

Diamond-silicon Reaction at High Pressure –High Temperature Kinetics of SiC Formation

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Introduction

Nowadays there is a growing interest in diamond composites due to their huge variety of applications in diverse fields, e.g. heat sinks for electronic equipment, engineering components, grinding, cutting, machining, mining, drilling.[1-6] Typically the starting materials are silicon powder and diamond crystals of sizes ranging from tens of microns to nanometers.

In the last years several studies on the sintering process and the mechanical properties of diamond-SiC composites have been reported.[7-9] The silicon carbide is formed by the direct reaction of diamond and melted silicon, and starts on the surface of diamond crystals, near the surface defects,[10] which act as nucleation sites for SiC. Investigations of solid state reactions at high pressures and high temperatures are challenging, but due to recent developments in equipment and detection techniques studies of this type are more and more accessible and the focus has gradually shifted toward solid state reactions. The present study was motivated by the lack of information on the kinetics of formation of diamond-SiC composites.

Methods and Materials

In situ, energy-dispersive x-ray diffraction experiments were conducted in the DIA-type cubic anvil apparatus [11] at the bending magnet beamline 13-BM-D of the Advanced Photon Source (APS) at Argonne National Laboratory. Temperature was measured by a W/Re25%–W/Re3% thermocouple, and pressures were calculated from Decker's equation of state for NaCl.[12] The incident x-ray beam, collimated to dimensions of 100 $\mu\text{m} \times 100 \mu\text{m}$, and the scattered light was collected in an energy range up to 100 keV with a Ge solid-state detector. Typical duration for collecting a diffraction pattern with acceptable resolution was 30-60 s.

The kinetics of the reaction was investigated using the nucleation and growth model developed by Avrami and Erofeev.[13,14] It is assumed that the reaction starts at randomly distributed nucleation sites and that the growth is uniform and isotropic. Additionally, the coalescence and ingestion of new nuclei is taken in consideration. The degree of reaction is defined as the integrated intensity of the diffraction peak at time t divided by the integrated intensity of the same peak after the reaction ended, $\alpha(t)=I(t)/I(\infty)$. The reaction can be modeled by the following equation: $\alpha(t)=1-\exp[-(kt)^m]$, where k is the reaction rate and m the reaction exponent.

Synthetic diamond powders with crystal sizes of 30-40 μm from General Electric Co. and silicon powders of 1-20 μm from Alfa Aesar were mixed in the 1:1 weight ratio in acetone using a magnetic stirrer. The mixing time used was 24 hours. The goal of this process was to obtain a uniform mixture of the two

powders, namely diamond and silicon. After the mixing, acetone was evaporated.

Results

Three experiments were run at different temperatures: 1200, 1278 and 1319 K. The degree of the reaction as function of time of reaction is illustrated in Fig. 1.

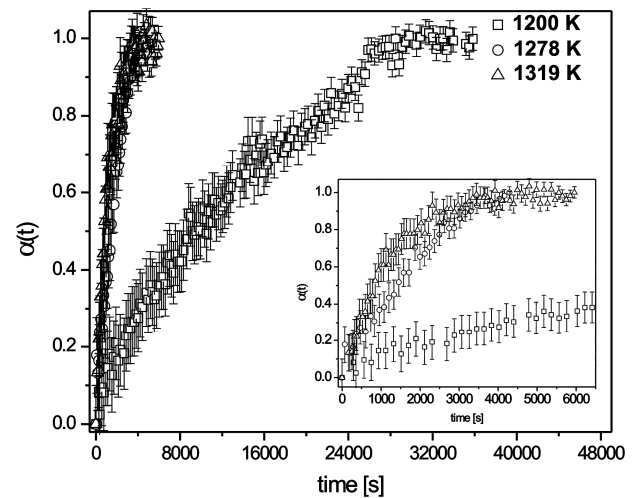


Fig. 1. Plot of the degree of reaction, α , vs. time for the (111) reflection of β -SiC. The inset represents the same runs, on a smaller time scale.

