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# *In situ* x-ray diffraction of graphite–diamond transformation using various catalysts under high pressures and high temperatures

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## Abstract

*In situ* x-ray diffraction studies of graphite–diamond transitions with various solvent catalysts under high pressures and high temperatures at the Photon Factory and SPring-8 are reviewed. By combining synchrotron radiation and a large-volume multi-anvil high-pressure apparatus, real-time observations have been successful in the diamond formation process with the help of various catalysts, such as transition metals, carbonates and aqueous fluids. The experimental procedures and the technical details are described. The diffraction data with various catalysts are shown and the problems and limitations of this method are discussed.

## 1. Introduction

Many studies have investigated diamond synthesis under high pressures and high temperatures since a General Electric team first reported their findings [1, 2]. Today, vast quantities of diamonds are synthesized using industrial high-pressure technology. However, many questions, such as the role of the catalyst, kinetics of the reaction and the possibility of a metastable phase, are still unanswered regarding the diamond formation process under high pressures. Previous experimental data based on the recovered specimens in ambient conditions do not provide enough information to answer these questions, but real-time *in situ* experiments in which the diamond formation process is directly observed under high pressures and temperatures are indispensable. In addition, it has been reported that inorganic compounds, such as carbonates and hydroxides, are effective catalysts for forming diamonds [3, 4].

The relationship between these non-metal catalysts and diamond formation in the Earth's interior has interested many geoscientists [5]. Various interpretations could be made of the experimental results, but their validity is unknown. In this case also, *in situ* observations should provide significant information. Although *in situ* experiments used to be very difficult since diamonds are formed in a thick and heavy high-pressure vessel, very powerful x-rays from a synchrotron radiation source have changed the situation.

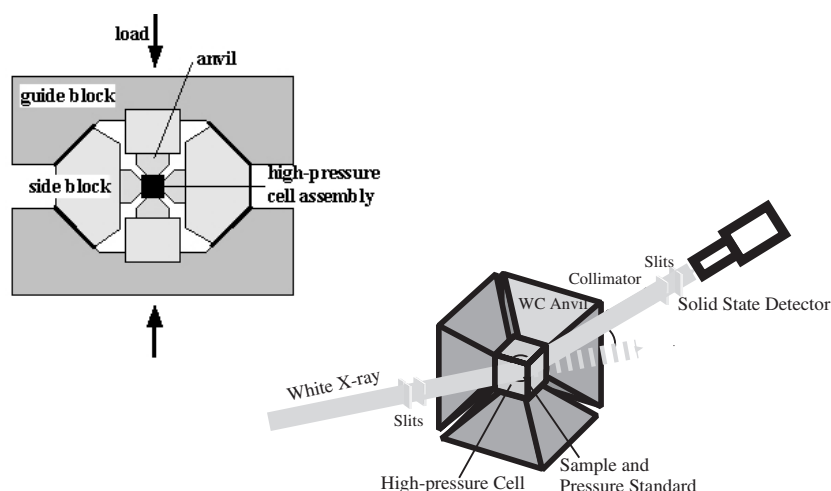
Yamaoka *et al* [6] pioneered *in situ* experiments using synchrotron radiation, but detailed information about the diamond formation process was not successfully obtained. This is mainly because the x-ray intensity was not strong enough due to their use of a bending magnet source at the second-generation synchrotron radiation ring. Owing to the higher-intensity x-rays from third-generation rings, several new *in situ* observations of diamond synthesis have been recently reported [7–10]. Here, our *in situ* x-ray diffraction studies of graphite–diamond transitions with various solvent catalysts under high pressures and high temperatures at the Photon Factory and SPring-8, which combined synchrotron radiation and a large-volume multi-anvil high-pressure apparatus, are reviewed. Many technical difficulties were overcome and now real-time observations of the graphite-to-diamond conversion process have been successfully made using various solvent catalysts such as conventional transition metals, carbonate materials and aqueous fluids. In this paper, the experimental procedure is described and the technical details are explained. The diffraction data with various catalysts are shown and the problems and limitation of this method are discussed.

## 2. Experimental procedure

Three large-volume multi-anvil high-pressure apparatuses, which are installed on the beamlines of the synchrotron radiation facilities; 'MAX90' placed on beamline BL14C at the Photon Factory in Tsukuba, Japan [11] and 'SMAP2' on beamline BL14B1 and 'SPEED1500' on beamline BL04B1 at the SPring-8 in Harima Science Garden City, Japan, have been used for the experiments [12, 13].

