

Kinetics of SiC formation during high P–T reaction between diamond and silicon

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Abstract

Time-resolved in situ X-ray diffraction at simultaneous high pressures (P) and high temperatures (T) was used to monitor kinetics of the reaction between diamond and silicon. Analysis of the data indicated that the reaction was diffusion controlled, and the diffusion was taking place through grain boundaries. For the nm size diamond the activation energy (170 kJ/mol) was smaller than that for μm size diamond (260 kJ/mol), and the reaction started at a temperature below the melting point of silicon. These effects are attributed to nanocrystalline structure and strained bonds within grain boundaries.

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1. Introduction

Diamond composites are a class of hard-materials with a huge variety of applications in diverse fields, such as mining, grinding, cutting, machining, drilling, engineering components, and heat sinks for electronic equipment [1–3]. Several different techniques have been used for diamond–SiC composites manufacturing, among them the most common is the high pressure–high temperature reactive infiltration technique [4]. Recent developments in the manufacturing process, such as addition of nanosize diamonds and silicon and structure engineering of grain boundaries, renewed interest in investigation of the process and mechanical properties of the product [5–8]. However, information on the kinetics of formation of diamond–SiC

composites is limited. It is generally accepted that the reaction between diamond and liquid silicon starts on the surface of diamond crystals, near the surface defects [9]. The surface defects that are promoting the reaction between diamond and melted silicon are of microscopic level and consist of growth steps, surface dislocations and/or places of increased roughness [10]. It has been observed that the reaction proceeds faster for diamond crystals of smaller sizes and when the temperature is increased.

In the last 25 years several studies on the kinetics of SiC formation at high temperature from different precursors were reported [11–14]. In general, there is an agreement that the controlling step of the reaction is the diffusion of carbon atoms through the newly formed SiC layer, with activation energies of 100–400 kJ/mol. Many authors have studied self-diffusion of carbon and silicon in β -SiC [15–18]. Despite numerous efforts over the past 25 years that process is still not fully understood. Although different authors provided different values of activation energies for diffusion, ranging from 600 to 900 kJ/mol, they all agreed

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that the activation energies for C and Si are similar and that carbon diffuses faster than silicon. Some authors attributed these large values to the vacancy mechanism, which requires breaking of four SiC bonds. The activation energy combines the vacancy formation energy and migration energy of an atom to the surface. Slower diffusivity of silicon was explained by larger atomic radius of Si, which increased the contribution of long-range interactions and thus slowed down its motion. Another mechanism, self-diffusion of interstitial Si and C in SiC was investigated by Lento et al. [19]. They found that the formation energies for interstitial Si and C are just between the formation energies for carbon and silicon vacancies.

It is the purpose of this paper to calculate, for the first time, the activation energy of the β -SiC formation from diamond and melted silicon precursors, at simultaneous high temperature and high pressure, and to explain the discrepancies between the activation energies mentioned above. At the same time, the effect of the size will be investigated, using micron-size and nano-size diamond powders. It is expected that the nano-size powders will have a higher number of strained bonds/defects on the surface, which will affect the activation energy, thus the kinetics of the reaction.

2. Experimental

2.1. Sample preparation

In this work we investigate the kinetics of the reaction between diamond and silicon of micron- and nano-size powders using time-resolved in situ X-ray diffraction, at conditions similar to the ones used in diamond composites sintering. Synthetic diamond powders with crystal sizes of 5–10 and 30–40 μm from General Electric Co., 0–50 nm, MicroDiamant, Switzerland, and silicon powders of 1–20 μm , Alfa Aesar were used in the experiments. Sintering experiments were run on a DIA-type, cubic-anvil, high pressure/high temperature apparatus, SAM85 [20]. A hexagonal boron nitride (hBN) sample chamber is used to surround the sample. The hBN is a soft material and provides a pseudo-hydrostatic state at high pressures, and provides high thermal conductivity that promotes homogeneous temperature inside the cell. Temperature was measured by a W/Re 25%–W/Re 3% thermocouple, and pressure was determined using the equation of state for NaCl [21]. Pressure was fixed at 8.0 ± 0.5 GPa in all experiments we performed. Errors in temperature measurements were estimated to be ± 10 K and the uncertainty in pressure measurements was less than 0.2 GPa [22].

