Formation of diamond powders from melamine under high pressure and high temperature*

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Abstract: High pressure pyrolysis of melamine has been attracting great interest recently, due to it being considered as a suitable precursor to realize the g-C_3N_4 and even superhard C_3N_4. In this work, we studied the detailed pyrolysis behavior of melamine at 22 GPa. Melamine was stable at 800 ℃, and decomposed to diamond in the form of powder at 1500–2000 ℃ under this pressure condition. At 2000 ℃, the pure cubic diamond powders with 0.1–0.5 μm grain size were obtained. The diamond particles exhibited euhedral forms and dispersed to each other, we proposed that these novel features were caused by the presence of liquid N_2 and NH_3 during diamond formation. The high pressure pyrolysis of melamine may provide a new means of producing micrometer-sized diamond powders.

Key words: melamine, decomposition, high pressure, diamond powder

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1 Introduction

Melamine ($C_3N_6H_6$; 2, 4, 6-triamino-1, 3, 5-triazine) is traditionally considered as a good fire retardant additive for polymeric materials, so it was widely used as rugged dishware, formica, and fire retardants fabrics in industry [1–4]. Recently, melamine has excited great interest due to its new application for synthesizing the superhard C_3N_4, which was theoretically predicted by Liu and Cohen [5]. Melamine has a honeycomb structure which consists of a six-member CN aromatic ring (triazine) and three amino groups, the triazine is stable and has high degree symmetry (C-C and C-N bond lengths are all very close to 1.35 Å and the bond angles are all nearly 120 ℃) [6], this atomic arrangement is structurally similar to C_3N_4 with graphitic form (g-C_3N_4) [7]. Hence, melamine has been suggested as a suitable precursor to realize g-C_3N_4 and even superhard C_3N_4 phases. In analogy with the high pressure synthesis of diamond from graphite and cubic boron nitride from hexagonal boron nitride, the pyrolysis of melamine was widely studied under high pressure in order to synthesize the C_3N_4 compound. The g-C_3N_4 obtained at 820 ℃ and 3 GPa via high pressure solvothermal treatment of melamine was reported by H. Montigaud [8] and I. Alves [9], they suggested that melamine was not decomposed at a temperature below 800 ℃, but the nitrogen content decreased strongly at temperatures above 850 ℃. L. D. Yao [10] found that melamine partly decomposes from 750 ℃ at 4.5 GPa, and obtained g-C_3N_4, which embedded in undecomposed melamine, graphite and intermediate phases at 800 ° C with short heating time (e.g. less than 5 min). H. A. Ma [11] synthesized g-C_3N_4 with an unknown intermediate product and the starting melamine at 650 ℃ and 5 GPa. He found that, after being decomposed completely, melamine transforms into a black powder which consists of amorphous carbon and a small amount of nitrogen. However, the detailed pyrolysis behavior of melamine at high pressure (up to 20 GPa) has been rarely reported.

In this work, we studied the high pressure pyrolysis behavior of melamine at 22 GPa. The pure cubic diamond powders with 0.1–0.5 micro grain size as the decomposition product were obtained. It provides a novel route to synthesis the pure cubic diamond powder from organic compounds by high pressure and high temperature methods.

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2 Experimental method

The high pressure was generated by a Kawai-type multianvil apparatus at the Geodynamics Research Center (Ehime University, Japan). The 11/5 mm cell assembly which composed of eight WC anvils with 5 mm truncation edge-length and a MgO octahedron of 11 mm edge-length was used. The starting material melamine ($C_3N_6H_6$; white powder; purity $\geqslant$99 at%) was carefully enclosed in double platinum capsules, and then capsules were put into the middle of a cylindrical Rhenium heater. A MgO sleeve was used as an insulator between the Re heater and the Pt capsules. A schematic illustration of the cell assembly is shown in Fig. 1. The cell temperature was measured directly by using a $W_{97}Re_3$-$W_{75}Re_{25}$ thermocouple. The pressure calibration was performed at room temperature using conventional pressure standards (phase transition). After desired pressure and heating duration, the sample was quenched to room temperature by turning off the heating current and then decompressed to ambient pressure. The recovered samples were analyzed by X-ray diffraction (MAC Science M18XHF) using CuKα radiation (40 kV, 200 mA, collimated to 50 μm) and Raman spectroscopy (Renishaw RS-SYS1000) for phase identification. The microtexture observation and chemical composition of samples were examined by a field-emission SEM (JEOL JSM-7000F) which was equipped with an energy dispersive X-ray spectrometer (EDS).

