

Preparation of diamond nanocrystals from catalysed carbon black in a high magnetic field

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 8049

(<http://iopscience.iop.org/0953-8984/15/46/019>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 17:45

Please note that [terms and conditions apply](#).

Preparation of diamond nanocrystals from catalysed carbon black in a high magnetic field

Bin Wen¹, Tingju Li¹, Chuang Dong, Xingguo Zhang, Shan Yao, Zhiqiang Cao, Dehe Wang, Shouhua Ji and Junze Jin

Department of Materials Engineering, Dalian University of Technology, Dalian 116023, People's Republic of China

Received 16 September 2003

Published 7 November 2003

Online at stacks.iop.org/JPhysCM/15/8049

Abstract

Under a static high magnetic field of 10 T, diamond-like carbon (DLC) nanocrystals and graphite-coated n-diamond nanoparticles have been synthesized after a pyrogenation of carbon black and a nanometre-sized iron catalyst at atmospheric pressure and a temperature of 1100 °C. The product is analysed by x-ray diffraction, Raman spectroscopy, transmission electron microscopy and electron-probe microanalysis. The average size of the DLC nanopowders is about 20 nm, and that of the graphite-coated n-diamond particles is about 100 nm. The yield of diamond is as high as 30%.

1. Introduction

Carbon can exhibit a wide variety of forms, such as diamond, lonsdaleite (hexagonal diamond), graphite and carbynes [1–3]. Diamond materials in different forms can be synthesized by a variety of methods such as high-pressure and high-temperature processes (bulk samples) [4], explosive detonation (nanometre-sized powders) [5, 6], chemical vapour deposition (CVD) with CH₄ or C₂H₂ as the carbon source (polycrystalline films) [7–13], the reduction-pyrolysis-catalysis route (nanoparticles) [14] etc. In 1990, plasmas controlled by magnetic fields have been applied to CVD of diamond and have resulted in lowered substrate temperature and uniform films [15, 16], and an increased diamond deposition area [17]. Hirata and Yoshikawa [18] found that the application of high magnetic fields is effective in producing highly activated plasma suitable for diamond deposition.

Over the last decade, nanodiamonds have been synthesized by detonation of pure and composite CHNO explosives with a negative oxygen balance [5, 6]. Many authors [19–21] have studied the reaction conditions, finding that the diamond yield from the explosives depends on both their composition and density, and the best yields are obtained with carbon black as the additive [22]. Another method for producing nanodiamonds is the compression of carbon precursors by shock loading [3]. It was found that the addition of a metallic component could

¹ Authors to whom any correspondence should be addressed.

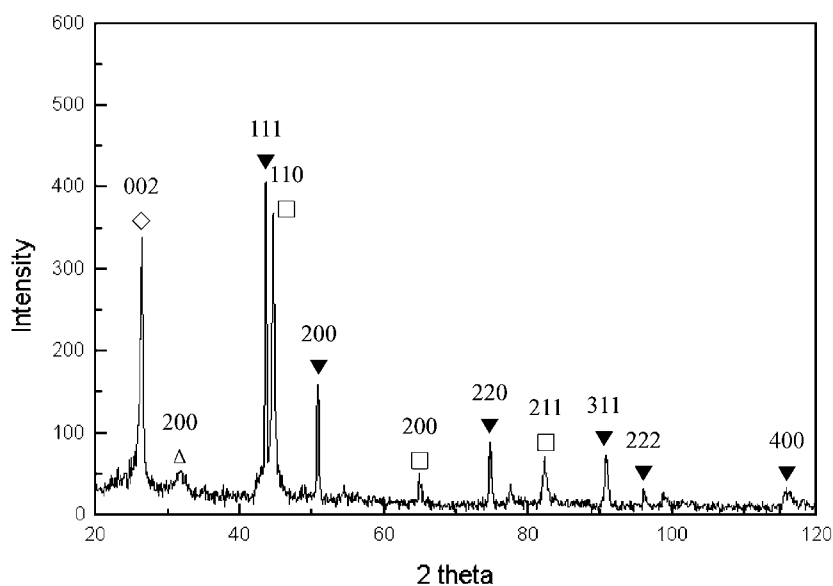


Figure 1. X-ray diffraction pattern of the sample. ▼, n-diamond; ◇, graphite; □, α -Fe; △, NaCl.

