

**IN SITU OBSERVATION OF DIAMOND FORMATION PROCESS UNDER HIGH-PRESSURES AND HIGH-TEMPERATURES**

Diamond formation under high-pressure and high-temperature has been extensively studied, resulting in large-scale synthesis of diamonds using industrial high-pressure technology [1,2]. However, most of the previous studies were based upon information obtained at ambient conditions from recovered specimens, and very few *in situ* experiments have been reported. Such experiments would be indispensable for the direct

study of the diamond formation process. A combination of a large volume press and synchrotron-derived X-ray radiation have made it possible to carry out real-time *in situ* observations of the catalytic graphite-diamond conversion process at high-pressure and high-temperature.

Experiments were performed using a large-volume multi-anvil high-pressure apparatus, SPEED1500, installed at beamline **BL04B1** [3]. Well-crystallized graphite of high purity (impurity concentration less than 5 ppm, graphitized index value 7.4) was used for the reaction substrate.  $K_2Mg(CO_3)_2$  (potassium magnesium carbonate)

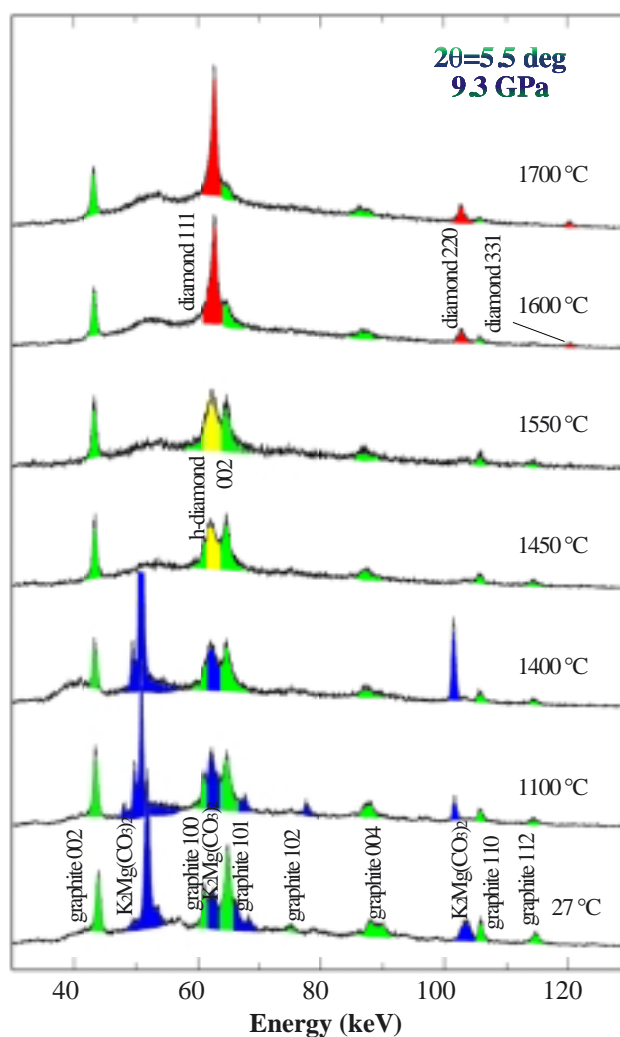


Fig. 1. Variation of the X-ray diffraction profiles of graphite- $K_2Mg(CO_3)_2$  system with increasing temperature at 9.3 GPa.

was used as a catalyst in the present study. The role of this carbonate compound in diamond formation in the earth's interior has interested many geoscientists [4,5]. Experiments were conducted by first increasing pressure at room temperature, and then increasing temperature under a constant applied load. Powder X-ray diffraction profiles of the specimen were obtained under each pressure-temperature condition by the energy dispersive method using the white synchrotron radiation beam from a bending magnet.

Figure 1 shows a series of X-ray diffraction profiles of the sample with increasing temperature at 9.3 GPa. At lower temperatures, sharp diffraction peaks of graphite and catalyst in the solid state were clearly observed. When temperature was increased to 1400 °C, several catalyst diffraction peaks became very strong due to grain growth. These strong peaks suddenly disappeared at 1450 °C, at which point the catalyst had melted completely. Although the catalyst melted, all the graphite peaks still persisted and no obvious cubic diamond peaks appeared at this temperature. Instead, a broad hexagonal diamond

002 peak was observed between the 100 and 101 peaks of graphite. Hexagonal diamond is known to be a meta-stable phase produced even at room temperature with non-catalytic compression [6]. Hence, this hexagonal diamond peak is interpreted to have existed before catalyst melting but was hidden by the solid catalyst peak. Cubic diamond peaks began to appear when temperature was further increased up to 1600 °C. The peaks of hexagonal 002 and cubic 111 forms were clearly distinguished; a clear shift in peak position and sudden decrease in peak width were observed when cubic diamond began to form. The formation of cubic diamond was confirmed by the appearance of other cubic diamond peaks (220, 311). These *in situ* observations demonstrate that catalyst melting is not sufficient for cubic diamond formation; a temperature higher than the melting point of  $K_2Mg(CO_3)_2$  is necessary if it is to be used as a catalyst for diamond synthesis at this pressure. This result can be contrasted to the behavior of metal catalysts such as nickel and cobalt, which trigger diamond formation at their respective melting points.

