

# Properties of nanostructured diamond-silicon carbide composites sintered by high pressure infiltration technique

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A high-pressure silicon infiltration technique was applied to sinter diamond–SiC composites with different diamond crystal sizes. Composite samples were sintered at pressure 8 GPa and temperature 2170 K. The structure of composites was studied by evaluating x-ray diffraction peak profiles using Fourier coefficients of ab initio theoretical size and strain profiles. The composite samples have pronounced nanocrystalline structure: the volume-weighted mean crystallite size is 41–106 nm for the diamond phase and 17–37 nm for the SiC phase. The decrease of diamond crystal size leads to increased dislocation density in the diamond phase, lowers average crystallite sizes in both phases, decreases composite hardness, and improves fracture toughness.

## I. INTRODUCTION

Diamond–silicon carbide composites have recently attracted a lot of attention due to their unique mechanical properties and a great potential for a variety of applications. The following methods of their processing have been reported: infiltration of diamond powders by silicon at high<sup>1–4</sup> and normal<sup>5,6</sup> pressures, high-pressure sintering of diamond/SiC powder mixtures,<sup>7–10</sup> synthesis of diamond/ $\beta$ -SiC composite films by microwave plasma assisted chemical vapor deposition.<sup>11</sup> To date, only the high-pressure silicon infiltration technique has been reported as a method of a large scale production of diamond–SiC composite inserts for rock drilling and other applications.<sup>1,3</sup> Composite inserts made by this method have uniform structure and are extremely hard and thermally stable. However, much room still remains for improvement of their mechanical properties, first of all strength and fracture toughness. This goal requires detailed study of structure and properties of composites as a function of manufacturing parameters. One of the most important factors is the size of the crystals of the

initial diamond powder. Uniform bulk composites have been produced by silicon infiltration of diamond powders with crystal size ranging from 15 to 60  $\mu\text{m}$ .<sup>1,3</sup> In this work, we broadened the range of diamond powder crystal size (from 1 to 60  $\mu\text{m}$ ) and studied how the size of the diamond grains affects the structure and properties of composites.

## II. EXPERIMENTAL

### A. Sample preparation and characterization techniques

All composite samples were made by the high-pressure silicon infiltration technique.<sup>3,4</sup> Synthetic diamond powders of crystal size 1–2  $\mu\text{m}$ , 10–14  $\mu\text{m}$ , and 40–60  $\mu\text{m}$  from the Institute for Superhard Materials, Kiev, Ukraine, and silicon powder of particle size less than 44  $\mu\text{m}$  from Alfa Aesar (Ward Hill, MA) were used in this study.

Sintering experiments were run in a toroid high pressure cell, which consisted of two identical anvils with toroidal grooves and the lithographic stone gasket that matched the contours of the grooves.<sup>12</sup> Pressure calibration of the cell was made by recording phase transitions of Bi and PbTe. Temperature calibration was made by measuring temperature in the center of the high pressure cell by a W<sub>3%</sub>Re/W<sub>25%</sub>Re thermocouple as a function of

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electric power dissipated in the apparatus. Obtained power–temperature and load–pressure plots were used as the calibration curves for subsequent high-pressure, high-temperature (HPHT) sintering.

The layers of silicon and diamond powders packed inside a cylindrical graphite heater were placed inside the center of the gasket. The experiments were run according to the following protocol. The pressure was raised to the value 8 GPa at room temperature. Next, temperature was increased to 2170 K at a rate of 200 K/s, and the samples were kept at that temperature for 30 s. Finally, temperature was decreased to the room level and the pressure was released.

After sintering samples were grinded to form tablets of diameter 7.5 mm and height 3 mm. Both bases of the tablets were polished using diamond powders and sprays with particle sizes decreasing gradually from 5 to 0.5  $\mu\text{m}$ . Three different samples of each material were prepared, and the results listed in this paper are the average data obtained for these specimens.

The density of the samples was measured by the Archimedes method on AT261 Delta Range made by Mettler Toledo (Columbus, OH). De-ionized water was used as the immersion medium. The Knoop and Vickers microindentation hardness were measured on a PMT3 microhardness tester; the loads applied to the indenter were, respectively, 4.9 and 49 N. The fracture toughness stress intensity factor  $K_{IC}$  was measured by the indentation method<sup>13</sup> with a load of 147 N on a Vickers diamond indenter.

