Effects of Mg on diamond growth and properties in Fe–C system under high pressure and high temperature condition*

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Diamond crystal crystallized in Fe–Mg–C system with Archimedes buoyancy as a driving force is established under high pressure and high temperature conditions. The experimental results indicate that the addition of the Mg element results in the nitrogen concentration increasing from 87 ppm to 271 ppm in the diamond structure. The occurrence of the {100} plane reveals that the surface character is remarkably changed due to the addition of Mg. Micro-Raman spectra indicate that the half width of full maximum is in a range of 3.01 cm^{-1}–3.26 cm^{-1}, implying an extremely good quality of diamond specimens in crystallization.

Keywords: high pressure and high temperature, Archimedes buoyancy process, diamond crystal, Mg metal

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1. Introduction

Diamond, as a typical traditional superhard material, can be synthesized by various techniques,[1–4] but the static-pressure-catalyst process is still the most popular way in the production of industrial diamond grits. In this method, the initial graphite and metallic catalyst experience high pressure and high temperature (HPHT) process either in a form of powder mixture or in a layer-by-layer assembly. The most effectively metallic solvent-catalysts used for diamond growth under the HPHT condition are prominently composed of Fe, Co, Ni, and Mn.[4–8] Besides, some oxygen-contained materials, such as Li_2CO_3, $SrCO_3$, Na_2CO_3, and Na_2SO_4, can also serve as the catalytic medium for diamond growth.[9,10] Recently, the kimberlitic medium was selected as a catalytic solvent to explore diamond crystallization.[11] It is well recognized that the crystallized medium significantly affects the morphology and crystalline habit of diamond crystal. In recent years, more and more research works have focused on metals with a low melt point such as Mg, Cu, and Sn, acting as solvent metal for diamond growth.[12–14] The solubility of carbon source dissolved in these metal solvents is extremely low, and the required pressure for diamond crystallization is relatively high, at least $\sim$ 7 GPa, when a single element is used as the catalyst.[14] However, the spontaneously nucleated pressure for diamond crystals was reduced to $\sim$ 6 GPa in the Cu–Mg–C system.[12] In these systems, the dominant role of Mg is not clear enough. Accordingly, we explore the effects of Mg on diamond growth and properties in the Fe–Mg–C system under the HPHT condition in this paper.

As for diamond growth under the HPHT condition, the traditional methods are the phase conversion process, which is generally termed the film growth process, and the temperature gradient method. In the process of phase conversion, the driving force for the formation of diamond crystal is derived from the difference in thermodynamic stability between the two phases of carbon. In the temperature gradient growth process, the crystal growth can be controlled by the temperature gradient. In our work, a new growth process, in which carbon atoms diffuse from the carbon source to the crystallized sites through the metal melt with Arhchimedes buoyancy as a driving force, is used to control crystal growth.

2. Experiment

The experiments on diamond growth were performed in a cubic anvil HPHT apparatus (SPD-6×1400). The assembly for the synthesis of diamond crystals by a buoyancy process was designed as presented in Fig. 1. The sub-heater was added only on the top side to avoid the presence of the temperature gradient in metal solvent. The synthesis chamber was constructed from a ceramic material, ZrO_2 + MgO, with an inner size of 13 mm in diameter. Pressure parameters were estimated by the curve based on the pressure-induced phase transitions of Bi, Tl, and Ba. The diamond crystals were crystallized at a pressure of $\sim$ 6.0 GPa and temperatures of $\sim$ 1335 °C–1435 °C. Diamond crystals were spontaneously crystallized on the top side of solvent metal with an assist of Archimedes

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buoyancy. The temperature gradient was nearly eliminated by adjusting the size of sub-heater on the top side. This fact was confirmed by an additional experiment that the assembly was placed upside down and pressed to the diamond stable region to insure no crystals were found.

