

Nano 6H Diamond Polytype Polycrystalline Powder

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ABSTRACT

In 1967, "Hexagonal diamond - a new form of carbon" was reported to be found in meteorites. This hexagonal form, 2H, was named Lonsdaleite, after the noted crystallographer, Kathleen Lonsdale. Since the corrected structures and x-ray diffraction data for all six possible non-cubic polytypes was published in 1992, the considerably increased interest in CVD diamond has resulted in finding others of the predicted polytypes, including 6H, 8H and 15R. The rapid crystallization and cooling characteristics of CVD diamond, and that produced by rapid implosion in meteorites and from man-made explosions, tend to produce non-cubic polytypes because of the rapid and short-lived transformation to the more dense crystal structure. Powder from the latter source has been characterized by infrared spectroscopy, and Rietveld x-ray and neutron diffraction. For particle size fractions in the range of 10 to 1000 nanometers, the non-cubic, 6H hexagonal polytype phase is present in amounts $\geq 50\%$ and the cubic diamond phase is present at the $\leq 50\%$ level. In all of these size ranges each particle is polycrystalline containing crystallites of nanometer and sub-nanometer dimensions.

Keywords: diamond, polytypes, nanopowder

1 INTRODUCTION

Cubic, 3C diamond is the most abundant crystalline form of diamond found in nature. It is also the form produced by high-pressure hot-pressing graphite in the diamond stable range. In 1967, "Hexagonal diamond - a new form of carbon" was reported to be found in meteorites.[1,2] This hexagonal form, 2H, was named Lonsdaleite, after the noted crystallographer, Kathleen Lonsdale. Other non-cubic polytypes were proposed in 1973[3] and 1990[4] but only the 2H and 6H polytypes had actually been found in CVD produced diamond[5,6] when the corrected structures and x-ray diffraction data for all six non-cubic polytypes was published in 1992.[7] Since that time the considerably increased interest in CVD diamond has resulted in finding several of the other predicted polytypes, including, 8H[8], 15R[9], and other forms such as "X - Diamond." [10] The rapid crystallization and cooling characteristics of CVD tends to produce some non-cubic polytypes.

In the mid 1980's it was theorized that diamond produced by rapid implosion from man-made explosions, like natural meteorite impacts on the earth's surface, would

be more likely to contain non-cubic diamond polytypes because of the rapid and short-lived transformation to the more dense crystal structure. Furthermore, these polytype powders might be used to toughen polycrystalline diamond or ceramic matrices because they could reverse transform more easily to higher volume graphite by a displacive transformation as opposed to the diffusive transformation required in the cubic diamond case. Consequently, a U.S. Patent was issued in 1990[11] and a paper was published in 1991[12] showing an example of toughening of carbides by this means which were hot-pressed at 5.5 GPa and 1500°C. In the latter it was shown that the toughening effect didn't show up until the diamond polytype additive particle size became very small, in the nanosize range. This paper also showed the comparison between one micron size GE diamond, which was 100% 3C and the implosively produced one micron diamond containing 12% hexagonal polytype thought to be 2H. It was thought, but never proven, that the smallest size ranges were effective in their role as toughening agents because they contained an even higher fraction of non-cubic polytypes. These implosively formed diamonds were produced by duPont using their widely used plastic wrap explosives to implode graphite particles entrained in a copper matrix. They were marketed as Mypolex suspensions of diamond powder in aqueous ammonium hydroxide or as dry powders. Although they were sold in various size fractions, duPont did not have a good handle on very small particle size measurement so their smaller size classifications were more than an order-of-magnitude in error.

In 1999, the Swiss firm, Rudolf Spring, AG, purchased duPont's Mypolex polycrystalline diamond powder business. Rudolf Spring has been micronizing diamond powders since the 1950's and 1960's and at the time of the Mypolex acquisition they had a very highly developed facility for micronizing and precisely classifying diamond powders. Since acquiring the Mypolex product they now manufacture three size classes smaller than the smallest ever available from duPont.

2 STRUCTURAL ANALYSES

The diamond polytype phases contained in these powders were determined qualitatively and quantitatively by three different analytical techniques. Infrared spectroscopy determined the existence of higher order polytypes. The Rietveld whole profile powder X-ray and neutron diffraction technique is able to resolve overlapping peaks of multiple phases. This technique determines the

percentage of each phase present. These powders are unique in that in spite of their nano-size, each particle is polycrystalline and therefore made up of even smaller crystallites. The technique also determines the crystallite size of each phase. The analyses were performed on five different particle size range classifications. They were designated by their mean particle size in nanometers.

