

The Thermal Conductivity of Graphite Fibers

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Introduction

The thermal conductivity is one of the less often studied parameters of graphite fibers, although its low temperature ($T \leq 40$ K) value is directly related to the defect structure of the fibers.¹ Of the three prevailing types of fibers, carbonized from spun polyacrylonitrile, from petroleum pitch, or chemically vapor deposited, the latter have been most extensively studied.^{1,2,3} This is due to the fact that, when highly heat-treated, their longitudinal thermal conductivity is exceptionally high, reaching the value of $1500 \text{ Wm}^{-1}\text{K}^{-1}$ at room temperature. Not only does this lead to possible applications, but it also eases the experimental difficulties of the measurements. The temperature dependence of highly heat-treated pitch fibers has recently been measured⁴ between 4 and 300 K. PAN-based fibers have been studied more extensively, by measurements on bundles or on composites.^{5,6,7}

Experiment

Table 1 of Reference 8 summarizes the properties of the fibers studied here. They are:

- a. Fibers grown from pyrolysis of natural gas (carbon chemical vapor deposited),⁹ further identified CVD, and the same heat-treated to 3000°C (CVD-HT).
- b. Pitch-based fibers, purchased from Union Carbide,¹⁰ uncoated: Thornel P55 and P100.
- c. PAN-based fibers: we study Celion 6000¹¹ which we also received uncoated (C6000), and heat-treated the same fibers at 3000°C (C6000-HT). Also included in the samples is a highly stretched PAN fiber produced by Fiber Materials Inc. (FMI).¹²

The thermal conductivity was measured in a closed-cycle refrigerator by a steady-state heater and sink method: a rigid fiber glass-epoxy frame supported the heater and the thermocouples. The heat losses of the system were calibrated by making a measurement with no sample mounted. The losses were mainly due to the frame and wires below 100 K, and to radiation above 100 K. A bundle of each type of fiber was glued to the heater, the sink, and the thermocouples by means of flexible silver paint, though the fibers were electrically insulated from the thermocouples. The CVD fibers, however, were mounted filament per filament.¹ The geometrical aspect ratio (area divided by length between contacts) was estimated by measuring the resistance of the bundle at 294 K and comparing that to the resistivity Reference 8. It is assumed that the thermal ratio is the same as the electrical one.

The results are shown in Figure 1. Both CVD fibers and P100 exhibit a behavior that is quite like that of pyrographites, with a $T^{2.3} - T^{2.6}$ law at low temperature. The PAN-based fibers display a lower temperature dependence, especially the not heat-treated Celion 6000. This result, confirmed by Reference 5 cannot be ascribed to an electronic contribution to the thermal conductivity,¹³ as we verified using the Wiedemann-Franz law with the free electron Lorentz number¹³ and the electrical resistivity.⁸ In the intermediate temperature range, where the sharper $T^{2.3}$ law is obeyed by all fibers but C6000, we can use the theoretical model of Kelly,¹⁴ assuming that in all fibers the graphite planes are dominantly aligned along the fiber axis, and so estimate the phonon mean free path L_ϕ . The latter value is limited by the density of defects in the fibers.

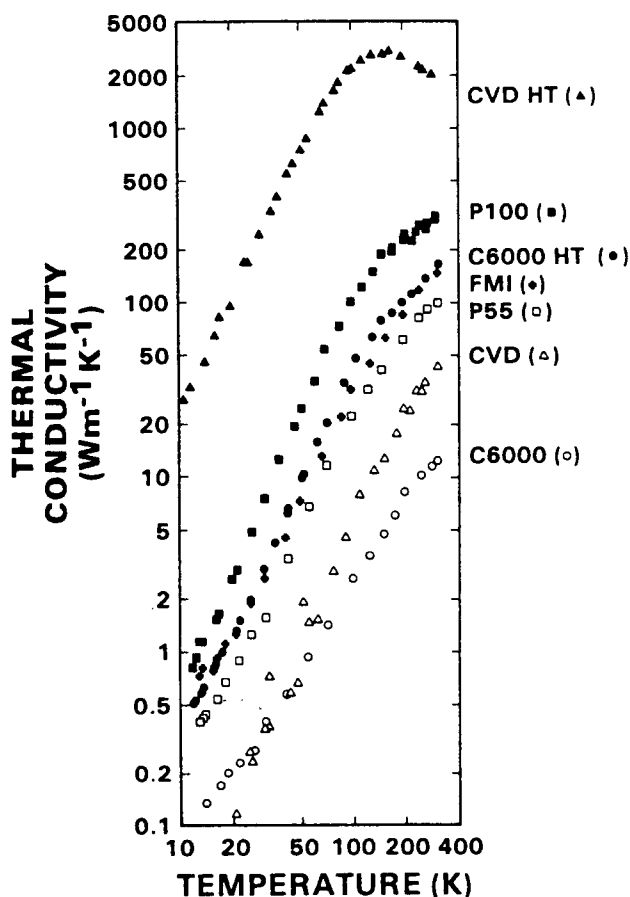


Figure 1. The temperature dependence of the thermal conductivity of various fibers identified as in Table 1 of Reference 8.

Conclusions

The present comparison suggests that even the highly heat-treated PAN and pitch-based fibers have their thermal conductivity at room temperature limited by defects. The more graphitizable vapor-grown fibers have a conductivity near room temperature that is probably limited by phonon-phonon Umklapp processes, and therefore such fibers even if heated to slightly lower temperatures, will still conduct heat much better than most commercially available materials.

Acknowledgments

The author acknowledges Dr. C. P. Beetz for discussion and critical reading of the manuscript, and Dr. G. G. Tibbetts and M. Devour for providing the vapor-grown fibers.

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