Different effect of NiMnCo or FeNiCo on the growth of type-IIa large diamonds with Ti/Cu as nitrogen getter*

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In order to synthesize high-quality type-IIa large diamond, the selection of catalyst is very important, in addition to the nitrogen getter. In this paper, type-IIa large diamonds are grown under high pressure and high temperature (HPHT) by using the temperature gradient method (TGM), with adopting Ti/Cu as the nitrogen getter in $Ni_{70}Mn_{25}Co_5$ (abbreviated as NiMnCo) or $Fe_{55}Ni_{29}Co_{16}$ (abbreviated FeNiCo) catalyst. The values of nitrogen concentration (N_c) in both synthesized high-quality diamonds are less than 1 ppm, when Ti/Cu (1.6 wt%) is added in the FeNiCo or Ti/Cu (1.8 wt%) is added in the NiMnCo. The difference in solubility of nitrogen between both catalysts at HPHT is the basic reason for the different effect of Ti/Cu on eliminating nitrogen. The nitrogen-removal efficiency of Ti/Cu in the NiMnCo catalyst is less than in the FeNiCo catalyst. Additionally, a high-quality type-IIa large diamond size of 5.0 mm is obtained by reducing the growth rate and keeping the nitrogen concentration of the diamond to be less than 1 ppm, when Ti/Cu (1.6 wt%) is added in the FeNiCo catalyst.

Keywords: high pressure and high temperature, catalyst, nitrogen getter, type-IIa large diamond

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1. Introduction

Almost all natural diamonds have some defects. Especially type-Ib diamond contains a large quantity of nitrogen impurities which greatly influence the applications of its many excellent properties. Type-IIa large diamond (size> 1 mm) contains less nitrogen atoms ($N_c < 1$ ppm) and is free of impurities or inclusions.[1–6] Comparing with type-Ib large diamond, the mechanical and physical properties of type-IIa large diamond are greatly promoted, due to its high crystal quality and almost no crystal defects. These remarkable features enable it to give the maximum limiting function of type-IIa diamond. So, it can be used as infrared spectral window material, monochromator of x-ray synchrotron radiation, diamond anvil cells (DAC) of high pressure equipment, coal mine drill, etc.[7–12] Considering the scarcity of the natural resources and expensive price of perfect type-IIa diamond, study of the synthesis of type-IIa large diamond has practical significance.

In order to synthesize high-quality type-IIa large diamond, the selection of nitrogen getter and catalyst are very important. Nitrogen getter, which is free in the chamber, can react with nitrogen by generating more stable nitride, so it can avoid the nitrogen entering into the diamond.[4–17] The previous studies on type-IIa large diamond often focused on the nitrogen getter, especially on the commonly used nitrogen getter of Al and Ti/Cu.[6–14] Otherwise, catalyst refers to metal or alloy that is able to reduce the synthesis temperature and pressure conditions of diamond synthesis. The influences of different catalysts on N_c of synthetic type-Ib large diamond have been reported.[18–21] However, the influence of catalyst composition on eliminating nitrogen has not been reported. In order to synthesize type-IIa large diamond, we choose Ti/Cu as the nitrogen getter and added it to the typical NiMnCo catalyst or FeNiCo catalyst. Then, the different efficiencies of Ti/Cu on eliminating nitrogen with NiMnCo and FeNiCo catalyst are investigated in detail. High quality colorless type-IIa large diamond is synthesized by controlling the crystal growth rate, choosing a suitable catalyst, and determining the ratio of nitrogen getter related to catalyst.

2. Experiment

The experiments on diamond crystal growth were carried out by TGM in a China-type cubic anvil high-pressure apparatus (CHPA) (SPD-6×1200). The assembly diagram of dia-

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mond synthesis is shown in Fig. 1. The samples were synthesized under conditions of pressure approximately at 5.5 GPa and temperature approximately at 1260 °C. The high-purity graphite (99.99%) was used as the carbon source and NiMnCo or FeNiCo alloy used as the solvent catalyst. A particle size of about 0.5 mm of high quality diamond was selected as the seed along the (100) crystal orientation to grow. Different quantities of Ti/Cu (the quantity of Ti/Cu is expressed as wt% in this paper, namely, this weight percentage is Ti or Cu accounted for the weight proportion of catalys and the weight ratio between Ti and Cu is 1/1) were introduced to synthesize type-IIa large diamond.