2.1 Infrared Spectroscopy

The diamond powder samples were dispersed in KBr powder and pressed into pellets. The pellets were placed in a Perkin Elmer 1760-x Infrared Fourier Transform spectrometer and the data was analyzed using Spectrum v. 2.00, Perkin Elmer Ltd. 1988 software.

The difference between the diamond polytypes is the stacking sequence between lattice planes. The cubic, 3C stacking sequence is ABC/ABC/... The hexagonal, 2H sequence is AaBb/AaBb/... where the lower case letters represent mirror images of their upper case counterparts. 3C stacking is "pure" cubic and 2H is "pure" hexagonal. They are the simplest and represent the two extremes or end members of the polytypes. The stacking sequences for the other polytypes are more complex because they are "mixtures" of the hexagonal and cubic stacking. The end member polytypes, 3C and 2H are not infrared active whereas all of the other higher order polytypes are infrared active in their first order spectra⁴. These powders displayed discrete IR peaks indicating that diamond polytypes other than the end member 3C and 2H were present. Therefore the powders must contain one or more of the higher order polytypes, 4H, 6H, 8H, 15R, or 21R.

2.2 Rietveld X-ray Diffraction

Five samples with different particle size ranges were analyzed. Their mean particle size ranged from 25 to 175 nanometers. All samples were run in a Siemens D5000 diffractometer with Cu K α radiation. Prior to running any experiments, the diffractometer was aligned and characterized with LaB₆ and Al₂O₃ standards from NIST. Three preliminary tests were run to characterize the diffractometer. These were a check of peak positions, peak half-widths, and peak intensities. Data from these scans were used by the Rietveld refinement to adjust for systematic errors and to confirm that the machine was well within the allowable alignment errors. A thin coating of a powdered sample was deposited onto a quartz zero background holder and then placed into the diffractometer. Tests were run with a divergence slit of 1 mm, an anti scatter slit of 0.1 mm, and a detector slit of 0.2 mm. The step size was 0.05° with a counting time between 30 and 120 seconds/step. The scans were run over the angular range from 10° to 100°. The Riqas software was used to

analyze the data. A pseudo-Voigt fitting program was chosen to model the crystalline peaks and a 5th order polynomial was used to fit the background. All the single crystal data was taken from the ICSD database. The very small amount of graphite phase revealed only the single strong peak. Therefore the graphite polytype, 2H or 3R could not be determined. The 2H form was chosen and the refinement constrained making the information on the graphite phase incomplete. It was sufficient, however to discern the particle size and amount. The superposition of many of the 3C and 6H peaks required that the 3C structure be fit and refined first and then constrained. Next the 6H was refined and constrained. This process was repeated a second time and then the refinements were allowed to continue unconstrained.

All of the sample patterns could be fit with the three phases, 3C and 6H diamond and 2H graphite. Several other combinations of diamond polytypes were tried but none were as satisfactory. The quality of the refinement as indicated by the weighted residual, Rwp, was in the 2.4% to 4.7% range as shown in Table 1. Figures 1, 2 and 3 show the structure of these three crystalline phases.

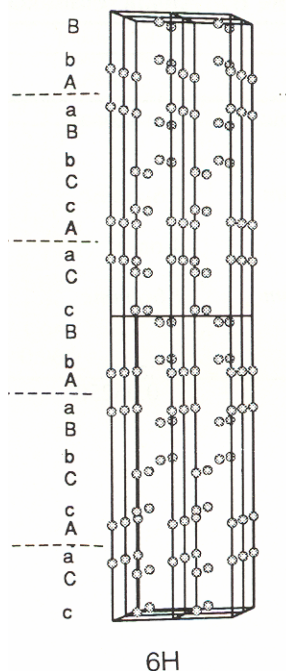


Figure 1 The 6H Diamond Polytype Unit Cell

Figure 4 shows a typical Rietveld fit of the XRD data. The expected scans of each of the three crystalline phases from the ICSD database are shown below the experimental scan which is fit by iteratively varying the amounts of each phase in the sample

