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2002 J. Phys.: Condens. Matter 14 11331

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***In situ* x-ray observations of the diamond formation process in the C–H₂O–MgO system**

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Received 18 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/11331

Abstract

The diamond formation process in aqueous fluid catalyst under high-pressure and high-temperature conditions has been observed for the first time. Quench experiments and *in situ* x-ray diffraction experiments using synchrotron radiation have been performed upon a mixture of brucite (Mg(OH)₂) and graphite as the starting material. It was confirmed that brucite decomposed into periclase and H₂O at 3.6 GPa and 1050 °C while its complete melting occurred at 6.2 GPa and 1150 °C, indicating that the solubility of MgO in H₂O greatly increases with increasing pressure. The conversion of carbon from its graphite to its diamond form in aqueous fluid was observed at 7.7 GPa and 1835 °C.

1. Introduction

The formation mechanism for natural diamonds in the Earth's mantle remains a topic of debate. On the basis of studies regarding diamond inclusion, it has been suggested that diamond formation had a strong relationship with the mantle fluids (e.g., [1, 2]). Recently, water in a supercritical state and fluids composed of carbon, oxygen and hydrogen were discovered to have a catalytic effect on diamond formation [3–7]. However, most of the previous studies have been based on the 'quench method'. If direct observation of the phenomena under high pressure and temperature could be achieved by means of *in situ* x-ray diffraction, significant information such as details of the diamond formation process from graphite or other carbon sources with the aid of mantle fluids could be determined. We report the first success of such an experiment, which was enabled through the technical development of a high-pressure cell assembly to seal fluids into a metal capsule and the use of synchrotron radiation.

Mantle fluids in environments conducive to diamond formation consist primarily of H₂O and CO₂, in addition to various dissolved mantle components. We adopted magnesium as one of these components, and carried out experiments with a simple C–H₂O–MgO system. In these experiments, a mixture of brucite (Mg(OH)₂) and graphite (C) was used as the starting material, and the graphite-to-diamond conversion process was observed in supercritical aqueous fluid formed by the dehydration of brucite under high pressure and temperature.

The dehydration of brucite under high pressure is also a subject of controversy. High-pressure quench experiments suggest that brucite dehydrates to solid phase MgO (periclase) and H₂O at high temperature (see, e.g., [8]). However, the possibility of MgO dissolution into aqueous fluid cannot be denied. It is critical to decide just from the information of the recovered specimen whether solid MgO coexisted with H₂O under high pressure and temperature. For the solubility of silicate in aqueous fluid, there are previous studies. Mibe *et al* [9] carried out high-pressure experiments for the system of Mg₂SiO₄–MgSiO₃–H₂O, and confirmed that solubility of silicates, especially the MgO component, in H₂O increased with pressure. For the brucite dehydration process, we suspect that brucite decomposes into periclase and H₂O even in high-pressure regions. In this study, we attempt to obtain direct evidence by means of *in situ* x-ray diffraction experiments of either brucite dehydration into periclase and H₂O or its complete melting under various high-pressure conditions.

2. Experimental details

In this study, the starting material was fine powdered brucite (Mg(OH)₂) mixed with a fine powder of graphite in a 1:1 weight ratio.

Preliminary quench experiments were carried out before the *in situ* observations. A 180 ton DIA-type cubic-anvil press installed on the BL14B1 beamline at the SPring-8 was used for pressure generation with six WC anvils of 4 mm truncation [10]. The pressure medium was a mixture of boron and epoxy resin. Cylindrical graphite was used as the furnace in conjunction with a molybdenum electrode. In order to generate very high temperatures (~2000 °C), the furnace was surrounded by LaCrO₃ as a thermal insulator. The starting material powder was compacted in advance to a disk shape and then packed into a molybdenum capsule. It has been confirmed that molybdenum does not act as a diamond forming catalyst [4]. Temperature was monitored by a W97Re3–W75Re25 thermocouple. Pressures were estimated by extrapolation from the load–temperature–pressure relations of the following *in situ* experiments. The recovered run products were investigated using a micro-focused x-ray diffractometer and a scanning electron microscope equipped with an energy dispersive spectrometer (SEM-EDS).

In situ x-ray diffraction experiments at high pressure and temperature were made using a modified high-pressure cell assembly. Since LaCrO₃ used as a thermal insulator has a large absorption coefficient with respect to x-rays, the LaCrO₃ cylinder has small holes as x-ray paths which were filled with semi-sintered MgO rods. The starting material, which was packed into a graphite capsule, was further inserted into another capsule made of molybdenum foil to avoid observation of the molybdenum capsule. A fine powder mixture of NaCl and hexagonal BN (3:7 by weight) as a pressure standard was placed close to the capsule. *In situ* x-ray observations were made by the energy dispersive powder diffraction method using white x-rays provided from a bending magnet source. The diffracted x-rays are collected by a pure Ge solid state detector at constant 2θ (6.0°). Pressures were calculated from the lattice constants of NaCl using the Decker scale [11]. Under very high-temperature conditions where direct pressure determination was impossible due to grain growth or melting of NaCl, pressure was estimated by an extrapolation from the pressure values at lower temperatures. Pressure was first increased at room temperature, then temperature was increased at a constant applied load. The rate of temperature increase was about 100 °C min⁻¹. Every 100 °C, the temperature was stabilized and the x-ray diffraction profile of the sample was measured in a 100 s exposure time.