A conventional powder diffractometer (Philips X'pert, Almelo, Holland) using  $\text{CuK}\alpha$  radiation and pyrolytic graphite secondary monochromator was used to obtain the x-ray spectra of the samples (Fig. 1). Composition of

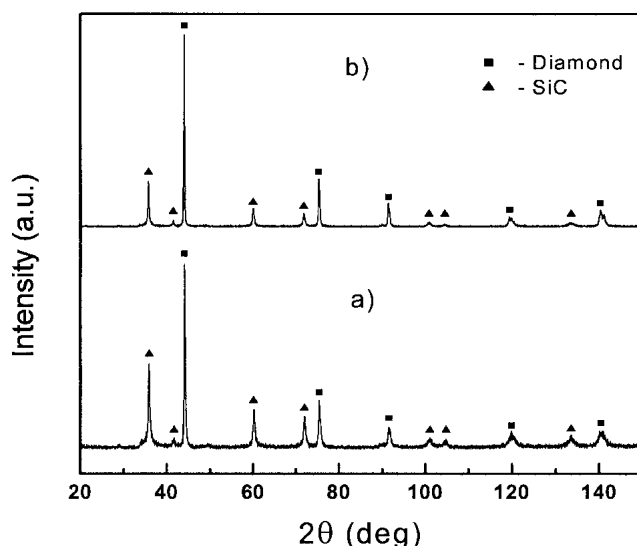


FIG. 1. X-ray spectra for composites of diamond, initial grain size (a) 1–2  $\mu\text{m}$  and (b) 40–60  $\mu\text{m}$ .

the samples was evaluated from integral intensities of diamond and SiC peaks. Diamond– $\beta$ –SiC powder mixtures of different content were used for peak intensity calibration. The microstructure of the specimens produced from the diamond powders with crystal sizes of 1–2  $\mu\text{m}$  and 40–60  $\mu\text{m}$  were studied by x-ray diffraction peak profile analysis. The {111}, {220}, {311}, {400}, and {331} peaks of the diamond phase and {111}, {220}, {311}, {331}, {420}, and {422} of the silicon carbide phase were measured individually by a special double-crystal high-resolution diffractometer with a very small instrumental broadening (with the sample to detector distance  $l = 500 \text{ mm}$   $\Delta(2\theta)_{\text{instr}} = 0.012^\circ$ ) attached to a high brilliance rotating anode (Nonius, Delft, Holland). Monochromatic  $\text{CuK}\alpha_1$  incident radiation was used.

## B. Evaluation procedure of x-ray diffraction profiles

The evaluation of the peak profiles was performed by the multiple whole-profile fitting (MWP) procedure.<sup>14</sup> In this method the Fourier coefficients of the measured profiles were fitted by the product of the theoretical functions for size ( $A^S$ ) and strain (distortion,  $A^D$ ) broadening. In the calculations of the theoretical functions the crystallites were assumed to have spherical form with log-normal size distribution and the strains were assumed to be caused by dislocations. According to this model of the microstructure, the theoretical function for the size and strain Fourier coefficients are

$$A^S(L) \sim \frac{m^3 \exp(4.5\sigma^2)}{3} \text{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} - 1.5\sqrt{2}\sigma \right] - \frac{m^2 \exp(2\sigma^2)|L|}{2} \text{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} - \sqrt{2}\sigma \right] + \frac{|L|^3}{6} \text{erfc} \left[ \frac{\ln(|L|/m)}{\sqrt{2}\sigma} \right], \quad (1)$$