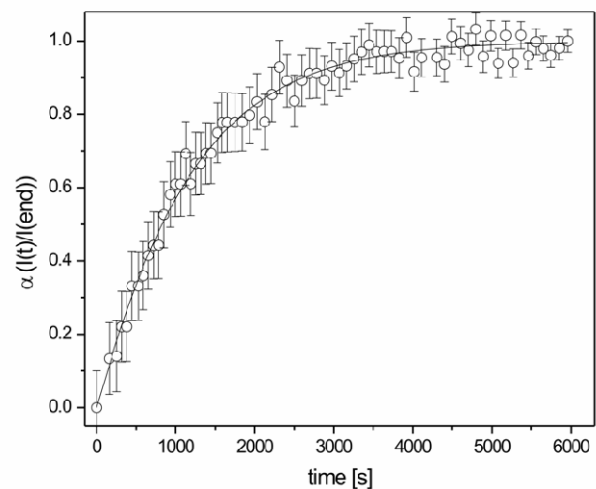


Fig. 2. Plot of the degree of reaction, α , vs. time for the (111) reflection of β -SiC for $T=1319 \text{ K}$, and 30-40 μm diamond powder. Solid line represents the best fit of the Avrami-Erofeev equation to experimental data.

The Avrami-Erofeev equation was used to fit the kinetics data for the (111) reflection of β -SiC in order to determine the reaction rate for each individual run. An example of the fitting quality is shown in Fig. 2. The quality of the fit was similar for the other two runs. The values of the reaction rate, k , and reaction exponent m , are given in Table 1.

Table 1. Kinetics parameters of the SiC formation from diamond and silicon presursors.

Sample	T [K]	k [s ⁻¹]	Δk [s ⁻¹]	m [-]	Δm [-]
K5	1200	8.0×10^{-5}	2.20×10^{-5}	1.06	0.16
K6	1278	4.2×10^{-4}	1.55×10^{-4}	0.98	0.09
K7	1319	8.5×10^{-4}	2.95×10^{-4}	1.04	0.08

By plotting logarithm of the rate constant vs. reciprocal temperature and fitting the data to a straight line the activation energy for SiC formation from diamond and melted silicon can be estimated, see Fig. 3. The activation energy obtained in the present experiment is 261 ± 71 kJ/mol. The present value is in good agreement with *in-situ* data obtained at National Synchrotron Light Source and *ex-situ* experiments from a toroidal anvil, at similar pressures and temperatures.

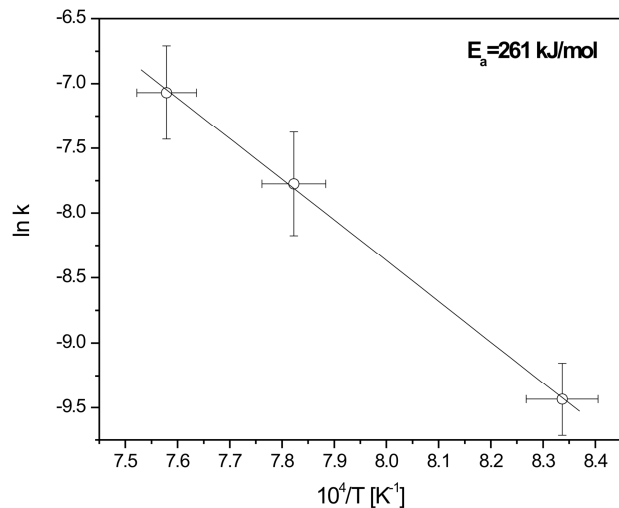


Fig. 3. Arrhenius plot of the SiC reaction rates obtained from diamond powder of average grain size 30-40 microns.

Discussion

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. However, in each run the first data point indicated that a significant amount of SiC was already produced, with a thickness of about 0.3 μm around diamond crystallites. Due to the fast process of nucleation we were not able to study this stage of the reaction. The second stage of the reaction proceeds through the diffusion of silicon atoms toward diamond or the diffusion of carbon atoms from the diamond phase through the SiC layer to liquid silicon.

Different authors provided different values of activation energies for diffusion of silicon and carbon atoms through SiC, of 600 kJ/mol to 900 kJ/mol.[15-18] These values 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.[16] 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 the 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.[19] Under high pressure - high temperature conditions the extensive grain boundaries are under considerable strain and relatively loosely packed. Dislocations present in the bulk and grain boundary dislocations will greatly enhance diffusivity of both atoms. Furthermore, it is reasonable to assume that during the experiments structure of dislocation was dynamic which further facilitated the diffusion process.

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