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Simultaneous Electrical Resistivity and Mass Uptake Measurements in Bromine Intercalated Fibers

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SIMULTANEOUS ELECTRICAL RESISTIVITY AND MASS UPTAKE MEASUREMENTS IN BROMINE INTERCALATED FIBERS

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SUMMARY

Changes in mass and electrical resistivity of several types of pitch-based and vapor-grown graphite fibers were monitored during reaction with bromine. The observed threshold pressure dependent reaction suggested that the fibers were intercalated. In the fully brominated compound, the mass was increased by 44 percent and the resistivity was improved by a factor of 17. In the residue compound, the mass was increased by 22 percent and the resistivity was improved by a factor of 5. Fibers possessing different degrees of graphitization had surprisingly similar changes in both mass and resistivity.

INTRODUCTION

Pitch-based graphite fibers have received considerable attention recently because of their suitability as a host for graphite intercalation compounds. Intercalation, the insertion of guest atoms or molecules between the graphene planes, yields graphite fibers with improved electrical conductivity. These improved fibers are being considered for a number of aerospace applications, such as lightning strike resistant aircraft surfaces, electromagnetic interference shielding, and de-icing.

Amoco (formerly Union Carbide) pitch-based P-100 fibers treated with bromine are exceptionally noteworthy due to their remarkable electrical performance and environmental stability (ref. 1). For example, these brominated fibers have an electrical resistivity comparable to stainless steel and exhibit thermal stability up to 200 °C, while maintaining the desirable properties of low density and high thermal conductivity. Other brominated pitch-based fibers also show considerable promise in terms of improved electrical properties and environmental stability (ref. 2).

This paper focuses on the incremental changes in electrical resistivity as a function of bromine mass uptake for several fiber types, including P-55, P-75, P-100, P-120, and vapor-grown fibers. In the "P" series of pitch-based fibers, the tensile modulus increases with designation number, and the degree of graphitization increases with increasing modulus. The vapor-grown fibers represented the highest level of graphitization owing to their annealing at 3000 °C. The bromine mass uptake of highly oriented pyrolytic graphite (HOPG) was also measured as well. Monitoring the change in both mass and resistivity should yield valuable information on threshold pressure dependence and brominated fiber composition for all of the fiber types tested.

MATERIALS AND METHODS

To monitor the changes in mass, an electronic microbalance (Perkin-Elmer model TGS-2) was modified such that the mass of a small bundle of fibers (46 to 1161 μg) could be measured while in contact with bromine vapor. The platinum hangdown wire assembly was extended so that several chambers could be added to protect the electronics from the bromine vapor (see fig. 1). A condenser, kept at -20 °C, was placed just above the bromine reaction chamber to remove most of the bromine vapor. A heated copper tube, kept at 120 °C, was placed above the condenser to scavenge any residual bromine vapor. As a final precaution, the vent for the nitrogen purge gas was placed above the heated copper tube.

Bromine was added to the reaction chamber by heating a small bromine reservoir. The reservoir was attached to the reaction chamber through a stopcock, so that the source of bromine vapor could be turned on during the bromination step and off during the purge step. The refluxing action of the bromine would continually add bromine vapor to the reaction chamber (and the condenser would continually remove it). This dynamic approach for the addition of bromine vapor was necessary because an unobstructed path for the hangdown wire to the microbalance was needed. However, it was difficult to precisely control the bromine vapor pressure with this approach. Since the temperature of the reaction chamber did not exceed room temperature, the vapor pressure of the bromine in the chamber could not have exceeded 165 torr. After bromination was judged to be complete, the bromine vapor was purged from the reaction chamber with a modest flow of nitrogen.

The electrical resistivity of a single fiber was simultaneously monitored using a four point resistance probe located in a sidearm adjacent to the sample pan. Carbon paint was used to mount the fiber across the four platinum leads. A Keithley model 220 constant current source supplied 100 μA to the outer two leads while a Keithley model 181 nanovoltmeter measured the voltage drop across the inner two leads. Both the four point probe and the microbalance were interfaced with an IBM microcomputer for data collection and storage.