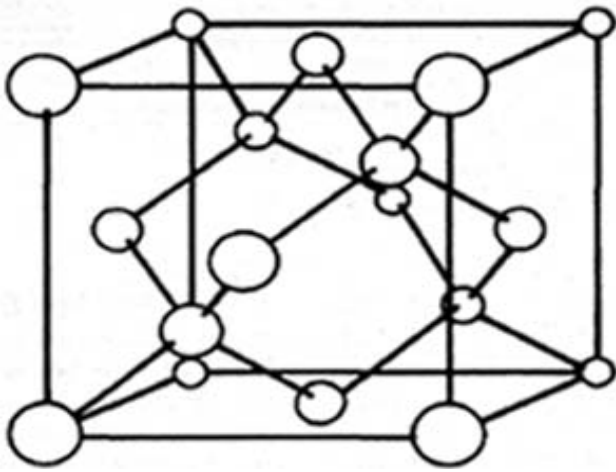


Figure 2 The Cubic Diamond, 3C, Unit Cell

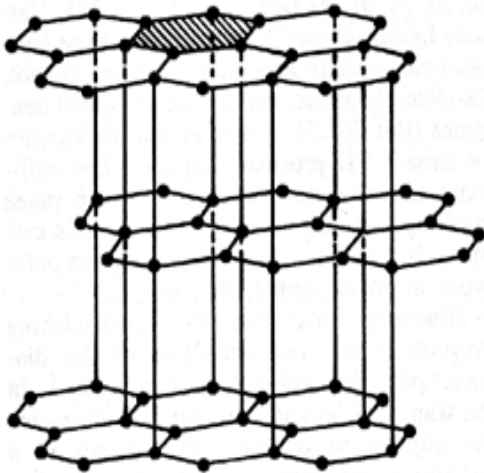


Figure 3 The Graphite Crystal Structure

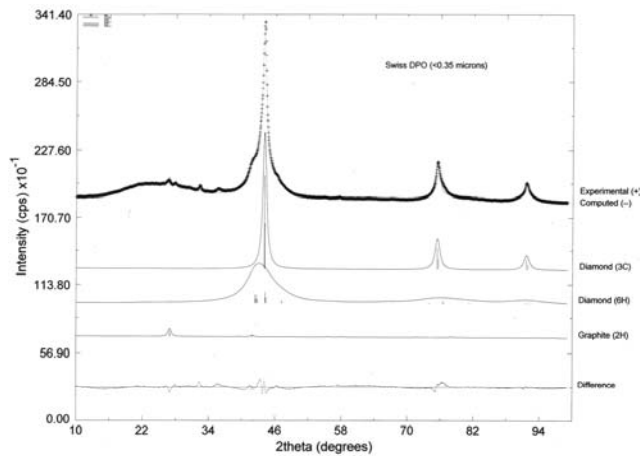


Figure 4 Rietveld Fit of Typical X-ray Diffraction Pattern

2.3 Rietveld Neutron Diffraction

Neutron data were collected using the high-resolution diffractometer[13] at the University of Missouri Research Reactor (MURR). This instrument uses a bent, perfect Si crystal monochromator and position sensitive detector, to take advantage of scattering space focusing of the neutron beam, achieving high throughput for small samples. The detector spans 20° (2θ) and the full spectrum is collected by moving the detector in five 20° steps to span the range from 5° to 105° . The incident neutron wavelength is 1.487\AA . Data collection with this instrument can be as short as 1 hour for well-crystallized materials, but in this case where weak second phase peaks are hard to detect and peak broadening effects are prominent, roughly 12 hours of data collection was used for each sample.

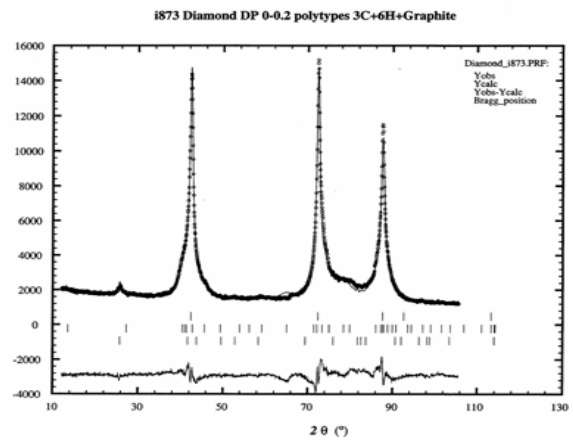


Figure 5 Rietveld Fit of Typical Neutron Diffraction Pattern

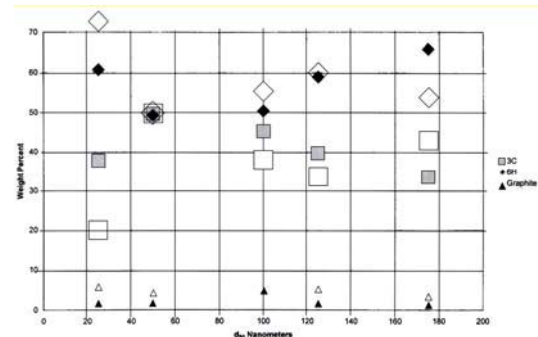


Figure 6 Phase % vs. Mean Particle Size (Symbols from XRD are solid and from Neutron diffraction are open)

The phase distribution difference between the XRD data and the ND may at least partially be accounted for by the ~ 2 yr space between obtaining the XRD and ND samples. When the XRD samples were obtained, the supplier is reported to have been mixing powder from another non-US source with that from the Pennsylvania plant.

