ELECTRONIC AND STRUCTURAL CHARACTERISTICS OF CARBON FIBERS FROM MESOPHASE PITCH*

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Electronic properties have long been used as a means for studying the structure of carbons. A recent series of studies of PAN-based carbon fibers[1] showed that all of the electronic and structural properties could be correlated with processing conditions. A single parameter, such as the resistivity ratio, was found to be a good indicator of the structural evolution of the fibers with processing. The present work is an attempt to apply the same principles to the study of mesophase pitch-based carbon and graphite fibers. The purpose is two-fold: first, to provide a better understanding of the structure of these fibers and its relation to the fiber properties; and second, to clarify the differences in structure and properties between pitch-based and PAN-based carbon fibers.

Several series of fibers were studied, each processed at various temperatures up to 3000°C. Fibers having both radial and random microstructures were included. Resistivity and magnetoresistance measurements were made on single filaments by four-contact ac and dc methods at temperatures between room temperature and 4.2K. Standard ESR techniques were used to measure the g-anisotropy, linewidth, and effective spin concentration of strands of fibers.

The resistivity ratio is defined as $\rho(300°K)/\rho(4.2°K)$. For fibers heat treated to 1000°C, this parameter has a value of about 0.4, increasing to 0.93 for HTT = 1700°C. Above 1700°C, the resistivity ratio decreases again, reaching values around 0.4 for HTT = 3000°C. Radial structure fibers have lower resistivity ratios (above 1700°C) than random structure fibers processed at the same temperature.

Figure 1 shows the transverse magnetoresistance at 4.2K for selected fibers. At low HTT's, the magnetoresistance (MR) is very small, becoming larger and negative as HTT increases to around 2000°C to 2500°C. At higher HTT's, the MR becomes positive at high fields, but remains negative at low fields until the highest HTT's. Radial fibers show a stronger tendency toward positive MR than equally processed random structure fibers. The results of Ingram and coworkers[1] on PAN fibers show a negative MR (at 77K) even for samples heat treated up to 3000°C.

The above results are illustrated more dramatically in Figure 2, where the transverse MR at 14kG is plotted against resistivity ratio. All samples fall precisely on the same curve. Two distinct regions are evident, corresponding approximately to HTT's below and above 2500°C. The low-temperature region is characterized by negative MR and larger resistivity ratios. The high-temperature region, in which the MR is positive, corresponds to the onset of three-dimensional ordering as evidenced by the appearance of three-dimensional X-ray diffraction lines. The results of Ingram and coworkers[1] for PAN fibers cannot be compared directly since they were measured at a different temperature, but they fall roughly in the low-HTT region for all samples.

Figure 3 shows the crystallite size in the c-axis direction, L_c, plotted against resistivity ratio. Again, all samples fall on a single curve. The results for PAN fibers[1] fall on a separate curve. Presumably, this is due to the fact that the resistivity ratio is more closely related to L_a than to L_c and reflects the difference between PAN and pitch in their crystallization behavior.

Crystallite size (L_c) and interlayer d-spacing results show similar correlation with electronic properties and offer further confirmation that radial structure fibers are capable of a higher degree of graphitic order than random structure fibers.

From ESR, the "effective spin concentration," calculated assuming no skin effect and Curie's law, was similar to that obtained by Robson et al.[1] for heat treated PAN fibers viz., a decrease from ~15 to ~10 x 10^{18}/g over an HTT range from 1800°C to 3000°C.

The linewidth is sensitive to impurities and narrows by as much as a factor of five when the sample is purified with chlorine. The effect is reversible when one diffuses impurities back into these same samples. The purification process has no effect on any of the other electrical or ESR properties, indicating the phenomenon is purely one of relaxation. The broad linewidths observed by Robson et al.[1] are most likely due to impurities.

In Figure 4, the fiber g-anisotropy is plotted against HTT. The dashed line indicates that the anisotropy was so large that the spread in g-values broadened the signal in the perpendicular orientation beyond detection. The g-anisotropy of the PAN derived fibers[1] saturates at high HTT's at a value equal to that of pitch-based fibers heat treated in the 2000°C to 2300°C range. This finding is consistent with the fact that mesophase pitch-based fibers are graphitizable whereas PAN-based fibers are not.

