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Citation: Chin. Phys. B . 2020, 29(1): 018101 . **doi:** 10.1088/1674-1056/ab592f
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Growth characteristics of type IIa large single crystal diamond with Ti/Cu as nitrogen getter in FeNi–C system*

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(Received 20 September 2019; revised manuscript received 12 November 2019; accepted manuscript online 20 November 2019)

High-quality type IIa large diamond crystals are synthesized with Ti/Cu as nitrogen getter doped in an FeNi–C system at temperature ranging from 1230 °C to 1380 °C and at pressure 5.3–5.9 GPa by temperature gradient method. Different ratios of Ti/Cu are added to the FeNi–C system to investigate the best ratio for high-quality type IIa diamond. Then, the different content of nitrogen getter Ti/Cu (Ti : Cu = 4 : 3) is added to this synthesis system to explore the effect on diamond growth. The macro and micro morphologies of synthesized diamonds with Ti/Cu added, whose nitrogen concentration is determined by Fourier transform infrared (FTIR), are analyzed by optical microscopy (OM) and scanning electron microscopy (SEM), respectively. It is found that the inclusions in the obtained crystals are minimal when the Ti/Cu ratio is 4:3. Furthermore, the temperature interval for diamond growth becomes narrower when using Ti as the nitrogen getter. Moreover, the lower edge of the synthesis temperature of type IIa diamond is 25 °C higher than that of type Ib diamond. With the increase of the content of Ti/Cu (Ti : Cu = 4 : 3), the color of the synthesized crystals changes from yellow and light yellow to colorless. When the Ti/Cu content is 1.7 wt%, the nitrogen concentration of the crystal is less than 1 ppm. The SEM results show that the synthesized crystals are mainly composed by (111) and (100) surfaces, including (311) surface, when the nitrogen getter is added into the synthesis system. At the same time, there are triangular pits and dendritic growth stripes on the crystal surface. This work will contribute to the further research and development of high-quality type IIa diamond.

Keywords: high temperature and high pressure, temperature gradient method, type IIa diamond

PACS: 81.05.ug, 61.72.S–, 61.05.C–, 07.35.+k **DOI:** 10.1088/1674-1056/ab592f

1. Introduction

Diamond is a kind of multi-functional material, which has excellent performance in mechanical, thermal, optical, chemical and electrical fields. Since the first large diamond was synthesized with metal catalyst and graphite by temperature gradient method (TGM) under high temperature and high pressure (HPHT) in 1971,[1] its synthesis characteristics have been widely concerned. During the synthesis process of diamond, the crystal contains metal inclusions and some chemical impurity elements such as nitrogen and nickel. The presence of these impurities in the crystal will significantly affect the properties of diamond.[2–6] In particular, the nitrogen content in diamonds would strongly affect their physical and chemical properties.[6] According to the concentration and existing forms of N and B atoms, diamonds are classified into type Ia (IaA and IaB), type Ib, type IIa and type IIb. Type IaA and IaB diamonds correspond to nitrogen atoms with pair atoms (A center) and four atoms accompanying vacancy (B center) respectively, while type Ib diamond contains nitrogen in a single substitution form (C center).[6] Type IIa is pure diamond that contains almost no nitrogen impurities. Additionally, type IIb diamond only contains boron impurity.[7–9] Most of the synthetic diamonds belong to type Ib, which are mainly used in the field of industrial processing. Type IIa diamond has a good crystal structure due to its low nitrogen concentration. Therefore, type IIa diamond has an irreplaceable role, for example, it can be used as an optical window material of laser transmitter and has more advantageous to synthesize new semiconductors by adding sulfur, phosphorus and boron.[10–13] Presently, a large number of researchers have devoted to study of type IIa synthetic diamond.

