Fabrication of diamond/SiC composites using HIP from the mixtures of diamond and Si powders

Ken Hirota [1, a *], Motoyasu Aoki [1, b], Masaki Kato [1, c],
Minoru Ueda [2, d] and Yoichi Nakamori [2,e]

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

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

[a]khirota@mail.doshisha.ac.jp, [b]ctwb0701@mail4.doshisha.ac.jp, [c]makato@mail.doshisha.ac.jp, [d]mueda@kinzoku.co.jp, [e]ynakamori@kinzoku.co.jp

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Abstract. Diamond/SiC=75/25~50/50vol% composites have been fabricated utilizing a liquid-phase reaction sintering during hot isostatic pressing (HIP) at 1450°C under 196 MPa for 2 h from the mixtures of diamond and Si powders. They were mixed for 30 min in ethanol. After drying, they were compacted uniaxially and isostatically (245 MPa). They were pre-heated at 950°C for 2 h (Process I) or solidified using pulsed electric-current pressure sintering (PECPS) at 1350 or 1450°C for 10 min under 50 MPa in a vacuum (Process II). Both compacts prepared via "Process I" or "II" were densified by Pyrex-glass capsule HIPing (1450°C/2h/196MPa/Ar). The high relative density has been achieved at the composition of diamond/SiC=55/45vol% using Process II. In order to increase Vickers hardness (H_v), a small amount of B_4C particles have been added to diamond/SiC= 55/45vol% composites using "Process II" at 1350°C and followed by HIP. The H_v values increased from 37.3 to 40.5 GPa at 5vol% B_4C addition.

Introduction

As for the continuously increasing need of new novel materials and properties, hard inorganic materials have been attracting a lot of attention. Among them, diamond is the hardest (Vickers hardness H_v: ~150 GPa) material with high mechanical properties as shown in Table 1. Since the invention of artificial diamond in 1955 by Bundy *et al*. [1], a lot of works have been done to fabricate polycrystalline diamond (PCD) under the diamond's thermodynamically stable state region [2], such as 5~6 GPa and 1800~1900°C [3]. On the other hand, a few experiments have been attempted in the metastable region [4]. Shimono and Kume [5] studied the fabrication of diamond/SiC composites from diamond and Si powders using a glass-capsule HIP. They reported the bulk density of 3.2~3.3 $g \cdot cm^{-3}$, i.e., the relative density ≥ 90 %, average H_v of 23.5 GPa, and bending strength σ_b of ~550 MPa, for the composites fabricated at 1450°C for 30 min at 50 MPa. Recently a new sintering method, *i.e*., pulsed electric-current pressure sintering, PECPS, has been developed in Japan [6]. This method has some features; it can solidify poor sinterable powders in a shorter soaking time at lower sintering temperature than those of conventional electric furnace [7, 8].

In the present study, we have applied this method to fabricate diamond/SiC composites and compared with those made using the nearly same method [5]. Furthermore, to improve the H_v value, the third hardest B_4C particles have been added to diamond/SiC composites based on thermochemical stability at high temperatures among diamond/SiC matrix. The present paper describes the properties of (PECPS+HIP) sintered diamond/SiC composites and also reports the H_v of B_4C added composites.

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Experimental procedure

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

As shown in Fig. 1, starting powders were diamond (average particle size P_s of 69 and 3.5 μm, Tomei Diamond, Tokyo, Japan), Si (P_s of 5.0 μm, High Purity Chemical Labo., Saitama, Japan), and B_4C (P_s of 0.5 μm, ibid.). The Si powder was pulverized into P_s of 0.6 μm using a beads-mill, (Easy Nano, AIMEX, Tokyo, Japan) at 1600 rpm for 1.0 h using 2.0 mmϕ zirconia balls in ethanol and Ar. The diamond powders of P_s of 69 and 3.5 μm were mixed into a 7:3 ratio [9]. The diamond and pulverized Si powders, furthermore B_4C particles were mixed homogeneously using a vibrating homogenizer in ethanol. After drying, they were mixed with a small amount of 3% acrylic binder and compacted uniaxially and isostatically (245MPa/1min). From our preliminary experimental results, they were pre-heated at 950°C for 2 h (Process I) or solidified using pulsed electric-current pressure sintering (PECPS) at 1350~1450°C for 10 min under 50 MPa in a vacuum (Process II). Both compacts prepared via "Process I" or "II" were densified by Pyrex-glass capsule HIPing (1450°C/2h/196MPa/Ar) as shown in Fig. 1, using a liquid-phase reaction sintering [10] between diamond and Si at higher temperatures than the melting point of Si (1414°C) by glass-capsule HIPing (1450°C/2 h/196 MPa/Ar).