This study has shown that reproducible correlations exist between various electrical, mechanical, and structural properties of mesophase pitch-based carbon fibers. Radial fibers are more graphitic than random fibers at a given HTT above 1700°C and reach a higher ultimate degree of graphitization at the highest HTT. These observations strongly imply that the graphitization process is inhibited from proceeding beyond a certain stage in the random fibers. The most likely explanation for this is that the random structure is more highly defected and grain growth is inhibited at an earlier stage than in the radial structure.

The exploratory ESR experiments described here

*Work supported in part by AFML, Wright Patterson Air Force Base, Ohio, Contract No. F33615-75-C-5109.

demonstrate that effects of preferred orientation, degree of graphitic character, nature of the unparied spins, and impurity and other defects are all apparent and seem to have interpretable effects on the observed ESR spectra.

Finally, the electrical measurements suggest that mesophase pitch fibers are very similar to pyrolytic carbons treated in the same temperature range. This is consistent with the high degree of graphitization attainable by these fibers. On the other hand, PAN-based fibers have been found[1] to exhibit a much lower ultimate degree of crystalline order, comparable to pitch fibers treated in the 1700°C to 2300°C range.

Reference

1. D. Robson, F.Y.I. Assabghy, and DJE Ingram, J. Phys. D: Appl. Phys. 4, 1426 (1971); 5, 169 (1972); 6, 1822 (1973).

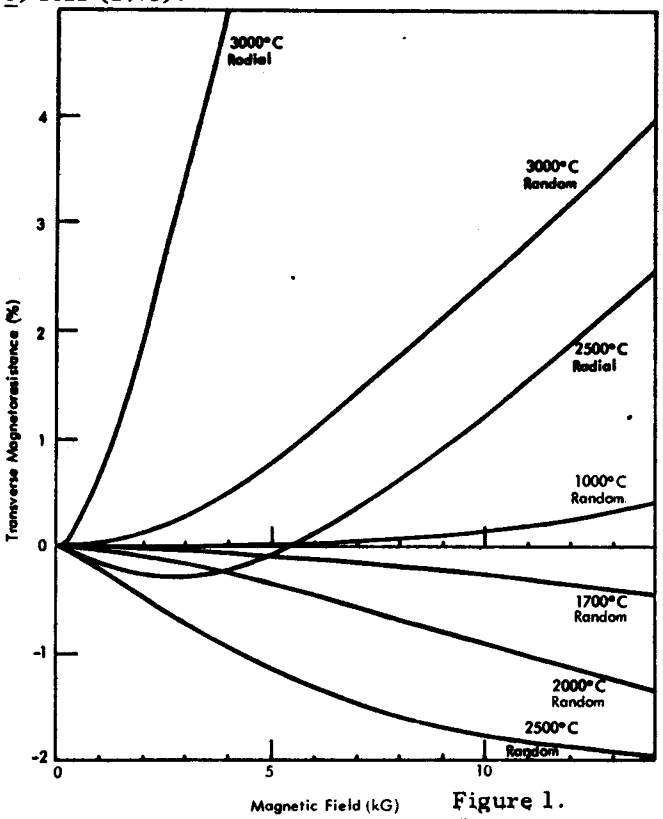

Figure 1.

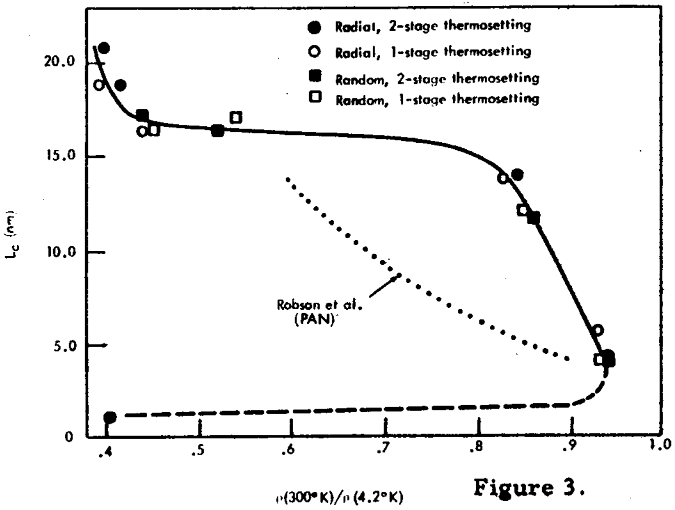

Figure 3.