During the diamond growth process, nitrogen impurities in the synthetic cavity are easy to enter into the crystal, which leads to high concentration of the isolated nitrogen defects and makes the crystal display yellow. Nitrogen impurities can be found in the pores of carbon source, solvent and synthetic cavity materials. Therefore, in order to synthesize colorless dia-

*Project supported by the Natural Science Foundation of Henan Province of China (Grant No. 182300410279), the Key Science and Technology Research Project of Henan Province of China (Grant No. 182102210311), the Key Scientific Research Project in Colleges and Universities of Henan Province of China (Grant Nos. 18A430017 and 20B140009), the Fundamental Research Funds for the Universities of Henan Province of China (Grant No. NSFRF180408), and the Fund for the Innovative Research Team (in Science and Technology) in the University of Henan Province of China (Grant No. 19IRTSTHN027).

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mond crystals, Ti is often added as nitrogen getter to eliminate nitrogen impurities and Cu is added to reduce the formation of TiC in the synthesis system.[14–19] Sumiya *et al.* successfully synthesized 6 mm type Ⅱa crystal by doping Ti in the FeCo–C system.[6] Wang *et al.* successfully synthesized a type Ⅱa large diamond single crystal, whose diameter is about 4 mm, with Ti/Cu as nitrogen getter in the FeNiCo–C system.[20] At present, the most common FeNi catalyst in the industry has been less researched in the synthesis of type Ⅱa diamond large single crystal.

In this paper, Ti and Cu were added to the FeNi–C system with different ratios to investigate the best ratio for high-quality type Ⅱa diamond. Then, different contents of nitrogen getter Ti/Cu (the best ratio) added was employed to this synthesis system to explore the effect on diamond growth. The synthesized diamonds are characterized by optical microscopy (OM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). We believe that the current research results will help to expedite the industrialization process of high-quality type Ⅱa diamond.

2. Experimental methods

The synthesis experiments of the colorless diamond were performed using a cubic-anvil high pressure apparatus (China type SPD–6 × 1200) by temperature gradient method (TGM). High-purity graphite powder (99.99%) and $Fe_{64}Ni_{36}$ alloy were used as carbon source and solvent, respectively. High-purity Ti metal was used as nitrogen getter during diamond crystallization. The growth surface (111) with better crystal surface was selected as the growth surface for diamond seed (0.5 mm × 0.5 mm). The synthetic pressure and temperature were 5.3–5.9 GPa and 1230–1380 °C, respectively. The synthesis time of crystal was controlled for six hours to avoid the influence of different growth time on the results. Crystal growth was placed in a circular cavity of insulating and sealing pyrophyllite blocks. The assembly diagram of the experiment is shown in Fig. 1. Ti was selected as nitrogen getter (nitrogen removal agent) to add into the diamond synthesis chamber. The pressure was estimated by the oil press load, which was calibrated by a curve that was established on the pressure-induced phase transitions of Bi, Tl, and Ba. The temperature was determined by a Pt6%Rh–Pt30%Rh thermocouple.

After HPHT synthesis, the samples were put into hot HNO_3 to separate the crystals from the catalytic melt. Then, the crystals were put into a mixture of H_2SO_4 and HNO_3 to eliminate the residual graphite on the crystal surface. The supersonic wave equipment was used to remove small residues on the surface of the crystal, and then optical microscopy (OM) was used to observe the crystal samples. The area ratio of (111) to (100) of the synthesized crystal was used to characterize the change of crystal form. A scanning electron microscope (SEM, FEI Quanta 250 FEG type) was used to observe the microscopic morphology of the crystal surface. Nitrogen concentration (C_N) in diamonds was measured by Fourier fransform infrared (FTIR) spectroscopy on a BRUKER IFS 66 V/S spectrometer fitted with a Hyperion 3000 microscope. The IR beam size was limited to 150 μm square by apertures so as to pass only one type Ⅱa diamond. The FTIR spectroscopy was carried out in the range of 400–4000 cm^{-1}, and the accuracy of the tester was 2 cm^{-1}.

