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Industrial diamonds grown in $Ni_{70}Mn_{25}Co_5$–graphite–sulfur system under HPHT

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This paper reports that diamond single crystals were synthesized from sulfur-added $Ni_{70}Mn_{25}Co_5$+C system under high pressure and high temperature (HPHT). It was found that additive sulfur had inhibited the nucleation and growth of diamond to some extent. X-ray diffraction of the collected sample indicated that under the synthesis conditions, a new compound MnS had been formed through the reaction of additive sulfur with manganese in the catalyst. The MnS has a fcc structure, and its average crystal size was about 30 nm. By scanning electron microscope, the {111} surface of diamond was found to be flat, while there was usually a large depression on the central region of {100}. Further observation showed that there were many small upside-down pyramidal pits in the expression. The results of x-ray photoelectron spectroscopy shows that MnS can only be detected in the depression in the range of detection precision. It was inferred that MnS had been dissolved in the melted alloy during the growth experiment, and precipitated in the sequent quenching process.

Keywords: sulfur, diamond, morphology, MnS
PACC: 8110D

1. Introduction

It is well known that diamond is a wide-bandgap semiconductor with unsurpassed physical and chemical properties. When doped, semiconducting diamond can lead to the realization of electronic and optoelectronic devices with exceptional properties.[1] As a potential shallow energy level donor element in diamond, sulfur has drawn many researchers' attention.[1−5] It has been found that under the conditions of 8–8.5 GPa and 1600–1800°C, sulfur can act as a catalyst for diamond growth alone.[6]

The solvent theory of diamond synthesis indicates that diamond formation is realized in molten catalyst under high pressure and high temperature (HPHT). The characters of catalyst directly influence the formation and growth of diamond. Introducing additive is an effective approach to synthesize special type diamond.

In this article, diamond synthesis was carried out in $Ni_{70}Mn_{25}Co_5$–C–additive sulfur system. Based on the results of x-ray diffraction (XRD), scanning electron microscope (SEM) and x-ray photoelectron spectroscopy (XPS), the experimental phenomenon were analysed and discussed. This research will be helpful for us to understand the action of additive sulfur on the synthesis of industrial diamonds.

2. Experimental

Diamond synthesis was carried out in a China-made SPD 6×1200 cubic high-pressure apparatus under the conditions of 5.5 GPa and 1750 K. The pressure was estimated based on the pressure-induced phase transitions of bismuth, thallium and barium. And the temperature was measured using a Pt6%R–Pt30%Rh thermocouple.[7]

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The experimental raw materials were $Ni_{70}Mn_{25}Co_5$ alloy powder and natural crystalline flake graphite powder. Both of them were 200 mesh in granularity and higher than 99.9% in purity. The additive was sedimentary sulfur, presented by much fine powder. Compared to the coarser sulfur types, it presents a larger active contacting surface for the same amount of sulfur. It is above 99% in purity. According to certain mass ratio, the alloy, graphite and sulfur powder were uniformly mixed by a rotational mixer for 4h. Then the mixture was shaped into disc form to fit in high pressure sample assembly.

After the synthesis, x-ray diffractometer was used to characterize the collected sample. Then the collected samples were treated in the boiling mixture of H_2SO_4 and HNO_3 to remove the remnant graphite and catalyst. SEM (LINK-ISIS JSM5310) and XP) were applied for observation and detection.

3. Results and discussions

3.1. Effect of additive S on spontaneous diamond nucleation

There were three kinds of sulfur-contained samples, corresponding to the sulfur content of 1wt%, 2wt% and 3wt% respectively. As a comparison, sulfur-free sample had also been prepared. All the samples were synthesized under the same conditions of 5.5 GPa and 1750 K for 10 min. Then the spontaneous diamond nucleation was investigated under optical microscope (Fig.1). It was found that the nucleated amount of diamond tended to decrease with the increase of sulfur content. When sulfur content reached 3wt%, graphite-diamond conversion could be completely prevented.

