The Thermal Conductivity of Vapor-Grown Graphite Fibers: Relation to their Microstructure

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Introduction

The thermal conductivity of vapor-grown carbon fibers subsequently heat-treated to 3000°C is remarkably high[1,2] along the fiber axis. Room temperature values up to 1500 $Wm^{-1}K^{-1}$ have been reported, and this compares favorably with the conductivity of natural single crystal and highly oriented pyrolytic graphite (HOPG). We report here measurements of the thermal conductivity along the axis of as-grown fibers as well as fibers heat-treated to 3000°C. We also deduce the phonon mean free path and correlate it directly to defects visible in SEM pictures, for the heat-treated fibers. For the as-grown fibers, it is possible in high-resolution TEM pictures of similar fibers not grown to macroscopic diameters, to identify a structure that may limit the phonon mean free path. Fiber growth was terminated at a very early stage of chemical vapor deposition in order to perform TEM on the single fiber.[3,4]

Experiment

The carbon fibers were grown by pyrolysis of natural gas.[5] One batch of about 100 fibers was heat-treated to 3000°C. A summary of the fiber properties is given in Table 1. X-ray diffraction yielded the inter-planar distance, and we estimated the c-axis correlation length L_c through a very elementary analysis of the <002> peak broadening.[6]

The thermal conductivity was measured using a steady-state heater and sink method. Careful measurements[2] made on single filaments and then on a bundle of 17 filaments showed no appreciable difference. We therefore decided to measure bundles of filaments individually mounted: 12 filaments for the heat-treated fibers; 57 filaments for the as-grown samples. The fibers we used were 10 to 50 μm in diameter.

We calibrated our system in the absence of fibers, to estimate the heat losses. The conductance through these losses was then subtracted from the total conductance to yield the fiber conductivity. In the worst case, the losses were responsible for half the heat transport; but usually their contribution was lower. An error of up to 15% may also be present in the absolute values due to the difficulty in estimating the cross-sectional area of the sample. Figure 1 shows the experimental data.

Table 1. Properties of the Fibers.

Sample	Units	1	2
Maximum process temperature	AC	1130	3000
d <002>	nm	0.347	0.335
<004>	nm	0.171	0.168
L_c	nm	4	48
ρ(294K)	Ωm	$1.02\ 10^{-5}$	$7.15\ 10^{-7}$
L_ϕ	m	$3.6\ 10^{-9}$	$2.9\ 10^{-6}$

Discussion

The theory of thermal conductivity in graphite is well developed[7] at least as long as defects are the only cause of phonon scattering. In the temperature range of our measurements, phonons are the dominant heat carriers. Also, in the present fibers, the graphite planes are dominantly aligned along the filament axis.[5] At low temperatures (T<40 K for the heat-treated fiber, T<100 K for the as-grown), our experimental data follow an approximate $T^{2.3}$ law, which corresponds well to the theoretical $T^{2.28}$ law valid when the elastic constant $C_{44} = 0$.[7] Since the thermal conductivity scales linearly with the phonon mean free path L_ϕ when defects dominate, we can deduce L_ϕ easily, and report it in Table 1.

We performed a goal-oriented microscopic search for the type of defects that could limit the mean-free path. Most of the fiber material was formed by a pyrolytic thickening or carbon chemical vapor deposition process. Of the material so deposited, in the case of benzene-derived fibers, lattice images are available in the literature.[4] Clearly 3 to 4 nm is indeed roughly the length over which each individual graphite plane extends before it is bent with a sharp (>20°) angle. The heat-treated fibers often appear quite smooth in the SEM. However, some fibers (Fig. 2) among those measured here, show facets whose size scales well with the 3-4 μm L_ϕ measured. If the facet boundaries are indeed the phonon limiting barrier, one should expect to find them in most fibers. In view of the thermal conductivity data, we suggest that this could indeed be the case, though such grains would often be