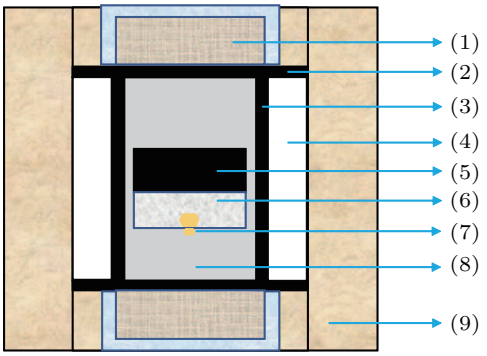


Fig. 1. Sample assembly for diamond synthesized by HPHT: (1) steel cap, (2) sheet graphite, (3) graphite heater, (4) NaCl + ZrO_2 sleeve, (5) carbon source, (6) alloy catalyst, (7) seed crystal, (8) ZrO_2 + MgO pillar, (9) pyrophyllite.

3. Results and discussion

3.1. Ti/Cu ratio on growth of type Ⅱa diamond

According to the previous report,[6] when Ti/Cu is used as a nitrogen getter in the FeCo–C system, the mass ratio of Ti to Cu is 1 : 1 to obtain a type Ⅱa crystal with no inclusions. However, there are a lot of inclusions in the crystal when the mass ratio of Ti/Cu is 1 : 1 in the FeNi–C system. It is well known that the following reactions occur during the synthesis of type Ⅱa diamond with Ti/Cu as nitrogen getter: $Ti + N \rightarrow TiN$, $Ti + C \rightarrow TiC$, $TiC + Cu \rightarrow Ti^- + Cu^+ + C$.[20] According to the above reaction equation, it can be known that Ti, as nitrogen getter, reacts with carbon and nitrogen elements to form TiN and TiC during the synthesis of type Ⅱa diamond. The purpose of Cu additive is to decompose the formed TiC in the synthesis system. According to this principle, the effect of Ti/Cu with different mass ratios on the diamond growth in the FeNi–C system is further discussed, so as to solve the problem of a large number of inclusions in the process of crystal growth. In this experiment, 1.8 wt% of Ti was used as the basic doping amount,[6] and the change of crystal after synthesis was investigated by changing the addition content of Cu. The experimental data, the photos of synthesized crystals and its results of FTIR are shown in Table 1, Figs. 2 and 3, respectively.

Table 1. The experimental results of synthesizing crystals doped with different ratios of Ti and Cu in the FeNi–C system.

Run	Ratio of Ti to Cu/wt%	Temperature/°C	Ratio of (111) to (100)	Color	Inclusions	C_N/ppm
(a)	1.80 : 1.80 (4/4)	1270	9.2 : 1.1	dark	a few	< 1
(b)	1.80 : 1.35 (4/3)	1270	6.1 : 1.2	colorless	no	< 1
(c)	1.80 : 0.90 (4/2)	1270	4.9 : 1.1	colorless	a few	< 1
(d)	1.80 : 0.45 (4/1)	1270	3.7 : 1.0	yellowish	a few	7

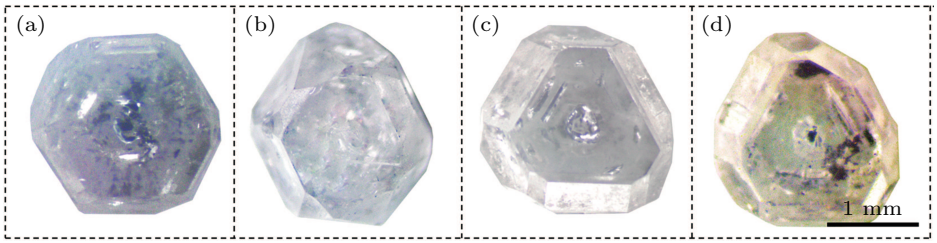


Fig. 2. Optical micrographs of synthetic diamonds in the FeNi–C system with the different ratios of Ti/Cu additives: (Ti/Cu) (a) 1.80 : 1.80 (4/4), (b) 1.80 : 1.35 (4/3), (c) 1.80 : 0.90 (4/2), (d) 1.8 : 0.45 (4/1).