Characterization of samples

Crystalline phases were identified by X-ray diffraction (XRD) analysis. Bulk densities of sintered samples were measured by Archimedes method. Microstructural observation on the fracture surfaces of sintered samples was performed with a field-emission type scanning electron microscope and their average grain sizes G_s were determined by an intercept method [11]. Then, H_v was evaluated with an applying load of 9.8 N and a duration time of 15 s with a Vickers hardness tester.

Table 1 Physical and mechanical properties of diamond, silicon carbide

Property	symbol	unit	diamond cubic	β-SiC cubic	B_4C hexa.
Theoretical density	D_x	$Mg \cdot m^{-3}$	3.513	3.21	2.515
Vickers hardness	H_v	GPa	~150	28	33.5
Melting temperature	T_m	°C	2450	2730	2450
Fracture toughness	K_{IC}	$MPa \cdot m^{1/2}$	2.0	4.0	3.1
Young's modulus	E	GPa	1050	430	385
Thermal expansion coefficient	α	$10^{-6} \cdot K^{-1}$	0.8~1.2	4.5	2.3
Thermal conductivity	σ_T	$W \cdot (mK)^{-1}$	600~2000	270	37

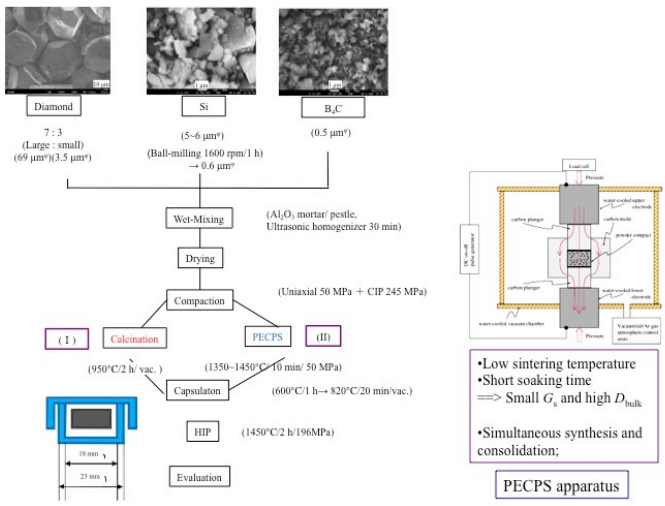

Fig. 1 Flow chart for the fabrication of diamond/SiC composites.

Results and discussion

Difference between Process I and II

Fig. 2 displays the XRD patterns of diamond/SiC composites with various SiC contents from 35 to 50 vol% or 35 to 100 vol%, fabricated as follows; (a)~(d), calcined (950°C/2h/vac.) via ”Process I”, and (e)~(h) sintered by PECPS (1450°C/10min/50MPa/vac.) via ”Process II”, then followed by HIP (1450°C/2h/196MPa/Ar). Big difference between “Process I” and “II” is; i) with increasing the intended content of SiC from 35 to 50 vol%,

amount of graphite 2H-C in the HIPed composites decreased in (a) to (d) via "I", on the contrary the amount of graphite increased in (e) and (f) via "II", and ii) the remained content of Si in the composites were still high in XRD patterns of (b)~(d) via "I", however, in "II" the amount of unreacted Si is not so high without the diamond/SiC=30/70 vol% composition, suggesting that when a small amount of Si was added to the diamond powders, and PECPSed at 1450°C unreacted diamond might transform into graphite. This might be explained by that the dense microstructures of diamond/SiC after PECPS at 1450°C might block a direct-contact between diamond and remained liquid Si and resulted in suppression of their liquid state reaction during HIPing. Fig. 3 (i) to (iv) display the relative densities D_r, *i.e.*, $D_r=D_{obs}/D_x$, here, D_{obs} and D_x are bulk and theoretical densities, respectively, of diamond/SiC composites fabricated by two processes, i.e., via "I" and "II" before and after HIPing denoted as (i), (ii) and (iii), (iv), respectively, as a function of intended content of SiC. In the D_r before HIPing the values of (i) only calcined materials are much lower than those of PECPSed (iii), it might be due to activated pressing during heat treatment.