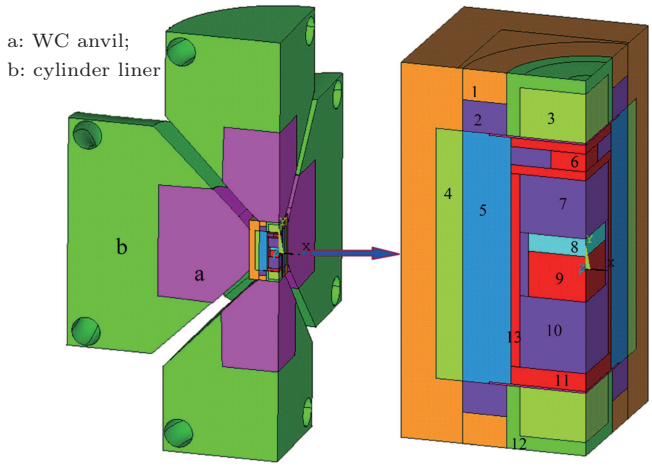


Fig. 1. (color online) Sample assembly of 1/4 part for diamond synthesis by HPHT. 1: pyrophyllite; 2: ZrO_2 sleeve; 3: end cap of dolomite; 4: dolomite sleeve; 5: NaCl+Al_2O_3 sleeve; 6: sub-heater of graphite; 7 and 10: cap of ZrO_2; 8: metal medium; 9: graphite of carbon source; 11: sheet graphite; 12: steel ring; 13: graphite heater.

The high-purity graphite was utilized as a carbon source, and $Fe_{1-x}Mg_x$ (x value is in a range of 0–0.092) was used as the catalyst medium. The graphite powder (99.99% purity) was pressed into a cylindrical sample as the initial material loaded into the ampoule. After the HPHT synthesis with a run duration of 10 h, the collected crude samples were first treated with dilute nitric acid to separate the diamond grains from the metal catalyst medium. The diamond crystals were subsequently refluxed in the strong acid solution to eliminate the residual impurities present on the crystal surface. The as-synthesized diamond crystals free from visible inclusions were selected for analysis using an optical microscope. Nitrogen and hydrogen in these diamonds were characterized by micro-infrared (IR) spectra recorded from a Fourier transform infrared (FTIR) spectrometer in a spectral range of 500 cm^{-1}–3500 cm^{-1} with a resolution of 2 cm^{-1} in a transmittance mode. For the IR measurements, a Bomem M110 FTIR spectrometer fitted with a microscope was employed. The IR beam size was rescaled to the range of 50 μm–150 μm in diameter for analyzing the absorptions only occurring in diamond crystal. Nitrogen concentrations (C_N) in single substitutional form (C-form) were estimated by absorption coefficients of 1130 cm^{-1} ($\mu_{(130)}$) with a conversion factor of 25, namely, $C_N(\text{ppm}) = 25 \times \mu_{(1130)}(\text{cm}^{-1})$. Morphologies and structural properties of the as-synthesized samples were characterized by scanning electron microscope (SEM). The crystalline quality of collected diamond samples was characterized by micro-Raman spectroscopy at room temperature.

3. Results and discussion

The diamond crystallization is established in the Fe–Mg–C system under the HPHT condition by the buoyancy process. Typical SEM images from collected samples are shown in Fig. 2. Observation on specimen morphologies indicates that the content of Mg (C_{Mg}) added in catalysts affects the surface properties of collected crystals. Lower C_{Mg} in metal can improve the surface smoothness (Figs. 2(b) and 2(c)), and the sharp ridges present in crystal. It is implied that the wettability of solvent-metal is enhanced as a result of the reduction of viscosity properties when the element of Mg is added. However, the surface property of crystal planes further changes with increasing C_{Mg}. The surface of each face becomes rough and the $\{100\}$ plane occurs in crystal (Figs. 2(d) and 2(e)) under the same HPHT condition of $C_{Mg} > 4.6$ mol%. The occurrence of $\{100\}$ planes indicates that the metal of Mg added in solvent can significantly affect the surface character of diamond crystal. This phenomenon is the same as that of diamond growth in a pure Mg system.[15] Considering the current concept on crystal growth, the specific surface energy of $\{100\}$ planes may be reduced due to the addition of Mg metal.