According to the experimental results of Wang *et al.*, the growth temperature range of type Ib crystal synthesized along (111) surface in the FeNi–C system is 1235–1360 °C.[21] The experiments were conducted in the FeNi–C system under a pressure of 5.6 GPa and a temperature of 1270 °C for 6 h. The changes of crystal color, inclusion amount and nitrogen concentration were investigated by doping different ratios of Ti to Cu. The ratio of crystalline Ti to Cu are shown in the optical micrographs of Figs. 2(a)–2(d) is (a) 1.8 : 1.8, (b) 1.8 : 1.35, (c) 1.8 : 0.9, and (d) 1.8 : 0.45, respectively. By comparing the crystal optical pictures in Fig. 2, it can be found that amount of inclusions in the corresponding crystals (Figs. 2(a)–2(d)) varies from a few, nothing to a few with the addition content of Cu decreasing from 1.8 wt% to 0.45 wt%. Additionally, the colors of the obtained diamond crystals transform from colorless to yellow. Figure 2(c) shows that the crystal with Ti/Cu ratio of 4:3 does not contain inclusions, and C_N calculated by infrared spectrum is less than 1 ppm.

The nitrogen element is the main impurity in the diamond crystal and is easily present in the crystal lattice. The main form of existence in crystals is determined by the spectral shape in the one phonon region (800–1400 cm^{-1}) of nitrogen concentration. According to the National Institute of Standards and Technology (NIST) infrared database, it can be found that the representative peaks of N element in diamond locate at 1130 cm^{-1} and 1344 cm^{-1}, resulting from C-center nitrogen. Nitrogen impurities are present in the crystal lattice of the single substitution form, and the concentration of nitrogen atoms in the crystal is proportional to the 1130 cm^{-1} and 1344 cm^{-1} in the ideal spectrum (type Ib diamond). The nitrogen impurity concentration can be evaluated based on the absorption coefficient of the FTIR spectrum as follows: $C_N = (25 \pm 2) \times \alpha(1130\ cm^{-1})$,[22] in which $\alpha(1130\ cm^{-1})$ is the absorption coefficient of the peak at 1130 cm^{-1}

$$u\left(1130\ cm^{-1}\right) = \left[A\left(1130\ cm^{-1}\right) - A\left(1400\ cm^{-1}\right)\right],$$
$$u(2000\ cm^{-1}) = [A(2000\ cm^{-1}) - A(1400\ cm^{-1})],$$
$$\alpha(1300\ cm^{-1}) = [u(1300\ cm^{-1})/u(2000\ cm^{-1}) \times 5.5].$$

Here, $A(1130\ cm^{-1})$ is the absorption intensity of the 1130 cm^{-1} peak; $A(1400\ cm^{-1})$ is the absorption intensity of the 1400 cm^{-1} peak; and $A(2000\ cm^{-1})$ is the absorption intensity of the 2000 cm^{-1} peak. Shown by curves (a)–(c) in Fig. 3, the corresponding FTIR spectra of C–N bonds locating at 1130 cm^{-1} and 1344 cm^{-1} were not detected when the addition amount of Ti was fixed at 1.8 wt% with the addition amount of Cu gradually decreasing. Based on this formula, the C_N of curve d in Fig. 3 is evaluated to be about 7 ppm. This indicates that the C_N in the crystal changes significantly, and the C_N in the crystal is less than 1 ppm.

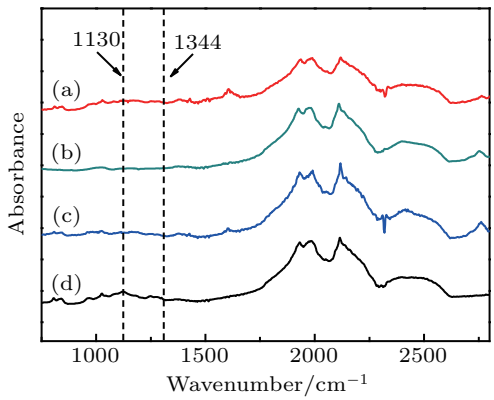


Fig. 3. Typical FTIR spectra recorded for diamond crystals synthesized in the FeNi–C system with the different ratios of Ti to Cu additives: (a) 1.80 : 1.80 (4/4), (b) 1.80 : 1.35 (4/3), (c) 1.80 : 0.90 (4/2), (d) 1.80 : 0.45 (4/1).