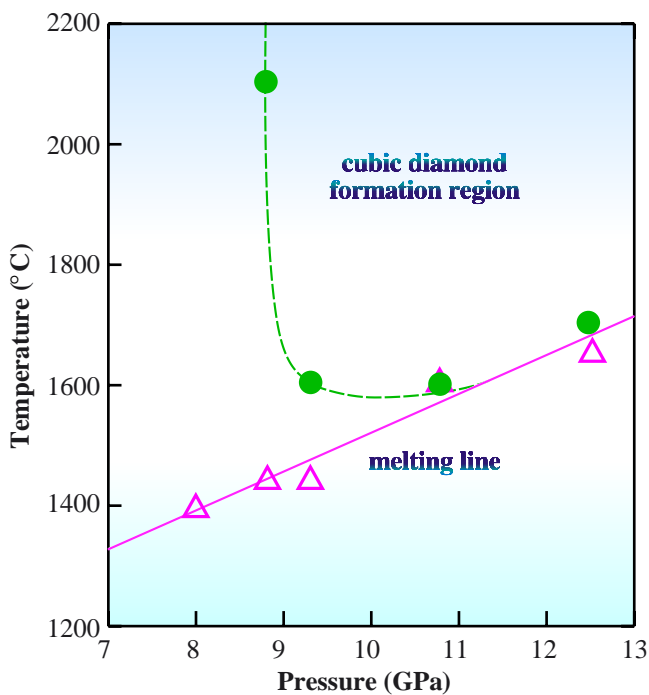


Fig. 2. Melting line of catalyst and diamond formation region for graphite-  $K_2Mg(CO_3)_2$  system.

The same experiments were repeated under different pressures so that the pressure dependence of two important temperatures – the melting point of the catalyst and the diamond formation temperature – was obtained (Fig. 2). The melting curve for the catalyst (*i.e.*, eutectic temperature of the graphite/ $K_2Mg(CO_3)_2$  system) has a positive slope. Solid circles in Fig. 2 represent the temperatures at which diamond formation began at each pressure. At pressures lower than 8.6 GPa, diamond formation was not conclusively observed. At pressures between 8.6 and 10.8 GPa, the diamond formation temperature is higher than the melting temperature of the catalyst. Below the diamond formation temperature, molten  $K_2Mg(CO_3)_2$  does not demonstrate catalytic activity. 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 take place almost simultaneously, similar to the action of metal catalysts.

A SEM photograph of the recovered sample is shown in Fig. 3. The newly-synthesized diamond grains exhibit octahedral or cubo-octahedral morphology, indicating that they grew up in the presence of molten  $K_2Mg(CO_3)_2$ .

Our present study demonstrates that *in situ* X-ray diffraction under high-pressure and high-temperature combined with a large volume press is a powerful tool for diamond research. This technique will be further developed and applied to the study of diamond formation in both academic and applied science.

Wataru Utsumi

SPring-8 / JAERI

E-mail: utsumi@spring8.or.jp

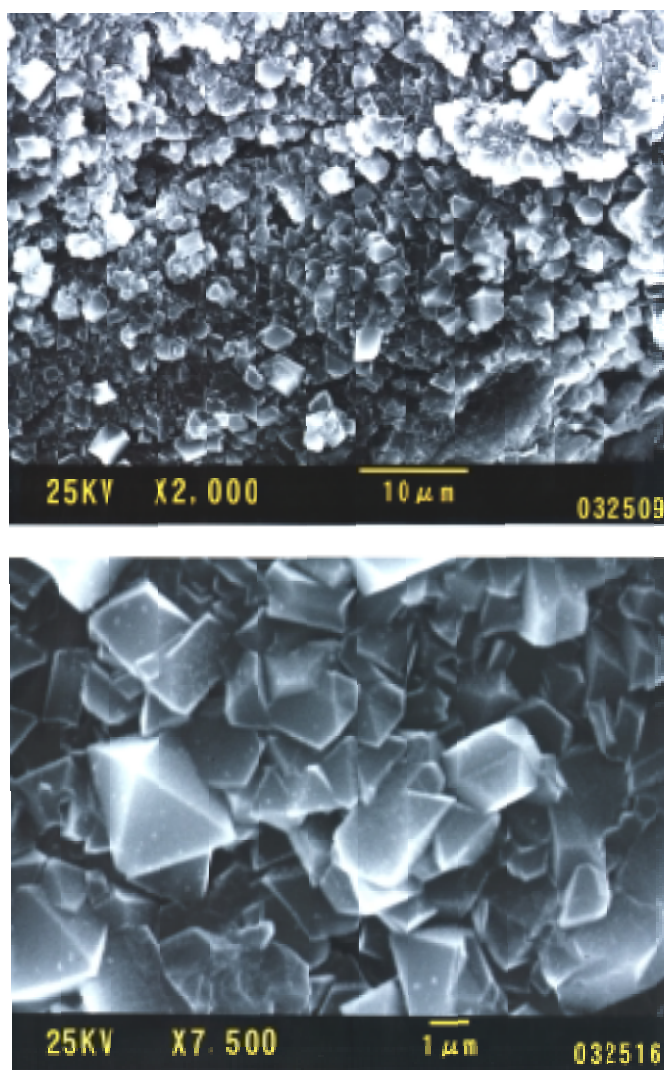


Fig. 3. SEM photograph of the synthesized diamond recovered to ambient conditions.

## References

- [1] F.B. Bundy *et al.*, Nature **176** (1955) 51.
- [2] F.B. Bundy *et al.*, J. Chem. Phys. **35** (1961) 383.
- [3] W. Utsumi *et al.*, Rev. High Press. Sci. Technol. **7** (1998) 1484.
- [4] M. Akaishi *et al.*, J. Cryst. Growth **104** (1990) 578.
- [5] T. Taniguchi *et al.*, J. Mater. Res. **11** (1996) 2622.
- [6] T. Yagi *et al.*, Phys. Rev. B **46** (1992) 6031.