The role of Mg during crystal development is appreciably different from those of non-metal materials, such as S and P. As is well known, crystals generally have octahedral growth habits, when those nonmetallic materials are added in metal-solvent or serve as catalysts.[16,17] It should be pointed out that the degree of regularity of crystal turns worse and more macro-defects appear on the crystal surface as shown in Fig. 2(e) when C_{Mg} is beyond 6.9 mol%. Therefore, one can deduce that an appropriate C_{Mg} added in pure Fe-metal solvent can improve the properties of catalyst; nevertheless, the excessive C_{Mg} added in solvent can change the catalytic character of metal medium, resulting in the deterioration of crystalline quality.

The IR detections of good-quality crystals which are collected from the Fe–Mg–C system indicate that nitrogen atom donors, even though without deliberate doping with nitrogen-related nitrides, are readily incorporated into diamond materials as a substitutional form, generally called C-center, characterized by 1130 cm^{-1} and 1344 cm^{-1} absorption peaks in one-phonon region as plotted in Fig. 3. It is indicated that the C_N incorporated into diamond structure depends on C_{Mg} in metal melt and the crystallizing temperature. Moreover, the IR spectra imply that hydrogen-related structure occurs in diamond crystal. According to Refs. [18] and [19], hydrogen-related absorption peaks at 2850 cm^{-1} and 2920 cm^{-1} in the three-phonon region indicate that hydrogen atoms in the diamond structure exist in the forms of sp^3 bonded $–CH_2$ and $–CH_3$ group. The source of hydrogen should come from the decomposition of H_2O.

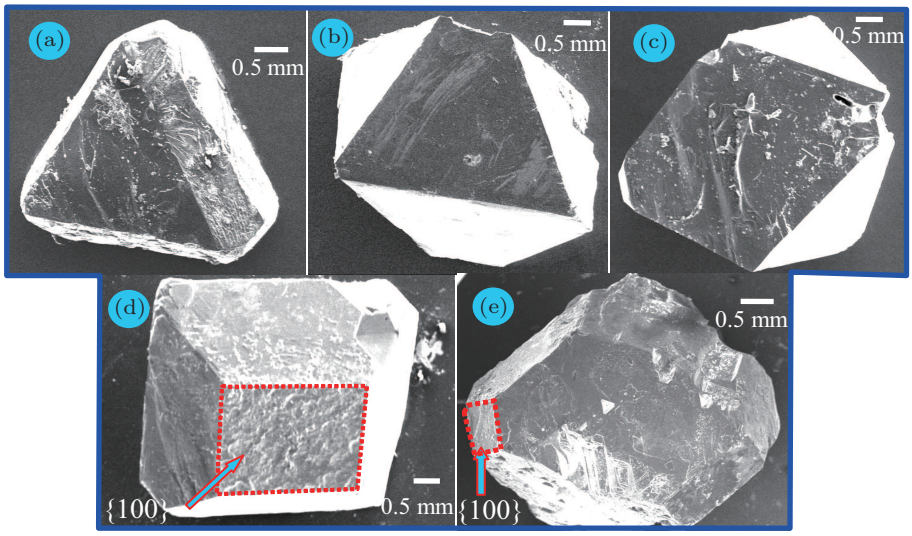


Fig. 2. (color online) SEM images of specimens crystallized in buoyancy systems of the metals of $Fe_{100-x}Mg_x$ with $x = 0$ (a), 2.3 (b), 4.6 (c), 6.9 (d), and 9.2 (e), under the same HPHT condition.

