and HIP; (a) 0, (b) 1.0, (c) 3.0, (d) 5.0, (d) 7.0, and (e) 10 vol% B₄C. At first it is clear that dense microstructures are recognized as compared with those without B₄C addition in Fig. 6. As described before, a back-scattered electron image (BEI) proves that the heavier elements give brighter images than the lighter elements. Therefore, both the large dark gray blocks and the small particles in the grain boundaries are large and small diamonds, respectively, and the bright grain-boundary matrix might be SiC. However, in these photographs B₄C particles could not be recognized or distinguished from small diamonds among the grain boundaries because both particles are fine and have nearly the same light elements as diamond.

Then a mechanical property, the hardness of the composites with the [diamond (69:3.5 $\mu\text{m}\phi = 7:3$)/SiC = 55/45 vol%]/B₄C = 100/0~90/10 vol%, was evaluated. Vickers hardness H_v is shown in Fig. 14 (a). Though some scattering in H_v values at 1, 5, and 10 vol% is observed, with increasing B₄C content their average

Fig. 13 SEM (BEI) photographs of [(diamond/SiC = 55/45 vol%)/B₄C] composites fabricated by PECPS (1623 K/0.6 × 10³ s/50 MPa/vac.) and sintered by HIP (1723 K/7.2 × 10³ s/196 MPa/Ar).

Fig. 14 (a) Vickers hardness H_v of [diamond (69:3.5 μmφ = 7:3)/SiC = 55/45 vol%]/B₄C and [diamond (69:9.2 μmφ = 7:3)/SiC = 55/45 vol%]/B₄C composites as shown by white and black circles, respectively. (b) SEM photos of Vickers indent under low (left) and high (right) magnifications, respectively.

H_v values increased gradually from around 38.7 to 51.3 GPa at 10 vol% B₄C addition. It should be noted that the highest H_v value was 51.3 GPa. As a reference, H_v values of composites with the [diamond (69:9.2 μmφ = 7:3)/SiC = 55/45 vol%]/B₄C = 100/0 and 93/7 vol%, 31.1 and 33.4, are also displayed in Fig. 14 (a); both values are much lower than those of the former. A comparison of these values of the two groups indicates that this H_v increment might originate from not only the harder B₄C addition compared

to that of SiC, *i.e.*, a 3.3 GPa increase from 31.1 to 33.4 GPa, but also from the effect of the SiC matrix microstructural evolution originating from the difference in starting diamond powder mixtures between (69:3.5 μmφ = 7:3) and (69:9.2 μmφ = 7:3); fine diamonds in the former are much more active during the liquid-phase reaction sintering of Si with diamond than fine diamonds in the latter. Fig. 14 (b) shows laser microscopic images of “Vickers indent (H_v : 51.3 GPa)” on the polished surface through low (left) and high (right) magnifications. From the left image, it is clear that the H_v indent in the black circle had been formed in the SiC matrix. The indent size in the right image is very small, proving high hardness. These photographs also indicate that small diamond, B₄C, and SiC are homogeneously dispersed. This homogeneous dispersion, the thermal expansion coefficient α difference between SiC ($\alpha = 4.5 \times 10^{-6} \text{ K}^{-1}$)¹⁹⁾ and B₄C ($\alpha = 2.3 \times 10^{-6} \text{ K}^{-1}$)¹⁷⁾, and the high Young’s modulus ($E_{\text{(B}_4\text{C)}} 385 \sim E_{\text{(SiC)}} 430 \text{ GPa}$ ^{19,21)}, Table 1) might induce high compression stress into the SiC/B₄C grain boundary, which might bring about a higher H_v value than those (about 37 GPa) reported previously⁵⁾.

4 Conclusions

Dense diamond/SiC = 55/45 vol% composites were fabricated from mixtures of various kinds of diamond powders, such as mono-modal, 3.5~69 μm and bi-modal (69:3.5 μmφ = 7:3), (69:9.2 μmφ = 7:3), and Si (0.6 μmφ) powders using pulsed electric-current pressure sintering (PECPS) at 1623 K for 0.6 × 10³ s under 50 MPa in a vacuum, followed by HIP at 1723 K for 7.2 × 10³ s under 196 MPa in Ar with liquid-phase sintering. This composite had a high Vickers hardness H_v of 38.7 GPa. Furthermore, a small addition of B₄C enhanced the H_v up to about 51.3 GPa due to high compression stress induced into the SiC/B₄C boundary matrix.

