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Effects of zinc additive on the HPHT synthesis of diamond in Fe–Ni–C and Fe–C systems ☆

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ABSTRACT

In the series of experiments at 5.0–7.0 GPa and 1300–1800 °C with the duration from 15 min to 2 h, the diamond crystals were synthesized in the Fe–Ni–C and Fe–C systems with zinc additive and the capability of zinc for converting graphite to diamond were also investigated in this work. Compared with the diamond synthesis using conventional catalysts, much higher temperatures are required for the nucleation and growth of diamond in Fe–Ni–Zn–C and Fe–Zn–C systems. The morphology of synthesized diamond crystals changes regularly from cub-octahedron to octahedron in the Fe–Ni–C system with increasing zinc additive, while only octahedral diamonds form in the Fe–Zn–C system. The diamond growth is accelerated by appropriate addition of zinc in conventional catalysts while the excessive zinc additive may have a suppressive effect on the diamond nucleation. We also estabish the essential dependence of diamond nucleation and morphology on the composition of crystallization medium in the Fe–Ni–Zn–C and Fe–Zn–C systems. Based on our analysis of the diamond surface configuration, we suggest that the formation of the different defects on the {100} and {111} faces is most likely due to the two simultaneous growth process on the {111} faces.

1. Introduction

It is well known that some mechanical and electronic properties are usually affected significantly by the special metals which play the role of "catalysts", for the diamond synthesized under high pressure and high temperature (HPHT) conditions. Research on the catalysts for the diamond synthesis has aroused great interest in connection with attempts to achieve some outstanding properties, such as mechanical, optical and electronic applications. Thus, an understanding of the function of catalyst forms an important research topic in the science and technology of diamond.

Since diamonds have been successfully synthesized using transition metals as catalysts in 1955 [1], the original list of catalysts for diamond synthesis discovered by General electric scientists includes nine Group VIIIB elements (Fe, Co, Ni, Ru, Th, Pd, Os, Ir, Pt) and three other transition metals (Mn, Cr and Ta) [2]. Various other materials, such as arbides, carbonates, water, hydrides, oxides, and various silicates (serpentine, muscovite, biotite, etc.), have been reported as having a catalytic effect on diamond growth [3–5]. Moreover, Wakatsuki has published that Nb, Cu and alloys with carbide forming elements (Ti, Zr, Hf, V, Nb, Mo and W) also act as catalysts [3]. It is interesting to note that diamond could form from Ta–C, Co–C, and Fe–C solid solutions [2,4,5], while some catalysts with low melting points (Zn, Cu, Ge, S, and P) [6–10] are classified into the other category and can be used as catalysts only if the temperature increases sufficiently. The melting temperature of the catalyst is, therefore, seen to be an important parameter in determining the growth conditions of diamond. Since the melting point of zinc is very low, 420 °C at ambient pressure and 600 °C at 6.0 GPa [11], the zinc is one typical catalyst in this category. In the previous work, it was found that the presence of zinc in the catalyst had a significant effect on the diamond nucleation process and crystal growth. The catalytic action of the zinc and the phase diagram of Zn–C system at 7.7 GPa were investigated in detail [12]. Furthermore, the growth regions for the diamond crystallization were found different from that in the conventional catalysts and a boundary named "Reaction line" was firstly introduced by Kanda et al. [7] to indicate where diamond started growing. However, only a 20-μm-thick growth layer was obtained on the seed crystal in 6 h in molten zinc without any spontaneous nucleation. The wettability of graphite by a melt of zinc has also been investigated and the spontaneous nucleation of diamond with bad quality was obtained at 8 GPa and 2100 K in the Zn–C system [13]. However, there is still a lack of a strict definition for the weak catalytic action of zinc for converting graphite to diamond. Thus, it is important to synthesize high quality diamonds to get a further understanding of catalytic action of zinc in the diamond formation process.

With respect to this, we have synthesized diamond in the Fe–Ni–C and Fe–C systems with zinc additive, in the range from 0 wt.% to 80 wt.% (weight ratio in catalysts). Growth runs of experiments were performed in the catalyst-carbon system at pressure ranging from 5.0 to 7.0 GPa and temperature from 1300 to 1800 °C with holding

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different time to synthesize diamond crystals. The objective of this work is to investigate the catalytic action of zinc and aims to obtain a new metallic catalyst which is effective and enables the production of diamond single crystal. It is also of importance to clarify the generation mechanism of diamond.

2. Experimental details

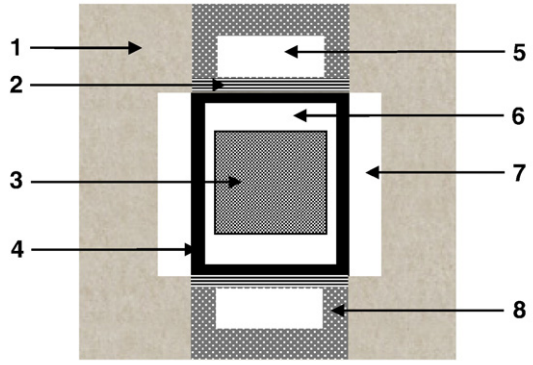
Experiments on diamond crystallization were carried out using a china-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1200). The starting materials were the high purity graphite rod (99.9% purity) as carbon source and $Fe_{70}Ni_{30}$ alloy powder (200 mesh) as catalyst. In order to obviously investigate the effect of zinc in the diamond growth, we choose zinc powders with 99.999% in purity (30 μm in size) as addition. The amount of zinc added in the catalyst powder varied from 0 to 100 wt.%. After mixing these powders for 4 h, they were shaped into disc form to fit in a cylindrical space surrounded by a ceramic material. The temperature was measured in each experiment using a Pt-30% RH/Pt-6% Rh thermocouple, whose junction was placed near crystallization sample. The design of the high-pressure cell for diamond synthesis is shown in Fig. 1. Pressure was calibrated at room temperature by the changes in resistance of standard substances and at high temperatures by the graphite-diamond equilibrium. After experiments, crystallization sample column were first cracked and examined with an optical microscope. Then the products were dissolved in hot nitric acid to remove the remaining graphite and metallic catalysts.