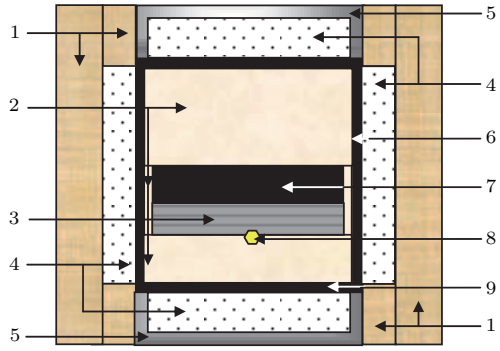


Fig. 1. (color online) Schematic diagram of assembly for synthesizing diamond by TGM. 1: sealing medium (pyrophyllite), 2: insulation material (MgO), 3: catalyst (FeNiCo or NiMnCo), 4: filling medium (dolomite), 5: conductive cap (iron), 6: heater tube (graphite), 7: carbon source (graphite), 8: seed (diamond), 9: conductive sheet (graphite).

In the experiments, the pressure was estimated by the load of oil press, which was calibrated by a curve that was established on the pressure-induced phase transitions of elements of Bi, Ba, and Tl. The temperature was determined from the relationship between temperature and input power, which was calibrated using a Pt6%Rh-Pt30%Rh thermocouple.[15] The N_c in diamond was measured by the results of micro Fourier transform infrared (FTIR) spectroscopy. It was reported that N_c was proportional to the intensities of absorbance at 1130 cm^{-1} and 1344 cm^{-1} in an ideal spectrum, and determined from the equation $N_c = (25.0 \pm 2) \times \alpha$ (1130 cm^{-1}).[11] In this formula, α (1130 cm^{-1}) represents the absorbed parameter at 1130 cm^{-1} peak.

TGM under HPHT is that graphite first became diamond and dissolved in the catalyst, then, it began to diffuse to the seed under the driving of temperature gradient and then grew in the seed.[4–6] In one-dimensional approximation, the diamond crystal growth rate is proportional to the temperature gradient:

$$v = \mathrm{d}w/\mathrm{d}t \propto \mathrm{d}T/\mathrm{d}z,$$

where v, w, t, and $\mathrm{d}T/\mathrm{d}z$ are the crystal growth velocity, crystal weight, crystal growth time, and axial temperature gradient, respectively.[16] The different temperature gradients in the chamber were acquired by adjusting the assembly to control the growth rate.

3. Results and discussion

Fe-based alloy or Ni-based alloy is usually selected as the catalyst to synthesize large diamond under HPHT by using TGM. Then, type-IIa large diamonds are synthesized in the representative NiMnCo or FeNiCo catalyst and Ti/Cu is adopted as the nitrogen getter, because the efficiency of Ti/Cu on eliminating nitrogen is better than that of Al.[11,14] The Ti/Cu is different from Al which will generate easily the decomposition of AlN during diamond crystal growing.[4–6] So, Ti/Cu is chosen as the nitrogen getter to synthesize large diamonds. For nitrogen getter Ti/Cu, Ti reacts with N to eliminate nitrogen, and Cu dissolves TiC which is generated by Ti and C.[4–6]

3.1. Efficiency in eliminating nitrogen of Ti/Cu in NiMnCo

Diamond syntheses are studied in NiMnCo alloy with the values of Ti/Cu ranging from 0.5 wt% to 2.0 wt%. Growth time and temperature of diamonds are 3 hour and 1280 °C, respectively. The temperature gradient is adjusted to 30 °C/mm and growth rate of diamonds was controlled to about 1.5 mg/h. The experimental results are shown in Table 1.

Table 1. Results of diamond growth with different quantities of Ti/Cu in NiMnCo.