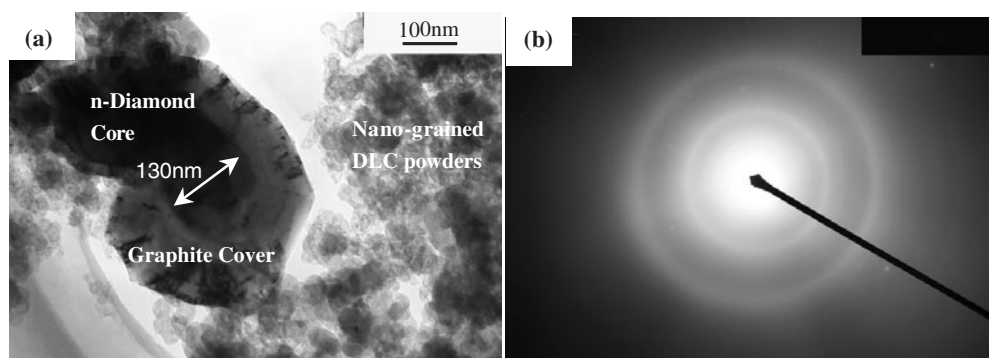


Figure 2. (a) TEM image, showing two types of particles, spherical DLC nanoparticles and graphite-coated n-diamond particles, and (b) the SAED pattern of nano DLC.

increase the diamond yield [23]. Furthermore, Donnet and co-workers [22] found that diamond could be obtained with carbon black as the precursor.

These studies suggest that a catalyst mechanism, both chemically and physically, favours the phase transition from carbon black to diamond. In addition, the CVD method implies that diamond materials might be produced even at atmospheric pressure or lower. Here, we report on a unique experimental procedure which was designed to synthesize diamond and diamond related structures at atmospheric pressure with carbon black as the carbon source. The catalyst was nano-sized iron which was the product of the reduction of colloidal $\text{Fe}(\text{OH})_3$ by carbon black. In order to control the thermodynamics of the transformation, a high magnetic field was introduced into the system. X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and electron-probe microanalysis (EPMA) were used to characterize the final powders.