3. Results and discussion

The experimental conditions and the phase relations observed in the present study are summarized in figure 1. The quench experiments were carried out at three different conditions

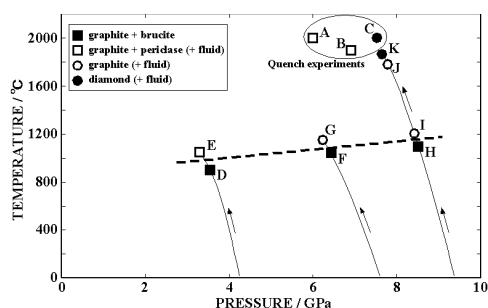


Figure 1. The experimental conditions and the observed phase relations.

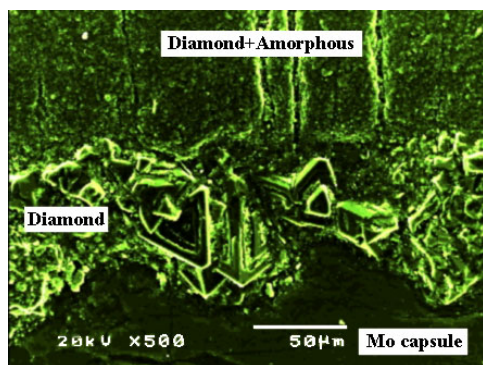


Figure 2. SEM photograph of the run product for conditions C (7.5 GPa, 2000 °C, 10 s).

(This figure is in colour only in the electronic version)

(figure 1: A: 6.0 GPa, 2000 °C, 300 s; B: 6.9 GPa, 1900 °C, 1200 s; C: 7.5 GPa, 2000 °C, 10 s). The micro-focused XRD analyses on the run products for conditions A and B showed that graphite and solid phase MgO (periclase) existed in the samples. This indicates that periclase and H₂O were formed due to the dehydration of brucite under high pressure and temperature, which was also reported in the previous quench experiments on pure Mg(OH)₂ (e.g., [8]). No diamond was detected in these run products. On the other hand, in the run product for conditions C, only diamond phase was detected by the XRD analysis. Figure 2 shows a SEM photograph of this specimen. Although no periclase peak was found in the XRD analysis in this specimen, the qualitative chemical analysis using the SEM–EDS detected the element Mg. This suggests that amorphized materials from the brucite melt coexisted with diamond. From these quench experiments, it is thought that the behaviour of brucite decomposition varies with pressure, and that the diamond formation has relevance to the complete melting of brucite. In order to confirm these hypotheses directly, we carried out *in situ* diffraction experiments to observe the decomposition of brucite at various pressures and to confirm the coexisting phases when the diamond formation occurs.

In situ x-ray diffraction experiments for the brucite decomposition were carried out at about 3.6 and 6.2 GPa. In the experiment at around 3.6 GPa, the diffraction peaks of Mg(OH)₂ (brucite) and graphite were clearly observed at 900 °C (figure 1, D), indicating that brucite maintained its original solid state. On increasing the temperature from 900 to 1050 °C, the brucite peaks disappeared while the diffraction peaks of solid MgO (periclase) appeared (figure 1, E). At this temperature, peaks corresponding to graphite were unchanged, suggesting no diamond formation. Supercritical aqueous fluid was supposed to coexist with periclase under this condition. This variation of the diffraction peaks corresponds to the dehydration decomposition reaction of brucite, which was also reported in the previous quench experiments (e.g., [8]). On the other hand, in the experiment at around 6.2 GPa, the diffraction peaks