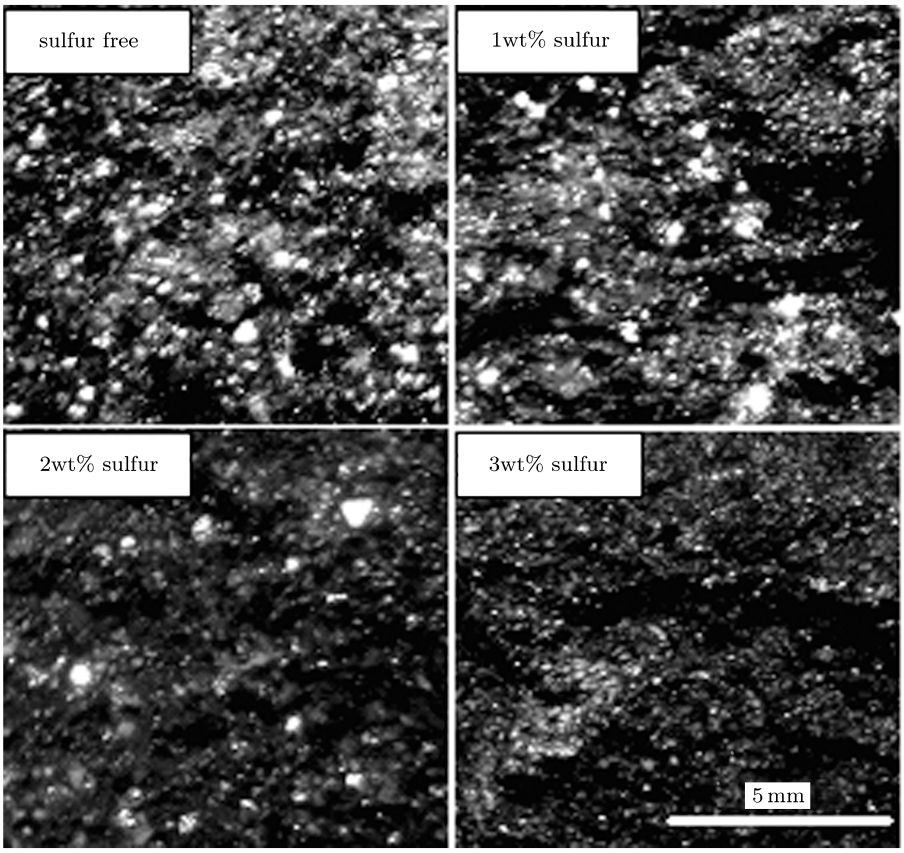


Fig.1. Spontaneous diamond nucleation in $Ni_{70}Mn_{25}Co_5$–C–S system.

3.2. XRD of collected sample

After synthesis, the collected sample (1wt% sulfur) was characterized by XRD. The XRD pattern is shown in Fig.2. It is found that there is a new compound MnS, besides diamond, graphite and $Ni_{70}Mn_{25}Co_5$ alloy, in the collected sample. The MnS has a fcc structure, and its average crystal size is about 30 nm according to Scherrer formula $D_{hkl} = \frac{0.89\lambda}{\beta_{hkl}\cos\theta}$.

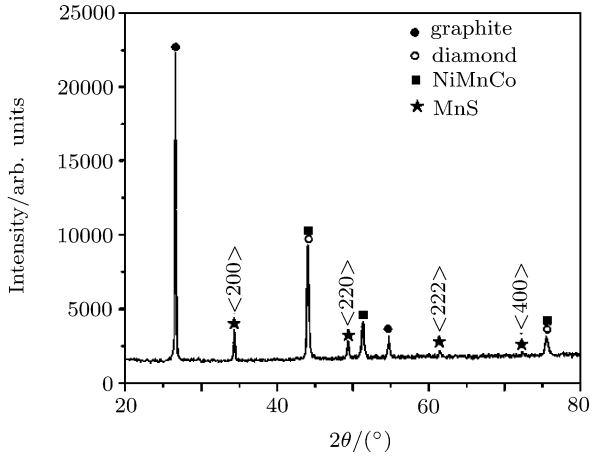


Fig.2. XRD of collected sample.

