

Hydrostatic Pressure Piezoresistance of Carbon Fibers

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Introduction

Several studies have been made of the tensile piezoresistance (TPR) behavior of carbon fibers [1-8]. The TPR is positive for carbonized fibers; decreases with increasing heat treatment temperature HTT; then becomes negative beyond a critical stage of structural development (resistivity $\leq 800 \mu\Omega\text{cm}$; HTT $\geq 2700^\circ\text{C}$ for PAN). The hydrostatic pressure piezoresistance (HPPR) behavior of fibers has not been reported, though there have been several investigations on pyrocarbons (PC) and graphites [9,10]. This paper presents the results of an initial investigation of the HPPR behavior of fibers from PAN; and of an as-deposited PC and a glass-like carbon (GLC) selected as reference 'bulk' materials.

Experimental Procedure

The fibers studied were T-300, in the as-received condition, and after HTT $\approx 3200^\circ\text{C}$. The former is representative of carbonized fibers with +TPR, while the latter should have -TPR. Thin stick samples ($\sim 0.4 \times 0.5 \times 12 \text{ mm}^3$) cut from plates of a GLC (Beckwith, HTT $\sim 1800^\circ\text{C}$) and a PC (Le Carbone, deposited at 2100°C from methane) were also measured.

Resistances were measured by four-terminal (4T) methods, using a digital multimeter (DMM, Keithley 191) for the fiber and GLC samples. For the PC, a voltmeter/ammeter method was used with a constant current source (Keithley 225), 0.1Ω standard resistor and DMM measurement of the voltage drops. The length between the potential contacts was $1 \pm 0.2 \text{ cm}$ for all samples. The fibers were mounted on glass substrates and fine Ag lead wires were attached with Ag paint and protected with a coating of epoxy resin. (bare contacts were unstable).

The resistances R_c of the potential contacts were monitored by measuring all of the two-terminal (2T) resistances, because of evidence that contact stability could be a problem. $R_c \leq 20 \Omega$ at ambient, dropping to $\leq 1 \Omega$ at $P \geq 0.5 \text{ kb}$ were obtained by applying paint to the junctions of wires laid across the fibers. These R_c were well within the stated compensation capability of the DMM, but the hysteresis and relatively high R_c at low P were undesirable. An improved method (type 2; paint applied to the substrate first, then as above) gave $R_c \leq 1 \Omega$ at all P . Wrapped wire plus Ag paint, and epoxy coating, was used for the GLC and PC contacts; R_c was similar to the type 2 fiber contacts. The 4T R values were $\sim 0.2 \Omega$ for the PC and $\sim 1.6 \Omega$ for the GLC; the fiber R were 4.7 (as-received) and 1.7 (graphitized) $\text{k}\Omega/\text{cm}$.

The temperature coefficient of resistance (TCR) of the fibers around room temperature was measured to evaluate their structural state [4-7], and to assess the influence of adventitious temperature variations on the results. The TCR were $\sim -0.04\%/^\circ\text{C}$ (as-received) and $-0.163\%/^\circ\text{C}$ (graphitized fiber), consistent with previous results. Temperature variations of $\sim \pm 1^\circ\text{C}$ caused easily detectable changes in the graphitized fiber R .

R was measured as a function of P up to $\sim 3 \text{ kb}$, in mineral oil at room temperature, using a Swiss Nova manual apparatus with a Harwood manganin P gage and a steel sample chamber designed and fabricated at the laboratory. Room temperature was monitored with a thermometer contacting the chamber. Transient R changes with a decay time of $\sim 10 \text{ min}$ occurred during the P dependence measurements due to adiabatic temperature changes within the chamber ($\Delta T \sim \pm 4^\circ\text{C}$ for the usual P increments of $\sim \pm 0.2 \text{ kb}$).

Results and Discussion

The HPPR of the graphitized fibers was found to be small and positive, while that of the carbonized fiber was larger and negative -- just the reverse of the TPR behavior. The possible influences of contact resistance and temperature variations were evaluated to confirm the validity of these results.

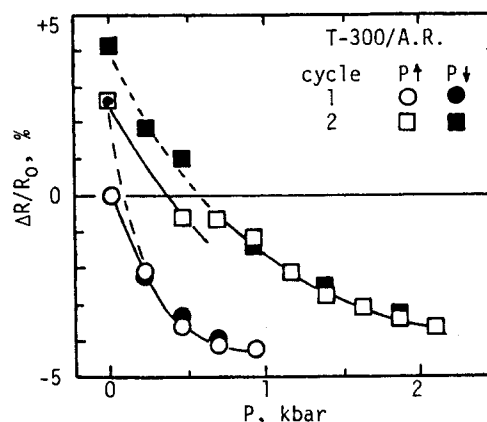


Fig. 1. Pressure dependence of the resistance of an as-received (carbonized) fiber.