Morphology and structural properties of the synthesized samples were characterized by scanning electron microscopy (SEM). The infrared spectra were obtained on a Perkin-Elmer 2000 Fourier-transform infrared (FTIR) spectrometer in the spectral range between 400 and 4000 cm^{-1} with a spectral resolution of 2 cm^{-1} in the transmittance mode.

3. Results and discussion

3.1. Diamond crystallization in the Fe–Ni–Zn–C and Fe–Zn–C systems

The experimental results performed in the catalyst-carbon system at pressure ranging from 5.0 GPa to 7.0 GPa and temperature from 1300 °C to 1800 °C are summarized in Tables 1 and 2. Duration of the experiments is from 15 min to 2 h. Long run times are applied to study the diamond nucleation in the Zn–C system. In experiments performed at 5.2 GPa (N-1), the diamond nucleation and growth are both established in the Fe–Ni–C system, green in color (Fig. 2a). The morphology of the synthesized diamond exhibits cubic, cub-octahedral, and octahedral shape at 1300 °C, 1350 °C, and 1400 °C, respectively. Both the growth habits and color for the synthesized diamonds



1. pyrophyllite; 2. metal plate; 3. sample; 4. graphite heater; 5, 6, 7. ceramic cylinder and cover; 8. steel ring

Fig. 1. The sample assembly for diamond synthesis by HPHT.

Table 1
Experimental results on the crystallization of diamond in the Fe–Ni–C system with zinc additive.

Run	Zinc (wt.%)	Pressure (GPa)	Temperature (°C)	Time (°C)	Obtain diamond crystals		
					Morphology	Color	Size
N-1	0	5.2	1300–1410	15	{100} and {111}	Green	0.2
N-2	5	5.1	1320–1440	15	{100} and {111}	Greenish yellow	0.1
N-3	10	5.15	1360–1500	15	{100} and {111}	Yellow	0.15
N-4	20	5.3	1420–1530	15	Dominate {111} with minor {100}	Bright yellow	0.25
N-5	40	5.5	1440–1570	15	{111}	Light yellow	0.4
N-6	60	5.7	1500–1600	15	{111}	Colorless	0.5
N-7	80	6.0	1570–1650	15	{111}	Colorless	0.3

significantly change with the increase of zinc additive in catalysts. The nucleation of diamond increases with 5 wt.% and 10 wt.% zinc additive (N-2 and N-3) in the catalyst and decreases gradually with more zinc additive. The synthesized diamonds have yellow color with different intensities from greenish yellow to light yellow with increasing the zinc additive. The diamond synthesized with 20 wt.% zinc additive in the Fe–Ni–C system (N-4) are bright yellow, transparent, and nearly don't contain any inclusions (Fig. 2b). The obtained diamond exhibit octahedral shape with dominated {111} and minor {100} faces. As the zinc additive was increased up to 40 wt.%, the synthesized diamond (N-5) exhibit octahedral shape only with the {111} faces left, nearly colorless (Fig. 2c). To further examine the effect of zinc additive on the diamond synthesis, we adjust the synthetic pressure to control the yield of diamond, and the resulting crystals were well-distributed in the samples. The degree of the graphite-to-diamond conversation in the systems is approximately 50%. The maximum size of synthesized diamond is about 400–500 μm with 40 wt.% and 60 wt.% zinc additive (Fig. 2c and d), while that size is only about 100–200 μm in a 15 min run in the Fe–Ni–C system without zinc additive.

At 5.5 GPa, the diamond could grow in the Fe–C system (S-1), and the synthetic diamonds are light yellow in color, with cub-octahedral and octahedral morphology at 1370 °C and 1400 °C, respectively. When zinc is added up to 10 wt.%, the synthesized diamonds exhibit octahedral shape, nearly colorless, and the transparence is not as good as the crystals synthesized without zinc additive (see Fig. 2e). Note that the synthesis pressure and temperature are both increasing with the increase of zinc additive, but the nucleation of diamond decreases gradually with zinc additive more than 30 wt.%. The maximum size of the synthesized diamond is 700–800 μm in a 15 min growth process with 50 wt.% zinc additive (Fig. 2f). The rate of diamond growth is

Table 2
Experimental results on the crystallization of diamond in the Fe–C system with zinc additive and Zn–C system.

Run	Zinc (wt.%)	Pressure (GPa)	Temperature (°C)	Time (min)	Obtain diamond crystals		
					Morphology	Color	Size
S-1	0	5.5	1370–1480	15	{100} and {111}	Light yellow	0.3–0.4
S-2	1	5.5	1380–1490	15	Dominate {111} with minor {100}	Colorless	0.35–0.5
S-3	5	5.6	1350–1490	15	Dominate {111} with minor {100}	Colorless	0.35–0.5
S-4	10	5.7	1450–1560	15	{111}	Colorless	0.4–0.6
S-5	30	5.9	1530–1600	15	{111}	Colorless	0.5–0.7
S-6	50	6.1	1580–1670	15	{111}	Colorless	0.7–0.8
S-7	100	7.2	1300–1800	15–120	–	–	–