'MAX90' and 'SMAP2' are hydraulic presses with DIA type guide-blocks, where a cubic shaped pressure medium is compressed. Tungsten carbide anvils that have a top area of 6 mm × 6 mm or 4 mm × 4 mm are commonly used to generate pressure, and the pressure medium consists of either pyrophyllite or a mixture of amorphous boron and epoxy resin. 'SPEED1500' is a 1500 ton press for a two-stage octahedral compression (Kawai system), in which tungsten carbide cubes with truncated edge lengths of 8 mm are used as the second-stage anvils. The pressure medium is usually made of semi-sintered magnesia and pyrophyllite pre-formed gaskets were used to generate a stable pressure. In both cases, a cylindrical graphite furnace embedded in a pressure medium achieves high temperatures. A typical sample size is about 1.0 mm in diameter and 0.45 mm in height and the exact dimensions depend on the cell assembly and the experimental conditions.

*In situ* powder x-ray diffraction profiles of the specimen are obtained by the energy dispersive method using a white synchrotron radiation beam. The effective x-ray energy range for the high-pressure experiments is 30–150 and 30–200 keV for Photon Factory and SPring-8, respectively. Figure 1 shows a schematic illustration of the *in situ* x-ray diffraction system combined with a DIA type multi-anvil high-pressure apparatus. The incident x-ray beam collimated by the front slits passes through the anvil gap and then irradiates the sample in the high-pressure cell. A typical slit size is 0.05 mm in width × 0.30 mm in height. A pure germanium solid-state detector mounted on a goniometer collected the diffracted x-ray collimated by the receiving slits. The diffraction angle  $2\theta$  is fixed at an appropriate value, which is selected for the best diffraction profiles in the region under investigation.



**Figure 1.** A schematic illustration of the *in situ* x-ray diffraction system combined with a DIA type multi-anvil high-pressure apparatus.

The real-time variations of the diffraction profile are observed in a display mode and can be saved onto a computer. 10–300 s, depending on the conditions, are needed for the exposure time for each diffraction profile. Pressure values are calculated from an internal pressure standard such as NaCl and Au. A thermocouple placed close to the sample measures the temperature, but at extremely high temperatures the temperature is extrapolated from the input power versus temperature relationship since the thermocouple is destroyed. Experiments are usually conducted by initially increasing the pressure at room temperature and then increasing the temperature under a constant applied load. The *in situ* powder x-ray diffraction profiles of the sample are measured for each set of pressure/temperature conditions.

### 3. Results and discussion

#### 3.1. Metal solvent catalysts

Transition metals such as nickel, cobalt and their alloys are the most common catalysts in industrial processes for synthesizing diamonds. We initially used nickel for our *in situ* investigations because we thought the nickel reaction would not be too challenging since high-pressure diamond synthesis with nickel is an established technique. Nevertheless, there were many serious problems for *in situ* x-ray experiments.

The first encountered was the difficulty in the high-pressure cell design for the *in situ* observations. As mentioned above, a mixture of amorphous boron and epoxy resin is commonly used as the pressure medium for the *in situ* high-pressure experiments since this mixture has a low absorption of x-rays. However, it has been pointed out since the first experiment by Yamaoka *et al* [6] that the graphite–diamond conversion with a metal solvent is not trivial in a boron-epoxy pressure medium. Our experiments confirmed their findings when the inner furnace with the sample chamber was placed directly in the boron-epoxy pressure medium. Although the pressure–temperature conditions were sufficient, frequently diamond crystals did not form. The reason is unclear, but it is possible that the hydrogen formed by the decomposition of the epoxy resin at high temperatures negatively affects diamond formation. A sleeve made of