RESULTS AND DISCUSSION

The idea of monitoring the change in mass of a graphite sample upon intercalation is not new. Forsman et al., for example, used the length of a quartz spring as a visual indicator of the mass change during a nitric acid intercalation (ref. 3). This technique, however, is inadequate for studying microgram quantities of fibers because the change in mass would be too small to detect. Furthermore, monitoring a change in length visually is not conducive to computerized data collection. The electronic microbalance modified for this study was capable of detecting a mass change on the order of a few micrograms and was easily interfaced with a computer. However, with the enhanced sensitivity of this approach, adsorption presented a problem. The bromine uptake of the fibers alone was actually obscured by adsorption of bromine on the platform hangdown wire and pan. Through careful analysis of the data, mass uptake and electrical resistivity of the "fully brominated" fibers and the "residue compound" were obtained.

Figure 2 shows both the change in mass and electrical resistance for a typical sample of P-100 fibers placed in the bromine environment. Several features of this diagram are worth noting. When the bromine first entered the reaction chamber, a mass increase of approximately 35 μg was observed; however, no change in electrical resistance was observed (region A). This mass increase was independent of sample size and was observed in the absence of fibers. It was attributed to the initial adsorption of bromine on the platinum hangdown wire and pan. (There is no threshold pressure requirement for adsorption.)

As the vapor pressure of bromine was increased, the threshold pressure for the intercalation reaction was exceeded (refs. 4 and 5), and both the mass and resistivity began to change, signaling the onset of intercalation (region B). With the four point probe positioned in a side-arm of the reaction chamber, a slight lag between the change in mass and the change in resistivity was observed. The one factor which limited the usefulness of the data collected in this region was the additional adsorption of bromine on the hangdown wire. There was no way to clearly distinguish fiber mass uptake from multilayer adsorption on the platinum. Much of the multilayer adsorption may be attributed to bromine freezing out on the hangdown wire in the vicinity of the cold-trap. It was not possible to subtract out an empty reference pan for this region because the shape of the curve was dependent on time and bromine vapor pressure.

After the fiber on the four point probe reached its equilibrium resistance value, the bromine source was shut off and the bromine in the reaction chamber was slowly vented. As shown in figure 2 (region C), the mass of the sample pan abruptly decreased. No corresponding change in resistivity confirmed that this mass change was independent of the fibers. A similar decrease in mass was also seen in the absence of fibers. The abrupt decrease in mass was attributed to the loss of the multilayer adsorbed bromine. Then the mass leveled out to a value representing the "fully brominated" fiber compound (region D). This mass value of approximately 44 percent corresponded to a resistivity value of 18 μΩ-cm and a stochiometry of $C_{30}Br_2$.

As the last traces of bromine were purged from the reaction vessel, another decrease in mass was observed (region E). This mass loss had a corresponding increase in fiber resistance and was clearly dependent on the fibers. This step corresponded to the loss of bromine from the skin of the fibers (refs. 4 and 6) (as well as the loss of the monolayer of adsorbed bromine). The mass and electrical resistivity values at the final plateau (region F) represented the "residue" compound. The mass value of approximately 22 percent corresponded to a resistivity value of 50 μΩ-cm. The mass value of 22 percent reported here is slightly larger than the 18 percent reported by Hung (ref. 7), and the discrepancy can be explained by the asymptotic loss of bromine which occurs over the first few hours in air (ref. 8).

The changes in mass and electrical resistivity obtained with the P-75 and P-120 fibers were similar to the changes shown in figure 2. The changes in mass for the HOPG and vapor-grown samples were also similar to P-100, except that they had an additional mass plateau between the fully brominated and residue plateaus, perhaps suggesting a stage transition. No electrical resistivity data were collected with the HOPG sample because the geometry of HOPG was inappropriate for the four point probe. The P-55 fibers showed no substantial increase in either mass or conductivity.