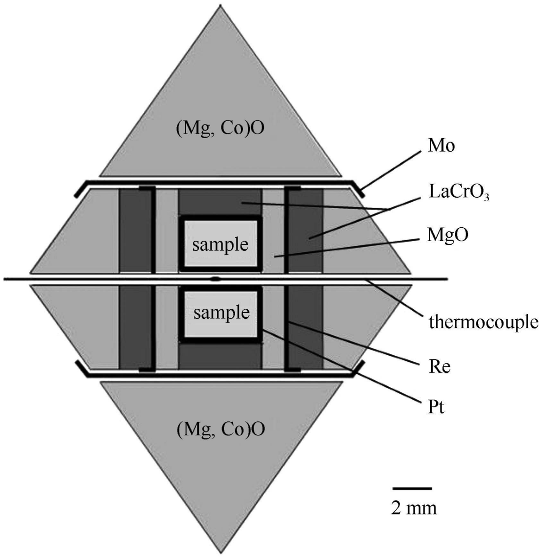

Fig. 1. Schematic illustration of the cell assembly was used in this study.

3 Results and discussion

The experiments were carried out at the pressure of 22 GPa, and the heating temperatures were 800, 1500, 2000 ℃ for 30 min, respectively. After high pressure and high temperature treatment, we opened the Pt capsules carefully and found the samples. Contrary to the sample being a black color when the melamine decomposed as reported in Ref. [11], our samples were a white color and in the form of powder which could be seen by a naked eye. The XRD, Raman, and SEM-EDS data of samples are shown below.

Figure 2 shows the X-ray diffraction patterns of the recovered samples heated at 800 ℃ (1), 1500 ℃ (2), 2000 ℃ (3), respectively. It can be found that only melamine peaks were detected for samples heated at 800 ℃, apart from several smaller peaks derived from the surrounding Pt capsule, which reveal that melamine maintained its stability at this P-T condition. This result is different from previous studies that the onset temperature for melamine decomposition was around or below 800 ℃ [8–11]. The most probable reason is that the pressure we performed under was much lower than in previous studies, and the closed reaction environment (Pt capsules) in this study may also play an important effect in preventing melamine decomposition. Upon heating to 1500 ℃, the melamine peaks completely disappeared and were replaced by broad diamond peaks. This indicates that melamine decomposed and transformed directly to diamond. When the sample was further heated to 2000 ℃, the diamond peaks become sharper and more intense, implying that the great grain growth of diamond crystals had occurred. Compared with nano-polycrystalline diamond (NPD) [12]

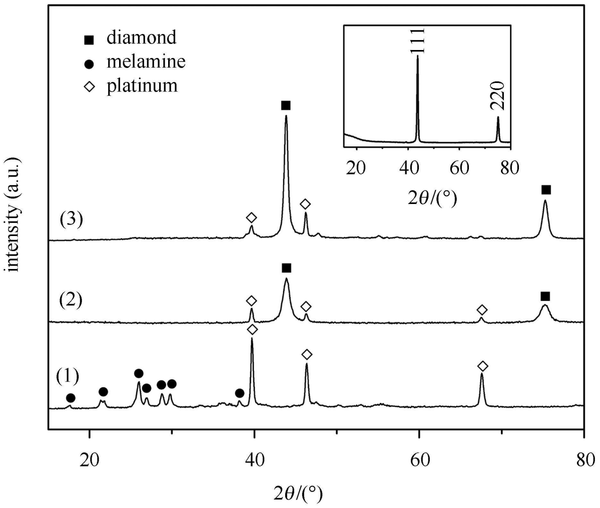

Fig. 2. The X-ray diffraction patterns of melamine which was treated from 22 GPa and 800 ℃ (1), 1500 ℃ (2), 2000 ℃ (3), respectively. The peaks from platinum in the patterns derived from the surrounding Pt capsule which was used to sealing melamine in an enclosed condition. As comparison, the inset figure is XRD pattern of nano-polycrystalline diamond (NPD) [12].

inserted in Fig. 2, the pure cubic diamond was obtained after decomposition of melamine, no other phases were detected even at this P-T condition.

Figure 3 shows the Raman spectra of recovered samples which were heated to 800 ℃ (1), 1500 ℃ (2), 2000 ℃ (3) at 22 GPa, respectively. When the sample was heated to 800 ℃, the spectrum shows no visible band; probably due to its strong fluorescence and photoluminescence induced by high pressure treatment of melamine. The sample heated to 1500 ℃ shows a peak at 1331 cm^{-1}, which is typical Raman peak of diamond. Continuous broad bands in the 1400–1600 cm^{-1} range were also observed, indicating the presence of minor amounts of disordered (amorphous) carbon in this sample. As heating temperature increases to 2000 ℃, only a sharp diamond peak at 1331 cm^{-1} was detected, indicating again that the pure cubic diamond with good crystalline was obtained at 2000 ℃ and 22 GPa.