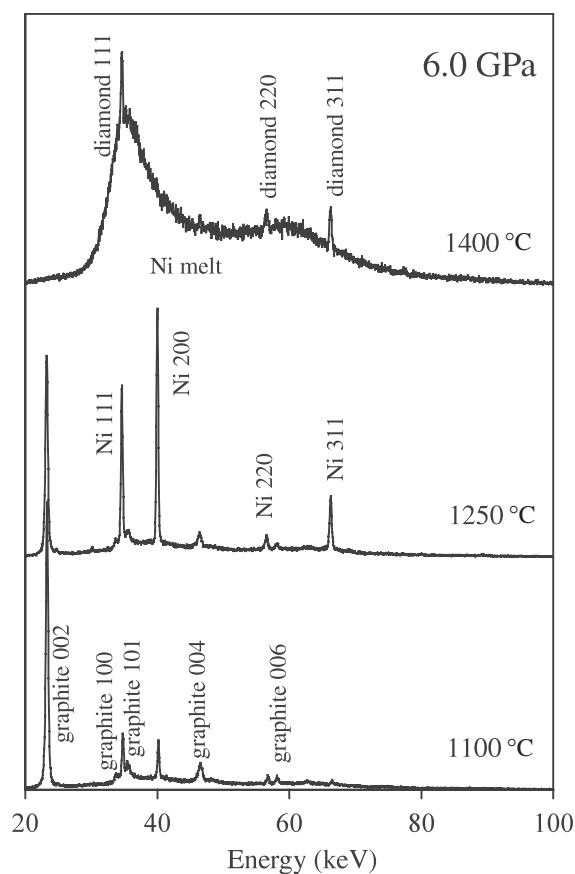
NaCl was inserted between the boron-epoxy medium and the furnace to prevent the hydrogen from entering the sample area. (A previous study [14] determined that hydrogen cannot pass through NaCl under high pressures.) With the addition of the NaCl sleeve, we were able to reproducibly synthesize diamonds.

Since the x-ray scattering factor is proportional to the atomic number, the intensity of the diffraction peak from carbon (diamond or graphite) is much smaller than that from nickel and the big difference between the x-ray scattering factors of carbon and metal caused the second problem. In the experiment using a powder mixture of graphite and nickel with a 1:1 weight ratio, the nickel diffraction peaks were too strong to clearly observe the graphite diffraction peaks. Reducing the nickel ratio to increase the graphite intensity caused diamonds to form inefficiently. In order to solve this problem, we adopted a 'film growth' geometry in which the nickel plate was sandwiched by the graphite discs. In this method, incident x-rays irradiated the boundary between the upper graphite disc and the metal plate where diamonds were formed. We could optimize the diffraction profile when the peak intensities of graphite and nickel were comparable by changing the press height

Figure 2 shows the variations in the x-ray diffraction profile as the temperature increases at 6.0 GPa for an *in situ* observation with a nickel catalyst. This measurement was made with 'MAX90' at the Photon Factory. The exposure time for each profile was 300 s. At 1100 °C, sharp diffraction peaks of graphite and solid nickel (fcc structure) were observed. When temperature was increased to 1250 °C, several diffraction peaks of the catalyst became very strong due to its grain growth. At around 1400 °C, these sharp peaks suddenly disappeared and showed a continuous broad diffraction profile, which indicated the catalyst melted. The moment the catalyst melted, the graphite peaks became weak and three diamond peaks appeared. The diamond formed within the first 300 s of exposure time after the nickel catalyst had melted. Below the melting temperature, the solid nickel maintained a fcc structure and chemical reactions were not observed between nickel and graphite. Also, diamonds did not form in this temperature range. We have conducted similar experiments using other transition metals (cobalt and iron) under the same conditions. When cobalt was used, a phase transition from a hcp to fcc structure was observed around 600 °C and nothing else happened until cobalt melted followed by diamond formation. However, for iron, after the bcc to fcc transition in solid iron occurred, the catalyst chemically reacted with graphite and iron carbide formed at higher temperatures. The melting of this carbide compound triggered diamond formation.