Sample	Quantity Ti/Cu/wt%	Temperature/°C	Temperature gradient/(°C/mm)	growth rate /(mg/h)	N_c/ppm	Color	Diamond defects
A	0.5	1280	30	1.5	151.2	yellow	no
B	1.0	1280	30	1.5	85.7	light yellow	no
C	1.5	1280	30	1.5	52.9	slight yellow	no
D	1.8	1280	30	1.5	< 1	colourless	no pit but a few inclusions
E	2.0	1280	30	1.5	< 1	colourless	some pits and inclusions

In order to determine the N_c content values in diamonds with different amounts of nitrogen getter in NiMnCo catalyst, all synthetic diamonds in Table 1 are tested by micro FTIR. The FTIR absorption spectra of the synthetic diamond crystals are shown in Fig. 2. According to these curves of FTIR absorption spectra and N_c formula, N_c content values in diamonds (collected in Table 1) with the different amounts of nitrogen getter are 151.2 ppm (Ti/Cu: 0.5 wt%), 85.7 ppm (Ti/Cu: 1.0 wt%), 52.9 ppm (Ti/Cu: 1.5 wt%), < 1 ppm (Ti/Cu: 1.8 wt%), < 1 ppm (Ti/Cu: 2.0 wt%), respectively.

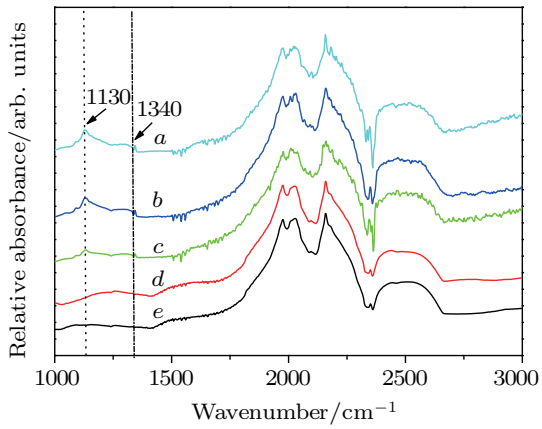


Fig. 2. (color online) FTIR absorption spectra of large diamonds synthesized with different quantities of Ti/Cu nitrogen getter in NiMnCo catalyst (curve *a*) 0.5 wt%, (curve *b*) 1.0 wt%, (curve *c*) 1.5 wt%, (curve *d*) 1.8 wt%, (curve *e*) 2.0 wt%).

As shown in Table 1, with increasing the content of additive Ti/Cu, the color of diamond crystals changes from yellow to light yellow to slight yellow, then to colorless. It can be seen from the results of FTIR that the N_c in the diamond gradually decreases with the increase of Ti/Cu additive. However, inclusions and pits are found when the Ti/Cu content increases to 2.0 wt%. The ability of diamond to capture metallic inclusions increases with the increase of Ti/Cu additive, which is consistent with the results reported by Sumiya *et al.*[4,10] However, the pit emerges when adding too much Ti/Cu, and it seriously affects the quality of crystals.

In order to synthesize high-quality colorless type-IIa large diamond without metallic inclusions or pits on its surface, we reduce the crystal growth rate and determine the content of Ti/Cu additive. The temperature gradient is reduced to about 25 °C/mm by adjusting the assembly. Finally, the growth rate drops to 1.2 mg/h. While the quantity of Ti/Cu additive is 1.8 wt%, the size of the superior diamond reaches 2.0 mm with a growth time of 12 hours. As shown in Fig. 3, there are no visible inclusions in the diamond, and crystallization of the surface is very flat without pits.

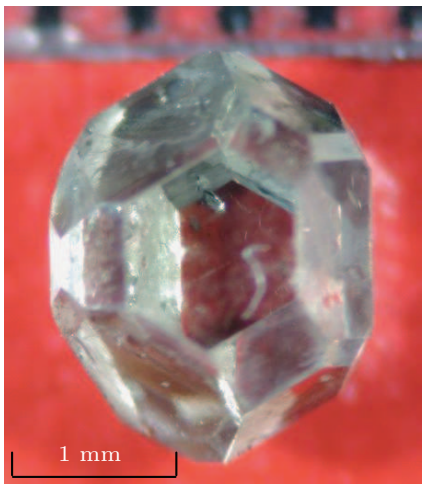


Fig. 3. (color online) Photo of diamond at 1.8 wt% of Ti/Cu in NiMnCo (12 h).