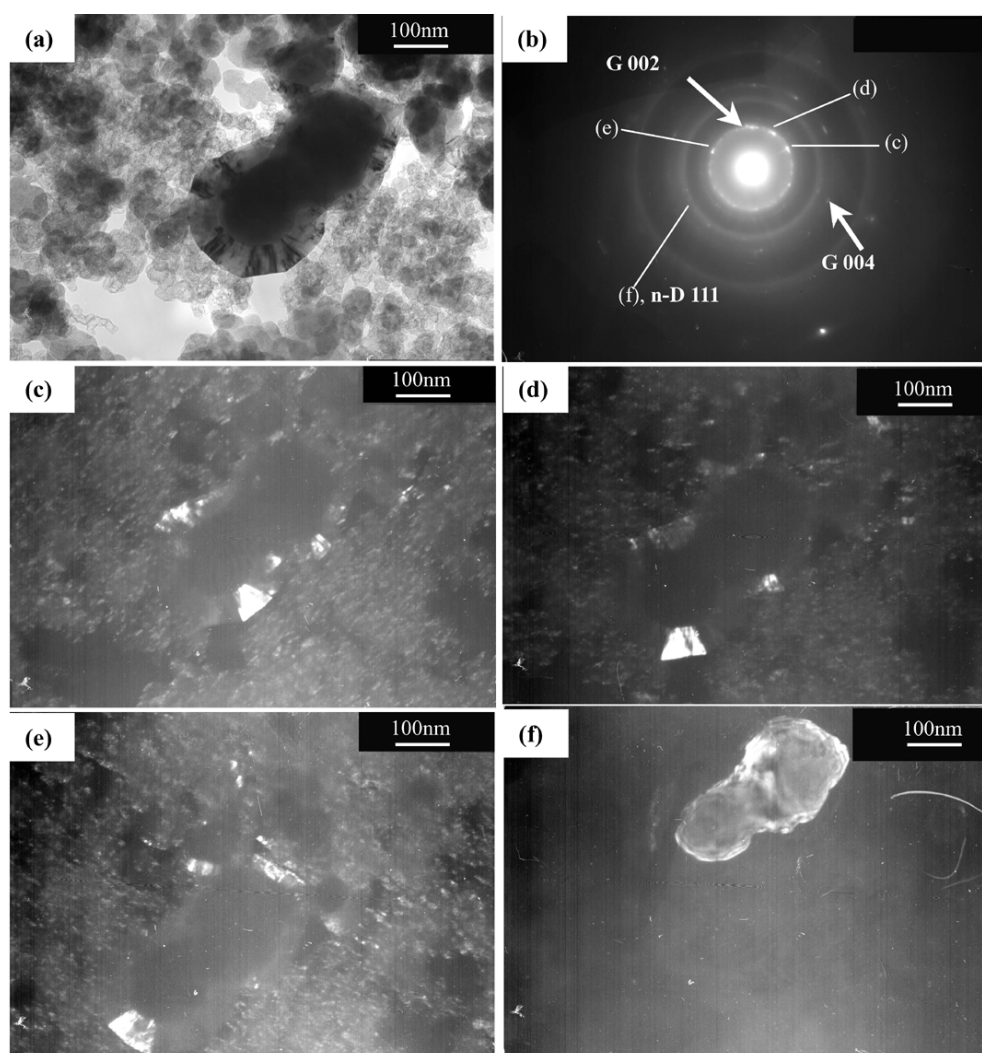


Figure 3. (a) Bright-field TEM image of a graphite (G)-coated n-diamond particle, (b) the corresponding SAED pattern and (c)–(f) the dark field images taken at spots indicated in (b).

2. Experiment

An admixture of the carbon black N231 powders and colloidal $\text{Fe}(\text{OH})_3$ (the reaction product of FeCl_3 solution and NaOH solution) were compressed into an open stainless steel tank of 100 ml capacity. The mass ratio of carbon and iron in the mixture was 10:1. The tank was maintained at $300\text{ }^\circ\text{C}$ for 100 min and sealed in air. In a high magnetic field of 10 T, the tank was maintained at $1100\text{ }^\circ\text{C}$ for 100 min and then cooled to room temperature in the furnace. The products were washed with $6\text{ mol l}^{-1}\text{ H}_2\text{SO}_4$ and then rinsed with distilled water. The final powders were dried in an oven at $110\text{ }^\circ\text{C}$. The EPMA indicated that the content of elemental Fe in the final black powders is 0.2 wt%.

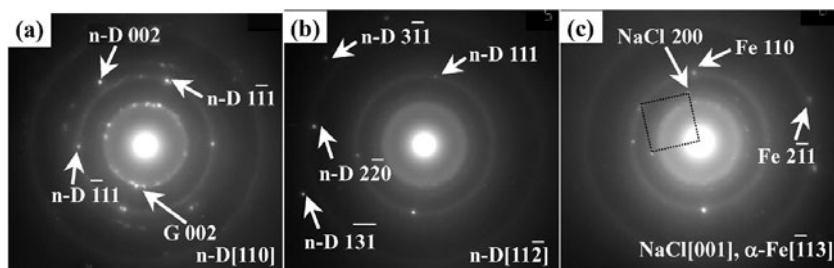


Figure 4. (a)–(b) The SAED pattern of the n-diamond. The inner ring in (a) is from the nanographite covering; the broad rings are from DLC nanoparticles. (c) SAED pattern revealing the presence of α -Fe and NaCl.

