Preparation of SiO$_2$-diamond composites by spark plasma sintering

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ABSTRACT

SiO$_2$-diamond composites with 65–85 mass% diamond were fabricated by spark plasma sintering at 1873 K under 130 MPa for 300 s using bimodal diamond particle size of 2 and 25 µm in diameter. The diamond particles were coated with a SiC layer by chemical vapor deposition. The effects of diamond content on relative density, microstructure, and Vickers hardness of the SiO$_2$-diamond composites were investigated. The SiO$_2$-diamond composites exhibited relative density of 96%, and Vickers hardness of 36.2 ± 3.6 GPa at 75 mass% diamond content.

1. Introduction

Diamond is an outstanding material to use in cutting tools owing to its excellent hardness and high wear resistance. Polycrystalline diamond (PCD) cutting tools have been employed in industrial machining of materials such as nonferrous metals, hard refractory ceramics, and natural stones. The bonding between diamond grains in synthesized PCD can be achieved by sintering diamond powder under high temperature and pressure in the presence of metallic binders such as cobalt. However, PCD is susceptible to brittle fracture and deterioration at high temperature during operation, which limits its cutting performance. Many studies show that the strength increases as diamond grain size decreases, but there is no direct relationship between strength and binder content. In terms of fracture toughness, increasing the grain size of PCD tends to increase its toughness, while using less binder improves it [1]. Although there is a common relationship between mechanical properties and grain size or binder content, in the individual case, the binder type and fabrication process may confound the results. The effect of these parameters on the mechanical properties of each material must be carefully investigated.

The manufacturing of diamond and silicon carbide (SiC) composites by reaction infiltration technique is usually performed since a composite with a high content of diamond (up to 50 vol%) can be achieved at ambient or low pressure [2–7]. SiC is mostly associate with diamond since it has excellent mechanical properties, thermal stability, and compatibility with diamond [2]. To prepare the composite, liquid or vapor silicon (Si) is infiltrated into preformed diamond at 1000–1650°C, then the reaction of diamond surface with infiltrated Si results in the formation of SiC. However, the residual Si is inevitably remain in the composites which might lead to the degradation of composite in alkaline solution [8].

The compaction of diamond particle is difficult to consolidate by a pressureless sintering due to the intrinsic covalent nature, low self-diffusion, and the phase transformation to soft graphite at high temperature. Diamond is, therefore, used as composites with glasses, ceramics, resins, and metals. The glass- and ceramic-diamond composites have higher refractoriness and endurace than resin- and metal-bonded diamond composites [9]. Glass-diamond composites using borosilicate glass by pressureless sintering [10–13] have widely been investigated, because of low sintering temperatures at 873 to 1073 K, and no phase transformation from diamond to graphite. However, the hardness of glass-diamond composites is low (1–9 GPa) due to the limited mechanical strength of glasses. Diamond composites using refractory and high-hardness ceramics, e.g. yttria-stabilized zirconia (YSZ) [14], silicon nitride (Si$_3$N$_4$) [15,16], alumina (Al$_2$O$_3$) [17], and cemented carbide (WC–Co) [18–21], have been fabricated by hot press (HP) or spark plasma sintering at moderate pressures (30–150 MPa). The mechanical, thermal, and wear properties of these composites are reported to be superior to those of monolithic ceramics [16,22].

Diamond- as well as cubic BN-based composites are divided into two broad classes of low (<40 – 50 vol%) and high (>50 vol%) hard phase content composites
[23]. There have been many papers of low hard-phase content composites [24–26]. Since the thermal and chemical resistance of composites relies on the bonding phase, the low hard-phase content composites have modest mechanical and other properties, while the high hard-phase content composites are featured for mechanical properties. Although an increase in the hard phase in the composite may increase the hardness and mechanical properties, directly contacted hard phases cannot be sintered, which leaves voids in between hard phases. It is usually difficult to make dense composites with high hard-phase content. The surface coating of hard phases could be effective to prevent the direct contact of hard phases. We have coated diamond particle with silicon carbide (SiC) by rotary chemical vapor deposition (CVD) to prevent the direct contact of diamond particle [27]. SiC coating also serves as an intermediate layer forming a strong bonding between the diamond particles and binder phase. The Si₃N₄ composite with the SiC-coated diamond exhibits high wear resistance due to the strong interfacial bonding of diamond particles to the matrix [16].

