

Evidence of sp^3 Bonding in Vapor Grown Carbon Fibers

David P. Anderson*, J.-M. Ting**, Max L. Lake**, and Robert L. Alig**

* University of Dayton Research Institute
300 College Park Avenue
Dayton, OH 45469-0168

** Applied Sciences Inc.
P.O. Box 579
Cedarville, OH 45314-0579

INTRODUCTION

Vapor grown carbon fiber (VGCF) is produced by a catalytic process from hydrocarbons in the vapor state. The resulting fiber has a unique lamellar morphology and is highly graphitic. Properties include high tensile strength and tensile modulus and low electrical resistivity and extremely high thermal conductivity of 1950 W/m-K. This is the highest value found in nature except for diamond. Applications for this type of reinforcement are in automotive components such as rubber compounds, brake linings, and body panels; as well as in high thermal conductivity materials for electronics packaging, among many others. Because of the simplicity of synthesis and the potential to be produced directly from low cost hydrocarbons, VGCF may be produced at a fraction of the cost of current commercial carbon fibers with comparable properties.

This process begins with vapor phase metals, generally iron, which, upon exposure to a hydrocarbon gas at a temperature in the 1000-1150°C range, catalyze the growth of long, slender, partially graphitic filaments which are not supported by a substrate[1]. The diameter of VGCF produced by this method generally averages 0.2 μm as produced, and the length/diameter ratio ranges in excess of 40. This is in sharp contrast to commercial fibers, which are in the range of 8 μm in diameter. Also, the VGCF becomes entangled during the production process and the individual fibers are not continuous like carbon fibers derived from pitch or PAN. Due to the unique nature of the process whereby pure carbon is transformed into fiber by condensation at the catalyst, VGCF has a highly graphitic structure, without inclusions from foreign material as occurs with commercial fibers during extrusion of the filaments. This process generally produced fiber over a wide diameter range of 0.15 to 0.32 μm and an L/D ratio of 10 - 75 with a bulk density around 1.6 kg/m^3 (0.0016 g/cm^3).

It was subsequently discovered that the fiber could be continuously produced by intermittently purging the reactor by interrupting the flow of the reactant gases and during the interruption, conducting a forced purge by flowing air through the reactor at a pressure that blasts the

fiber out of the reactor. Fiber of superior quality was developed by injecting anhydrous ammonia into the reactor during the growth stage with the hydrocarbon, catalytic nuclei, and hydrogen sulfide[2]. Depending on the conditions selected, the fibers are formed with a 0.2 μm diameter with a narrow standard deviation range of 0.05 μm and an L/D ratio up to 200, and a bulk density of 0.4 kg/m^3 (0.0004 g/cm^3 or 40 ft^3/lb).

EXPERIMENTAL

The fibers were produced in a semi-continuous process of chemical vapor growth. Hydrocarbon source, catalysts, and carrier gas injected into the furnace; some with and some without the anhydrous ammonia as described above.

For x-ray diffraction, the fiber samples were pressed into bundle mats, the fibers all laying approximately in a plane but randomly oriented within the plane. The bundle mats were scanned in symmetric transmission on a Huber 4-circle x-ray diffractometer. Incident beam crystal monochromated $\text{CuK}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) from a Rigaku RU-200 rotating anode generator at a power of 45 kV and 70 mA. The data was corrected for absorption, polarization, incoherent scattering, and Lorentz factors. Curve fitting was used to get d-spacings and peak widths[3-5].

RESULTS AND DISCUSSION

These fibers are mostly graphitic in nature although not 100% true graphite. Small, reproducible changes in the processing conditions produced fibers with significant differences in their x-ray diffraction scans. The x-ray diffraction scans from several fibers are shown in Figure 1. X-ray diffraction of the vapor grown carbon fiber samples was undertaken to determine the degree of graphitization and level of 3-dimensional crystal growth. The fiber samples obtained with anhydrous ammonia in their feed streams had peaks that are not normally observed in graphitic fibers.

It is expected that the (00,l) peaks will be shifted to lower angles (larger d-spacings) as a result of imperfect

graphitic stacking; this is the basis for the degree of graphitization, g_p , calculations[6]. The shift of the (00,2) and (00,4) peaks can be seen in Figure 1. The diffraction patterns shown are of fibers all about $g_p = 0.6$.