Furthermore, if a relative density of more than 99.5% can be achieved in these composites, H_v values higher than 60 GPa may be a dream come true.

Acknowledgment

This work was financially supported by the Program for the Strategic Research Foundation at Private Universities, 2013-2017, from the Ministry of Education, Culture, Sports, Science, and Technology, Japan (MEXT). The authors thank Ms. M. Toda and Ms. J. Morita of the Doshisha University Research Centre for Interfacial Phenomena for FE-SEM and laser microscope observations of the samples.

References

- 1) F. P. Bundy, H. T. Hall, H. M. Strong, R. H. Wentorf Jr.: *Nature*, **176** (1955) 51-55.
- 2) H. Sumiya, N. Toda, S. Satoh: *J. Crystal Growth*, **237-239** (2002) 1281-1285.
- 3) R. Berman, F. Simon: *Zeit. Electrochem.*, **59** (1950) 333-38.
- 4) S. Kume, K. Suzuki, H. Yoshida: pp. 53-55 in *Physical Properties of Composites, Proceedings of the 125th TMS Annual Meetings Symposium, The Minerals, Metals and Materials Society, Warrendale, PA, 1996.*
- 5) M. Shimono, S. Kume: *J. Am. Ceram. Soc.*, **87** (2004) 752-755.
- 6) M. Tokita: *J. Soc. Powder Tech. Jpn.*, **30** (1993) 790-804.
- 7) K. Hirota, K. Shibaya, M. Kato, H. Taguchi: *Processing and Properties of Advanced Ceramics and Composites VI, The American Ceramic Society's Ceramic Transactions*, **249** (2013)3-13.
- 8) Y. Zhou, K. Hirao, M. Toriyama, H. Tanaka: *J. Am. Ceram. Soc.*, **83** (2000) 654-656.
- 9) K. Hirota, Y. Takaura, M. Kato, Y. Miyamoto: *J Mater Sci*, **42** (2007) 4792-4800.
- 10) K. Hirota, H. Hara, M. Kato: *Materials Science and Engineering, A* **458** (2007) 216-225.
- 11) K. Hirota, T. Shibata, M. Kato, T. Nishimura: *Materials Science and Technology (MS&T)* (2007) 309-320.
- 12) K. Hirota, Y. Nakayama, S. Nakane, M. Kato, T. Nishimura: *Int. J. Appl. Ceram. Technol.*, **6** (2009) 607-616.
- 13) K. Hirota, M. Shima, X. Chen, N. Goto, M. Kato, T. Nishimura: *Mater. Sci. Eng. A*, **628** (2015) 41-49.
- 14) K. Hirota, M. Obata, M. Kato, H. Taguchi: *Int. J. Appl. Technol. Online*, **6** DEC (2011) 1-13.
- 15) R. Ohshima, H. Yamanaka, S. Hosomi: *J. Soc. Mat. Sci., Japan*, **49** (2000) 602-605.
- 16) V. Novikov: *Naukova Dumka* (1987) 147.
- 17) S. Yerazunis, J. W. Bartlett, A. H. Nissan: *Nature*, **195** (1962) 33-35.
- 18) J. E. Marion, C. H. Hsueh, A. G. Evans: *J. Am. Ceram. Soc.*, **70** (1987) 708-713.
- 19) J. F. Shackelford, W. Alexander: *CRC Materials Science and Engineering Handbook 3rd ed.*, Table 116. Thermal expansion of ceramics, CRC Press, Boca Raton, Florida 3343, 2001, p. 449.
- 20) Y. Zhou, H. Tanaka, S. Otani, Y. Bando: *J. Am. Ceram. Soc.*, **82** (1999) 1959-1964.
- 21) J. F. Shackelford, W. Alexander: *CRC Materials Science and Engineering Handbook 3rd ed.*, Table 116. Thermal expansion of ceramics, CRC Press, Boca Raton, Florida 3343, 2001, p. 449.