2.2. In situ X-ray diffraction experiments

In situ high P – T X-ray diffraction experiments in energy-dispersive mode were conducted at National Syn-

chrotron Light Source (NSLS)—beamline X17B2, and Advanced Photon Source (APS)—beamline 13 BM-GSE-CARS. The data were collected at a fixed scattering angle ranging from 5.8° to 6.5° , in the energy range 0–100 keV. The incident X-ray beam was collimated to $100 \times 100 \mu\text{m}^2$. Typical duration for collecting a diffraction pattern was 30 s. The three sets of experiments done for different mixtures of diamond and silicon powders are referred as ‘Series 1’ (for 30–40 μm diamond)-APS, ‘Series 2’ (for diamond 5–10 μm)-NSLS, and ‘Series 3’ (for diamond 0–50 nm)-NSLS.

3. Results and discussion

A typical energy-dispersive X-ray diffraction pattern obtained during the experiments is shown in Fig. 1. SiC formed as a result of the reaction between carbon atoms from diamond crystals and silicon was the cubic polytype, β -SiC. No evidence of the α -phase (hexagonal type) of SiC was observed. Peak positions for the hexagonal phase of SiC can be found in Ref. [23]. None of them were found in our diffractograms.

We focused our study on four SiC peaks, (111), (200), (220), and (311), which are marked in Fig. 1. Peaks with lower d-spacings were of very small intensities and their analysis led to large errors; therefore they were not taken into consideration. The diamond (111) peak, the strongest peak of diamond, was also analyzed. As it can be seen in Fig. 1, in addition to diamond and silicon carbide peaks, several peaks due to hBN and Al_2O_3 were also present. Intensities of hBN peaks were quite strong due to the fact that the capsule was closer to the sample than alumina.

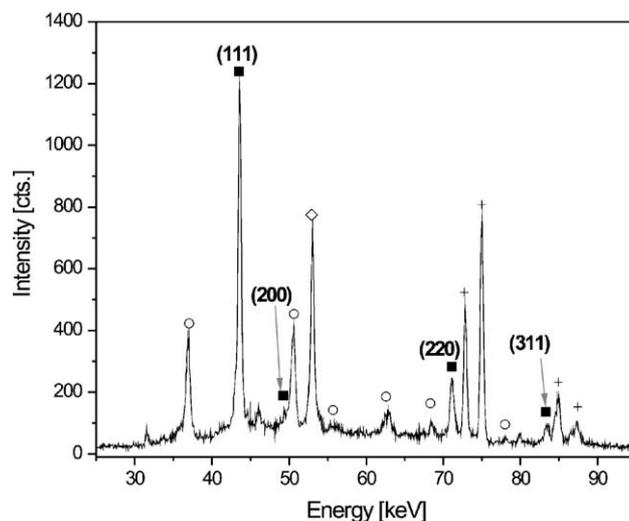


Fig. 1. Diffraction pattern of diamond–SiC sample obtained at 8 GPa and 1360 K. The acquisition time was 60 s. ■— β -SiC, ◇—diamond (111) reflection, ○—hBN. The remaining unmarked peaks are from Al_2O_3 and other materials constituting the cell.

The degree of the reaction is defined as

$$\alpha(t) = \frac{I(t)}{I(\infty)} \quad (1)$$

where $I(t)$ is the integrated intensity of the diffraction peak at time t and $I(\infty)$ represents the integrated intensity of the same peak after the reaction ended. Time dependencies of $\alpha(t)$ calculated from intensities of the (111) and (220) reflections are shown in Fig. 2. Within experimental errors the two curves are identical, see insert in Fig. 2. The other two reflections, (200) and (311) also gave similar dependencies. However scatter in the data was larger because these peaks had smaller intensities and partially overlapped with other peaks, which led to increased error in determining their intensities.