By analyzing the color change and the amount of inclusions of crystals synthesized in different proportions, it is found that the inclusions of the synthesized diamond crystal

are the least and the crystals exhibit colorless. According to the infrared spectra of 1130 cm^{-1} and 1344 cm^{-1} in the (111) surface of different proportions of crystals, indicating that the C_N in crystal is less than 1 ppm at 4 : 3 of Ti/Cu ratio. The results show that the optimum doping ratio of Ti/Cu crystal is 4 : 3.

3.2. Effect of Ti/Cu content on diamond growth

Synthesis experiments were carried out with the different addition amounts of Ti/Cu (4 : 3) in the FeNi–C system at pressure of 5.6 GPa and temperature of 1270 °C. The growth time of the crystals was determined to be 6 h. The synthetic conditions of diamond added with different amounts of Ti/Cu are listed in Table 2. The corresponding crystal optical photos are shown in Fig. 4.

According to Table 2, the addition amounts of Ti as nitrogen getter from a to g are 0 wt%, 1.0 wt%, 1.5 wt%, 1.6 wt%, 1.7 wt%, 1.8 wt%, and 1.9 wt%, respectively. Correspondingly, the addition amounts of Cu as TiC decomposer from a to g are 0 wt%, 0.75 wt%, 1.13 wt%, 1.20 wt%, 1.28 wt%, 1.35 wt%, and 1.43 wt%, respectively. It is observed from Fig. 4 that the yellow color of the crystals gradually becomes light during the change of Ti from 1.0–1.6 wt%. When the amount of Ti is increased to 1.7 wt%, the color of the diamond crystal becomes colorless. Furthermore, the color of the crystal does not change with further increase of amount of the additive. Additionally, it is noticed that the growth rate of the diamond crystal is significantly reduced, resulting from the addition of the nitrogen getter in the FeNi–C system.

Table 2. Experimental results of synthesizing type IIa diamond crystals by adding different contents of Ti/Cu (Ti : Cu = 4 : 3) in the FeNi–C system.

Run	(Ti/Cu)/wt%	Pressure/GPa	Temperature/°C	Ratio of (111) to (100)	Color	C_N/ppm
a	0	5.6	1270	8.2:1.4	yellow	188
b	1.00/0.75	5.6	1270	13 : 1.8	yellowish	12
c	1.50/1.13	5.6	1270	7.2 : 1.4	yellowish	7
d	1.60/1.20	5.6	1270	8.5 : 1.2	yellowish	3
e	1.70/1.28	5.6	1270	8.6 : 1.1	colorless	< 1
f	1.80/1.35	5.6	1270	8.5 : 1.2	colorless	< 1
g	1.90/1.43	5.6	1270	7.6 : 1.4	colorless	< 1

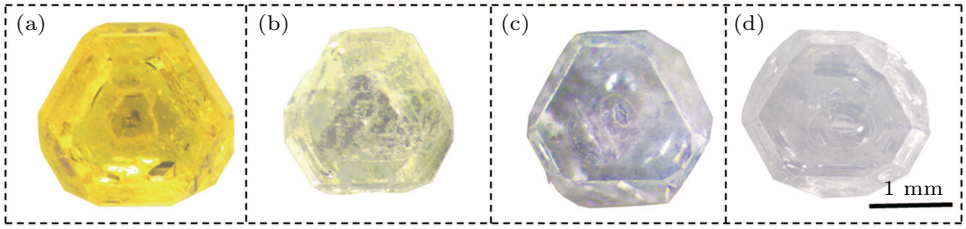


Fig. 4. Optical micrographs of synthetic diamonds in the FeNi–C system with the different contents of Ti/Cu (Ti : Cu = 4 : 3) additive: (a) 0 wt%, (b) 1.00/0.75 wt%, (c) 1.50/1.13 wt%, (d) 1.70/1.28 wt% (corresponding to e in Table 2).