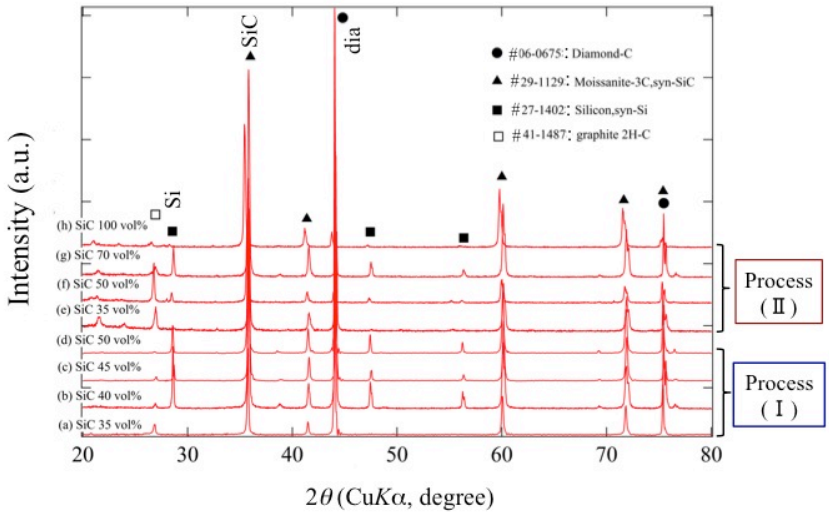

Fig. 2 XRD patterns of diamond/SiC composites: (a)~(d), calcined (950°C/2 h/vac.) and (e)~(h) sintered by PECPS (1450°C/10min/50MPa/ vac.), followed by HIP (1450°C/2h/196MPa/Ar).

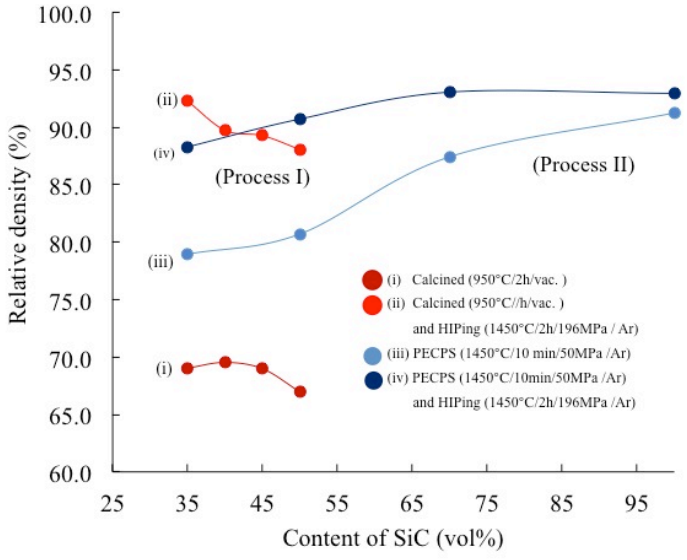

Fig. 3 Relative densities of diamond/SiC composites fabricated under various conditions as a function of SiC content.

However, after HIPing the difference in the D_r between "I" and "II" as shown in (ii) and (iv) is a little. Here, it should be noted that in "I", there is a decline tendency of D_r for both (i) and (ii), on the contrary, an accession tendency of D_r for both (iii) and (iv) in the SiC rich region.

Then their microstructures were observed. Fig. 4 shows SEM photographs of the fracture surfaces of diamond/SiC composites with 65/35 and 50/50 vol% compositions. The upper photographs (a) and (b) are the composites fabricated via "I", and the lower (c) and (d) via

"II", both followed by HIPing. Large diamond particles and small (gray: SiC and black: diamond) grains are observed, and their relative densities D_r are also shown to the right side of photograph. In "I", a high D_r (93.3%) is achieved in diamond/SiC=65/35vol%, and in "II" a high D_r (90.7%) is achieved in diamond/SiC=50/50vol%. It is clear that dense grain-boundary consisting of fine SiC and small diamond grains could bring a high D_r, in addition to this, good contact, or good adhesiveness between large diamond particle and grain-boundary also has much effect on the densification. Based on these data, in the SiC rich composites, "II" was expected to show higher D_r. Fig. 5 shows XRD patterns of diamond/SiC composites added with B_4C, their content changed from 0, 1, 3 and 5 vol%: (a)~(d) materials sintered by PECPS at 1350°C and (e)~(f) sintered by additional HIP (1450°C/2h/196MPa/Ar). With increasing the amount of B_4C addition after PECPS, a lot of Si and B_4C diffraction peaks were observed around 2θ=26.5° and 2θ=37.5°, respectively.