A bimodal diamond particle size mixture can improve the packing density of composites. The maximum packing density of bimodal particle size can be realized by filling small particles in between large particles [28]. For more than 80 vol% packing density, the ratios of size diameters of large to small particles (d₁/d₃) should be higher than 7 [29]. Mizuuchi et al. [30] reported that using bimodal diamond particle size dispersed in aluminum metal (Al) matrix increased the diamond content up to 75 mass% and also improved thermal conductivity. However, diamond particle more than 65 mass% with glass and ceramic binder has never been consolidated.

In this study, bimodal diamond particle size were coated with SiC and consolidated by SPS using SiO₂ binder; further, a sintered sample containing up to 85 mass% diamond was prepared. This paper reports the microstructure and mechanical property (hardness) of the SiO₂-diamond composite using bimodal diamond particle size.

2. Experimental procedure

Two kinds of diamond particles (MICRON+MDA M24 and MICRON+MDA M2535; 2 and 25 μm in mean diameters, respectively; Element six, Luxembourg) and SiO₂ powder (YAO50C-SP3; 50 nm in diameter; Admatechs, Japan) were used in this study. Diamond particles were coated with SiC by rotary CVD using hexamethyldisilane (Si₂H₆) as a precursor [31]. HMDS was heated to 303 K and carried in a CVD reactor by Ar gas at a flow rate of 1.7 × 10⁻⁷ m³ s⁻¹. The total pressure in the reactor was 400 Pa. The deposition temperature was 970 K and the deposition time was 7.2 ks. The bimodal diamond particle sizes (2 and 25 μm in diameters, d₁/d₃ = 12.5) was rotated in the CVD reactor at 45 rpm.

Diamond particles with 2 and 25 μm in diameters were mixed at a volume ratio of 30–70% leading to bimodal diamond particle size. A monomodal diamond particle size 25 μm in diameter was also used for comparison. The SiC-coated diamond particles were mixed with SiO₂ in an agate mortar with a small amount of ethanol. The mixed powders were then dried and sieved through a 200 mesh. The powder mixtures were sintered using SPS (SPS–210 LX; Fuji Electronic Industrial, Japan) with a heating rate of 1.67 K s⁻¹ to 1873 K in a vacuum for 300 s. A pressure of 130 MPa was applied throughout the sintering. The temperature was measured by an optical pyrometer and the displacement (shrinkage) of specimen was monitored during the sintering. The specimen diameter was approximately 10 mm and its thickness was 2 mm. Sintered samples with diamond content of 65–85 mass% were prepared.

The density was measured by the Archimedes method, and the relative density was calculated from the theoretical density of diamond (3.52 Mg m⁻³), SiC (2.75 Mg m⁻³), and SiO₂ (2.20 Mg m⁻³). The given densities for SiC and SiO₂ are for the amorphous materials. The theoretical density of composite was calculated by the rule of mixture. The volume of diamond and SiC were calculated from the average particle size of diamond and the average thickness of SiC layer, respectively. Then, the volume fraction of each composition was calculated from the mass of the mixture. The calculated volume fraction of phase composition and calculated theoretical density are given in the appendix.

The phase compositions were examined using X-ray diffraction (XRD; RAD–2 C, Rigaku, Tokyo, Japan) with CuKα radiation, with scanning 2θ in the range of 10–90 degree using a step interval of 0.02 degree and scanning speed of 10 degree/min. The diamond to graphite transformation in the sintered sample was examined using micro-Raman spectroscopy (inVia Reflex SL, Renishaw, UK) using a laser wavelength of 532 nm with a laser spot size of ~1 μm. The laser beam was focused on the interface between diamond and SiO₂. The diamond sample was too hard to polish by diamond paste; hence, a flat surface was obtained by Ar ion etching using a cross-section polisher (IB-19500CP, JEOL, Akishima, Japan). The microstructures were observed using a scanning electron microscope (SEM; S-3400 N, Hitachi, Tokyo, Japan) equipped with energy dispersive X-ray spectrometer (EDS; EDAX Inc., USA) and a transmission electron microscope (TEM; EM-002B, TOP-CON, Tokyo, Japan). Vickers hardness was measured using a microhardness tester (HM-221, Mitutoyo, Tokyo, Japan) at a load of 4.9 N. The average
of five indentation points on each specimen was calculated.

