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Effects of the additive NaN_3-added in powder catalysts on the morphology and inclusions of diamonds synthesized under HPHT

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Abstract

In this paper, the effects of the additive NaN_3 added in powder catalysts to synthesize nitric diamond were studied in a cubic anvil high-pressure and high-temperature apparatus (SPD-6 × 1200). Diamond crystals with perfect shape were successfully synthesized using NaN_3-added $Fe_{90}Ni_{10}$ catalyst under pressure 5.4 GPa and temperature 1600 K for 15 min. The temperature and pressure of crystals growth were increased with an increase of the content of NaN_3. The V-shape section for the diamond's growth, which is the region between the solvent/carbon eutectic melting line and diamond/graphite equilibrium line under pressure and temperature, was moved upwards. The synthetic diamonds exhibited perfect cubo-octahedral shape or octahedral shape with green or densely green in color. However, some orderly accidented lines were observed on the surfaces of most of the diamond crystals synthesized with NaN_3-added in $Fe_{90}Ni_{10}$. These lines might be formed during the procedure of crystal growth according to the results of the scanning electron microscope images. Moreover, the Mössbauer spectrometry for these diamonds indicated that the concentrations of inclusions formed by iron in diamonds were changed and iron nitride was detected.

Keywords: Diamond; Powder catalyst; Nitrogen; Inclusion

1. Introduction

It is well known that there are a lot of impurities in diamonds synthesized by the high-pressure and high-temperature (HPHT). Parts of impurities can enter into diamond with the types of substitutes or inclusions [1–8]. Different impurities have different influences on the properties of diamond. Some properties of diamond can be improved by certain elements in the diamond. For example, n-type or p-type diamonds doped with phosphorus and boron, respectively, used as electronic and optoelectronic devices, have been prepared by chemical vapor deposition (CVD) [9]. Furthermore, the lithium, phosphorus and nitrogen have been considered extensively for enhancing the emission capability of diamond films [10,11]. Therefore, it is significant for enriching the kinds and expanding the applied fields of diamond that some atoms are doped in the diamond. Although there are many reports on the preparation of n-type or p-type diamonds by CVD, the preparation of n-type diamonds by HPHT are seldom reported. In general, the doped diamond synthesized by HPHT was mainly carried out by adding additive to the mixture of the graphite powder and the catalyst powder. Consequently, the growth of diamond was affected directly by these additives added. For example, the nucleation of diamond was effectively enhanced by the additives of B_4C, β-SiC and C_{60} fullerence particles added by a spot-coating process [12]. Furthermore, the characteristics of catalyst were changed by some elements added in the catalyst with very small concentration [13]. The trace elements in the catalyst will result in the changes on the color, shape and intensity of diamond and the distribution of the inclusion in the diamond.

Nitrogen is one of the most common impurities in natural and synthetic diamond. Nitrogen influences the physical

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properties of diamond significantly [1–6,9], including mechanical, electric and thermal properties, especially most optical properties of diamond [14,15]. It will influence the potential applications of diamond in industry and high-tech fields [2–5]. Therefore, many researchers have focused on the nitrogen in diamond synthesized by HPHT. However, up to date, how to dope nitrogen into diamond is an open question.

In this paper, it was reported that diamond doped nitrogen, which was from the additive azide added in powder catalysts, was synthesized by HPHT. High purity NaN_3 was performed as the source of nitrogen, and diamond crystals with perfect shape were synthesized with NaN_3-added $Fe_{90}Ni_{10}$ catalyst under a pressure of up to 5.4 GPa and a temperature of around 1600 K for 15 min. This work might be helpful to the further study on the doping-nitrogen diamond.