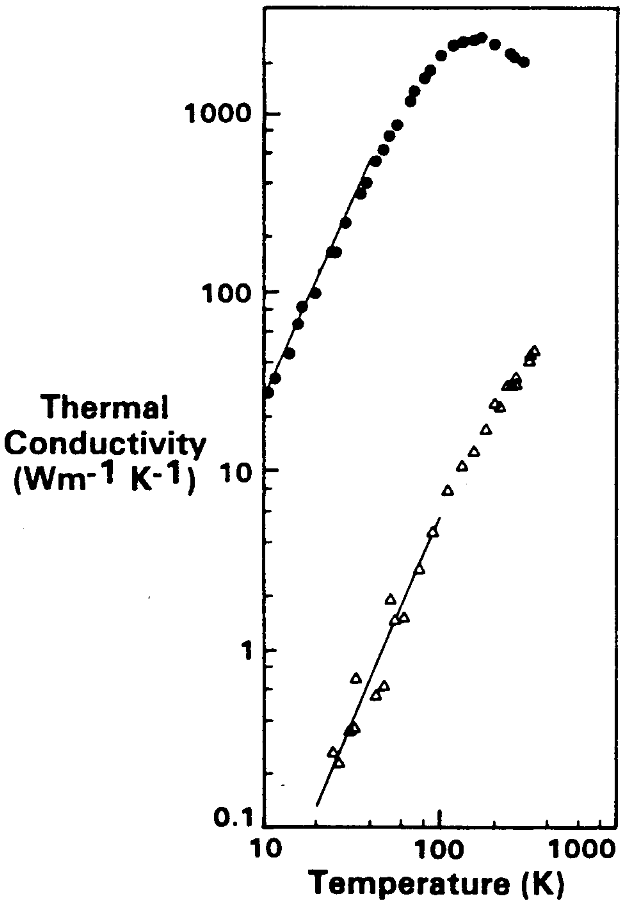

Figure 1. The temperature dependence of the thermal conductivity of vapor grown fibers (bottom) and the same, heat-treated to 3000°C (top). The lines represent the low-temperature theoretical behavior[7] assuming $C_{44} = 0$ and the phonon mean-free paths given in Table 1.

masked by a more sooty deposit on the outer fiber surface.

Conclusions

We have illustrated how the temperature dependence of the thermal conductivity for as prepared and 3000°C heat-treated vapor phase grown carbon fibers can lead to a determination of the average defect structure of the graphite fibers. Such an average value for the grain size is a useful complement to the information yielded by direct SEM and TEM microscopic observations of fiber structure.

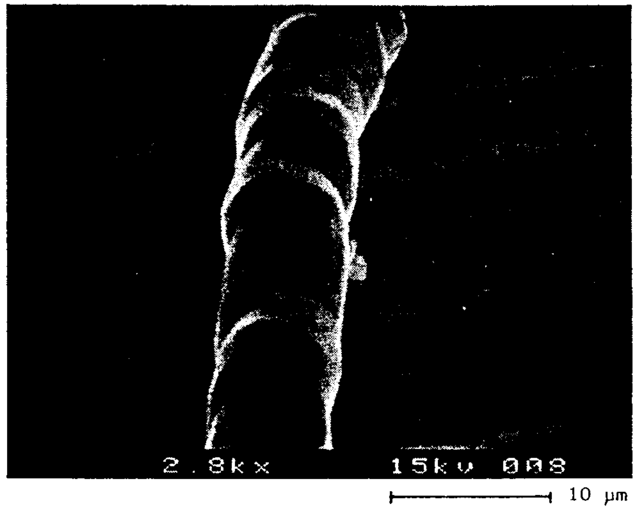

Figure 2. SEM picture of one heat-treated fiber on which the thermal conductivity was measured, showing clearly the highly faceted structure that develops on heat treatment. The average facet size is on the same order as the phonon mean-free path calculated from the data in Fig. 1.

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References

1. J. C. Bowman, J. A. Krumhansl and J. T. Meers, "Industrial Carbon and Graphite", Society of Chemical Industry, London (1958), p. 52.

2. L. Piraux, B. Nysten, A. Haquenne, J.-P. Issi, M. S. Dresselhaus and M. Endo, Solid State Commun. 50, 697 (1984).

3. J. R. Bradley and Y. L. Chen, private communication.

4. A. Oberlin, M. Endo and T. Koyama, J. of Crystal Growth, 32, 335 (1976).

5. G. G. Tibbetts, Appl. Phys. Lett. 42, 666 (1983).

6. B. D. Cullity, "Elements of X-Ray Diffraction", Addison-Wesley, Reading, MA (1956).

7. B. T. Kelly, "Physics of Graphite", Applied Science Publishers, London (1981).