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 at amounts ≥ 50% and the cubic diamond phase is present at the ≤ 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
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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 spectra. 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
diffactometer with Cu Kα 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
diffactometer. 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.
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 20º (2θ) and the full spectrum is collected by moving the detector in five 20º steps to span the range from 5º to 105º. The incident neutron wavelength is 1.487Å. 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.

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
  \[d_{50}\] 3C 6H
  10 128 11
  25 116 16
  50 102 9
  75 98 9
- From Neutron Diffraction

Table 1: Crystallite size in nanometers

<table>
<thead>
<tr>
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<th>3C</th>
<th>6H</th>
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<tr>
<td>From X-ray</td>
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<tr>
<td>Diffraction</td>
<td>Rwp</td>
<td>2.4% to 4.7%</td>
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<tr>
<td>From Neutron</td>
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<tr>
<td>Diffraction</td>
<td>Rwp</td>
<td>5.8% to 6.1%</td>
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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 ≤ 50% 3C, cubic diamond structure and ≥ 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


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