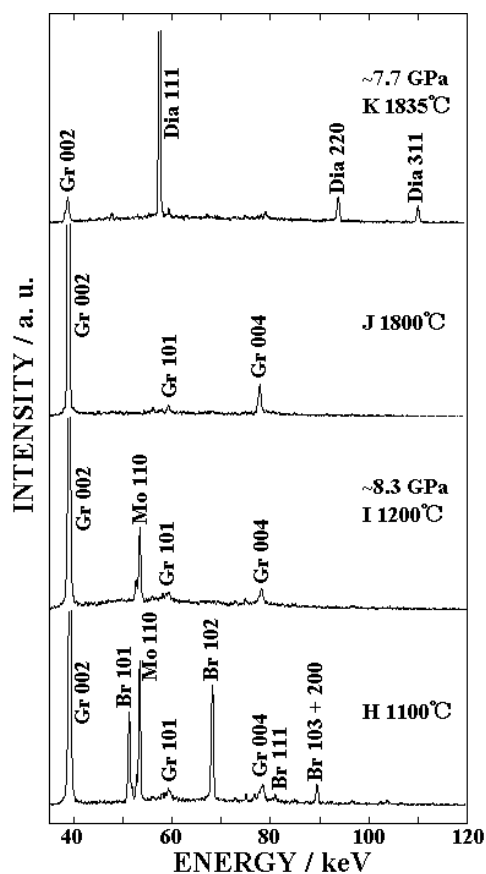


Figure 3. Variation of the x-ray diffraction patterns for the sample with variable temperature under constant applied load. Gr, Br, Mo and Dia denote diffraction lines of graphite, brucite, molybdenum and diamond, respectively.

of brucite disappeared when the temperature was increased from 1050 to 1150 °C (figure 1, F, G). In contrast to the former result at 3.6 GPa, crystallization of periclase was not observed at 6.2 GPa; instead, brucite was completely melted. This means that the aqueous fluid dissolves more than equal molar amounts of the MgO component at this pressure. Therefore, the present results show that the solubility of MgO in the aqueous fluid increases with increasing pressure. This is consistent with previous studies on the $\text{Mg}_2\text{SiO}_4\text{--MgSiO}_3\text{--H}_2\text{O}$ system which show the solubility of silicate, especially the MgO component, in aqueous fluid increases with pressure increasing from 3 to 8 GPa [9].

In the experiment at around 8.3 GPa, it was observed that brucite melts completely during the temperature increase from 1100 to 1200 °C (figure 1, H–I; figure 3, H–I). In this run, the temperature was further increased in order to observe the diamond formation. Only graphite diffraction peaks were clearly observed after the melting of brucite (figure 1, J; 3, J), thus diamond was not formed at the melting temperature of brucite. That is, the melting of brucite did not trigger the diamond formation, which is in contrast to the cases using conventional metal catalysts such as nickel or cobalt. When the temperature reached 1835 °C, since diamond diffraction peaks suddenly appeared, we stopped increasing the temperature. About 3 min after the first appearance of diamond peaks, the graphite peaks became nearly zero while three diamond peaks (111, 220, 311) were clearly observed (figure 1, K; 3, K). In figure 4, variation of the peak intensities of graphite 002 are plotted as a function of temperature. There are no significant differences between the peak intensities of graphite before and after the melting of

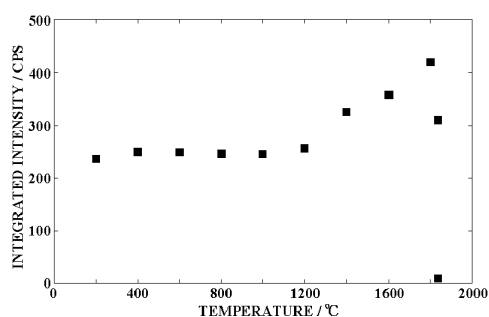


Figure 4. Variation of the integrated peak intensities of graphite 002 as a function of temperature.

brucite at around 1150 °C. This suggests that the amount of carbon dissolved into fluid was so small that it could not be estimated from the reduction of the peak intensity of graphite. If the solubility of carbon increased significantly with increasing temperature, the peak intensity of graphite should consequently decrease. From our results, however, it increased significantly. This is not a result of the decrease of the solubility of carbon, but should be interpreted as the effect of the recrystallization of graphite, which was reported by Yamaoka *et al* (2000) [6]. The occurrence of graphite recrystallization caused the increase in graphite peak intensity, because the recrystallized graphite had a better crystallinity than the original one.

4. Conclusions

In C–H₂O–MgO system, it was confirmed that Mg(OH)₂ (brucite) decomposes to solid MgO (periclase) and H₂O under relatively low pressure, which was also reported in the previous quench experiments. However, under high pressure above about 5 GPa, the complete melting of brucite occurs. This indicates that the solubility of MgO in the aqueous fluid increases with increasing pressure, and the aqueous fluid dissolves more than equal molar amounts of the MgO component above about 5 GPa.

It was suggested that the amount of carbon dissolved into fluid was extremely small on the basis of the variation of the diffraction peak intensities of graphite with temperature. The present study is the first successful *in situ* x-ray observation of the diamond formation process under high pressure and temperature using aqueous fluid as a catalyst. Our technical development has made it possible to seal a fluid component in the metal capsule and to carry out its *in situ* x-ray observation using synchrotron radiation. This technique can be expected to be a powerful tool for the detailed study of the diamond formation process, particularly of kinetic phenomena related to diamond nucleation and growth.

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