3.2. Efficiency in eliminating nitrogen of Ti/Cu in FeNiCo

According to the literature,[20] the N_c in type-Ib large diamond of FeNiCo as catalyst is less than that in diamond of NiMnCo as catalyst. In order to investigate whether the catalyst composition has any influence on the efficiency in eliminating nitrogen, the catalyst component is replaced by FeNiCo alloy. The Ti/Cu quantity is changed to synthesize the type-IIa large diamond. In order to facilitate comparison and analysis, the quantity of Ti/Cu ranging from 0.5 wt% to 2.0 wt% was added in FeNiCo alloy to synthesize diamonds, respectively. The growth time and temperature of diamonds are 3 hour and 1280 °C, respectively. The temperature gradient is adjusted to 33 °C/mm and the growth rate of diamonds is controlled to about 1.8 mg/h. The experimental results are shown in Table 2.

Table 2. Results of diamond growth with different quantities of Ti/Cu in FeNiCo.

Sample	Quantity (Ti/Cu)/wt%	Temperature/°C	Temperature gradien/(°C/mm)	Growth rate/(mg/h)	N_c/ppm	Color	Diamond defects
A	0.5	1280	33	1.8	77.7	yellow	no
B	0.8	1280	33	1.8	66.3	light yellow	no
C	1.3	1280	33	1.8	24.6	slight yellow	no
D	1.6	1280	33	1.8	< 1	colourless	no pit but a few inclusions
E	2.0	1280	33	1.8	< 1	colourless	some pits and inclusions

In order to determine the N_c content values in diamonds with the different quantities of nitrogen getter in FeNiCo catalyst, all synthetic diamonds in Table 2 are tested by micro FTIR. The FTIR absorption spectra of the synthetic diamond crystals are seen in Fig. 4. According to these curves of FTIR absorption spectra and N_c formula, N_c content values in diamonds (seen in Table 2) with the different quantities of nitrogen getter are 77.7 ppm (Ti/Cu: 0.5 wt%), 66.3 ppm (Ti/Cu: 1.0 wt%), 24.6 ppm (Ti/Cu: 1.3 wt%), < 1 ppm (Ti/Cu: 1.6 wt%), and < 1 ppm (Ti/Cu: 2.0 wt%), respectively.

It can be seen in Table 2, the color of diamond is slight yellow with a quantity of Ti/Cu additive of 1.3 wt% in FeNiCo. While the quantities of Ti/Cu are 1.6 wt% and 2.0 wt%, the color of diamond is colorless but defective. Comparing with type-Ib large diamonds, the growth rate of type-IIa large diamond greatly decreases. Therefore, the assembly is adjusted to

reduce the growth rate for synthesizing superior type-IIa diamond crystal. While the quantity of Ti/Cu additive is 1.6 wt%, and the growth rate dropped to 1.6 mg/h, the synthesized diamond is colorless without inclusion or pit. The size of the superior diamond arrives at 2.2 mm with a growth time of 12 h. As shown in Fig. 5, there are no visible inclusions in the diamond, and the crystallization of the surface is perfect (without any defect). While the quantity of Ti/Cu additive is up to 2.0 wt% and the growth rate is still 1.6 mg/h, metal inclusion often appears in diamond. Therefore, it is shown that the most appropriate quantity of Ti/Cu additive in FeNiCo catalyst is 1.6 wt%.

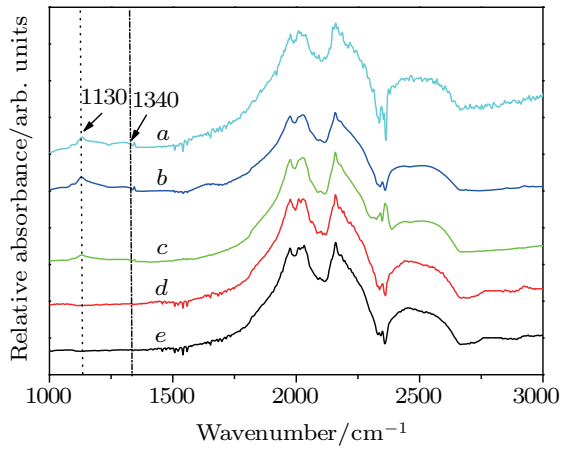


Fig. 4. (color online) FTIR absorption spectra of large diamonds synthesized with different quantities of Ti/Cu nitrogen getter in FeNiCo catalyst ((curve *a*) 0.5 wt%, (curve *b*) 1.0 wt%, (curve *c*) 1.3 wt%, (curve *d*) 1.6 wt%, and (curve *e*) 2.0 wt%), respectively.