Each tiny powder particle is not a single crystal, but polycrystalline, containing many smaller crystallites with different orientations & structures.

• From X-ray Diffraction	<u>d50</u>	<u>3C</u>	<u>6H</u>
	10	128	11
	25	116	16
	50	102	9
	75	98	9
• From Neutron Diffraction			8
			8

Table 1: Crystallite size in nanometers

• From X-ray Diffraction	Rwp	2.4% to 4.7%
• From Neutron Diffraction	Rwp	5.8% to 6.1%

Table 2 Rietveld Degree of Confidence

3 CONCLUSIONS

Diamond powder manufactured by explosive shock wave has a different structural character than static, high temperature and high pressure formed diamond powder. Statically formed diamond powder is all in the 3C cubic diamond crystal structure. Moreover, each particle is typically a single crystal. Crystalline diamond powder particles in the size range of 10 to 1000 nanometers formed by explosive shock wave have been shown to contain $\leq 50\%$ 3C, cubic diamond structure and $\geq 50\%$ higher order non-cubic polytype. The single higher order polytype that fits both the X-ray and Neutron diffraction data remarkably well is the 6H polytype. These individual nanosize powder particles are not single crystals but contain crystallites of nanometer and sub-nanometer dimensions. The cubic, 3C crystallites appear to be concentrated in the higher size range of each size fraction, while the hexagonal, 6H polytypes are concentrated in the smaller size side of each range. This work is first in characterizing a commercial source of the 6H diamond polytype powder.

REFERENCES

[1] F. P. Bundy and J. S. Kasper, "Hexagonal Diamond – A new Form of Carbon," J. Chem. Phys. 46, 3437-46, 1967.

[2] R. E. Hanneman, H. M. Strong, and F. P. Bundy, "Hexagonal Diamond in Meteorites: Implications," Science 155, 995-97, 1967.

[3] C. E. Holcombe, "Calculated X-ray Diffraction Data for Polymorphic Forms of Carbon," Report No. Y-1887, Oak Ridge Y-12 Plant, Oak Ridge, TN, 1973.

[4] K. E. Spear, A. W. Phelps, and W. B. White, "Diamond Polytypes and Their Vibrational Spectra," J. Mater. Res. 5, 2272-85, 1990.

[5] M. Frenklach, R. Kematich, D. Huang, W. Howard, K. E. Spear, R. Koba, and A. W. Phelps, "Homogeneous Nucleation of Diamond Powder in the Gas Phase," J. Appl. Phys. 66, 395-99, 1989.

[6] W. Howard, D. Huang, J. Yuan, M. Frenklach, K. E. Spear, R. Koba, and A. W. Phelps, "Synthesis of Diamond Powder in Acetylene Oxygen Plasma," J. Appl. Phys. 68, 1247-51, 1990.

[7] P. D. Ownby, Xi Yang and J. Liu, "Calculated X-ray Diffraction Data for Diamond Polytypes," J. Am. Ceram. Soc. 75, 1876-83, 1992.

[8] R. Kapil, B.R. Mehta, and V.D. Vankar, "Growth of 8H Polytype of Diamond using Growth Etch Cyclic Oxy-Acetylene Flame Setup, Thin Solid Films 312, 106-110, 1998.

[9] R. Kapil, B.R. Mehta, and V.D. Vankar, "Synthesis of 15R Polytype of Diamond in Oxy-Acetylene Flame Grown Diamond," Thin-Films, Appl. Phys. Lett. 68, 2520-2522, 1996.

[10] M. Rossi, G. Vitali, M. L. Terranova and V. Sessa, "Experimental Evidence of Different Crystalline Forms in Chemical Vapor Deposited Diamond Films," Appl. Phys. Lett. 63, 2765-2767, 1993.

[11] P.D. Ownby, "Fracture Toughening of High Pressure Sintered Diamond and Carbide Ceramics", U.S. Patent No. 4,968,647, Issued Nov. 6, 1990.

[12] P.D Ownby, and J. Liu, "Nano Diamond Enhanced Silicon Carbide Matrix Composites" Ceram. Eng. Sci. Proc. 12, 1345-1355, 1991.

[13] Yelon, W.B., Berliner R., and Popovici M., "A Perfect Match for High Resolution Neutron Powder Diffraction: Position Sensitive Detection and Focusing Monochromators", Physica B241-3, 237 1997.

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