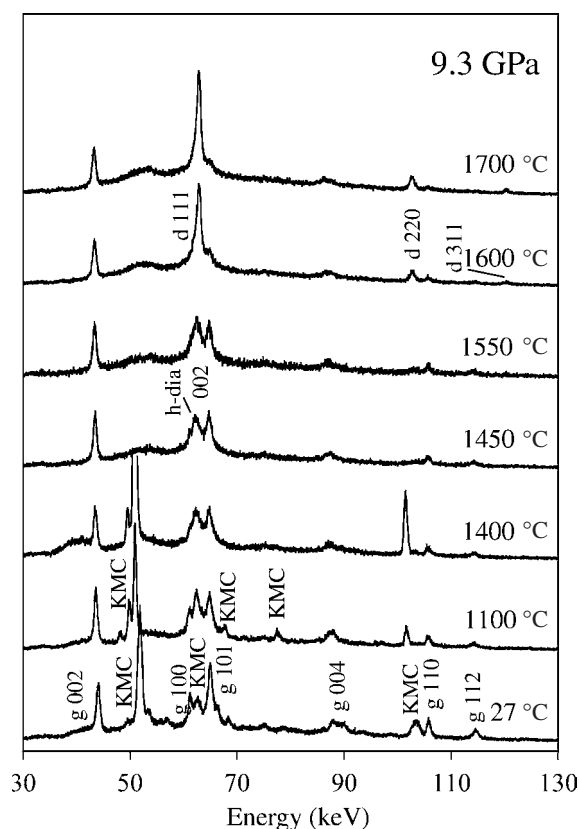
The following model is generally accepted as the diamond formation mechanism under high pressure and temperature. First, the metal catalyst must melt. Then, this molten metal dissolves the graphite. As more and more graphite is dissolved, the graphite solution in the metal becomes saturated. There is a slight solubility difference between graphite and diamond, and thus this situation is supersaturated for diamond. As a result, small crystals nucleate and begin to grow. Since the temperature and pressure are maintained in the region where diamond is in a stable phase, the growing crystals are diamonds. The present *in situ* observations are in good agreement with this diamond formation model.

It is worth summarizing the problems related to the intensities of the diffraction peaks obtained by the energy dispersive method. The diffraction angle  $2\theta$  is fixed and the present system does not have a sample oscillation mechanism. Thus, only diffracted x-rays from the lattice planes that lie in a certain direction can be observed. The 'powder condition' is satisfied as long as the particle size remains small compared with the glancing area where the effective diffraction is observed (approximately 1 mm (length)  $\times$  0.3 mm (width)  $\times$  0.05 mm (height)). In this case, the observed intensities of all diffraction peaks are reliable. However, if the glancing area is occupied by crystals that have a large grain size, the powder condition is not satisfied. Then some of the diffraction peaks would be observed very strongly or not



**Figure 2.** Variations in the x-ray diffraction profiles of a carbon–nickel system as the temperature increases at 6.0 GPa. X-ray diffractions were collected by an energy dispersive method with a constant  $2\theta$  of  $10.0^\circ$ . Sharp graphite and fcc nickel peaks were observed below the melting temperature of nickel. Nickel melted at around  $1400^\circ\text{C}$  and these sharp peaks were suddenly replaced by a continuous broad diffraction profile. The moment the catalyst melted, the graphite peaks became weak and three diamond peaks appeared.

at all. In the present experiment with nickel, the average grain size of a diamond by a SEM measurement of the quenched product was about  $20\ \mu\text{m}$ . This is near the limit for satisfying the powder conditions since the sample is not small enough in relation to the glancing area. If the diamond grains grow larger than  $100\ \mu\text{m}$ , which is common in diamond synthesis using conventional metal catalysts, then the observed peak intensities are very anomalous. Therefore, the intensities of the diffraction peaks cannot estimate the amount of diamond formed. There is also a potentially serious problem with the preferred orientations. Since the samples are fixed in the high-pressure press, it is impossible to average the peak intensities by rotating the sample. This preferred orientation causes large fluctuations in peak intensities. In conclusion, a detailed discussion of the kinetics of diamond formation with conventional metal solvent catalysts based on the information of the peak intensity variation can be very deceiving. Turkevich *et al* [9] conducted a similar experiment with Fe–Al alloy as a catalyst using ‘SMAP2’ at the SPring-8 and kinetically analysed the graphite–diamond transition. Their success was due to the small diamond grains formed ( $<10\ \mu\text{m}$ ) and the slow conversion speed from graphite to diamond.