3. Results and discussion

Figure 1 displays the morphology of diamond particle 25 μm in diameter after coating with SiC. The as-deposited SiC was amorphous. SiC coating on the small diamond particle (2 μm in diameter) was uniform and the average SiC layer thickness was 26 nm. However, the large diamond particle (25 μm in diameter) were covered with a thick SiC layer about 50 nm in thickness. The surface area of small diamond particle was greater than that of the large diamond particle; thus, for the same supplied precursor, the large-diameter diamond particle yielded a thicker SiC coating.

Figure 2 displays the densification behavior of samples using monomodal and bimodal diamond particle sizes at 873–1873 K, and the time dependence of isothermal displacement at 1873 K, up to 300 s. Displacement, i.e. shrinkage, for all specimens began around 1473 K. The shrinkage of all samples with monomodal diamond particle size had nearly ceased around 1673 K. Moreover, the samples with monomodal diamond particle size containing 75 and 85 mass% diamond exhibited only slight shrinkage, implying poor densification. The shrinkage of bimodal diamond particle size samples containing 65 and 75 mass% diamond proceeded until 1873 K. Additionally, samples with bimodal diamond particle size containing 65 mass% diamond continued to densify at 1873 K in isothermal holding, and ultimately showed the highest shrinkage. At the same diamond content, the samples with bimodal diamond particle size was more densified than those with monomodal diamond particle size.

Figure 3 displays the XRD patterns of samples with monomodal and bimodal diamond particle sizes sintered at 1873 K. The samples comprised diamond and SiO₂ (amorphous or cristobalite). Since the deposition temperature of SiC is 970 K, the as-deposited SiC layer was amorphous. The content of SiC could be too small.
to identify by XRD. Only a tiny SiC peak (3 C-SiC) was identified after sintering 85 mass % bimodal diamond at 1873 K. Crystalline SiO$_2$ (cristobalite) peaks was identified in the samples with 65 and 70 mass% monomodal diamond particle size, whereas only a broad peak of amorphous SiO$_2$ was found in the samples with bimodal diamond particle size. Since amorphous SiO$_2$ would crystalize to cristobalite with volume reduction of about 6% [32], the crystallization of SiO$_2$ may cause poor bonding between diamond and SiO$_2$. However, the amorphous SiO$_2$ in the bimodal diamond did not crystallize, and small diamonds were finely dispersed in the SiO$_2$ matrix (see Figure 6). The amorphous SiO$_2$ could be more strongly bonded to the small diamond particle via SiC, and could not be readily crystalized (shrinked) to cristobalite SiO$_2$.

Figure 4 displays the Raman shift of the samples with monomodal and bimodal diamond particle sizes at 65 mass% diamond sintered at 1873 K. The sharp peak at 1333 cm$^{-1}$ corresponds to the first order Raman spectrum (D band) of the diamond [33] and no G band spectrum ($\sim$1580 cm$^{-1}$) can be identified, suggesting no significant transformation of diamond to graphite. The samples with monomodal diamond particle size had a low intensity broad peak at 1400–1500 cm$^{-1}$. Barger and Yarbrough [34] reported a broad peak around 1520 cm$^{-1}$ in a diamond film by CVD, which was assigned to crystal defects of diamond or the formation of nondiamond carbon. In a vacuum without pressure, it is known that diamond begins to transform to graphite around 1773–2073 K and the transition would complete at 2173 K [35]. When diamond particle is sintered at moderate pressures, the transition temperature depends on density and binder material. Shi et al. [23] reported that uncoated diamond sintered with WC–Co by SPS at 30 MPa transformed to graphite at 1373 K, whereas W-coated diamond transformed at 1553 K. Huang et al. [15] prepared Si$_3$N$_4$-diamond composite by SPS at 100 MPa and the transformation started at 1923 K. In our study, the bimodal diamond particle size sintered with SiO$_2$ did not show the transformation to graphite at 1873 K. The rapid heating rate and short sintering time of SPS could have prevented the transformation of diamond particle.

Figure 5 displays the effect of diamond content on the relative density of samples with monomodal and bimodal diamond particle size sintered at 1873 K. The relative densities of the samples with monomodal
diamond particle size decreased from 96 to 73% with an increase in diamond content. However, the samples with bimodal diamond particle size containing 65–75 mass% diamond had high relative densities of 96–99%, while for diamond content of 85 mass%, the relative densities decreased to 86%.

Figure 5. Effect of diamond content on the relative density of samples with monomodal and bimodal diamond particle sizes sintered at 1873 K.