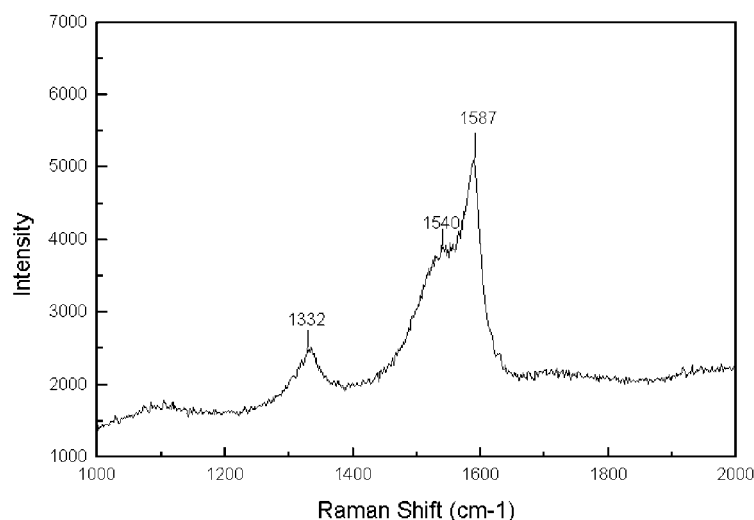


Figure 5. Raman spectrum of the dried powders.

3. Results and discussion

The phase composition of the dried sample was first examined with an XRD-6000 diffractometer using Cu $K\alpha$ radiation (wavelength 0.154 nm). The XRD pattern of the dried sample shown in figure 1 points to the presence of graphite, amorphous carbon, NaCl, α -Fe and the fcc n-diamond phase. Graphite is one of the reaction products, NaCl is the remnant of the reaction $\text{FeCl}_3 + \text{NaOH}$ and α -Fe is the remnant catalyst. The fcc n-diamond is characterized by its (200) peak, absent in normal diamond. Its fcc lattice constant is 0.3594 nm, which falls close to the reported values [24]. The phase content and the indexing of the XRD pattern of figure 1 is shown in table 1. The yield of n-diamond materials is about 30% as estimated from the integral area of the XRD peaks of n-diamond. To further support the presence of the n-diamond phase instead of the normal diamond, as well as to clarify the phase nature of the amorphous carbon, TEM and Raman spectroscopy were used to characterize the sample.

Figure 2(a) shows a bright-field image. The final product consists of two types of particles: spherical nanoparticles with a size of about 20 nm and coated particles with a size of about 130 nm. The corresponding electron diffraction pattern (figure 2(b)) of the nanoparticles reveals two broad rings, typical of an amorphous carbon. The images and selected area electron diffraction (SAED) pattern shown in figure 3 were taken from a coated particle. The

Table 1. The phase content and indexing of the XRD pattern of figure 1.

Sample			Graphite			n-diamond			NaCl			α -Fe		
2θ	d	Int	d	Int	HKL	d	Int	HKL	d	Int	HKL	d	Int	HKL
26.42	3.371	59	3.376	100	002				3.26	13	111			
29.15	3.061													
31.45	2.8421	5							2.82	100	200			
35.22	2.546													
37.61	2.389	3												
42.8	2.111	3	2.139	2	100									
43.57	2.075	100				2.06	100	111						
44.53	2.033	69	2.039	6	101							2.01	100	110
45.72	1.983								1.994	55	220			
46.68	1.944													
48.45	1.877													
49	1.857													
50.765	1.797	41	1.807	<1	102	1.784		200						
54.34	1.687		1.681	4	004				1.701	2	311			
56.29	1.633								1.628	15	222			
64.81	1.437	8												
65.14	1.431	4	1.548	1	103							1.43	15	200
67.82	1.381								1.41	6	400			
69.11	1.358								1.294	1	331			
74.69	1.269	20				1.261	25	220	1.261	11	420			
77.47	1.231	5	1.234	3	110									
77.75	1.227													
79.83	1.201													
82.21	1.172	15	1.160	3	112							1.17	38	211
83.76	1.154		1.121	<1	006				1.152	7	422			
90.77	1.082	17	1.057	<1	201	1.075	16	311	1.086	1	511			
96.03	1.036	4												
98.84	1.014	3							0.997	2	440	1.01	10	220
116.07	0.908	3				0.892	8	400	0.892	4	620	0.9	8	310

thin covering is identified to be graphite (figures 3(c)–(e)); the core consists of nano-sized grains of the n-diamond (figures 3(a), (f)). Figure 4 provides SAED patterns of n-diamond (figures 4(a), (b)) and NaCl and α -Fe (figure 4(c)). The TEM examination further validates the XRD results.