As the amount of graphitic nature increases, the 3-D (or off axis) peaks develop. The (10,1) and (11,2) peaks become visible at angles just above the (10,0) and (11,0) peaks, respectively, and gradually get larger until they exceed the (hk,0) peaks. Also the (10,0) and (11,0) peaks are typically displaced to higher angles as a result of the 2-D nature of the turbostratic carbon planes[4]. They move to lower angles and allow the off axis peaks to more completely separate.

The additional peaks observed were the peak near $50^\circ 2\theta$, which might have been the graphitic (10,3) peak but is not normally seen in fibers, and the small peak near $74^\circ 2\theta$, which did not correspond to any graphitic peak. Most significant was the development of the peak near $43^\circ 2\theta$, between the graphitic (10,0) and (10,1) peaks corresponding to the largest diamond peak, (111). The $50^\circ 2\theta$ peak suggested a face-centered-cubic (200) peak normally absent from diamond (see Cullity [7] for the distinction between FCC and diamond cubic reflections).

Assuming the $\sim 50^\circ$ and $\sim 74^\circ 2\theta$ peaks were the (200) and (220) peaks from a diamond-like FCC phase, the unit cell dimensions and other FCC reflections were calculated. A lattice size of 0.363 nm was found instead of the JCPDS 6-0675 diamond value of 0.35667 nm or 1.8% larger. Other peaks which should also be visible are the (111) near 43° , already observed, and the (311), just below 90° , which may be present as a small peak in the scans in Figure 1.

CONCLUSIONS

Fibers produced by chemical vapor growth are mostly graphitic. The carbon fibers produced by CVG with anhydrous ammonia contained a small, but detectable amount of diamond-like material. Since the diamond-like x-ray structure is reproducible, it is now possible to produce a fiber with mixed graphitic and diamond-like structures whenever desired.

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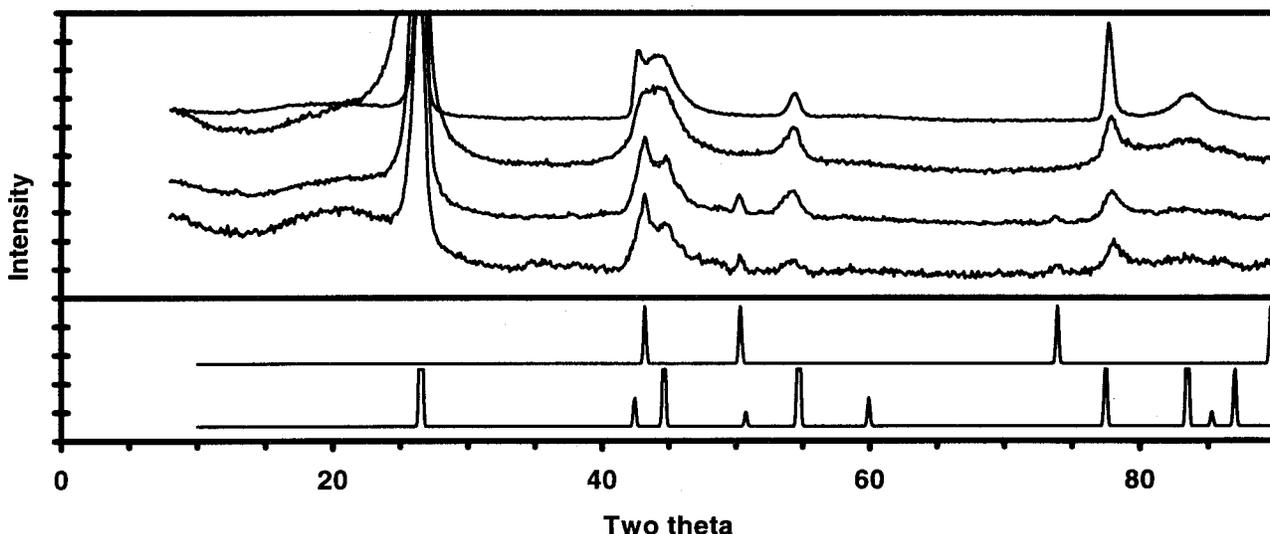


Figure 1. XRD scans of several fibers and the JCPDS based scans of FCC (diamond-like) and graphite.