The curves in Fig. 5 are the infrared spectra of diamonds synthesized with Ti/Cu added at different contents. The absorption intensities of 1130 cm^{-1} corresponding to curves (b)–(d) in Fig. 5 gradually weaken. The absorption peaks of 1130 cm^{-1} and 1344 cm^{-1} of curve (e) in Fig. 5 could not be detected (less than 1 ppm). The C_N of curves (b)–(d) in Fig. 5 can be calculated to be 12 ppm, 7 ppm, and 3 ppm, respectively. According to the change of the peak intensity of the infrared spectra in Fig. 5, the total C_N of the crystal decreases gradually with the increase of the nitrogen getter Ti/Cu (Ti : Cu = 4 : 3). The C_N in the crystal is less than 1 ppm when the amount of nitrogen getter is not less than 1.70 wt%.

It is found from the crystal colors of Fig. 5 that the crystal color translates from yellow to yellowish, and finally to colorless with the increasing addition amount of Ti additive. When the addition amount of nitrogen getter Ti is not less than 1.70 wt%, the C–N bond in the infrared spectra of the crystals cannot be detected, which means that the C_N in the crystal is less than 1 ppm. Therefore, 1.70 wt% of Ti and 1.30 wt% of Cu is the best amount for synthesizing high-quality type IIa diamond.

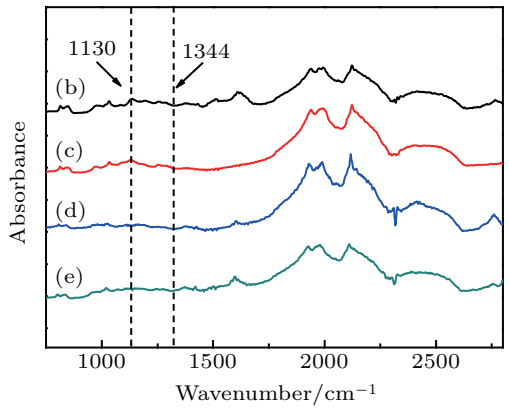


Fig. 5. Typical FTIR spectra recorded for diamond crystals synthesized in the FeNi–C system with (b) 1.0/0.75 wt%, (c) 1.50/1.13 wt%, (d) 1.60/1.20 wt%, (e) 1.70/1.28 wt% Ti/Cu (Ti : Cu = 4 : 3) additive.

3.3. Effect of Ti/Cu Addition on V-shaped Region

The V-shaped region is diamond growth region, which is bounded by the solvent-carbon eutectic melting line and the diamond–graphite equilibrium line. The effect of Ti/Cu (Ti : Cu = 4 : 3) additive on the V-shaped region of type IIa diamond was studied in the FeNi–C system at different temperatures and pressures. Type IIa diamond crystals have been synthesized with Ti/Cu (1.70 wt%/1.28 wt%) added in the FeNi–C system at different temperatures and at pressure of 5.3 GPa (group 2), 5.6 GPa (group 3) and 5.9 GPa (group 4). By contrast, type Ib diamonds have been grown without doping Ti/Cu at different temperatures and at pressure of 5.6 GPa (group 1). The data and results of experiments are listed in Table 3.

Table 3. Experimental results of synthesizing type IIa diamond crystals by adding Ti/Cu into the FeNi–C system at different pressures.