We performed a micro-Raman analysis with a Spex 1403 Raman spectrometer using the 514.5 nm radiation from an Ar-ion laser. The Raman spectrum (figure 5) exhibits an intense, sharp peak at 1332 cm^{-1} , indicating that the amorphous carbon was DLC [25–30]. The broad peak at 1587 cm^{-1} shows that some sp^2 amorphous carbon and graphite exists in the sample [29, 30].

4. Conclusion

In summary, we have shown the synthesis of DLC and n-diamond nanopowders from carbon black at atmospheric pressure and a temperature of 1100°C , using an Fe-catalysed process, assisted by a high magnetic field. It is a new and economic method with high efficiency. The peculiar graphite-coated n-diamond particles might imply brand new applications.

Acknowledgments

The National Natural Science Foundation of China, Project No 50234020 and Young Teacher Foundation of Dalian University of Technology, Project No 893202, supported this work.

References

- [1] Bundy F P 1989 *Physica A* **156** 169
- [2] Hirai H and Kondo K 1993 *Science* **253** 772
- [3] DeCarli P S and Jamieson J C 1961 *Science* **133** 1821
- [4] Bundy F P, Hall H T, Strong H M and Wentorf R H 1955 *Nature* **176** 51
- [5] Gneiner N R, Phillips D S, Johnson J D and Volk F 1988 *Nature* **333** 440
- [6] Thiel M V and Ree F H 1987 *J. Appl. Phys.* **62** 1761
- [7] Angus J C, Wiu H A and Stanko W S 1968 *J. Appl. Phys.* **39** 2915
- [8] Aisenberg A and Chabot K 1971 *J. Appl. Phys.* **42** 2953
- [9] Spitsyn B V, Bouilov L L and Deryagin B V 1981 *J. Cryst. Growth* **53** 219
- [10] Harris S J 1990 *Appl. Phys. Lett.* **56** 2298
- [11] Knight D S and White W B 1989 *J. Mater. Res.* **4** 385
- [12] Bachmann P K and Van Enkevort W 1992 *Diamond Relat. Mater.* **1** 1020
- [13] Wild C *et al* 1992 *Diamond Relat. Mater.* **2** 158
- [14] Li Y *et al* 1998 *Science* **281** 246
- [15] Wei J, Kawarada H, Suzuki J and Hiraki A 1990 *Japan. J. Appl. Phys.* **29** 1486
- [16] Chang J J, Mantei T D, Vuppuladhadiam R and Jackson H E 1991 *Appl. Phys. Lett.* **59** 1170
- [17] Abe T, Suemitsu M, Miyamoto N and Sato N 1991 *Appl. Phys. Lett.* **59** 911
- [18] Hirata A and Yoshikawa M 1998 *Diamond Relat. Mater.* **7** 139
- [19] Volk F and Schedlbauer F 1989 *9th Symp. on Detonation (Portland, 1989)* p 962
- [20] Kuznetsov V L, Chuvilin A L, Moroz E M, Kolomiichuk V N, Shaikhutdinov Sh K, Butenko Yu V and Mal'kov I Yu 1994 *Carbon* **32** 873
- [21] Petrov E A, Sakovitch G V and Brylyakov P M 1992 *Shock-Wave and High-Strain-Rate Phenomena in Materials* ed M A Meyers, L E Murr and K P Staudhammer (New York: Dekker) p 48
- [22] Donnet J B *et al* 2000 *Diamond Relat. Mater.* **9** 887
- [23] Morris D G 1980 *J. Appl. Phys.* **51** 2059
- [24] Joint Committee on Powder Diffraction Standards (JCPDS) see supplementary x-ray data 43-1104
- [25] Knight D S and White W B 1989 *J. Mater. Res.* **4** 385
- [26] Sato H *et al* 2001 *J. Mol. Struct.* **598** 93
- [27] Pickard C D O, Davis T J, Wang W N and Steeds J W 1998 *Diamond Relat. Mater.* **71** 238
- [28] Mermoux M, Roy F, Marcus B, Abello L and Lucazeau G 1992 *Diamond Relat. Mater.* **1** 519
- [29] Xu T *et al* 2001 *Diamond Relat. Mater.* **10** 1441
- [30] Sun Z, Sun Y and Wilson S R 2000 *Thin Solid Films* **377/378** 203