2. Experimental

The scalelike graphite powders and the catalyst powders $Fe_{90}Ni_{10}$ with 75 μm in diameter were used in our study. The additive azide is NaN_3 (99.99% in purity). The graphite powder and the catalyst powder (1 : 1, wt/wt) were mixed for 4 h firstly, and then were shaped with the form of pole for synthesizing diamond. The content of NaN_3 added in catalysts is in the range of 0.1∼2 wt%. The sample assembly for diamond synthesis by HPHT is shown in Fig. 1. A graphite tube was introduced as heater. To figure out the effect of nitride NaN_3, two kinds of diamonds were prepared. One kind of sample was synthesized from the graphite and catalysts powders directly and another sample was synthesized with additive NaN_3 added in powder catalysts. The diamonds were synthesized in a cubic anvil high-pressure and high-temperature apparatus (SPD-6 × 1200) with a sample chamber of 23 mm on an edge (Fig. 2) under pressure 5.4 GPa and temperature 1600 K for 15 min. The pressure was estimated by the oil press load, which was calibrated by a curve that was established based on the pressure-induced phase transitions of bismuth, thallium, and barium. The temperature was determined from a relation between the temperature and input power, which had been calibrated using a Pt6%Rh–Pt30%Rh thermocouple [13]. The measurement error in temperature and pressure was less than 5%.

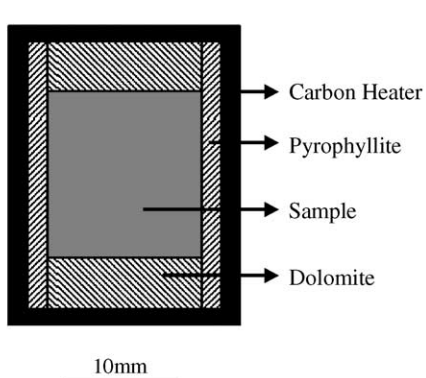

Fig. 1. The sample assembly for diamond synthesized by HPHT.

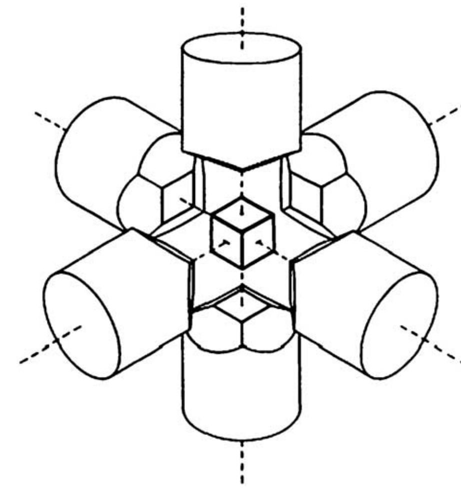

Fig. 2. The schematic diagram of a reaction cell for diamond growth by HPHT in high-pressure and high-temperature apparatus (SPD-6 × 1200).

The collected samples were disposed in a bottle of boiling mixture of H_2SO_4 and HNO_3, and then observed with an optical microscopy and scanning electron microscope on a LINK-ISIS JSM5310. The iron-inclusions in diamond crystal were characterized on an OXFORD MS-500 transmission Mössbauer spectroscopy at room temperature. The spectra were recorded using a $^{57}Co/Pd$ source.

3. Results and discussion

3.1. The effect of the additive NaN_3 on the conditions of synthesis

The pressure and temperature for diamonds synthesized by HPHT were studied firstly. The synthetic conditions for diamonds with different contents of additive NaN_3 were shown in Table 1. It was found that the pressure and temperature for diamond synthesized with additive NaN_3 were obviously higher than that without additive NaN_3. The nucleation of diamond was decreased by additive NaN_3 added in powder graphite and catalyst with the same pressure. The more additive NaN_3 was added, the

Table 1
The synthetic conditions of diamond with different NaN_3 content ($C_4 > C_3 > C_2 > C_1 > C_0 = 0$)

Content additive NaN_3 (wt%)	The synthesis conditions	
	Pressure (GPa)	Temperature (K)
$C_0 = 0$	5.10	1520
C_1	5.25	1570
C_2	5.40	1600
C_3	5.63	1650
C_4	5.70	1740