Early models of solid state reactions focused on spherical particles. Later models included corrections for the reduction of particle size due to consumption of the reagents. Other improvements took into account different densities of the reagents and the product, stoichiometry, shape of the particles, and other factors [24,25]. The most general model has been developed by Avrami [26] and Erofeev [27]. It assumes that the reaction starts at a limited number of nucleation sites which are randomly distributed throughout the volume. The growth of the product is uniform and isotropic. As the product grows new nucleation sites are formed and the product growing on different sites is allowed to coalesce. The general form of the equation can be represented by:

$$\alpha(t) = 1 - \exp[-(k \cdot t)^m] \quad (2)$$

where k is the reaction rate, and m is a parameter referred as reaction exponent. For the diffusion controlled reaction this parameter varies between 2.5 and 1.5 for three-dimensional

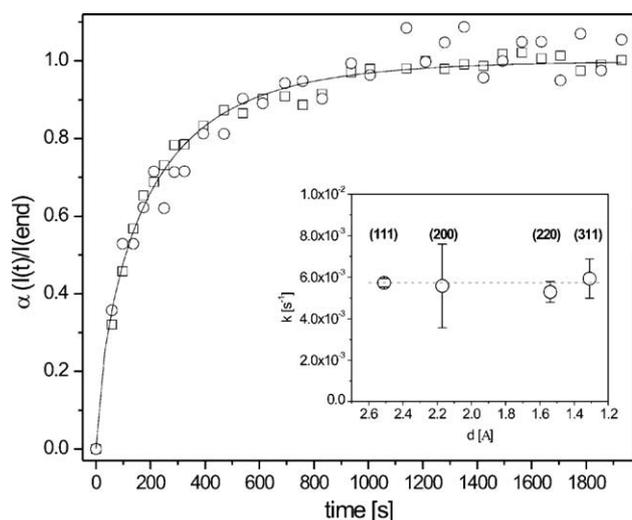


Fig. 2. Plot of degree of reaction, α , vs. time. \square —(111) reflection, \circ —(220) reflection of β -SiC for the run at 1357 K in ‘Experimental series 2’. Solid line represents the best fit of the Avrami–Erofeev equation to experimental data for the (111) reflection. The inset shows the error bars in reaction rate, k , determination for different reflections of SiC.

Table 1

Kinetics parameters obtained from the Avrami–Erofeev model by fitting experimental data to Eq. (2)

	T [K]	k [s^{-1}]	m
Series 1 (diamond 30–40 $\mu\text{m} + \text{Si}$)	1200	8.00×10^{-5}	1.06
	1278	4.20×10^{-4}	0.98
	1319	8.50×10^{-4}	1.04
Series 2 (diamond 5–10 $\mu\text{m} + \text{Si}$)	1193	0.25×10^{-3}	1.24
	1305	1.98×10^{-3}	0.82
	1357	5.73×10^{-3}	0.75
	1415	15.00×10^{-3}	1.23
Series 3 (diamond 0–50 nm + Si)	1283	1.70×10^{-4}	1.01
	1386	5.60×10^{-4}	1.26

growth; between 2 and 1 for two-dimensional growth; and between 1.5 and 0.5 for one-dimensional growth [25].

The fit of α values for the (111) reflection to the Avrami–Erofeev model is very good, see Fig. 2. The fitting parameters obtained for other reflections of the sample kept at the same thermodynamic conditions were practically identical. Since the (111) reflection of SiC gives a signal that is stronger than for other peaks its intensity can be determined with a better precision and consequently the fitting procedure is more accurate than for the other peaks. In Table 1 we list results obtained for this reflection. The fitting parameter, m , was independent of crystal size and temperature and varied between 0.75 and 1.25.

By plotting logarithm of the rate constant vs. reciprocal temperature and fitting the data to a straight line we estimated the activation energy. Fig. 3 illustrates the fitting of the data obtained in ‘Series 2’ for diamond powder of grain size 5–10 microns. In Table 2 we list the activation energies obtained for all three experimental runs. In parenthesis are estimated errors, which mainly come from the errors in temperature determination. For micron size crystals (Series 1 and 2) the activation energies are practically identical, but a somewhat smaller value was obtained for