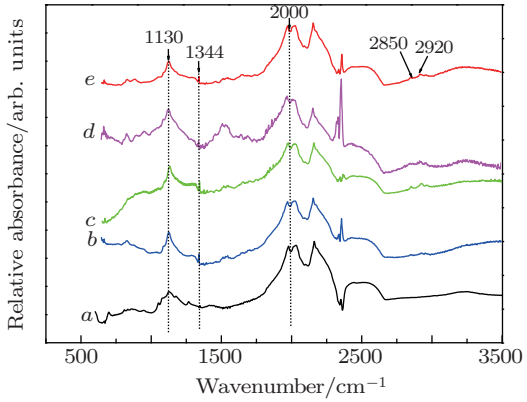


Fig. 3. (color online) Typical IR spectra recorded for good-quality crystals grown by $Fe_{100-x}Mg_x$, with $x = 0$ (curve *a*), 2.3 (curve *b*), 4.6 (curve *c*), 6.9 (curve *d*), and 9.2 (curve *e*).

Evaluation on nitrogen content indicates that with increasing C_{Mg} in crystallization medium, C_N progressively increases from 86 ppm to 271 ppm, before $C_{Mg} < 6.9$ mol%. The detailed variation of C_N with the increasing of C_{Mg} added in solvent metal is presented in Fig. 4. Exceeding this critical doping content of metal Mg, the detected C_N in diamond structure begins to decrease, owing to the influence of higher crystallizing temperature condition. The declining of C_N with crystallized temperature increasing has been already discovered.[20] It is considered that with crystallization temperature increasing, the solubility of nitrogen solved in metal melt gradually increases, giving rise to the decline of C_N incorporated into diamond structure. This explanation does not seem to be adequate enough. We argue that the incorporation of nitrogen atom into diamond material will undergo two processes: dissolution and absorption. Beside the dissolution process, the absorption process can also affect the incorporated C_N in crystals. It is a fact that the quantity of adsorbed atoms will decrease as a result of temperature increasing, whether physical absorption or chemical absorption of nitrogen atoms, is experienced. It is apparently interpreted that the variation of C_N is affected by the crystallizing temperature when the absorption process of nitrogen atoms is considered.

The reason for causing the increase of C_N while Mg is added into the crystallization medium is worth considering. Discussing the question on the possible role of the Mg element in catalysts, it is of interest to consider the role that the Ni element plays in Fe–Ni catalyst. As is well known, diamond crystal crystallized in pure Fe metal solvent generally has a lower C_N, only at a level of tens of ppm. When Ni or Co is added into the catalyst/solvent, the C_N in synthetic crystal will progressively increase up to around 200 ppm–300 ppm. The detailed C_N in crystal depends on the crystallization temperature and the content of Ni and Co added in solvents. According to this experimental result, one can conclusively confirm that the role that the Mg element plays in the Fe–Mg catalyst system resembles the roles that Ni and Co metal play in the nitrogen incorporation process. Nevertheless, the addition of the Mg element does not enhance nitrogen aggregation like the Ni solvent. As reported, the synthetic diamond specimens are free from nitrogen in the Mg–C system, which is different from our result.[21] Considering the different conditions of diamond growth, for the Fe–Mg system we suggest that the Mg element plays a significant role in reducing the viscosity of solvent, leading to enhancement of the adsorption capacity in nitrogen impurity and therefore causing C_N to rise in the crystal. As is well known, an appropriate content of Ni or Co added in pure Fe catalyst can reduce the crystallization condition. However, the experimental results in an Fe–Mg–C system indicate that the addition of Mg leads to the *P*–*T* range for diamond crystallization slightly moving upward.

