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2002 J. Phys.: Condens. Matter 14 10941

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Growth of diamond layers on diamond and cBN seeds using iron carbide under high pressure and high temperature

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Received 29 May 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/10941

Abstract

Iron carbide without any graphite was studied under high pressure and high temperature (HPHT); diamond layers were obtained both on diamond and on cubic boron nitride seeds at 5.5 GPa and 1700–1750 K. The results showed that transition-metal carbide was the main intermediate in the course of the transformation from graphite to diamond under HPHT.

1. Introduction

Since the first successful synthesis of diamond by Hall in 1954, a great deal of interest and activity has centred on the nucleation and growth of diamond under high pressure and high temperature (HPHT). Though the most commonly used starting materials are graphite and catalyst metals, many studies have been undertaken to investigate the mechanism of synthesis of diamond by application of HPHT. Hong and Wakatsuki [1] reported synthesis of diamond by means of SiC and a catalyst based on Fe; Yanzhang Ma *et al* [2] reported the process of change of fullerene to diamond under HPHT with a NiMnCo catalyst; Xiangjie Lou [3] succeeded in synthesizing diamond with B₄C and a catalyst under HPHT. In all these experiments, the carbon source and catalyst are different materials, which makes analysis of the process more difficult. Though the mechanism of the catalysis is not very clear, the carbides of the catalyst metal play an important role. Metals of group VIII in the periodic table such as iron and nickel can form stable carbides under HPHT [4], and if these carbides are the intermediate compounds in the system used for the formation of diamond, diamond may be synthesized with just metal carbides. Since cementite is one of the few stable types of catalyst metal carbide at room temperature, we started with iron carbide.

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In this paper we present the growth of diamond layers on surfaces of diamond and cubic born nitride (cBN) seeds under HPHT using iron carbide as both the carbon source and catalyst.

2. Experimental details

For the experiments presented here, iron carbide with cementite content 70 at.%, powder size 80–100 mesh and carbon content 4.33 wt% was prepared by a rapid-cooling method. Metallography analysis showed that the sample was composed of fine cementite and martensite. The results of the x-ray diffraction (XRD) measurements are shown as figure 1. The peaks of the XRD corresponded to cementite and martensite. Because the iron carbide was made by a non-equilibrium method, the peaks were broadened due to distorted crystal lattices. Since there are no graphite peaks, there was no graphite in this sample.

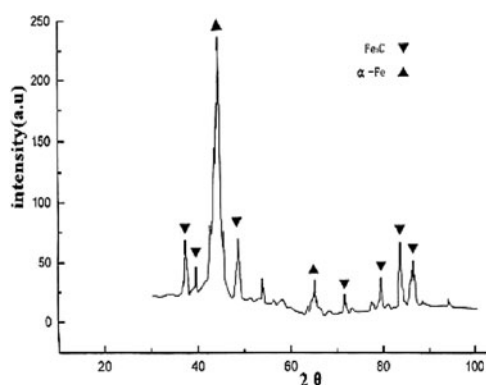


Figure 1. The XRD curve of iron carbide.

We put several crystals of cBN or diamond into samples of iron carbide powder. Two flakes of titanium were placed on either side of each sample to prevent any impurity entering the samples under HPHT conditions. Outside the Ti flakes, we placed flakes of NiMnCo alloy and graphite, one by one. Then we put the samples into a high-pressure cell. A KY-7200 6×1200 ton hexahedral high-pressure apparatus was used in the experiments with an electric current heating device. The sample was heated for 8 min. For samples with diamond seeds, the temperature and pressure adopted were $T = 1700$ K, $P = 5.5$ GPa; for samples with cBN seeds, $T = 1750$ K, $P = 5.5$ GPa.

Following removal from the high-pressure cell, the samples were marinated in a solution of HNO_3 and H_2SO_4 for 20 min, cleaned with deionized water and dried in the atmosphere at room temperature. The diamond and cBN seeds in the samples were monitored by scanning electron microscopy (SEM) and Raman spectroscopy.

3. Results

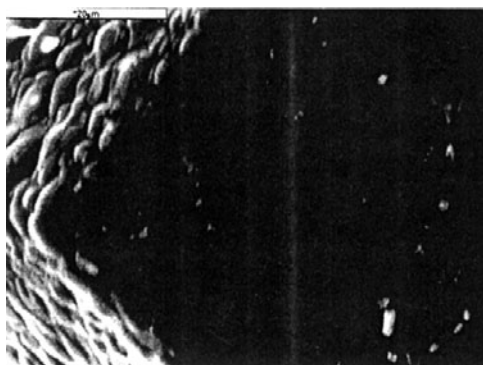
3.1. Diamond seeds in iron carbide

After the HPHT process, the surfaces of most of the diamond seeds were very smooth as before, but some became rough, and these surfaces are distinctly higher than the original ones. Figure 2 is a typical SEM image for these surfaces. It shows that a new layer was grown on the original diamond seed.

The SEM with the energy-dispersive x-ray (EDX) analysis function was used to measure the elemental content of the layer. The results obtained for two points on the surface shown in figure 1 are given in table 1; the content of carbon is above 90%. Because this sample was taken from a position near the Ti flakes, a small content of titanium was found.

Table 1. The elemental contents of the surfaces of diamond seeds in iron carbide after the HPHT process.