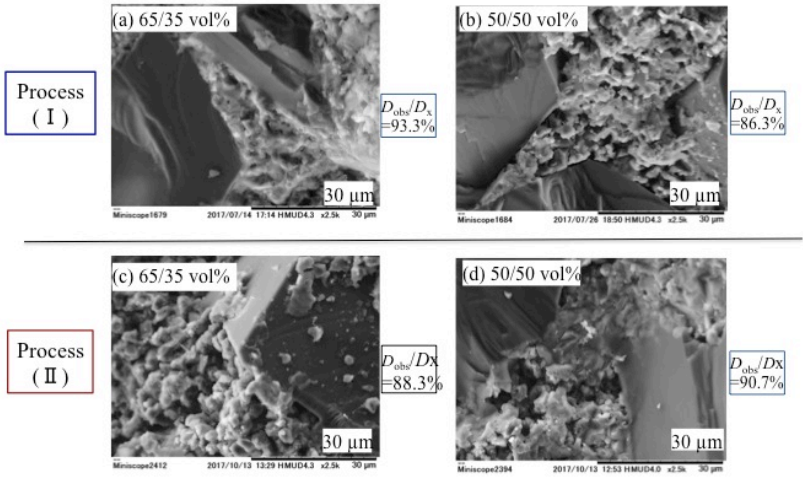

Fig. 4 SEM photographs for the fracture surfaces of diamond/SiC composites: (a)~(b), calcined (950°C/ 2h/vac.) and (c)~(d) sintered by PECPS (1450°C/ 10min/196MPa/Ar), followed by HIPing (1450°C/ 2h/196MPa/Ar).

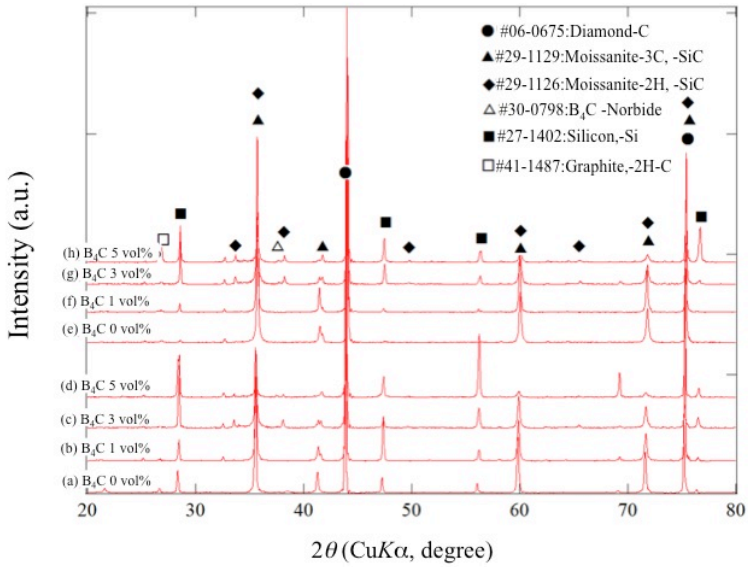

Fig. 5 XRD patterns of diamond/SiC=55/45vol% composites added with B_4C: (a)~(d) sintered by PECPS at 1350 ° C and (e)~(f) sintered by HIP (1450°C/2h /196MPa /Ar).

Furthermore, it should be noted that the B_4C addition enhanced the formation of both cubic (#29-1129) and hexagonal (#29-1126) SiC at the same time at 1350°C PECPS.After HIP at 1450°C, B_4C, SiC and graphite were recognized in the composites up to 5 vol% addition. The values of D_{obs} and D_r of composites were measured and calculated, respectively.

Fig. 6 represents the D_r for composites as a function of B_4C content. They were decreased once at 1.0 vol%, and then gradually increased until about 92.4% with 5.0vol% addition. Fig. 7 shows their microstructures observed by SEM using back-scattered electron image (BEI); (a) 0, (b) 1.0, (c) 3.0 and (d) 5.0 vol% B_4C added composites; as BEI proves that the heavier elements give brighter image than those of the lighter elements, therefore, both large dark

gray blocks and small particles in the grain-boundaries, are large and small diamonds, respectively, and bright grain-boundary matrix might be SiC. However, in these photographs B_4C particles could not be recognized or distinguished from small diamonds among gain-boundaries due to both fine particles and as the nearly same light elements as diamond.