Run	Pressure/GPa	(Ti/Cu)/wt%	Temperature/°C	Ratio of (111) to (100)
G–1	5.6	0	1230	skeleton crystal
			1235	1.2 : 8.9
			1270	4.5 : 5.1
			1360	9.2 : 1.1
			1365	–
G–2	5.3	1.70/1.28	1265	skeleton crystal
			1290	2.2 : 15.1
			1320	5.7 : 4.9
			1350	8.6 : 2.1
			1360	–
G–3	5.6	1.70/1.28	1255	skeleton crystal
			1260	1.5 : 8.4
			1280	6.5 : 7.7
			1363	8.9 : 1.4
			1370	–
G–4	5.9	1.70/1.28	1245	skeleton crystal
			1250	2.1 : 8.9
			1305	4.5 : 5.1
			1365	9.7 : 1.8
			1375	–

When the addition amount of nitrogen getter is 0 wt% at 5.6 GPa, the skeletal crystal appears at 1230 °C, and the crystal does not grow at 1365 °C, so the growth temperature range is from 1235 °C to 1360 °C. When the TiCu content in the crystal is 1.7 wt% and the pressure is 5.6 GPa, the skeletal crystal appears at 1255 °C and the diamond cannot growth at the temperature of 1370 °C. The results show that the synthesis low temperature of type IIa crystal is increased by about 25 °C compared with the low temperature of the skeleton crystal with the same amount of 0 wt%. This result is consistent with Sumiya's report, that is, the addition of Ti/Cu increases the low-temperature region of diamond growth by 20–30 °C.[6] By comparing the experiments of groups 2–4, it is found that with the increase of synthesis pressure, the temperature range of diamond crystals growth becomes wider and wider.

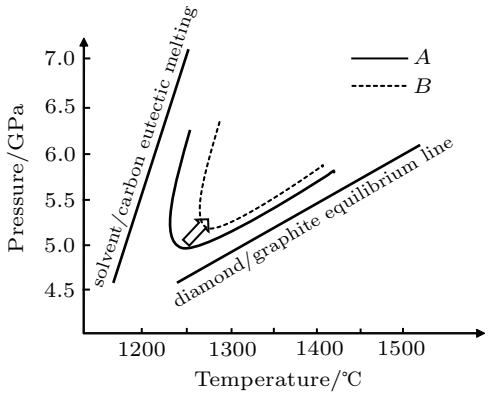


Fig. 6. The V-shape regions for diamond synthesis in FeNi–C with Ti and without additive system (the V-shape region of *A*: diamond growth from the FeNi–C system; V-shape region of *B*: diamond growth from the FeNi–C system doped Ti).

The change of V-shaped region for type IIa and type Ib is shown in Fig. 6. Adding Ti/Cu additives to the growth system will cause the V-shaped region to move to upper and right (curve *A* moves to curve *B* in Fig. 6). In the FeNi–C system, Ti/Cu addition causes the change of properties of FeNi alloy solvent under HPHT, which makes the V-shaped growth region of crystals move.

3.4. Crystal morphology and surface morphology of type IIa diamond

In order to analyze the influence of Ti/Cu additives on the crystal surface structure, the crystal with 0 wt% and 1.0 wt% Ti/Cu (Ti : Cu = 4 : 3) doping was analyzed by SEM. Figures 7(a) and Fig. 7(b) show the SEM photograph of synthesized diamonds in the FeNi–C system with Ti/Cu doped at different quantities.

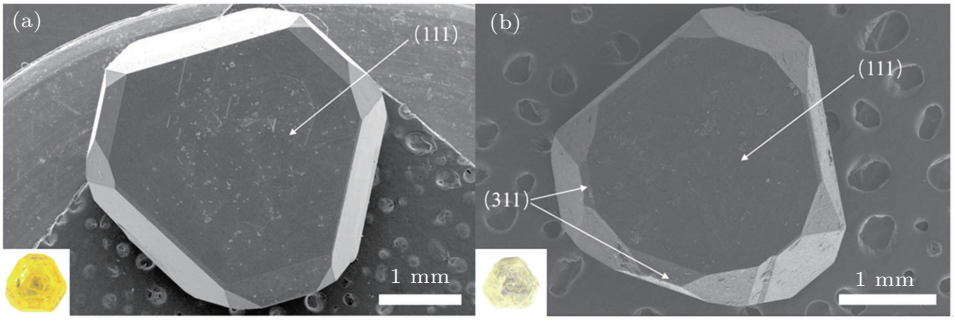


Fig. 7. SEM images of the diamond surface synthesized along (111) surface in the FeNi–C system with and without Ti/Cu (Ti : Cu = 4 : 3) additive: (a) 0 wt%, (b) 1.0 wt%.