Number	Element	wt%	at.%
1	Carbon	71.6	91.11
	Titanium	24.63	7.86
	Iron	3.77	1.03
2	Carbon	71.3	91.03
	Titanium	24	7.68
	Iron	4.71	1.29

**Figure 2.** SEM images of diamond seeds in iron carbide after the HPHT process.

Since there is no reliable method for distinguishing diamond layers with thicknesses of several micrometres on a diamond substrate, we tried to grow diamond layers on cBN seeds to allow clear conclusions to be reached.

3.2. Cubic boron nitride seeds in iron carbide

Optical microscopy observation indicates that most of the cBN seeds remain primarily amber after the HPHT process; but we found two crystals of cBN showing straw yellow colour, which is dissimilar to the original colour. EDX images of these seeds (figures 3 and 4) showed that they were cBN seeds, and that there was carbon positioned symmetrically on the surfaces.

To check the structure of the carbon, we have studied Raman spectra. The Raman spectrum shown in figure 4 revealed the characteristic peak centred at 1332 cm^{-1} which corresponds to cubic diamond. This proved that a new diamond layer had been grown on the surface of the cBN seed. The electron beam can penetrate the surface of the material to about $1\text{ }\mu\text{m}$. Now that EDX analysis reveals not only carbon, but also boron and nitrogen, we can establish that the thickness of the diamond layers was below $1\text{ }\mu\text{m}$. The surfaces of the cBN seeds were very smooth; we verified that the quality of the diamond layers was high.

3.3. Discussion

From the experiments described above, it is apparent that iron carbide without graphite can be used to grow diamond layers. As there is no other carbon source, the carbon atoms forming the diamond must be from the iron carbide. At high temperature, the iron carbide is decomposed into iron and carbon atoms. The state of the carbon atoms in the lattice of cementite resembles that in the diamond lattice [5], so it is easy to achieve transformation to diamond on appropriate surfaces. Since the melting point of cementite is very high ($\sim 1900\text{ K}$), the fluidity in the high-

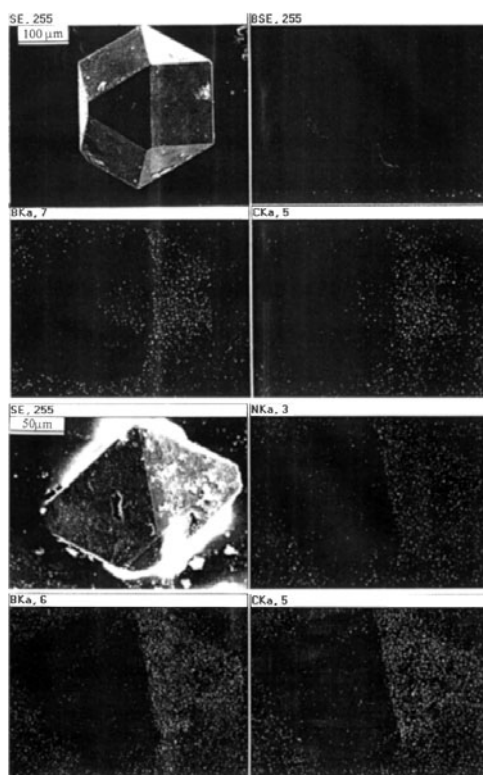


Figure 3. SEM and EDX images of two cBN seeds in iron carbide after the HPHT process.

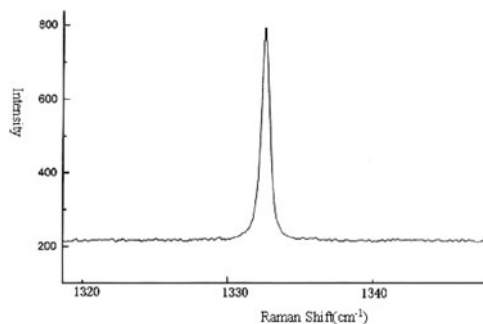


Figure 4. The Raman spectrum of the surface of a cBN seed.

pressure cell was very slight; atoms of carbon could move only by means of solid diffusion. When most of the iron carbide near the surface of the seeds was decomposed, the process of growth stopped. So the thickness of the diamond layers is very low ($\sim\mu\text{m}$).

Comparison of SEM images indicates the topographies of the diamond layers on the surfaces of diamond and cBN seeds to be very different. This perhaps indicates that the mechanisms of formation of the diamond on these two materials are not the same. For cBN, the layers are very smooth—it seems that the diamond layers were formed by deposition of carbon atoms one by one; while for the diamond, the layers became rough and it seems that the formation was by deposition of large groups of carbon atoms created in iron carbide. This difference is probably related to surface stress arising from the difference in lattice size between diamond and cBN.

From the results above, we think that the catalyst metal carbide was the intermediate composite in the system used for synthesizing diamond with graphite and a catalyst. Graphite and the catalyst metal formed metal carbide, and this was transported to the position of the substrate surface by the flowing of the melting catalyst metal. The carbide decomposed to form diamond on seeds under HPHT. Since the fluidity of iron carbide was very poor, we suggest using metal carbides with low melting point as raw materials—such as magnesium carbide. Work on this is under way.

4. Summary and conclusions

It is concluded that iron carbide has been converted to diamond on the surface of diamond and cBN seeds under HPHT. Moreover, iron carbide has probably been transformed into diamond directly in the process. It is firmly believed that iron carbide could be another new carbon source for use in synthesis of diamond under HPHT.

Acknowledgment

This work was financially supported by the National Science Foundation of China under grant no 59572036.

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