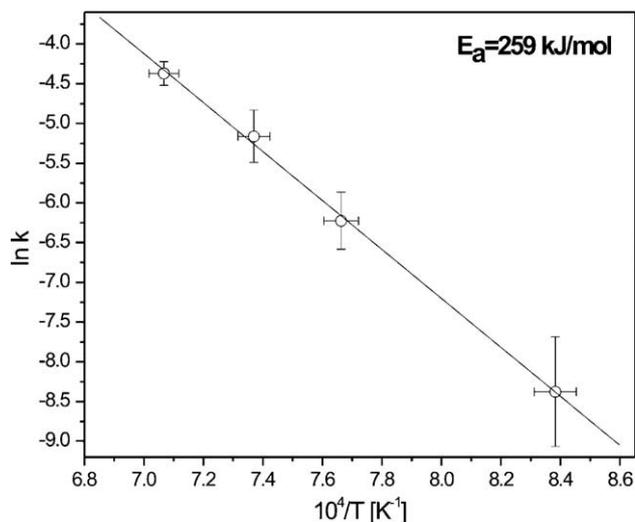


Fig. 3. Arrhenius plot of the reaction rates obtained in ‘Experimental series 2’ for diamond powder of average grain size 5–10 μm .

Table 2

Activation energy values obtained for different runs by fitting reaction rates to the Arrhenius equation

	E_a [kJ/mol]
Experimental series 1 (diamond 30–40 $\mu\text{m} + \text{Si}$)	261 (50)
Experimental series 2 (diamond 5–10 $\mu\text{m} + \text{Si}$)	259 (27)
Experimental series 3 (diamond 0–50 nm + Si)	170 (40)

The numbers in parenthesis reflect uncertainty in activation energy determination; they are caused by ± 10 K precision in temperature measurements.

‘Series 3’. The precision of reaction rate determination is very good in all cases, see for example the $\ln k$ versus $1/T$ dependence in Fig. 3, where all data points are very close to a straight line. The main source of errors is the uncertainty in temperature determination, which was ± 10 K in all experiments. Although only two points were available in ‘Series 3’, they were recorded with high accuracy allowing determining the activation energy. Please note that the precision in the activation energy determination was similar for various experiments.

So far we made the following observations: (1) similar values of reaction rates were obtained for different reflections; (2) the same activation energy was found for the 30–40 and 5–10 μm crystals; (3) the reaction exponent, m , was close to 1 for all runs. All these observations indicate that we studied diffusion-controlled reaction resulting in a two-dimensional growth. Additionally, the temperatures selected for the runs were all close to the melting point of silicon where the reaction was expected to proceed slowly; slow enough to collect a sufficient number of experimental points. Despite these efforts, in each run the first data point indicated that a significant amount of SiC had already been present, and covered the diamond crystallites entirely. The heating process was very fast and depending on the desired temperature it took less than 10–20 s to reach that value. Another 30 s were necessary to record the signal. Thus, the first points in the $\alpha(t)$ plots were taken after about 50 s from the start of heating in the experiment. For example, we estimated that the amount of SiC corresponding to the first point was sufficient to cover surface of all diamond crystals with 0.35 μm thick SiC layer. At the conclusion of the reaction the SiC layer was 1–1.5 μm thick. It means that in our experiments we did not study the initial stages of the reaction when diamond crystals were in contact with liquid silicon, but rather the stage in which these two phases were separated by a SiC layer. Further growth of the product could proceed by diffusion of carbon atoms from the diamond phase through the SiC layer to liquid silicon and/or diffusion of silicon atoms toward diamond. The thickness of SiC at different times of the reaction was estimated based on the assumption that diamond particles are in the form of a sphere and that SiC is growing uniformly on the surface of these spheres. The quantity of diamond and SiC in the sample was determined from the relative intensity ratio of diamond (111) and SiC (111) peaks.

The values of 600–900 kJ/mol for the activation energy for self-diffusion of carbon and silicon in β -SiC reported in Refs. [13–16] are too large to explain the reaction rates measured in this study. However, it is possible that the diffusion proceeds not through bulk crystals but through grain boundaries. The activation energies for grain boundary diffusion are about 40% lower than those for the bulk diffusion [14]. The estimated values for grain boundary diffusion are still larger than the activation energies found in this study. But one has to take into account the fact that all previous studies on self-diffusion of silicon and carbon in silicon carbide were done on single crystals or polycrystalline samples. In our experiments grain boundaries account for a significant fraction of the sample volume, and atoms residing in grain boundaries, which may have thickness of about 0.5 nm, define the effective diffusivity [28]. Under high pressure–high temperature conditions extensive grain boundaries are under considerable strain and relatively loosely packed. Dislocations present in the bulk and grain boundary regions will greatly enhance diffusivity of both atoms. Furthermore, it is reasonable to assume that during the experiments the structure of dislocations was dynamic which further facilitated the diffusion process.

