The Temperature Dependence of the Thermoelectric Power and Electrical Conductivity of Graphite Fibers

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Introduction

Carbon fibers are usually obtained either from organic precursor fibers made from polyacrylonitrile (PAN) or specially treated petroleum pitch, or grown by vapor phase pyrolysis of natural gas or benzene. Most fibers have planes of hexagonal carbon running nearly parallel to the fiber axis, the direction along which the present results are taken. The dependence of the room-temperature thermopower of PAN-based fibers[1] illustrates that these do not easily graphitize. The benzene-grown fibers were studied more extensively[2] and are fully graphitized by heat-treatment to 2800-3000°C. While experimental galvanomagnetic properties of PAN[3,4] pitch[5] and benzene[6,7] derived fibers are well documented, our current understanding of the electronic properties of less ordered carbon fibers is less advanced. Here, we present some new systematic data on the temperature dependence of the thermopower of PAN and pitch based fibers, and fibers grown by thermal decomposition of natural gas.

Experiment

We measured the temperature dependence of the electrical conductivity and thermoelectric power of the same fibers as used in Ref. (8). A summary of the relevant properties of the samples is given Table 1: the c-axis spacing d and c-axis correlation length L_c. We measured the room-temperature (294 K) resistivity ρ (R.T.) of several single filaments of our samples, using a 4-probe technique and optical microscope or SEM pictures to deduce the diameters. While the accuracy of the measurement and reproducibility from filament to filament were of the order of 15% for most fibers, the results on the FMI fibers were much more variable: an average value of $3\ 10^{-6}$ Ωm was measured, but individual fibers could have a resistivity as low as $1\ 10^{-6}$ Ωm. The temperature dependence of the electrical conductivity and of the thermopower was measured in a closed-cycle refrigerator on a bundle of filaments of each type of fibers. The results are shown in Figure 1a for pitch-based and vapor-deposited fibers, and Figure 1b for PAN-based fibers. The data for the absolute thermoelectric power are reported in Figure 2.

The electrical conductivity data on the pitch fibers agree quite well with those measured previously[5] and so does the correlation between L_c and ρ(10 K)/ρ(300 K). We also confirm the electrical measurements on vapor-grown fibers[12], and on PAN-based Celion 6000[3] fibers, including the unusual behavior around 30 K.

Table 1. Properties of the fibers: we used vapor-grown (CVD), pitch (P55, P100 Ref. (9)) and PAN-based (C6000 Ref. (10), FMI (Fibers Materials, Inc., Ref. 11)) fibers, and report the maximum temperatures they were processed at in our laboratory. R. T. stands for room temperature, here 294 K. (a) identifies the properties as measured by us on the fibers used in this paper, (b) as reported by manufacturers.

Property	Units	CVD	CVD-HT	P55	P100	C6000	C6000-HT	FMI
Max.Process.Temp.	°C	1130	3000				3000	
d<002>	nm	.347	.335	.341	.337	.353	.339	.341
L_c(002)	nm	4	>50	8	18	2	7	5.4
ρ(R.T.)(a)	10^{-7} Ω m	102	7.1	96	36	180	59	30
(b)	10^{-7} Ω m			75	25	150		

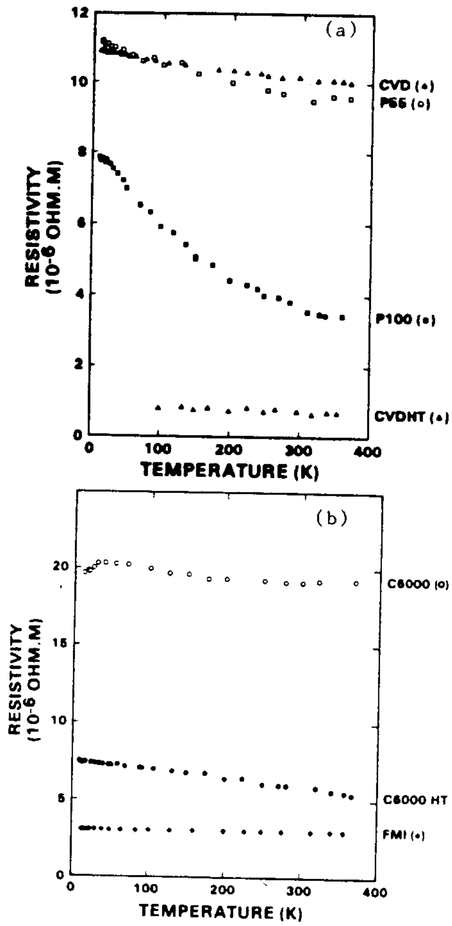

Figure 1. The temperature dependence of the resistivity of (a) pitch-based and vapor-grown fibers, and (b) pan-based fibers.

On PAN-based fibers, the room-temperature values of the thermopower differ slightly from those of.[1] The fibers deposited from natural gas have a temperature dependence of the thermopower that closely resembles that of benzene-derived fibers,[2] although the absolute values are not quite the same for the heat-treated CVD fibers. This descrepancy remains within the differences observed in other very perfect graphites,[13] where the thermopower is sensitive to the asymmetry between the properties of electrons and holes. P100 exhibits a positive thermopower, raising for T<100 K, then levelling of. This is the behavior one expects for the diffusion thermopower of a solid whose carrier density increases linearly with temperature above 100 K, as does graphite. If we are dealing with a two-carrier system, we have to add the assumption that the asymmetry in this case is temperature-independent. Finally P55, the FMI fiber, and less clearly the heat-treated Celion 6000, have a rather linearly increasing thermopower. This was the case for benzene-derived fibers heat-treated around 1700°C.[2] It suggests a metallic, hole-dominated diffusion thermopower.

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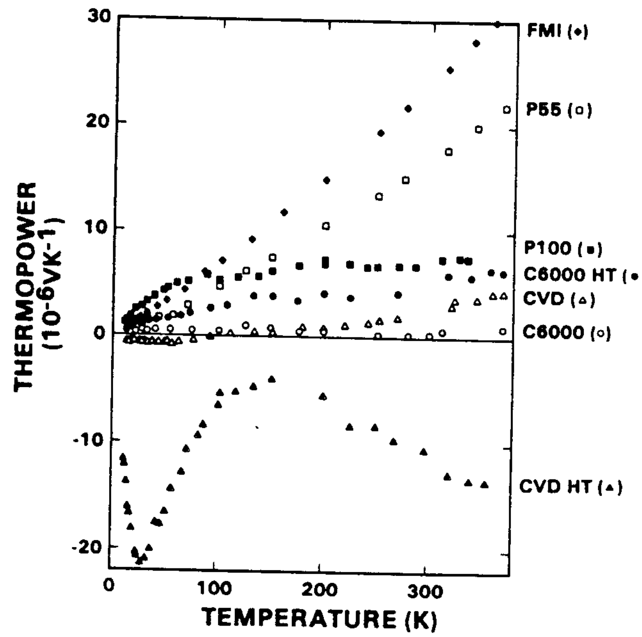

Figure 2. The temperature dependence of the thermoelectric power of vapor-grown, pitch-based and PAN-based fibers.

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