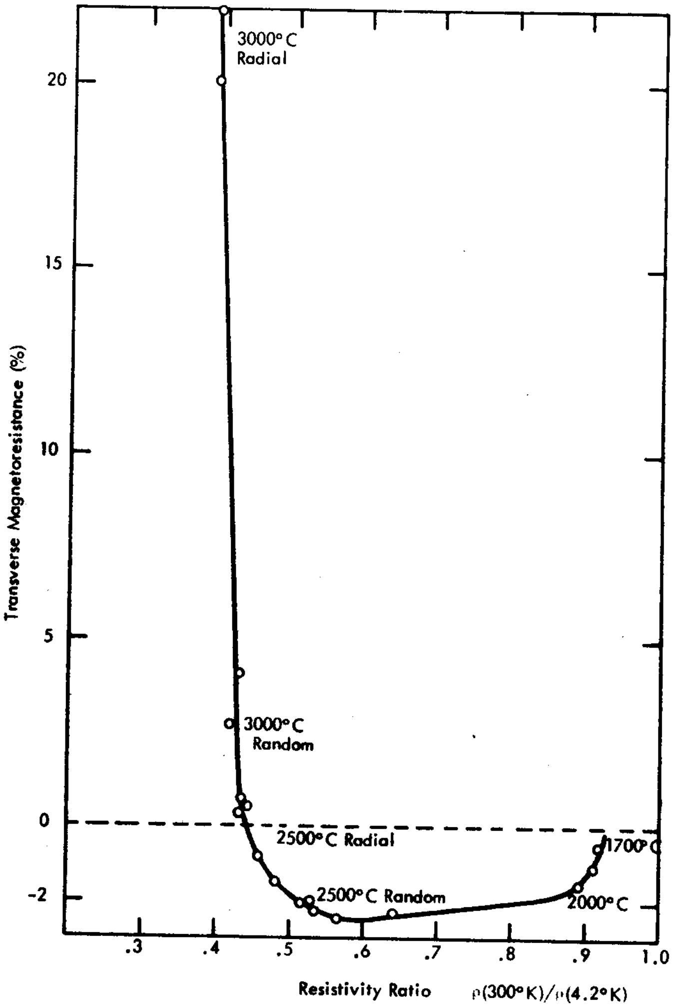

Figure 2.

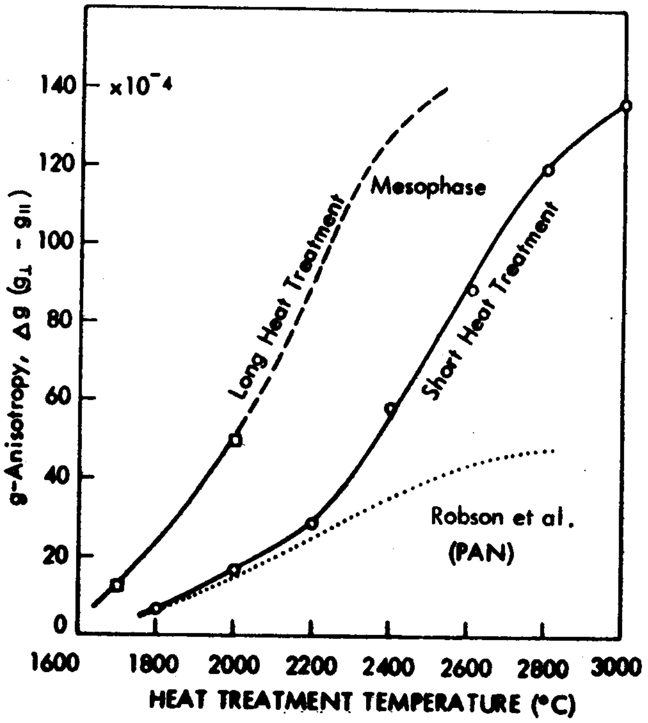

Figure 4.