For ‘Series 3’ we used nano-size diamond crystals, 0–50 nm. The calculated activation energy of 170 ± 40 kJ/mol, was lower than for micron size crystals, probably reflecting the fact that silicon carbide had nanocrystalline structure. From line shape analysis we estimated that average crystallites were smaller than 10 nm. Presence of nanocrystalline SiC is probably a consequence of high population of nucleation sites. Nucleation sites are surface defects and due to large surface area their population is also large [9]. Under high pressure conditions population of disloca-

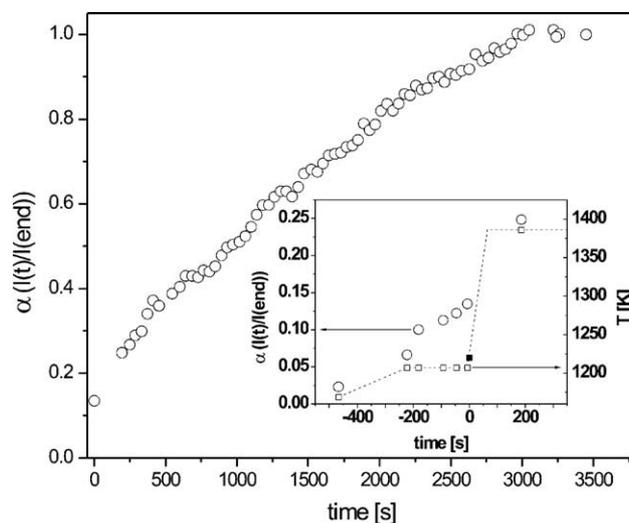


Fig. 4. Plot of degree of reaction, α , vs. time for the (111) reflection of β -SiC in ‘Experimental series 3’ at 1386 K. The insert represents the β -SiC formation at the temperature about 50 K below the melting point of silicon; \circ —degree of reaction, \square —temperature, \blacksquare —melting point of silicon. The broken line represents the history of temperature increase. Zero on the time axis corresponds to the time when silicon melted (1220 K at 7.8 GPa).

tions in nanostructured SiC may increase by one to two orders of magnitude [10,29]. A combination of the nanocrystalline structure, severe surface strain, and large population of dislocations may account for the lower energy of activation observed in ‘Series 3’.

Analysis of data obtained for nanosize diamonds revealed that the reaction started about 50 K below the melting point of silicon, see insert in Fig. 4. No such effect has been observed for micron-size diamonds. According to the core-shell model [30,31] nanocrystals consist of a uniform core surrounded by a surface shell. Crystallographic structure of the surface shell is the same as that of the core but interatomic distances in the surface layer are different than those in the center of the crystal. For diamond the surface layer is known to have a slightly expanded structure with longer interatomic distances [30]. Less dense surface layer of nanosize diamond crystals increases their reactivity because the bonds are deformed and strained. Thus, the reaction starts even though silicon is still in the solid phase.

4. Conclusion

Formation of silicon carbide during high-pressure/high-temperature reaction between diamond and silicon starts at the defect sites on the surface of diamond crystals. SiC grows both in lateral and vertical directions and as SiC islands overlap they quickly cover all surfaces of diamond crystals and further growth can be well characterized by the diffusion mechanism. This diffusion-controlled growth could be regarded as a two-dimensional growth. Dislocations and grain boundaries with strained bonds provide pipelines for silicon and carbon transport from one phase to another. For nanosize diamonds the activation energy was significantly lower. In that case the silicon carbide layer had nanocrystalline structure and the grain boundaries accounted for a significant fraction of produced SiC phase. We expect that these conclusions are applicable to other reactions conducted at normal pressure and resulting in production of various carbide or silicide ceramics.

In the case of nanosize diamond the reaction started below the melting point of silicon. No such effect was observed for micron size diamonds. To the best of our knowledge this effect has never been observed before. It was explained in terms of expanded structure of surface layer of nanosize diamond crystals, which enabled them to readily react with silicon. It is worth noticing that recently, we observed that other forms of carbon (carbon nanotubes, fiber) also start reacting with silicon at temperatures below its melting point [32].

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