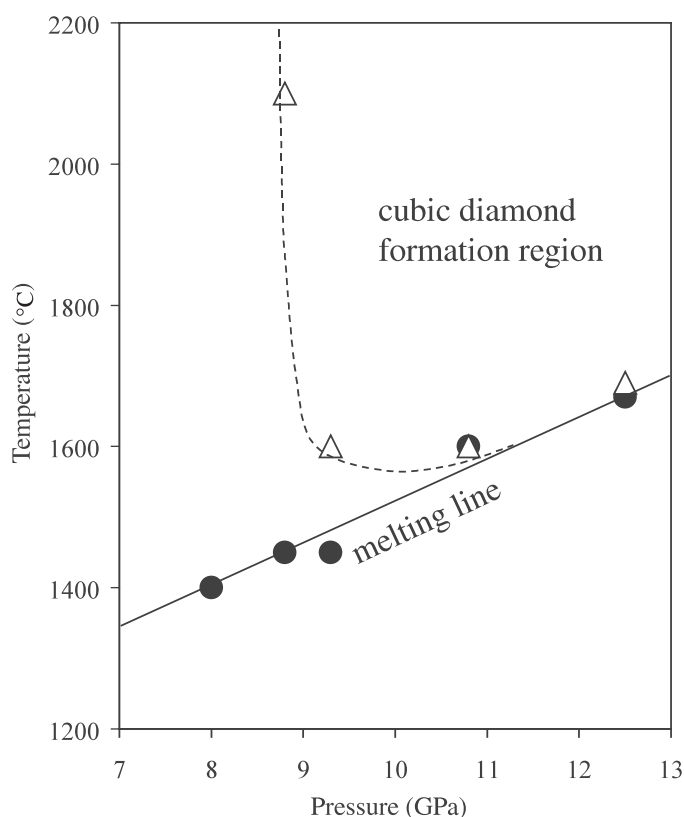


**Figure 3.** Variations in the x-ray diffraction profiles of a carbon– $\text{K}_2\text{Mg}(\text{CO}_3)_2$  system as the temperature increases at 9.3 GPa.  $2\theta$  was fixed at  $5.5^\circ$ . At low temperatures, sharp diffraction peaks from graphite and the catalyst in the solid state (denoted by KMC) were clearly observed. At 1400 °C, some of the catalyst peaks became very strong due to its grain growth before melting (peak intensity of KMC 110 is out of scale in this figure). Although the catalyst melted at 1450 °C, which was indicated by the sudden disappearance of the sharp catalytic peaks, cubic diamond did not form at this temperature. When the temperature was increased to 1600 °C, three diffraction peaks of cubic diamond appeared. Even at the highest temperature (1700 °C), non-converted graphite peaks still remained.

### 3.2. Carbonate catalysts

Experimental simulation of diamond formation with carbonate materials is very important because the research may provide information on the genesis of natural diamond formation since carbonate minerals are common in the mantle and might play the role of solvent catalyst and/or carbon source. We performed *in situ* experiments using  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  (potassium magnesium carbonate) and  $\text{MgCO}_3$  (magnesite) as the diamond forming catalysts. Quenching experiments previously confirmed that diamonds are formed with both carbonates [15, 16].

Figure 3 shows *in situ* x-ray data of a carbon– $\text{K}_2\text{Mg}(\text{CO}_3)_2$  system obtained by ‘SPEED1500’ at the SPring-8. It represents the variations in the diffraction profiles as the temperature increases at 9.3 GPa. At low temperatures, graphite and the catalyst display sharp diffraction peaks. Around 1400 °C, the peak intensity of the catalyst abruptly increases due to its grain growth and these peaks suddenly disappear at 1450 °C, the temperature where the catalyst melted completely. Although the catalyst melted, all the graphite peaks survived and