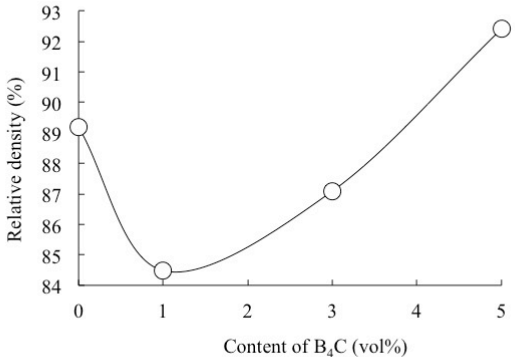

Fig. 6 Relative densities of B_4C-added diamond/SiC =55/45vol% composites as a function of B_4C content fabricated using PECPS at 1350°C for 10 min under 50 MPa in a vacuum, followed by HIP (1450°C/2h/196 MPa/Ar).

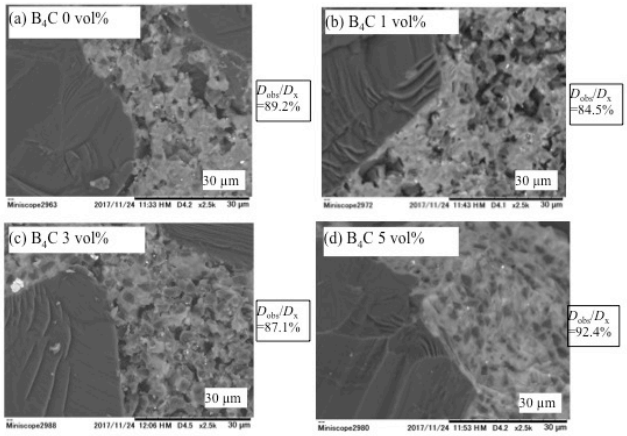

Fig. 7 SEM (back-scattered image:BEI) photograph of for the fracture surfaces of B_4C-added diamond/SiC=55/45 vol% composites fabricated using PECPS at 1350°C for 10 min under 50 MPa in a vacuum, followed by HIP (1450°C/ 2h/196MPa/Ar).

Then, their mechanical property, especially, hardness was measured. Vickers hardness H_v of composites was shown in Fig. 8 [I]. Though much scattering is observed with increasing B_4C content, the average value of H_v increased gradually from around 37.3 to 40.5 GPa at 5 vol% B_4C addition. In Fig. 8 [II], an laser microscopic image of 'Vickers indent", a SEM (BEI) and an energy-dispersive spectroscopic (EDS) images of the microstructure of 5.0 vol% B_4C added composite are presented. The indent size is very small which proves high hardness, and by comparing SEI and EDS images, it is clear that each particle, such as small diamond, B_4C and SiC are homogeneously dispersed. This homogeneous dispersion, thermal expansion coefficient α difference between SiC (α:4.3×10^{-6} K^{-1}) and B_4C (α:2.3×10^{-6} K^{-1}) and high Young's modulus (385~430 GPa) induced high compression stress into SiC grain-boundary, which might bring higher H_v value than those (about 23.5 GPa) reported previously [5]

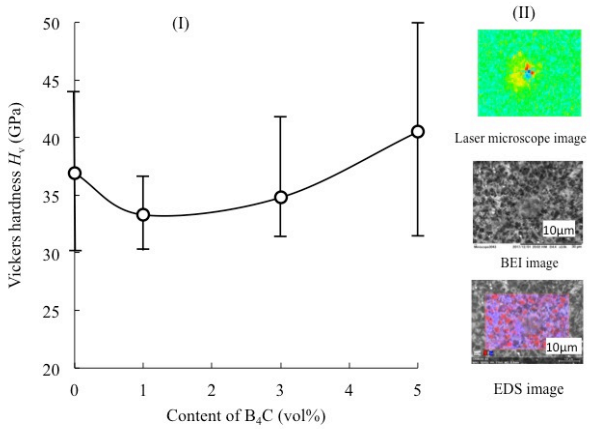

Fig. 8 (I); Vickers hardness H_v of diamond/SiC=55/45vol% composites sintered by both PECPS & HIP as a function of B_4C content, (II); microphotographs of Vickers indents, upper: laser microscope, middle: BEI figure, lower: EDS image.

Conclusion

Dense diamond/SiC=50/50vol% composites have been fabricated from the mixtures of diamond and Si powders using pulsed electric-current pressure sintering (PECPS) at 1350°C for 10 min under 50 MPa in a vacuum, followed by HIP at 1450°C for 2 h under 196 MPa in Ar with a liquid state sintering. This composite reveals high Vickers hardness H_v of 37.3 GPa. Furthermore, a small amount of B_4C addition enhanced the H_v up to about 40.5 GPa due to high compression stress induced into SiC boundary matrix.

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