and

$$A^D(L) = \exp[-\rho B L^2 f(\eta) K^2 \bar{C}] \quad (2)$$

respectively, where  $L$  is the Fourier variable,  $m$  is the median, and  $\sigma$  is the variance of the log-normal size distribution function,  $\text{erfc}$  is the complementary error function,  $\rho$  is the dislocation density,  $B = \pi b^2/2$ ,  $b$  is the absolute value of the Burgers vector,  $K$  is the absolute value of the diffraction vector,  $\eta \sim L/R_e$ ,  $R_e$  is the effective outer cut-off radius of dislocations and  $f(\eta)$  is a function derived explicitly by Wilkens [see Eqs. (A.6–A.8) in Ref. 15.]  $\bar{C}$  is the average dislocation contrast factor which is introduced to take into account the strain anisotropy of dislocations. Based on the theory of peak broadening caused by dislocations, it can be shown that in an untextured cubic polycrystalline specimen the values of  $\bar{C}$  are simple functions of the invariants of the

fourth order polynomials of the indices of reflections  $hkl$ <sup>16</sup>

$$\bar{C} = \bar{C}_{h00} \{1 - q(h^2k^2 + h^2l^2 + k^2l^2)/(h^2 + k^2 + l^2)^2\} \quad (3)$$

where  $\bar{C}_{h00}$  is the average dislocation contrast factor for the  $h00$  reflections, and  $q$  is a parameter depending on the elastic constants of the crystal and on the character of dislocations (e.g., edge or screw type). Details of the method have been published previously and can be found in Ref. 14. In the case when only a specific dislocation slip system is populated in crystals, individual contrast factors have to be considered. However, when different slip systems are randomly populated by dislocations or when polycrystalline materials are texture free, the average contrast factors can be used.<sup>14</sup> With the values for the elastic stiffness constants given in Refs. 17 and 18 and assuming that the most common dislocation slip system in both diamond and  $\beta$ -SiC has the Burgers vector  $b = a/2 \langle 110 \rangle \{111\}$  (both diamond and  $\beta$ -SiC have face-centered cubic unit cells), the values of the  $q$  factor for pure edge and pure screw dislocations are 0.30 and 1.35 for diamond and 1.1 and 2.1 for  $\beta$ -SiC, respectively.<sup>19</sup> Assuming the half edge-half screw character of dislocations the  $q$  values were taken as 0.8 for pure diamond phase and 1.6 for SiC phase. Here we note that if pure edge or screw character of dislocations is assumed for any of the two phases, the quality of the fitting is only slightly changed, and the parameters of the microstructure remain within the error range of  $\pm 10\%$  of the values determined for the half edge-half screw case. This is mainly caused by the relatively low elastic anisotropy of diamond and silicon carbide ( $A = 2c_{44}/(c_{11} - c_{12}) = 1.2$  and 2.2 for diamond and silicon carbide, respectively).

As a result of the multiple whole profile (MWP) fitting procedure the median ( $m$ ) and the variance ( $\sigma$ ) of the size distribution, and the density ( $\rho$ ) of dislocations were obtained. These parameters were used to calculate the volume weighted mean crystallite sizes<sup>14</sup>

$$\langle x \rangle_{\text{vol}} = m \exp(3.5\sigma^2) \quad (4)$$

### III. RESULTS AND DISCUSSION

Crystallite sizes and dislocation densities were determined by fitting the Fourier coefficients of whole profiles obtained by high-resolution x-ray measurements. The quality of the fits is fairly good as shown for a typical case in Fig. 2. The (331) profiles of diamond and SiC for the two specimens prepared from 1–2  $\mu\text{m}$  and 40–60  $\mu\text{m}$  diamond powders are shown in Fig. 3. The profiles corresponding to the smaller initial grain size are considerably broader, especially in the case of diamond peaks.

The average crystallite sizes and dislocation densities

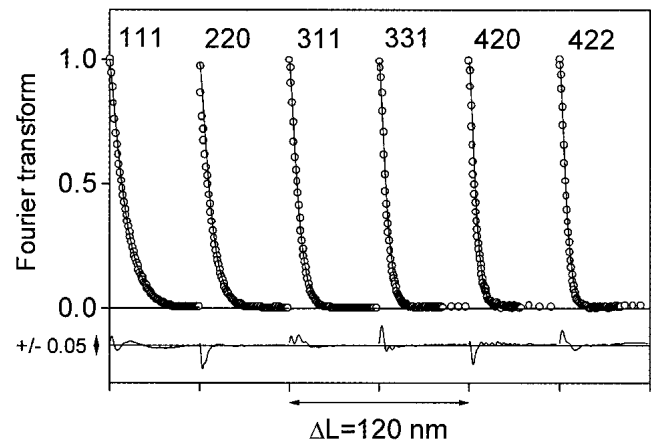


FIG. 2. Measured (open circles) and fitted (solid line) Fourier transforms of the silicon carbide diffraction profiles for the composite of diamond, initial grain size 1–2  $\mu\text{m}$ . The difference between the two sets of curves is shown in the bottom part of the figure.