By adjusting the assembly and reducing the growth rate (1.6 mg/h), the type-IIa large diamond is synthesized in a CHPA for 12 hours (Ti/Cu for 1.6 wt%) as shown in Fig. 5.

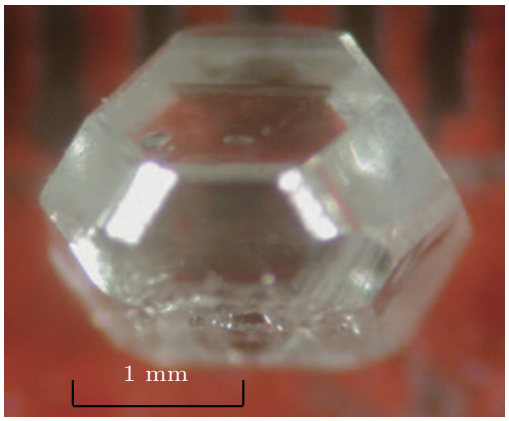


Fig. 5. (color online) Photo of diamond at 1.6 wt% of Ti/Cu additive in FeNiCo (12 h).

3.3. Analysis of efficiency on eliminating nitrogen with Ti/Cu in different catalysts

First, without considering the quality of crystal, it can be shown from Tables 1 and 2, and Figs. 2 and 4 that N_c content values in diamonds with NiMnCo catalyst are more than in diamonds with FeNiCo catalyst and the quantities of nitrogen getter in NiMnCo for diamonds are more than in FeNiCo for diamonds. It indicates that with the same quantity of nitrogen getter, the FeNiCo catalyst is more suitable for synthesizing low N_c of diamond than the NiMnCo catalyst.

It can be explained that the different ability to melt soluble nitrogen leads to the different efficiencies on eliminating nitrogen of Ti/Cu in both catalysts. According to the literature,[3] outer electronic shell structures of Fe, Co, Ni are $3d^64s^2$, $3d^74s^2$, and $3d^84s^2$, respectively, and the numbers of these electrons in the d shell increase gradually. The lower the electron number is in the d shell, the smaller the atomic number is in the row elements of the periodic table. Therefore, nitrogen is easier to enter into, to dissolve and to stay in catalytic melt of the Fe base than that of the Ni base, and it is hard for nitrogen impurities to enter into diamond with the Fe base as catalyst. According to this theory, the ability of metal to dissolve nitrogen should be in the sequence of Fe>Co>Ni.[15] So, the N_c content in diamond with Fe-base as catalyst should be lower than in diamond with Ni-based as catalyst. This shows that the N_c content in diamond with FeNiCo as catalyst is lower than that with NiMnCo as catalyst without nitrogen getter.

Without nitrogen getter, the N_c content in diamond with NiMnCo as catalyst is 430 ppm but the N_c content is only 140 ppm in diamond with FeNiCo as catalyst according to the report.[20] This is consistent with the above discussion and analysis. More content of Ti/Cu additive is required in NiMnCo catalyst than that in FeNiCo to synthesize type-IIa diamond. Metal inclusions appear easily in diamond as the content of Ti/Cu increases.[3,10] Therefore, our study results confirm that the FeNiCo catalyst is more suitable than the NiMnCo catalyst for growing high-quality colorless type of IIa large diamond.

In order to grow high-quality type-IIa crystals with Ni-based and Fe-based catalyst, respectively, the process of large diamond should be optimized. By choosing the right amount of Ti/Cu and reducing the growth rate, type-IIa high-quality diamond crystals (Figs. 3 and 5) can be synthesized with NiMnCo or FeNiCo, respectively. These results of diamonds are summarized in Table 3.

Table 3. Different efficiencies on eliminating nitrogen of Ti/Cu in both catalysts.