Figure 7(a) shows that the surfaces of the crystal without Ti/Cu added, which is flat and smooth, are predominantly composed of (111) and (100) surfaces. Figure 7(b) shows that (111) is the main crystal surface with (100) and transition (311) surfaces after adding Ti as nitrogen getter. According to the principle of "slow surface exposure and fast surface submergence" of crystal growth, the growth rate of (311) surface and (111) surface of crystal slowed down after doping Ti in the process of crystal growth.[24]

Figure 8 shows the micrographs of crystals with (111) surface as growth surface. Figures 8(a)–8(d) are partial magnification micrographs of crystals with Ti/Cu content 0 wt%, 1.0 wt%, 1.5 wt%, and 1.7 wt%. Figure 8(a) is a local view of the (111) surface of the top of the crystal without doped, which is smooth. Figure 8(b) shows obvious growth steps and triangular pit defects on the crystal surface. Figure 8(c) is the pitting defect of the obvious growth step and a small number of dendritic growth stripe triangles on the edge of the crystal surface. Figure 8(d) shows smooth surface and some dendritic growth stripes.

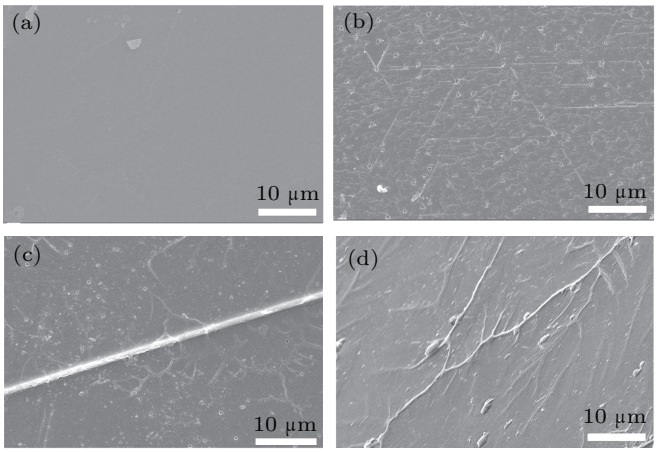


Fig. 8. SEM images (partial magnification) of the diamond surface synthesized along (111) surface in the FeNi–C system with Ti/Cu (Ti : Cu = 4 : 3) additive: (a) 0 wt%, (b) 1.0 wt%, (c) 1.5 wt%, (d) 1.7 wt%.

According to the results of SEM in Fig. 8, it can be known that the surface of the crystal doped with Ti nitrogen getter will have pits and lamellar defects, as well as dendrite growth stripes. The reason may be that the incorporation of Ti/Cu changes the crystal growth rate.

4. Conclusions

The growth characteristics of type Ⅱa large diamonds with Ti/Cu as nitrogen getter in the FeNi–C system are investigated. When the addition content is 1.70 wt% of Ti and 1.28 wt% of Cu with a ratio of 4:3, high-quality type Ⅱa diamond single crystals, in which C_N is less than 1 ppm, are synthesized in the FeNi–C system. Compared the V-shape region of type Ib diamond, the V-shape region of type Ⅱa diamond moves to right and upward with Ti/Cu addition, and the low edge of growth region for type Ⅱa diamond at 5.6 GPa rises 25 °C upward; Ti/Cu doping causes growth steps and triangular pitting on the crystal surface. The main crystal planes of the synthesized type Ⅱa crystals are (111) and (100) accompanying with the transition (311) crystal planes.

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