Hydrothermal behavior of diamond

Yury Gogotsi a, Thorsten Kraft b,*, Klaus G. Nickel b, Mary Ellen Zvanut c

a University of Illinois at Chicago, Department of Mechanical Engineering, 842 West Taylor Street, Chicago, IL 60607-7022, USA
b Eberhard-Karls-Universität Tübingen, Institut für Mineralogie, Petrologie und Geochemie, Wilhelmstr. 56, D-72074 Tübingen, Germany
c University of Alabama at Birmingham, Department of Physics, 310 Campbell Hall, 1300 University Blvd, Birmingham, AL 35294-1170, USA

Received 20 February 1998; accepted 4 May 1998

Abstract

The interaction of two diamond powders and synthetic diamond single crystals with H2O has been studied in the temperature range of 650–850 °C under pressures up to 500 MPa. The reaction products were characterized using electron paramagnetic resonance (EPR), Raman and Fourier transform infra-red spectroscopy, X-ray diffraction, scanning electron microscopy, transmission electron microscopy (TEM) and selected area diffraction. A noticeable interaction of fine grain diamond powders with H2O starts at approx. 700 °C while single crystals are stable up to 800 °C. At 800–850 °C, etching pits appear on the single crystal diamond surface. Thermodynamic calculations predict the formation of hydrogen, carbon oxides and hydrocarbons. Formation of graphitic carbon via the fluid is observed. Redeposition of nanocrystalline diamond and healing of crystal defects are suggested by TEM and EPR investigations. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Diamond; Carbon; Hydrothermal fluid; Water; Dissolution

1. Introduction

There exists evidence for the hydrothermal origin of natural graphite, poorly crystallized carbons and diamond [1–3]. A fast growth of natural diamond seed crystals embedded in graphite in the presence of water was observed experimentally at 7.7 GPa and 2200 °C [4]. On the other hand, at 5.5 GPa and 1000 °C interaction of water with diamond single crystals resulted in etching of the crystals and deposition of non-diamond carbon [5]. At 5 GPa and 1500 °C, complete dissolution of diamond occurs [6]. These experimental investigations were carried out above the Berman–Simon p–T line in the stability field of diamond. However, formation of diamond from different precursors with and without diamond seeding has been reported under hydrothermal conditions at pressures <500 MPa and temperatures <1000 °C [7–14]. This is far below the Berman–Simon p–T line, i.e., in the stability field of graphite. Based on these findings and some geochemical hints, Szymanski [8] suggested the presence of an additional field in the p–T diagram of carbon, defining a region of metastable diamond nucleation and growth under hydrothermal conditions [14]. However, detailed knowledge about hydrothermal behavior of carbon allotropes in this p–T range is essential for optimization of growth parameters. While there are publications on the behavior of graphite under hydrothermal conditions [15], only a very few deal with diamond [6,9]. Ref [9] reports no effect of water on single crystals after 24 h at 800 °C and 100 MPa, but significantly enhanced diamond X-ray diffraction (XRD) reflections after hydrothermal treatment of mixtures of diamond seeds and glassy carbon for 72 h at 1000 °C and 144 MPa. However, diamond crystals could not be detected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM); thus, the formation of extremely small (few nm) diamond crystals in fairly high concentrations was suggested.

Here, we report our investigations of diamond powders and crystals that were treated in supercritical water at 650–850 °C under pressures of up to 500 MPa.

2. Experimental

Synthetic diamond single crystals of 1–2 mm size about 20 mg (0.1 carat, General Electric, USA), syn-
thetic microcrystalline diamond powder with a narrow grain size distribution between 2 and 3 μm (Institute of Superhard Materials, Ukraine) and natural nanocrystalline diamond powder with a grain size of ≤0.1 μm (Rudolf Spring AG, Switzerland) were used in this study. Some experiments were carried out in the presence of graphite powder of spectral purity (Ringdorf, Germany).

Samples were placed with distilled water in gold capsules of 3 or 5 mm in diameter and about 25 mm in length. The gold capsules were welded to prevent loss of material and heated in tube-type, cold seal pressure vessels made of René 41 superalloy [16].

The condensed reaction products were analyzed using XRD (CuKα radiation), SEM and Raman spectroscopy (LabRam micro-Raman spectrometer, Dilor, France, excitation at 632.8 or 514.5 nm using He-Ne or Ar-ion lasers). Selected samples were analyzed using TEM, selected area diffraction (SAD) and electron paramagnetic resonance (EPR). EPR is a versatile method for analyzing defects in diamonds [17].