Figure 3 summarizes the mass uptake data obtained from all the fiber hosts (except P-55) and HOPG, as a function of initial mass, for both the fully brominated compounds and the residue compounds. P-75, P-100, and P-120 fibers have mass uptake values which are colinear. The slopes of these two lines yield the average mass increase for each type of compound: 44 percent for the fully brominated compound and 22 percent for the residue compound. The results from the HOPG sample also appear to be colinear in mass uptake, however the results from the vapor-grown fibers are slightly anomalous.

Ismail (ref. 9) has examined the pore volume and surface area of P-55 fibers and P-55 fibers graphitized to 2700 °C. Based on the pore volume measurements and the density of bromine, one can estimate the total mass of bromine that could occupy the pores of these pitch-based fibers. If bromine solely occupied the pores, then the weight percent of bromine in the P-55 fibers and graphitized P-55 fibers would be 0.7 and 0.6 percent, respectively. The contribution from the surface area is an order of magnitude less. The 44 percent mass increase observed in this work for the P-75, P-100, and P-120 pitch-based fibers is far too large to be attributed to the adsorption of bromine into the pores of the fibers alone. Some other mechanism, such as intercalation, must be responsible.

The three pitch-based fiber types also exhibit similar decreases in resistivity, as summarized by the resistance ratio (resistance, R/initial resistance, R_o) data in table I: seventeen-fold for the fully brominated compound and five-fold for the residue compound. The change in resistivity upon bromination is remarkably similar in these fibers even though they have different degrees of graphitization. Reliable resistance ratio data for the vapor-grown fibers were difficult to obtain owing to the slow reaction kinetics imposed by their morphology (ref. 8).

That the P-75, P-100, and P-120 pitch-based fibers had a similar bromine uptake and a similar change in resistivity leads one to believe that a similar number of charge carriers was added to each. This is quite surprising considering the different degrees of graphitization represented by the "P" series. Even more surprising is the similarity in mass uptake observed between these pitch-based fibers and HOPG. Because the fibers had different absolute resistivities, the mobility of the charge carriers must have been dominated by the degree of graphitization.

CONCLUSIONS

Adsorption of bromine on the platinum wire was apparent at the slightest visual indication of bromine. However, mass uptake in the fibers only occurred after a substantial amount of bromine had been introduced, suggesting a threshold pressure dependent intercalation reaction. Changes in the mass of the pitch-based P-75, P-100, and P-120 fibers were similar to the changes observed in HOPG. The fully brominated compound had a mass increase of 44 percent, and the residue compound had a mass increase of 22 percent. The P-55 fibers showed no detectable mass increase. The vapor-grown fibers acquired more bromine initially, but eventually reached the same residue compound composition. The mass increase observed in both the fully brominated compound and the residue compound could not be attributed to adsorption of bromine alone, based on the pore volume measurements of Ismail. Some other mechanism, such as intercalation, must be used to explain the observed mass increase. Changes in the

electrical resistivity of the P-75, P-100, and P-120 fibers were also similar, seventeen-fold for the fully brominated compound and five-fold for the residue compound. The similarity between the pitch-based fibers is surprising, considering the differences in graphitization.

ACKNOWLEDGMENTS

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TABLE I. - RESISTANCE RATIO (R/R_o)
FOR SEVERAL PITCH-BASED FIBERS
TREATED WITH BROMINE

Fiber type	Fully brominated	Residue compound
P-75	0.057	0.197
P-75	.057	.206
P-100	.058	.198
P-100	.069	.180
P-100	.051	.179
P-100	.051	.172
P-100	.055	.189
P-120	.057	.205
P-120	.065	.207
P-120	.062	.206

