

DIAMOND STRUCTURE OBSERVED IN PYROGRAF-III™ VAPOR-GROWN CARBON FIBERS

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Introduction

In a previous paper the presence of diamond was reported for vapor-grown carbon fiber (VGCF) [1]. At that time the only evidence was a minor phase identified by x-ray diffraction (XRD) which included the forbidden (200) diamond peak. This paper includes Raman evidence as well as XRD showing diamond as a major crystalline phase in some VGCFs.

VGCF is produced by a catalytic process from hydrocarbons in the vapor state. The resulting fiber typically has a lamellar morphology and is highly graphitic. Properties are expected to include high tensile strength and tensile modulus and low electrical resistivity. Extremely high thermal conductivity of 1950 W/m-K has been measured on some heat-treated VGCFs which is the highest value found in nature except for diamond.

The fiber formation process begins with a vapor phase metal (iron) which is exposed to a hydrocarbon gas at temperatures in the 1000-1150°C range which catalyzes the growth process. Long, slender, partially graphitic filaments which are not supported by a substrate are formed [2]. Sulfur may be added to the reaction stream as H₂S [3] or by using high sulfur coal for part of the hydrocarbon stream [4] which increases the fiber yield. The addition of anhydrous ammonia to the feed gas stream produced the fibers examined here [1].

The diameter of VGCFs produced by this method averages 0.1-0.2 μm and the length/diameter ratio is in

excess of 100. Commercial fibers are in the range of 8 μm in diameter. VGCF becomes entangled during the production process, and the individual fibers are not continuous like carbon fibers derived from pitch or PAN. VGCF has a highly graphitic structure without inclusions from foreign material, as occurs with commercial fibers during extrusion of the filaments. The fibers were produced in a semi-continuous process by chemical vapor growth. The fibers were obtained directly from the manufacturer, Applied Sciences, Inc., Cedarville, OH.

Experimental

X-ray Diffraction

The fiber samples were pressed into randomly oriented bundle mats. The fibers all lay approximately in the same plane. The bundle mats were scanned in symmetric transmission on a Huber 4-circle x-ray diffractometer. A Rigaku RU-200 rotating anode generator produced the incident beam crystal monochromated CuKα radiation ($\lambda = 0.15418$ nm) at a power of 45 kV and 70 mA. The data were corrected for absorption, polarization, incoherent scattering, and Lorentz factors. Curve fitting was used to get d-spacings and peak widths [5].

Raman Spectroscopy

A Spex Model 1403 double monochromator with a Spex Micramate microsampling system was used for this study. The micro-Raman system collects a backscattered

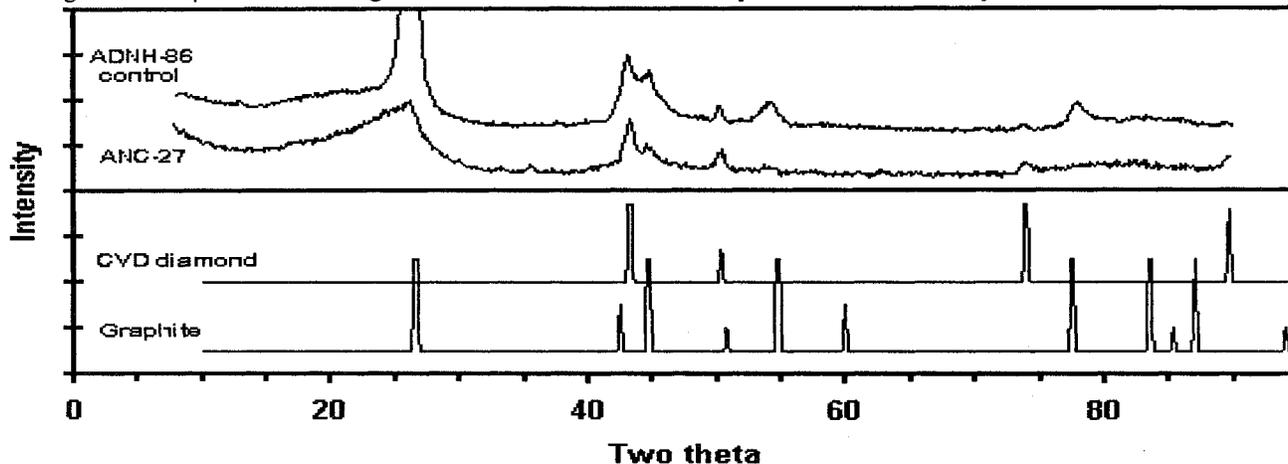


Figure 1. Phase identification of diamond and graphite in VGCF.

light through a microscope. The analysis spot is approximately 5 μm in diameter for this particular instrument. Initially, an argon ion laser tuned to the 0.514 μm green line was operated at a power of 100 mW at the sample surface. However, the laser power had to be turned down to only a few tens of milliwatts to avoid sample deterioration. The slit settings were 200 μm , 150 μm , 150 μm , 200 μm for this series of scans (producing a resolution of about 3 cm^{-1} [6]). Scans were taken with 0.5 cm^{-1} steps and 0.75 s integration times. A single crystal diamond was used as a calibration standard.