Room temperature EPR was performed at 10 GHz microwave frequency. The g tensor and nuclear hyperfine tensor (A), were obtained by computer simulation using standard powder pattern techniques. Defects were identified by comparing the measured g and A tensors with those found in the literature. The total concentration of centers was determined by comparison of the diamond powder spectra to that of a standard, weak pitch. A uniform concentration of centers is assumed. Thermodynamic calculations were carried out using ChemSage-4.0 [18].

3. Results and discussion

3.1. Thermodynamic calculations

The thermodynamic analysis of the system reveals the dependencies of the formation of diamond on T, p and the ratio C:H₂O. The calculations here have been performed using diamond as the only condensed species to simulate its higher thermodynamic reactivity compared with graphitic carbon. All of the major gas species of COₓ, CHₓ and CHₓOᵧ have been considered.

The system C–H–O is best understood from the pressure dependence. In Fig. 1 we have chosen a very wide range of pressures to illustrate that the basic control is given by the behavior of CO and H₂, which are the equilibrium species at low pressure. It is obvious from Fig. 1 that a 1:1 mixture of CO and H₂ converts at higher pressures to a four-species assemblage involving CO₂, CH₄, H₂O and diamond.

The reason for this is that two independent reactions may be formulated:

\[ \text{CO} + \text{H}_2 = \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{CO}_2 \]  
\[ \text{CO} + \text{H}_2 = \text{Diamond} + \text{H}_2\text{O} \]  

Both reactions have the same nominal pressure dependence as 2 mols of gas are converted into 1 mol of gas. The energetic characteristics are also very similar (Fig. 2), i.e. the \( \Delta G \) of both reactions at 100 MPa is similar in the temperature range of interest with Eq. (1) dominating at higher and Eq. (2) at low temperatures.

Thus the overall reaction governing the system to a first approximation is:

\[ 2\text{CO} + 2\text{H}_2 = \frac{1}{2} \text{CH}_4 + \frac{1}{2} \text{CO}_2 + \text{Diamond} + \text{H}_2\text{O} \]  

which explains why \( \text{Diamond} \) is not used up at a C:H₂O ratio of C:H₂O 1:1 as Eq. (2) would indicate.

![Fig. 1. Calculated pressure dependence of phase equilibria in the diamond–water system for a condition C:H₂O = 1:1 at 700 °C. Diamond has been used as the only condensed and solid species.](image1)

![Fig. 2. Gibbs free energies of competing reactions in the C–H–O system at 100 MPa.](image2)
The influence of temperature is shown in Fig. 3. At 100 MPa the individual contributions of Eq. (1) and Eq. (2) in Eq. (3) are clearly visible as the equilibrium amounts run in the pairs CH$_4$+CO$_2$, C$_{diamond}$+H$_2$O, and CO+H$_2$. At higher temperatures there is a deviation, which stems from the influence of the Boudouard equilibrium.

$$2CO = C_{diamond} + CO_2$$  \hspace{1cm} (4)

Clearly higher temperatures will tend to oxidize diamond to yield CO.

Looking more closely at Eq. (3) then gives us the understanding for the dependence of the equilibrium amount of species on the C:H$_2$O ratio. An externally increased amount and pressure of H$_2$O will yield lower amounts of CH$_4$, CO$_2$ and diamond and higher amounts of CO and H$_2$ simply to maintain the equilibrium constant K of Eq. (3). The result is a decrease in the equilibrium amount of diamond with decreasing C:H$_2$O-ratio. Accordingly, also the temperatures for the elimination of diamond from the assemblage decrease with decreasing C:H$_2$O-ratio (Fig. 4).

Repeating the calculation with the data for graphitic carbon gives a similar result with shifted boundaries (e.g. we need a still lower C:H$_2$O ratio of approximately 1:2 to eliminate C at 700 $^\circ$C).

Summarizing, the hydrothermal behavior of diamond is predicted to depend crucially on temperature and C:H$_2$O ratio with a strong interaction of both variables, but is more or less pressure independent in the range of supercritical water. The temperature of complete diamond gasification decreases drastically with increasing amounts of incoming water but is also increasing to high temperatures as the C:H$_2$O ratio exceeds 1 and formation of higher hydrocarbons have to be taken into account.

Naturally the equilibrium calculations do not consider kinetic limitations, which we have investigated experimentally below.