3.3. Morphology of diamond

Figure 3 shows the SEM photos of diamonds grown in sulfur-free system (I) and 1wt% sulfur-contained system (II). Both of them were synthesized under the same conditions for 15 min. As can be seen from the figure, the crystal grown in sulfur-free system is about 400μm in size, with integrated crystal form. There are some dendrites growth patterns on its surface.

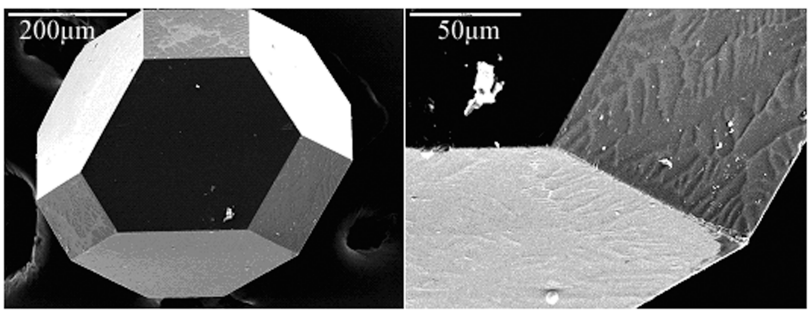
The crystal grown in the sulfur-contained system is less than 300 μm in size. And there is usually a bigger depression on the central region of {100} surface of diamond, while the {111} surface is flat. Scaling up step by step, the microstructure of the depression was further observed. In Fig.3(II)(e), it is found that there are plenty of small pits with upside-down pyramidal shape.

By comparison, it is clear that the introduction of additive sulfur has changed the surface morphology of synthetic diamond. On the other hand, diamond grown in the sulfur-contained system is smaller in size than that in the sulfur-free one in the same synthesis time. This indicates that additive sulfur has also decreased the growth rate of diamond.

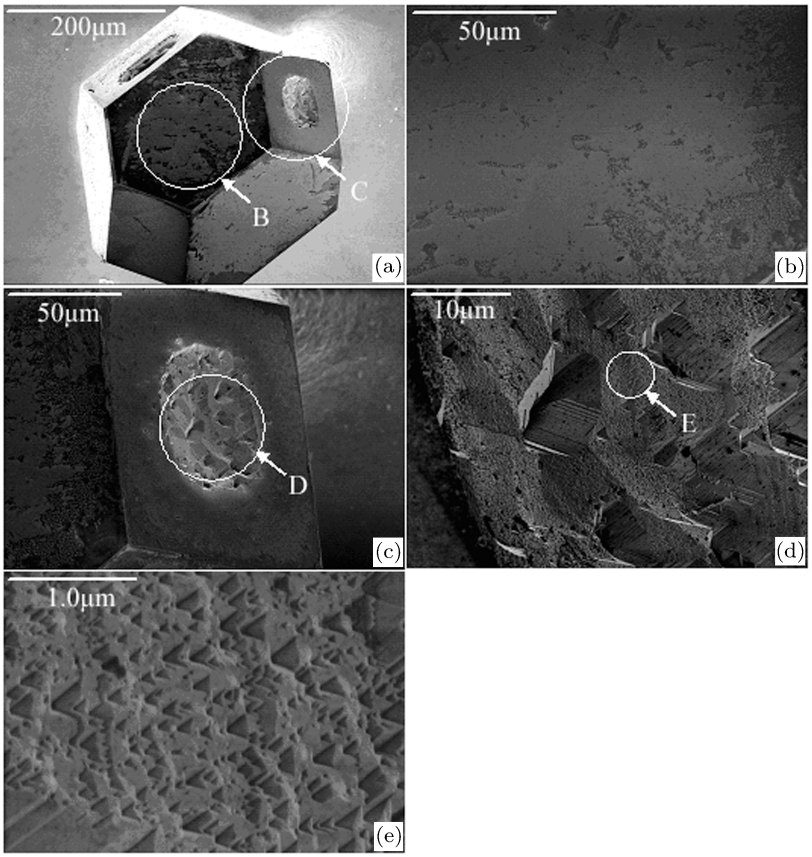
3.4. XPS measurement on synthetic diamond