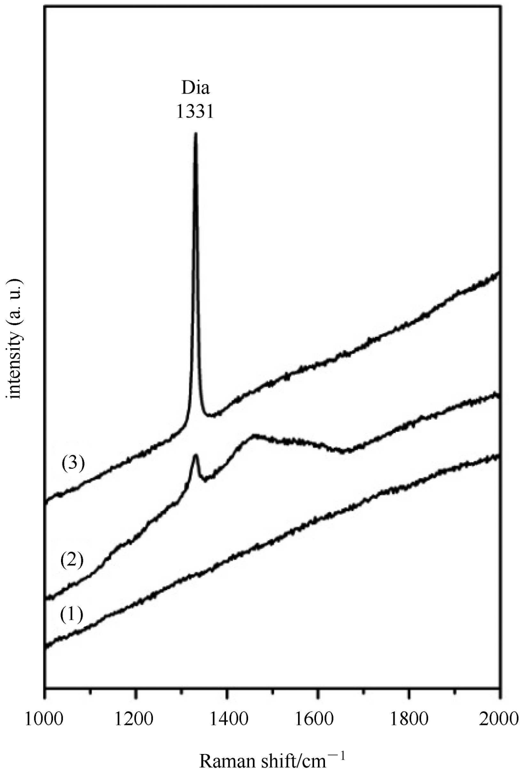

Fig. 3. Raman spectra collected from the recovered samples which were treated from 22 GPa and 800 ℃ (1), 1500 ℃ (2), 2000 ℃ (3), respectively.

In order to examine the microtexture and the chemical composition of the sample recovered from 2000 ℃ and 22 GPa, FE-SEM/EDS analyses were conducted. The SEM image (Fig. 4) shows that the diamond powders are in the form of euhedral crystals, the grain size are homogeneous and with a range of 0.1–0.5 micron. It was interesting that the diamond crystals are discrete and not bound to each other, which implies that the diamond crystallized in a free space such as a fluid medium. This morphological feature is quite different from the sintered NPD which was synthesized by direct conversion from pure graphite at the same P-T conditions [13]. Indeed, when melamine decomposed, N_2 and NH_3 were formed by the atomic arrangement breaking down. The liquid N_2 and NH_3 in the closed Pt capsule provided a fluid environment, made diamond crystallize to an euhedral form and led to a great grain growth of diamond crystals [14, 15]. EDS analysis conducted after gold coating (ca. 20 nm thickness) on the samples shows that the samples only contain carbon and no nitrogen, which suggested that these particles were pure diamond (Fig. 4). Thus, we can conclude that pure cubic diamond powders with micrometer-size were obtained by high pressure pyrolysis of melamine.

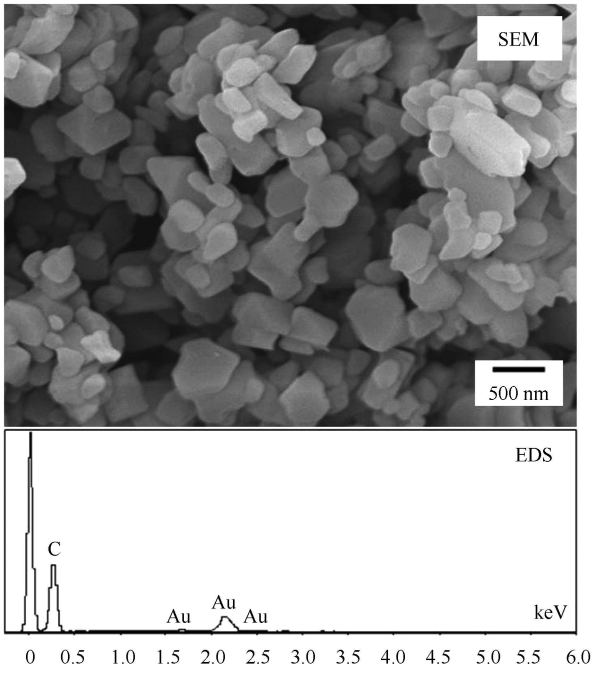

Fig. 4. SEM images (upper) and EDS analysis (lower) of samples recovered from 2000 ℃ and 22 GPa after gold coating.

As concluded in previous reports, diamond powders can be obtained by hydrothermal processes [16–18] and high pressure synthesis [19], but diamond seeds are needed and the purity of product is also a problem because of the presence of catalysts in these methods. The method of high pressure pyrolysis of organic compounds may provide a novel route of synthesizing pure cubic diamond powders.

4 Conclusions

In conclusion, we studied the high pressure pyrolysis behavior of melamine at 22 GPa pressure and 800, 1500, 2000 ℃ temperatures. Melamine maintains its structure at 800 ℃ and decomposes to diamond above 1500 ℃. Up to 2000 ℃, no phase transition of melamine was observed. Combined with XRD, Raman, and SEM-DES analyses, pure cubic diamond powders were obtained at 2000 ℃ and 22 GPa by decomposition of melamine. The diamond particles are discrete and exhibit euhedral forms. The grain size homogeneously ranges from 0.1–0.5 micron. Compared with the previous method used to synthesize diamond powders, pyrolysis organic compounds under high pressure and high temperature may provide a new means of producing micrometer-sized diamond powders.

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