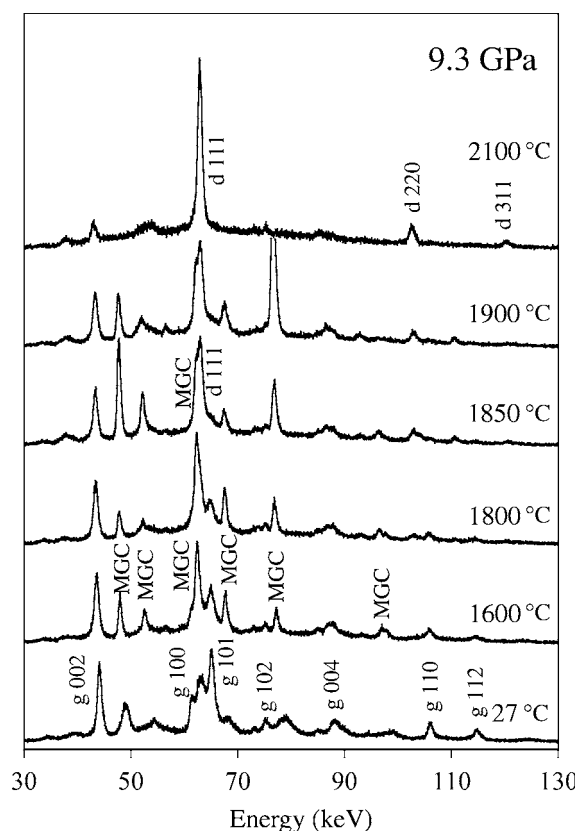


**Figure 4.** Melting line of the catalyst and diamond formation region for a graphite– $\text{K}_2\text{Mg}(\text{CO}_3)_2$  system. Full circles represent the temperatures where the catalyst melted, which was confirmed by the present *in situ* x-ray diffraction. Open triangles represent the temperatures where the diffraction peaks of cubic diamond initially appear under various high-pressure conditions.

obvious cubic diamond peaks did not appear at this temperature. Instead, a broad hexagonal diamond 002 peak was observed between the 100 and 101 peaks of graphite. Hexagonal diamond is a metastable phase that is produced even at room temperature without catalytic compression [17, 18]. Hence, this hexagonal diamond peak must have existed before the catalyst melted, but was hidden by the solid catalyst peak. Cubic diamond peaks began to appear when the temperature was increased to 1600 °C. The peaks of hexagonal 002 and cubic 111 were clearly distinguished by the shift in peak position and the sudden decrease in the peak width when cubic diamond began to form. The appearance of other cubic diamond peaks (220, 311) also confirmed that cubic diamond was formed. This *in situ* observation demonstrates that the melting of the catalyst is insufficient for cubic diamond formation, but a temperature greater than the melting point of  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  is necessary to catalyze diamond formation at this pressure. This result shows that carbonates do not behave like conventional metal catalysts such as nickel and cobalt, which trigger diamond formation at their respective melting points.

The pressure dependences of the two important temperatures, the melting temperature of catalysts and the diamond formation temperature, were determined by repeating the experiments at different pressures (figure 4). The melting line of the catalyst (i.e. eutectic temperature of the graphite and  $\text{K}_2\text{Mg}(\text{CO}_3)_2$  system) has a positive slope. The open triangles represent the temperatures where diamonds initially form at each pressure. For pressures

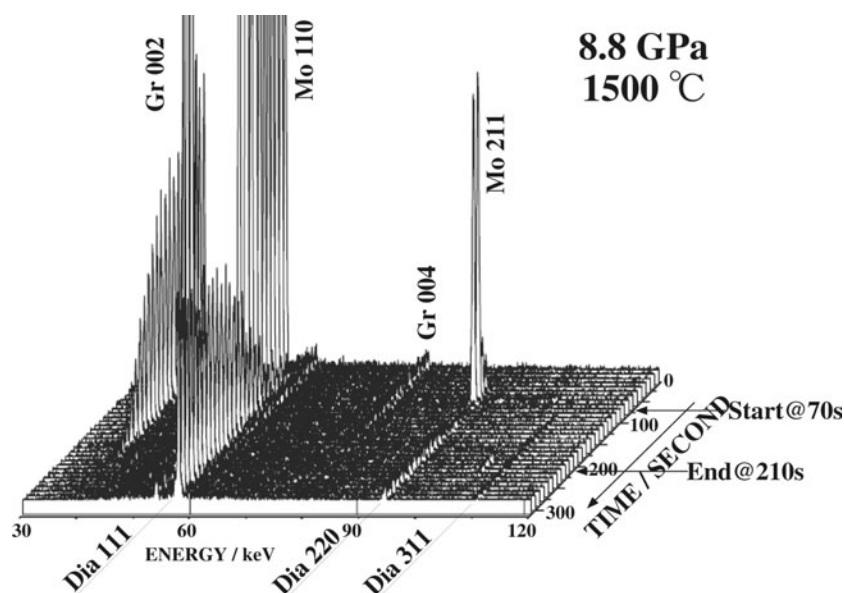




**Figure 5.** Variations in the x-ray diffraction profiles of a carbon–MgCO<sub>3</sub> system as the temperature increases at 9.3 GPa. Cubic diamond formation started at 1800 °C, well below the melting temperature of MgCO<sub>3</sub>, which melts at 2100 °C.