The Raman band position for diamond is 1332.5 cm^{-1} [7]. Sp^2 bound carbon may exhibit several Raman bands. Graphite and carbon fibers have a Raman band at 1580 cm^{-1} (G band) and occasionally an additional band at 1357 cm^{-1} representing disordered graphite (D band) [7,8]. Diamond-like carbon and amorphous carbons tend to have a Raman band around 1343 to 1346 cm^{-1} [7].

Results and Discussion

Figure 1 shows the XRD intensities for two VGCF samples. In the first sample, graphite is the major crystalline phase with a diamond minor phase. In the second sample, ANC 27, diamond is the major crystalline phase, although some graphite is also present. Amorphous carbon is indicated by the broad diffraction below the (00,2) graphitic peak in both samples. Several samples of VGCF were found to contain diamond as a minor phase. In every case the unit cell was found to have increased slightly from the accepted JCPDS value of 0.35667 nm, and the forbidden (200) peak was present. The (200) peak has also been reported for CVD diamond elsewhere [9].

The spectrum on the bottom of Figure 2 is a typical Raman spectrum for these carbon fibers. The G and the D bands are both clearly developed. The top spectrum is unusual in that there is a very distinct, repeatable Raman band around 1332 cm^{-1} and a second band around 1345

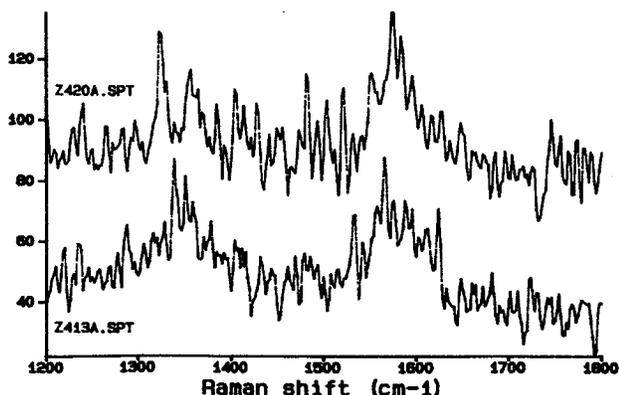


Figure 2. Raman spectra of VGCF. Bottom spectrum - typical VGCF fiber; Top spectrum - VGCF fiber with diamond character.

cm^{-1} . The presence of these two bands strongly suggests the presence of diamond or a significant degree of diamond-type sp^3 bonding in these fibers.

Conclusions

A series of catalytically-grown carbon fibers were observed to have x-ray reflections and Raman spectra indicative of the presence of diamond. X-ray reflections typical for the diamond lattice were observed that indicate a slightly larger (1-2%) unit cell than single crystal diamond. Raman spectra show a distinct diamond Raman band that strongly suggests the presence of a microcrystalline form of diamond. This appears to be a novel occurrence of widespread sp^3 bonding which does not necessarily appear to be related to the formation of diamond-like carbon.

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References

1. Anderson, D. P., J.-M. Ting, M. L. Lake, and R. L. Alig, in *Carbon '95 (Ext. Abstr. 22nd Biennial Conf. Carbon)*, San Diego, CA (1995) pp. 304-305.
2. Kaae, J. L., *Carbon*, **23**, 665 (1985).
3. Alig, R. L., G. G. Tibbetts, and D. W. Gorkiewicz, U.S. Patent 5,374,415, Dec. 20 (1994).
4. Alig, R. L., and D. J. Burton, "Producing vapor grown carbon fibers with high sulfur coal" in *Carbon '97 (Ext. Abstr. 23rd Biennial Conf. Carbon)*, University Park, PA (1997). (in Press).
5. Anderson, D. P., *X-ray Analysis Software: Operation and Theory Involved in Program "DIFF"*, AFWAL-TR-85-4079, USAF Tech. Report (June 1985).
6. Strommen, D. P. and K. Nakamoto, *Laboratory Raman Spectroscopy*, John Wiley & Sons, New York (1984).
7. Knight, D. S. and W. B. White, *J. Mat. Res.*, **4**, 385 (1989).
8. Tuinstra, F. and J. L. Koenig, *J. Composite Mater.*, **4**, 492 (1970).
9. Badzian, A. R. et al., *SPIE Proceedings*, **683**, 127 (1986).