We used XPS to detect the depression on the {100} of the synthetic diamond. The detection results are shown in Fig.4. As can be seen from the figure, it is clear that there are two types of chemical bonding of S–O and S^{2-} with the binding energies of 168.3 and 162.4 eV, respectively (Fig.4(a)). As for S–O bond, it is considered to have come from the oxidation in raw materials or the oxygen molecules sealed in the sample assembly. XPS results also show that Mn^{2+} is the only positive ion in the depression; its corresponding binding energy is 641.2eV (Fig.4(b)). It can be inferred that MnS exists in the depression on {100}.

We have also detected the other position of diamond surface besides the depression on {100}. No sulfur-related chemical bonding had been detected, nor did the Mn^{2+} in the range of detection precision. That is to say, there is no MnS in the other position on the diamond surface except for the depression on {100}.



(I)



(II)

Fig.3. SEM photos of diamond crystals.

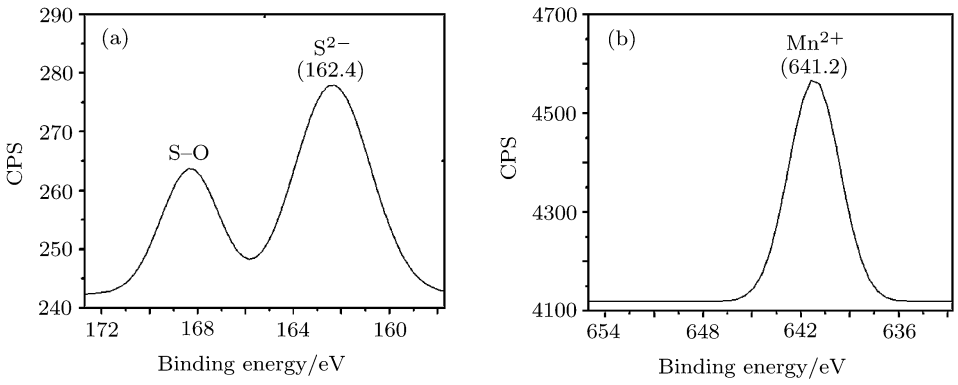


Fig.4. XPS narrow scan spectra of the depression on {100}.

3.5. State of MnS under HPHT

According to the phase diagram of Mn–S system under normal pressure (Fig.5), in the temperature range 1515–1843 K, the mixing phases L_1+MnS would be formed in the Mn–S binary system. In this paper, diamond synthesis is realized under the conditions of 5.5 GPa and 1750 K. So we inferred that under the synthesis conditions, MnS might be dissolved in the melted alloy solution in the form of solute.

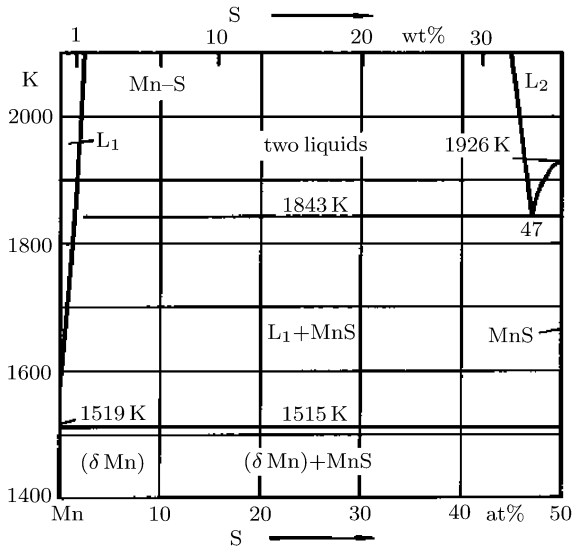


Fig.5. Mn-S phase diagram.