lower than 8.6 GPa, diamond formation was not confirmed. At pressures between 8.6 and 10.8 GPa, the diamond-forming temperature is higher than the melting temperature of the catalyst. Molten K<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub> does not demonstrate catalytic activity below the diamond forming temperature. At pressures higher than 10.8 GPa, the diamond formation temperature coincides with the melting temperature of the catalyst. That is, cubic diamond formation and catalyst melting occur simultaneously, which is similar to the action of transition metal catalysts.

On the other hand, when MgCO<sub>3</sub> was used as a catalyst, the diffraction profiles showed different variations (figure 5). MgCO<sub>3</sub> did not melt until 2100 °C at 9.3 GPa. However, at around 1800 °C, which was well below the melting temperature, clear cubic diamond peaks appeared. At this temperature, MgCO<sub>3</sub> peaks were clearly observed, indicating that MgCO<sub>3</sub> was still in a solid phase. Another experimental run was performed where half of the sample chamber was filled with only graphite and the other half was filled with the powder mixture of MgCO<sub>3</sub> and graphite. Cubic diamond formation was confirmed at 1800 °C in the mixture of MgCO<sub>3</sub> and graphite, while such evidence was not found in the pure graphite side. This result may indicate that solid MgCO<sub>3</sub> plays the role of a diamond formation catalyst, but it is more likely that a small amount of MgCO<sub>3</sub> partially decomposed and was accompanied by the formation of CO<sub>2</sub> fluid, which helped the diamond conversion.



**Figure 6.** A series of x-ray diffraction profiles over time during the graphite–diamond conversion process with the help of aqueous fluids. The diffractions were recorded every 10 s at 8.8 GPa and 1500 °C. The intensity of the graphite peak was clearly reduced and the diamond peak became larger, reflecting the amount of diamond present.

### 3.3. Aqueous fluid

Aqueous fluid is also an important candidate as a catalyst for forming natural diamonds [19, 20]. Water in a supercritical state and fluids composed of carbon, oxygen and hydrogen was experimentally discovered to have a catalytic effect on diamond formation [21–23].

We carried out *in situ* experiments using an aqueous fluid as a diamond forming catalyst; a mixture of brucite ( $\text{Mg}(\text{OH})_2$ ) and graphite (C) was used as the starting material and the graphite to diamond conversion in a supercritical aqueous fluid formed by dehydrating brucite was observed [8, 10]. In this experiment, two important technical developments in the high-pressure cell were made. One is the adoption of  $\text{LaCrO}_3$  as a thermal insulator to stably generate very high temperatures ( $\sim 2000$  °C). Since  $\text{LaCrO}_3$  has a large absorption coefficient with respect to x-rays, the  $\text{LaCrO}_3$  cylinder had small holes that were filled with semi-sintered MgO rods to form x-ray paths. The other development is the sealing technique for the fluid. The sample was packed in a cylindrical molybdenum capsule, which was covered with a molybdenum inner cap on both ends to prevent the volatile components from leaking. Owing to the high energy and high flux density of the synchrotron radiation beam at the SPring-8, x-rays can pass through the molybdenum and allow reliable diffraction profiles of the sample in the capsule to be obtained.

Figure 6 shows the variations in the diffraction profiles with time at 8.8 GPa and 1500 °C. The temperature was rapidly increased to the target temperature at the fixed press load and then stabilized at 1500 °C. The diffraction profiles were consecutively recorded every 10 s. The first plot was obtained when the temperature was stabilized. The diamond diffraction peaks initially appeared 70 s after the target temperature was achieved, which implies that there is a 70 s incubation time for spontaneous diamond nucleation. The intensity of the graphite

002 peak clearly diminished while the diamond 111 peak became larger. Approximately 140 s after the initial appearance of the diamond peaks, the graphite peaks were not observed, but three diamond peaks (111, 220, 311) were clearly seen, suggesting the completion of the transformation. This time-resolved x-ray diffraction data had high enough quality for kinetic analysis of the transformation, which provided much useful information related to the nucleation and growth process of diamond at high pressures and temperatures. The details of the kinetic analysis will be reported elsewhere [24].

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