Figure 6 displays the BSE-SEM images of the samples with monomodal and bimodal diamond particle sizes. The dark and light gray phases were diamond and SiO₂, respectively. The samples with monomodal diamond with 65 mass% diamond (Figure 6(a)) showed dense compaction; furthermore, large pores were observed with increasing diamond content (Figure 6(b–c)). The samples with bimodal diamond particle size containing 65 to 75 mass% diamond (Figure 6(d–e)) had a dense microstructure and uniform distribution of small diamond particles between large diamond particles. However, at diamond content higher than 75 mass% (Figure 6(f)), the pores were observed mainly at the contacts between large and small diamond particle. To achieve a fully dense microstructure, diamond content should be limited to 65 mass% for samples with monomodal diamond particle size but could extend to 75 mass% for samples with bimodal diamond particle size. In our previous study, a high-magnification micrograph of diamond and SiO₂ composites using SiC-coated diamond (monomodal diamond particle size of 2 μm) was reported [36,37]. At the interface between diamond and SiO₂, a scanning transmission electron microscope (STEM) image and elemental mapping by electron energy-loss spectroscopy (EELS) confirmed the presence of a thin SiC interlayer. A high-resolution transmission electron microscope (TEM) bright field image also confirmed the existence of crystalline SiC layer at the

Figure 6. BSE–SEM images of samples with monomodal diamond particle size at (a) 65 mass %, (b) 75 mass %, and (c) 85 mass %, and bimodal diamond particle size at (c) 65 mass %, (d) 75 mass %, and (f) 85 mass % diamond content.
interface between diamond and SiO$_2$. Therefore, the SiC layer at the diamond grain boundary is assumed to be crystalline phase in this study. The image analysis processing by ImageJ software was used to assess the diamond volume content from the SEM micrograph. The volume contents of diamond in the samples with monomodal diamond particle size in Figure 6(a), 6(b), and 6(c) are 58%, 65%, and 77%, respectively, while the volume contents of diamond in the sample with bimodal diamond particle size in Figure 6(d,e and f) are 55%, 66%, and 75%, respectively. The volume contents determined by image analysis are corresponding to the volume fractions of diamond calculated from the mixture (Table A in appendix).

**Figure 7** displays the effect of diamond content on Vickers hardness of samples with monomodal and bimodal diamond particle size sintered at 1873 K. The increase in diamond content resulted in a significant decrease of Vickers hardness of the samples with monomodal diamond particle size from 32.3 ± 4.4 to 6.2 ± 1.6 GPa. Contrastingly, the samples with bimodal particle size containing 65 to 75 mass% diamond maintained high Vickers hardness in the range 31.5 ± 4.7 to 36.2 ± 3.6 GPa. At 75 mass% diamond, Vickers hardness of the samples with bimodal diamond particle size was about 2.3 times higher than that by monomodal diamond particle size. At 65 mass% diamond, the samples with monomodal diamond particle size showed a similar Vickers hardness to samples of similar density by bimodal diamond particle size. At higher diamond content, the decrease in hardness of the samples with monomodal diamond particle size owed to the decrease in density. For the samples with bimodal diamond particle size, small diamond particle size filled in between large diamond particle, resulting in dense samples of greater hardness than those by monomodal diamond particle size.

**Figure 8** shows the Vickers indentation on samples with monomodal and bimodal diamond particle size at 65 mass% diamond sintered at 1873 K. The Vickers hardness of the samples with bimodal diamond particle size (35.4 ± 6.2 GPa) was slightly higher than that by monomodal diamond particle size (32.3 ± 4.4 GPa). However, the cracking feature around the indentation was significantly different. The cracks would generally form and extend from the corners of indentation in brittle ceramics; however, cracks did not simply extend from the corner of indentation in the samples. The cracks mainly extended along large diamond particle in the samples with monomodal diamond particle size.