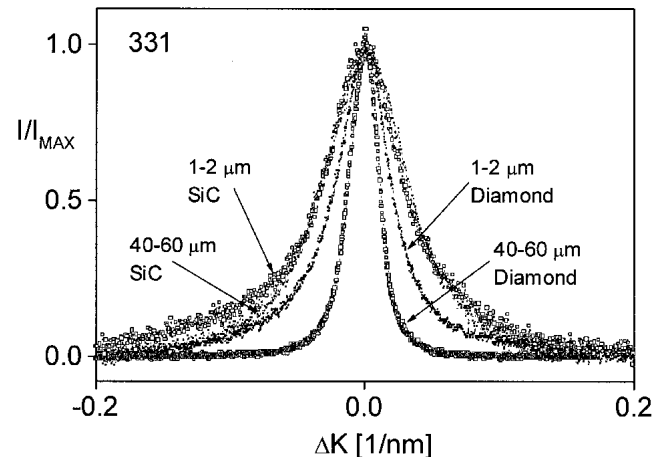


FIG. 3. Diamond (331) and SiC (331) peak profiles for composites of diamond, initial grain size 1–2  $\mu\text{m}$  and 40–60  $\mu\text{m}$ .

evaluated by the MWP method are listed in Table I. The results show that the composites have become nanocrystalline: the volume-weighted mean crystallite size is 41–106 nm for the diamond phase and 17–37 nm for the SiC phase. Fragmentation of diamond crystals of initial size 1–60  $\mu\text{m}$  to nanosize crystallites is the result of

TABLE I. Microstructural parameters for diamond–SiC composite samples sintered by Si reactive infiltration of different grain size diamond powders at pressure 8 GPa and temperature 2170 K for 60 seconds;  $\langle x \rangle_{\text{vol}}$ : volume-weighted mean crystallite size,  $\rho$ : density of dislocations.

Diamond powder grain size	Phase	$\langle x \rangle_{\text{vol}}$ (nm)	$\rho$ , $10^{14} \text{ m}^{-2}$
1–2 $\mu\text{m}$	Diamond	41 (4)	33 (5)
	SiC	17 (2)	42 (5)
40–60 $\mu\text{m}$	Diamond	106 (10)	9 (1)
	SiC	37 (4)	41 (5)

intense plastic deformation at the stage of heating at high pressure.<sup>4</sup> The specimen produced by the reactive infiltration method from diamond powder with smaller initial grain size has smaller crystallite size and higher dislocation density. This behavior of diamond at high temperatures and pressures seems to be similar to metallic materials during severe plastic deformation at ambient temperatures.<sup>20</sup>

The SiC phase forms after infiltration due to a reaction between diamond and silicon. Its nanocrystalline structure is the result of plentiful nucleation sites and restricted growth of crystals. Since the nucleation of SiC crystals starts at the diamond surface, first at defects, higher dislocation density in diamond crystals of size 1–2  $\mu\text{m}$  should result in more intense nucleation of SiC crystals. The decrease of crystallite sizes in diamond may also contribute to diminishing sizes of SiC crystallites due to oriented growth of silicon carbide on the diamond surface.<sup>21</sup>

Experimental densities and compositions of samples are listed in Table II. The content of the SiC phase in composites decreases with the increase of the initial diamond powder grain size. This trend has the following explanation. It has been shown that compaction of diamond powder at room temperature results in particle rearrangement, crushing of diamond, and filling of voids by debris of crushed crystals.<sup>22</sup> At a given pressure, larger crystals crush more readily than the smaller ones. Thus, porosity of compressed coarse powders is lower than that of fine powders.<sup>22</sup> It results in higher content of SiC in composites made from coarser diamond powders.