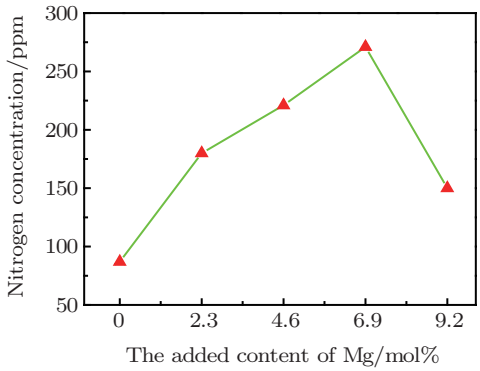


Fig. 4. (color online) Variation of C_N with C_{Mg} in catalytic medium.

The collected specimens are characterized by micro-Raman spectroscope in this study, and the results are displayed in Fig. 5. As is well known, the first-order Raman peak of purified diamond crystal is associated with sp^3-bonded carbon atom appearing at 1332.0 cm^{-1} usually under the assumption of free strain.[22] According to the Raman shift with purity of diamond crystal, it can be found that the synthetic diamond crystal crystallized in Fe–Mg solvent by the buoyancy process exhibits tensile stress, in that the first-order Raman shift appears at 1330.0 cm^{-1}. As for diamond specimen grown by the film growth process, it occurs at 1333.3 cm^{-1} as seen in the case of $x = 0$ in Fig. 5. It is currently accepted that the half width of full maximum (HWFM) of the first-order Raman peak is generally used to characterize the crystalline quality of diamond crystal. Micro-Raman spectra (Fig. 5) indicate that the HWFM is in a range of 3.01 cm^{-1}–3.26 cm^{-1} for specimens grown by the buoyancy process, whereas it is in a range of 5.52 cm^{-1}–8.89 cm^{-1} for film grown samples. It implies the extremely good quality in crystallization for samples grown by the buoyancy process. Moreover, micro-Raman spectra indicate the excessive amount of Mg added in solvent, $C_{Mg} > 6.9$ mol%, the crystalline quality will decline, for the HWFM becomes wider.

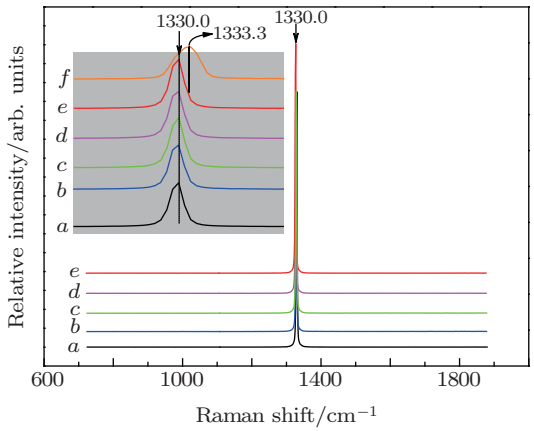


Fig. 5. (color online) Micro-Raman spectra of diamond crystals grown in the catalytic metal of $Fe_{100-x}Mg_x$ with $x = 0$ (curve *a*), 2.3 (curve *b*), 4.6 (curve *c*), 6.9 (curve *d*), and 9.2 (curve *e*). Spectrum (curve *f*) from diamond sample grown by the film growth process is used for comparison.

4. Conclusions

Diamond crystals readily crystallized in Fe–Mg–C system by using Archimedes buoyancy as a driving force. FTIR spectra indicate that the addition of Mg into the crystallization medium gives rise to an increase of C_N in diamond structure, but higher crystallization temperature applied can depress the incorporation of nitrogen impurities into diamond structure. SEM observation demonstrates that diamond samples with high-quality surfaces are generally produced when 2.3 mol%–4.6 mol% of Mg is added in metal solvent. Micro-Raman spectra reveal that the crystalline quality of diamond specimens grown by this process is high, although some macro-defects occur in diamond specimens. It is found that the addition of Mg leads to the *P*–*T* range for diamond crystallization slightly moving upward, nevertheless {100} planes are present in crystals grown under the condition of C_{Mg} in a range of 6.9 mol%–9.2 mol%.

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