Catalyst	Quantity Ti/Cu	N_c/ppm	Color	Growth rate/(mg/h)	Pit	Inclusion
NiMnCo	1.8	<1 ppm	colourless	1.2	no	no
FeNiCo	1.6	<1 ppm	colourless	1.6	no	no

The FTIR absorption spectra of diamond samples in Figs. 3 and 5 are shown in Fig. 6. It can be seen from Fig. 6 that the N_c content values in both diamonds are less than 1 ppm (the data are collected in Table 3).

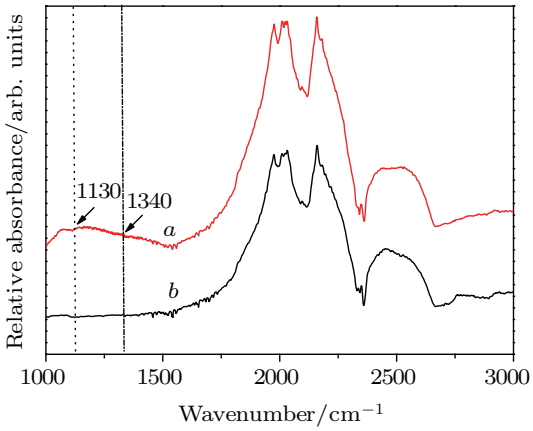


Fig. 6. (color online) FTIR absorption spectra of (a) diamond in Fig. 3 and (b) diamond in Fig. 5).

It can be seen from Table 3 that the quantity of Ti/Cu additive (1.6 wt%) in FeNiCo is less than in NiMnCo (1.8 wt%) when N_c content values are both lower than 1 ppm. Namely, the amount of nitrogen getter in NiMnCo for diamond in Fig. 3 is more than that in FeNiCo for diamond in Fig. 5 and the color of the former is inferior to that of the latter. Moreover, the growth rate of type-IIa diamond with FeNiCo catalyst is faster than that with NiMnCo. The reason is that the former needs to be added with a less amount of Ti/Cu than the latter. It indicates that the FeNiCo catalyst is more suitable for synthesizing low N_c diamond than NiMnCo catalyst.

Therefore, our study results confirm that the FeNiCo catalyst is more suitable than the NiMnCo catalyst for growing high-quality colorless type-IIa large diamond.

3.4. Synthesis of high-quality type-IIa large diamond

According to the above results and analyses, FeNiCo alloy, which is suitable for synthesizing type-IIa diamond, is selected as the catalyst. Therefore, using FeNiCo as the catalyst and Ti/Cu as the nitrogen getter, a high-quality type of IIa large diamond crystal with about 5 mm in size is synthesized after the growth time has extended to 50 hours. Then the colorless type-IIa large diamond without inclusion or pit is obtained as shown in Fig. 7

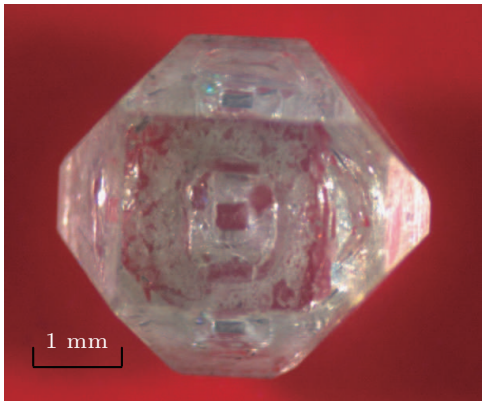


Fig. 7. (color online) Photo of diamond at 1.6 wt% of Ti/Cu additive in FeNiCo (50 h).

4. Conclusions

With adopting Ti/Cu as the nitrogen getter in NiMnCo or FeNiCo catalyst, large diamonds are grown by TGM under HPHT. Conclusions can be drawn as follows.

(i) With adopting Ti/Cu as the nitrogen getter in NiMnCo or FeNiCo catalyst, high-quality colorless type-IIa large diamonds are obtained.

(ii) The efficiency on eliminating nitrogen of Ti/Cu in the FeNiCo catalyst is better than in NiMnCo.

(iii) With adopting Ti/Cu as the nitrogen getter in the FeNiCo catalyst, high-quality colorless type-IIa large diamond with 5 mm in size is obtained.

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