![Image](https://example.com/image1.png)  
*Figure 7. Effect of diamond content on Vickers hardness of sintered samples with monomodal and bimodal diamond particle sizes.*

![Image](https://example.com/image2.png)  
*Figure 8. SEM morphologies of the Vickers indentation on sintered samples with (a) monomodal and (b) bimodal diamond particle sizes.*
In the samples with bimodal diamond particle size, on the other hand, some cracks extended along large diamond particle while some cracks penetrated and stopped in the large diamond particle, suggesting strong bonding between diamond particle and SiO$_2$ matrix. The samples with monomodal diamond particle size had crystalline (crystalobalte) SiO$_2$ (see Figure 3) and defect or non-diamond carbon (see Figure 4). The crystalline (crystalobalte) SiO$_2$ will be cracked by the transformation from $\beta$ to a form around 700 K, which would degrade the bonding between diamond and SiO$_2$ matrix, and the defect or non-diamond carbon would also weaken the bonding between diamond and SiO$_2$ matrix. The bimodal diamond particle size is beneficial not only to fabricate dense SiO$_2$-diamond composite but also to make strongly bonded diamond particle in the SiO$_2$ matrix.

Table 1 lists the Vickers hardness of glass- and ceramic-bonded diamond composites fabricated at less than 150 MPa, and the hardness of reaction infiltration diamond-SiC composites. Glass-bonded diamonds are usually prepared by pressureless sintering in air. The diameter of diamond ranged from 30 to 300 μm and the diamond content varied from 25 to 60 vol%. The coating on diamond particle by TiO$_2$/Al$_2$O$_3$ films prevented thermal oxidation of diamonds, thus improving the mechanical properties of glass-bonded diamonds [13]. However, the hardness of these glass-bonded diamonds were in the range of 1–9 GPa, which is comparable to that of borosilicate glass (5–8 GPa) [38]. In ceramic-bonded diamond samples, the hardness was 16–23 GPa [14,15,18,19] and was higher than that of glass-bonded diamond samples; however, the diamond content was 10–30 vol% owing to the poor wettability and sinterability between diamond and ceramics. The diamond-SiC composites prepared from the reaction infiltration exhibit high hardness value of about 50 GPa [3,4] due to the high content of diamond (50–55 vol%), and the SiC binder is typically high hardness phase. The hardness of composites is also improved by a strong bonding between diamond surface and SiC and the dense microstructure. In this study, the highest Vickers hardness of 36 GPa was achieved using bimodal diamond particle size containing 63 vol% (75 mass%) diamond.

4. Conclusions

SiO$_2$-diamond composite with 75 mass% diamond was fabricated by using SiO$_2$ and SiC-coated bimodal diamond particle size by SPS at 1873 K and 130 MPa for 300 s. With an increase in the diamond content from 65 to 75 mass%, the relative density of the samples with bimodal particle size decreased from 99 to 96%, whereas that of the samples with monomodal particle size decreased from 96 to 73%. The Vickers hardness of the samples with bimodal diamond particle size was 36.2 ± 3.6 GPa at 75 mass% diamond content. In the SiO$_2$-diamond composite by monomodal diamond particle size, partial crystallization of SiO$_2$ and defect or non-diamond carbon were identified, which would cause weak bonding between SiO$_2$ matrix and diamond particle, whereas that by bimodal diamond particle size, the bonding between diamond particle and SiO$_2$ matrix could be stronger than that by monomodal diamond particle size.

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Disclosure statement

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## Appendix

### Table A. Calculated volume fraction, theoretical densities, experimental densities measured from Archimedes method, and relative densities of composites.

| Diamond content (mass\% volume fraction (vol\%)) | Diamond | SiC | SiO₂ | Density (Mg m⁻³) | Relative density (%) |
|-----------------------------------------------|---------|-----|------|-------------------|---------------------|
| Monomodal diamond particle size                |         |     |      |                   |                     |
| 65                                            | 53.1    | 0.6 | 46.2 | 2.91              | 95.5                |
| 70                                            | 58.7    | 0.7 | 40.6 | 2.98              | 86.2                |
| 75                                            | 64.5    | 0.8 | 34.7 | 3.06              | 82.7                |
| 80                                            | 70.6    | 0.9 | 28.5 | 3.14              | 77.1                |
| 85                                            | 77.1    | 0.9 | 22.0 | 3.22              | 72.7                |
| Bimodal diamond particle size                  |         |     |      |                   |                     |
| 65                                            | 52.2    | 1.7 | 46.1 | 2.90              | 99.3                |
| 70                                            | 57.7    | 1.8 | 40.5 | 2.97              | 99.0                |
| 75                                            | 63.4    | 2.0 | 34.6 | 3.05              | 96.4                |
| 80                                            | 69.4    | 2.2 | 28.4 | 3.13              | 90.7                |
| 85                                            | 75.7    | 2.4 | 21.9 | 3.21              | 86.3                |