### 3.2. Nanocrystalline ($<0.1$ µm) diamond powder

Experiments were carried out at 650–850 $^\circ$C, under pressure of 100 –300 MPa. Some experiments were conducted in the presence of graphite.

Dissolution of nanocrystalline <0.1 µm diamond powder under hydrothermal conditions is apparent at 700 $^\circ$C. Significant evolution of gas was observed after 96 h at 700 $^\circ$C under 300 MPa, but even after a long high-temperature treatment (94 h, 850 $^\circ$C, 200 MPa) complete dissolution does not occur. With increasing temperature and reaction time the sharpness of the Raman band of diamond increases significantly, as indicated by the decrease of its full width at half maximum (FWHM). At the same time, the band moves from the downshifted value of 1323 cm$^{-1}$ to 1332 cm$^{-1}$, which is the normal value for diamond (Fig. 5). This can be explained by ordering and healing of the diamond structure. With increasing temperature and reaction time the amount of graphitic carbon increases. In addition to the indication by Raman spectroscopy, the (002) reflection of graphite was observed in the XRD pattern (Fig. 6). A SEM study of a sample treated for 111 h at 800 $^\circ$C under 120 MPa showed no significant change after the treatment. However, the magnification of $\times$10 000 was not sufficient to resolve fine changes in the particle shape. At the same time, TEM micrographs of hydrothermally treated samples showed sharpened particles (Fig. 7). This can result from either etching or recrystallization of defective and disordered diamond nanoparticles.

EPR spectra (Fig. 8) of nanocrystalline <0.1 µm diamond were measured before and after a hydrothermal treatment at 750 $^\circ$C. Table I lists the concentration of...
the two EPR centers observed in these samples. One is due to substitutional nitrogen (the P1 center) and the other is typically attributed to broken carbon bonds. The P1 center is identified by the three-line signal with isotropic $g$ value of 2.0024 and hyperfine tensor, $A_{\text{para}}=40.5$ G and $A_{\text{perp}}=28.9$ G [19]. The broken bond signal may be partially characterized by $g=2.0027$ and $A_{\text{para}}=225$ G and $A_{\text{perp}}=112$ G. Although a definitive assignment cannot be given, the EPR parameters are similar to that of the N5 center which represents broken bonds at the surface of diamond [20]. Comparison of the unannealed and annealed material suggests that an additional signal with $g=2.002$ is superimposed on the surface signal. The $g=2.002$ signal, most likely, is due to broken carbon bonds located throughout the volume of the nanocrystals. Such a signal is commonly observed in bulk crystalline diamond as well as polycrystalline diamond films [21]. No attempt has been made to
Table 1
Results of EPR analysis

<table>
<thead>
<tr>
<th>Powder</th>
<th>Treatment</th>
<th>Concentration of EPR centers [10^18/g]</th>
<th>Substitutional N</th>
<th>Broken C-C bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size</td>
<td>T [°C]</td>
<td>t [h]</td>
<td>p [MPa]</td>
<td></td>
</tr>
<tr>
<td>&lt;0.1 μm</td>
<td>as received</td>
<td>100</td>
<td>300</td>
<td>1.3</td>
</tr>
<tr>
<td>&lt;0.1 μm</td>
<td>750</td>
<td>100</td>
<td>300</td>
<td>2.4</td>
</tr>
<tr>
<td>2-3 μm</td>
<td>as received</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>2-3 μm</td>
<td>700</td>
<td>172</td>
<td>500</td>
<td>4.5</td>
</tr>
<tr>
<td>2-3 μm</td>
<td>750</td>
<td>172</td>
<td>500</td>
<td>4.5</td>
</tr>
</tbody>
</table>

resolve the surface and bulk broken bond signals; therefore, the concentration quoted in Table 1 represents the sum of the two centers. A third line, representing less than 1% of the total intensity, is present in the nanocrystalline <0.1 μm material, but it is not sufficiently well resolved for any assignment.

In nanocrystalline <0.1 μm diamond powders the majority of the total intensity of the EPR signals is attributed to damage centers. The broken carbon bond concentration decreased by a factor of 2 following hydrothermal treatment, while the concentration of the nitrogen centers remained the same within the estimated uncertainty. This behavior can be explained by two mechanisms which work together: on the one hand, we might have a gradient of defect concentration in each grain of the powder with the defects accumulated near the surface which is leached away first. On the other hand, the defect concentration may differ considerably from grain to grain. Assuming perfect grains being kinetically more stable than imperfect grains, grains with a high defect concentration will dissolve first. This mechanism would also explain the overall increase of the concentration of nitrogen centers by hydrothermal treatment when assuming a homogeneous and constant nitrogen substitution in well ordered grain domains, but a low concentration of nitrogen paramagnetic centers in highly defective particles by formation of nitrogen-hydrogen bonds.