The fractional change in resistance with pressure of an as-received fiber is shown in Fig. 1. The contacts were type 1, and 3/4 of the fiber was covered with epoxy. The discontinuity at $P \sim 0.6 \text{ kb}$ on

the second P cycle resulted from failure and repair of a current connecting lead. R decreases with increasing P, but there is appreciable hysteresis on reducing P below ~ 0.25 kb. Temperature drift had negligible effect on these data; and R_c changes, if uncompensated by the DMM, could account for R changes of $\sim \pm 0.8\%$ at most. Therefore, the R increase at ambient P must be attributed mainly to fiber damage; or, perhaps, to residual stresses associated with the compressible epoxy coating. 2T data indicated a much smaller residual ΔR for the bare end of the fiber, but this result is ambiguous because R_c of the current contact could not be measured. In any case, it may be concluded that the HPPR of the carbonized fiber is negative, with a mean slope $S' = d \ln R / dP \approx -1.4 \text{ \% / kb}$ for $P \geq 1$ kb.

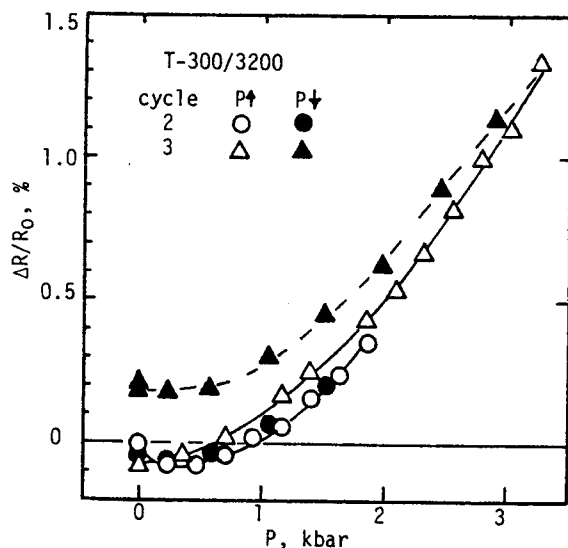


Fig. 2. Pressure dependence of the resistance of a graphitized fiber.

Fig. 2 shows the behavior of a bare graphitized fiber, corrected for room temperature drift. The contacts were type 2, and just the fiber ends, between the current and potential contacts, were epoxy coated. R_c was stable and negligible. The mean $S' \approx +0.6 \text{ \% / kb}$ for $P \geq 1$ kb. 2T data indicated a somewhat larger effect for the epoxy coated end segments. The hysteresis and residual $\Delta R \approx 0.2\%$ on returning to ambient from $P \approx 3$ kb suggest some damage to the fiber; however, there was no change in the TCR after the high P measurements. On the other hand, evidence was obtained for a reversible decrease with increasing P of the apparent temperature dependence. This could result from a decrease in TCR; or, perhaps more probably, an increase in heat transfer efficiency between the fiber and the oil at high P.

In order to obtain more information about the influence of microstructure on the HPPR characteristics, data were obtained on two model 'bulk' carbons: A GLC with an isotropic, microporous but impervious, very disordered structure; and a PC (a-direction) with a dense, anisotropic turbostratic structure. The results are shown in Fig. 3, in comparison with the fiber behavior. The HPPR of the GLC is similar to that of the carbonized fiber, but somewhat smaller: $S' \approx -0.7 \text{ \% / kb}$ in the range $P \geq 1$ kb, where R_c was constant. The large drop of R at low P for the PC was largely reversible, and is tentatively attributed to improved contact with the layer edges under pressure. DMM ohmmeter measurements confirmed that R_c decreased rapidly in this range, from $\sim 0.8 \Omega$ at

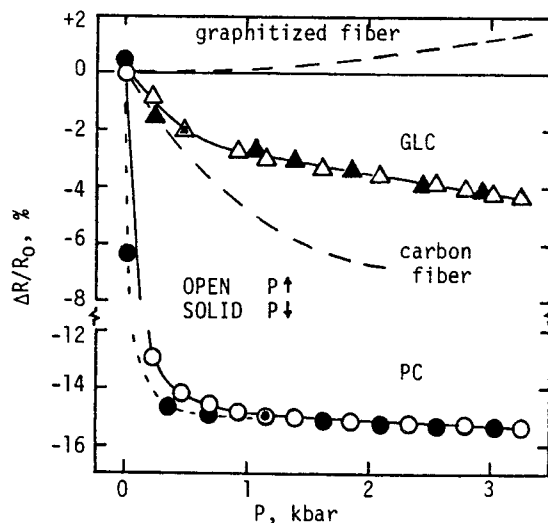


Fig. 3. Pressure dependence of the resistances of a glass-like carbon and a pyrocarbon, compared with the behavior of the fibers.

$P=0$, and was constant at $\sim 0.6 \Omega$ for $P \geq 1$ kb. The very small dependence at high P ($S' \approx -0.2 \text{ \% / kb}$) agrees with the room temperature values reported for various highly-oriented graphites [9] and PC [10]. It has been attributed to near-compensation of a carrier density increase by a mobility decrease. This suggests that the +HPPR of the graphitized fiber may be due to dominance of the mobility decrease, influenced perhaps by the combination of anisotropic compressibility and fiber-type orientation texture.

Conclusions

The electrical resistance of a graphitized carbon fiber from PAN increases with increasing hydrostatic pressure, whereas the resistances of the carbonized fiber, a glass-like carbon and a pyrocarbon all decrease. The hydrostatic pressure piezoresistance behavior of the fibers is just the reverse of that found for the tensile piezoresistance.

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