From the composition of samples, we calculated reference theoretical densities using the rule of mixtures. Porosities of the specimens were calculated using the expression:  $P = 1 - \gamma_{\text{exp}}/\gamma_{\text{th}}$ , where  $P$ ,  $\gamma_{\text{exp}}$ , and  $\gamma_{\text{th}}$  are porosity, experimental density, and theoretical density, respectively. They are listed in the same table. In the case of course-grained composites, porosity is very low but raises with decreasing size of diamond grains. This tendency could be explained by the diminishing pore sizes in diamond powder of decreasing grain size. It makes silicon infiltration more difficult, especially taking into account the bottleneck effect—closure of pore throats in

the process of the reaction between diamond and silicon. As a result, pores of smallest sizes remain unfilled by silicon during infiltration. It may also cause additional diamond crystal fragmentation and dislocation nucleation. Due to high pressure at the contact points on the surface of diamond crystals, shear stresses are developed and they are responsible for the dislocation production. These stresses are greatly lowered when voids between the diamond crystals are filled with silicon.<sup>4,10</sup> Unfilled pores for the specimen with 1–2  $\mu\text{m}$  initial crystal sizes may result in high contact shear stresses. The stresses remain in some diamond crystals after the silicon infiltration, and therefore higher dislocation densities are observed in these samples compared to the samples with 40–60  $\mu\text{m}$  initial crystal sizes.

Hardness and fracture toughness of composites are also listed in Table II. The decrease of diamond initial grain size results in noticeable decrease of composite hardness and increase of its fracture toughness. We offer the following explanation for this tendency. The phase content, porosity, and microstructure of the phases are the main factors affecting mechanical properties of the composites. All these factors simultaneously change when the size of crystals in initial diamond powder is altered. While the increase of porosity and content of “softer” silicon carbide phase usually leads to a reduced hardness of a composite, the decrease of crystallite size may result in increased hardness and fracture toughness.<sup>23</sup> It is the balance between these two opposite trends that defines mechanical properties of composites. Hardness of diamond-SiC composites gradually decreases with growing SiC content and porosity. On the other hand, the increase of fracture toughness can be explained by smaller pore size and/or crystallite size in the composite material produced from diamond powder with smaller initial grain size.

We propose the following strengthening mechanism in nanostructured diamond-SiC composites. Strong covalent bonding in diamond and SiC crystals results in cleavage along planes of low surface energy: usually {111}, and less often {110}, and other planes. The fragmentation to nanocrystallites hampers crystallographically oriented crack propagation, resulting in crack deflection

TABLE II. Phase content, density, porosity, hardness, and fracture toughness of diamond-SiC composites sintered by silicon reactive infiltration of diamond powders of different grain size.

Diamond powder grain size	Content (wt%)		Density ( $\text{g}/\text{cm}^3$ )		Porosity (%)	Knoop hardness $H_K$ , GPa ( $P = 4.9\text{N}$ )	Fracture toughness $K_{IC}$ ( $\text{MPam}^{0.5}$ )
	Diamond	SiC	Theor. <sup>a</sup>	Exp. <sup>b</sup>			
1–2 $\mu\text{m}$	76	24	3.44	3.34	2.9	$42 \pm 2$	$12 \pm 1$
10–14 $\mu\text{m}$	83	17	3.46	3.44	0.6	$50 \pm 2$	$11 \pm 1$
40–60 $\mu\text{m}$	86	14	3.47	3.46	0.3	$52 \pm 2$	$10 \pm 1$

<sup>a</sup>Theoretical

<sup>b</sup>Experimental

and more pronounced propagation along planes with higher surface energy.

#### IV. CONCLUSIONS

At high temperatures and pressures, diamond seems to deform in a similar manner as metallic materials under ambient conditions. Silicon reactive infiltration of compacted diamond powder with smaller initial grain size results in a composite with finer microstructure, higher dislocation density in the diamond phase, and increased fracture toughness. The specimens produced from the diamond powder with larger initial grain size show higher hardness due to smaller porosity and lower SiC content. Coarse-grained composites are more apt for applications requiring high hardness, while fine-grained ones are more preferable in cases when improved fracture toughness is needed.

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