According to the above results, dissolution of small and disordered particles and surfaces is strongly preferred. Formation of graphite particles and healing of nanocrystalline diamonds can be explained by redeposition of carbon from the hydrothermal fluid.

Mixtures of graphite (95%) and nanocrystalline <0.1 μm diamond (5%) were hydrothermally treated in the temperature range between 700 and 800 °C under 200 MPa for 72 h. It was observed that both graphite and diamond powders react with water. The intensities of Raman and XRD peaks of diamond decrease compared with those of graphite. Thus, the reaction of natural <0.1 μm nanocrystalline diamond with the supercritical water must be faster than that of graphite.

3.3. Microcrystalline (2-3 μm) diamond powder

The experiments were carried out between 700 and 850 °C at 100-500 MPa. Significant dissolution with weight loss and gas formation was first observed after a week at 750 °C and 500 MPa. Complete dissolution was never observed. TEM observations suggest the formation of nanocrystalline diamond (Fig. 9). After treatment at 850 °C, formation of graphite was clearly indicated by micro-Raman spectroscopy and combination of TEM and SAD (Fig. 10). EPR-investigations (Fig. 8, Table 1) showed that 80% of the total intensity of the EPR signal from the microcrystalline 2-3 μm diamond powder is attributed to substitutional nitrogen and 20% to broken carbon bonds. Hydrothermal treatment did not cause any significant changes, but it seems that it increases the substitutional nitrogen signal by approximately 50%.

Comparing the EPR spectra of microcrystalline

Fig. 9. TEM micrographs of small particles on the surface of microcrystalline diamond powder after hydrothermal treatment for 172 h at 750 °C under 500 MPa.
Below 800 °C, no alterations of the diamond crystal surface have been observed. However, after 15 h under 100 MPa at this temperature, formation of etching pits has been found. SEM micrographs (Fig. 11) showed the formation of trigons of several microns in size which are clearly deeper than those on the untreated surfaces. After 6 days at 800 °C under 250 MPa, a significant weight loss of approx. 7% was observed. In contrast, in the presence of nanocrystalline diamond powder or graphite, no change of the weight of the diamond single crystals has been observed, even after 6 days at 800 °C under 300 MPa. In some cases, deposition of carbon films on the walls of the gold capsules was observed under these p-T conditions, indicating the saturation of the fluid with carbon in thermodynamic equilibrium. Thus, preservation of monocrystalline diamond can be achieved by saturation of the fluid with carbon. This is in accordance with our thermodynamic calculations.

### 4. Summary and conclusions

The hydrothermal behavior of diamond depends strongly on the grain size. Disordered areas and surfaces are primary affected. While monocrystalline diamond of 1–2 mm size is kinetically stable up to 800 °C, dissolution of microcrystalline 2–3 μm and nanocrystalline <0.1 μm diamond powders starts at 750 and 700 °C, respectively. Complete dissolution of diamond was never observed. This is in agreement with thermodynamic calculations for high C:H ratios but can also be attributed to slow kinetics. However, after saturation of the liquid, redeposition of carbon may occur. Precipitation of graphitic carbon and healing of defective diamond crystals is clearly indicated. Some data suggest that nanocrystalline diamond may be formed from the fluid.
The resistance of diamond single crystals and microcrystalline diamond against dissolution under hydrothermal conditions can be increased by presaturation of the fluid with carbon. This can be done by using carbon of a lower kinetic and/or thermodynamic stability, such as graphite or natural <0.1 μm diamond powder. Stabilization of natural <0.1 μm nanocrystalline diamond powder by well-crystallized graphite was not observed.

The fact that no graphitization of the diamond surface was found in the whole range of temperature-pressure-concentration conditions under study indicates the possibility of the hydrothermal growth of diamond. However, epitaxial diamond growth was not observed. Thus, an intricate set of conditions not employed in the investigation thus far must be necessary for diamond synthesis from supercritical fluids.

Acknowledgement

Thanks are due to Dr. G.E. Khomenko (Institute of Materials Science, Kiev, Ukraine) and Dr. J. Plitzko (MPI für Metallforschung, Stuttgart, Germany) for help with TEM investigations. Deutsche Forschungsgemeinschaft (grant Nr 299/4) supported this research.

References