3.6. Discussion

The atoms on crystal surface are different from those in the interior. They lack for a certain amount of adjacent atoms, and have unsaturated atom complexion i.e. dangling bond. The existence of dangling bond makes surface atoms to show great chemical activity, and more likely to absorb alien substance. The more dangling bond there is on the surface, the stronger its adsorption capacity is. The atomic arrangement and dangling bond quantity on different crystal surface are usually different. Figure 6 shows the atomic arrangement and dangling bond on {100} and {111} surface of diamond. There are two dangling bonds for each atom on {100} surface, while each atom on the {111} only has one dangling bond. This means that the adsorption capacity of {100} surface is stronger than {111} surface.



Fig.6. Atomic arrangement and dangling bond on diamond surface.

On the other hand, the diamond growth process involves the formation of a tiny patch of a new layer on the crystal edge. Then the layer starts to spread out as an advancing step to cover the face of the crystal. Figure 7 is a sketch of processes occurring near a growth step. The desorption and diffusing away of the impurities are probably the limiting rate factors in growing sound crystals.[8,9]

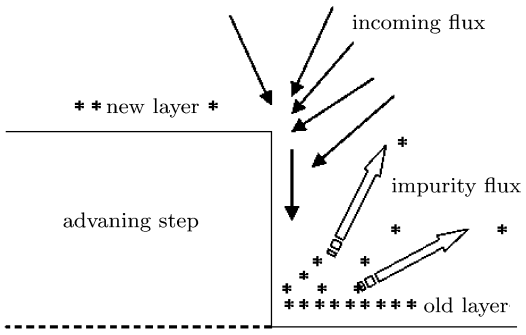


Fig.7. Sketch of processes occurring near a growth step.

Since the {100} surface has stronger adsorption capacity, during the growth of diamond, some melted alloy and the dissolved MnS would be easier to be trapped in it. This would destroy the growth of {100}, and lead to the formation of the depression. In the quenching process after the growth experiment, with the decrease of temperature, the solubility of MnS in the alloy reduces rapidly, and leads to the supersaturation of MnS, so MnS is precipitated in the depression.

4. Conclusion

Diamond single crystals were successfully synthesized from $Ni_{70}Mn_{25}Co_5$–C–S system. It was found that additive sulfur had inhibited both the nucleation and the growth of diamond to some extent. The {111} surface of the diamond grown in sulfur-contained system was flat, while there was usually a large depression on the centre of {100} surface. And there were many small upside-down pyramidal pits in the depression.

It is inferred that the MnS had been formed and dissolved in the melted alloy during the growth experiment, and precipitated in the sequent quenching process.

References

[1] Kalish R 1999 *Carbon* **37** 781

[2] Gheeraert E, Casanova N, Tajani A, Deneuville A, Bustarret E, Garrido J A, Nebel C E and Stutzmann M 2002 *Diamond Relat. Mater.* **11** 289

[3] Isao Sakaguchi, Mikka N. Gamo, Yuko Kikuchi, Eiji Yasu, Hajime Haneda, Toshimitsu Suzuki and Toshihiro Ando 1999 *Phys. Rev.* B **60** R2139

[4] Kalish R, Reznik A, Uzan-Saguy C and Cytermann C 2000 *Appl. Phys. Lett.* **76** 757

[5] Kalish R 2001 *Diamond Relat. Mater.* **10** 1749

[6] Sato K and Katsura T 2001 *J. Cryst. Growth* **223** 189

[7] Ma H A, Jia X P, Chen L X, Zhu P W, Guo W L, Guo X B, Wang Y D, Li S Q, Zou G T, Zhang Grace and Bex Phillip 2002 *J. Phys. Condens. Matter* **14** 11269

[8] Wentorf R H 1971 *J. Phys. Chem.* **75** 1833

[9] Devashish Choudhary and Jayesh Bellare 2000 *Ceramics International* **26** 73