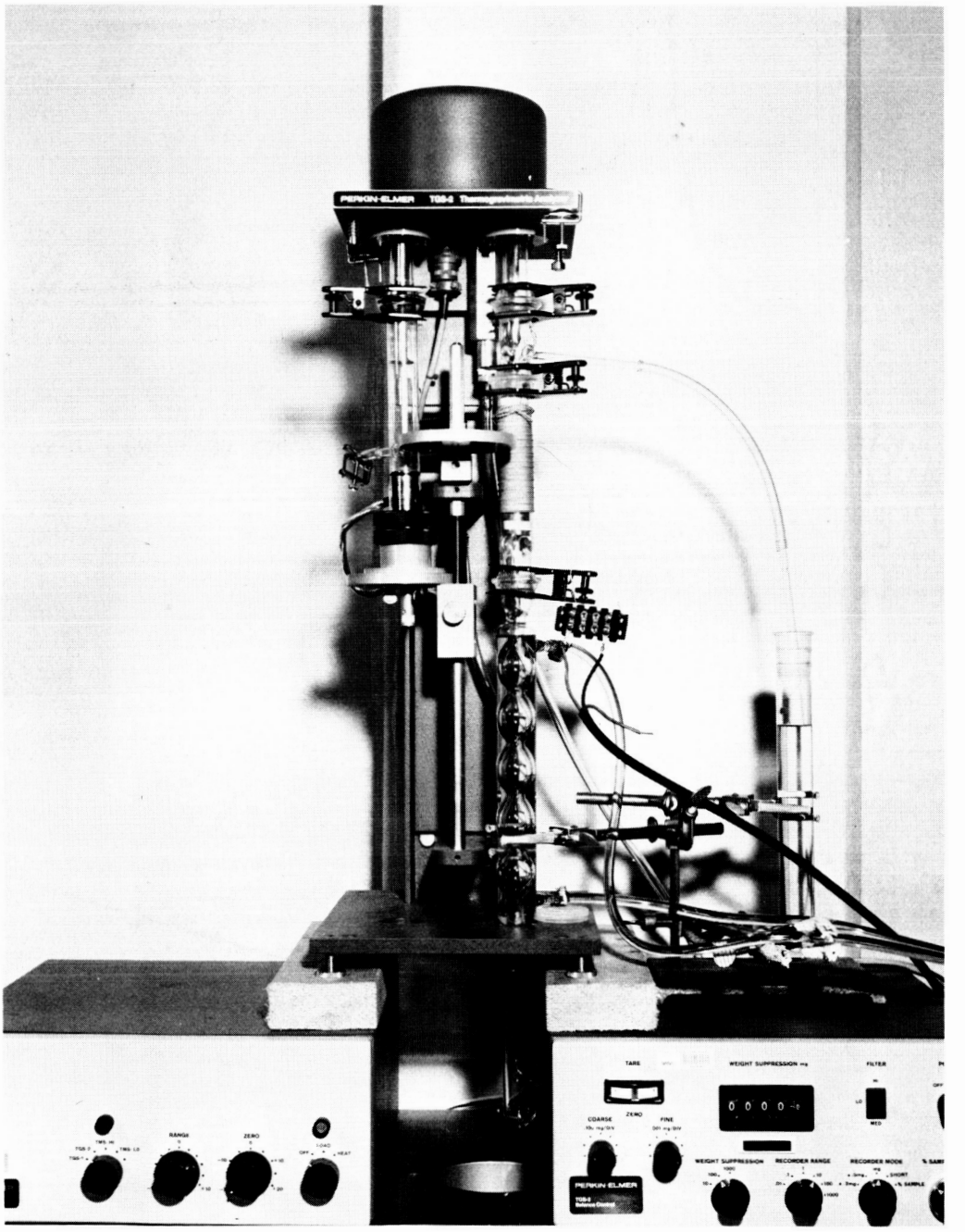

FIGURE 1. - MICROBALANCE MODIFIED FOR THE SIMULTANEOUS MASS UPTAKE, AND ELECTRICAL RESISTIVITY EXPERIMENTS.

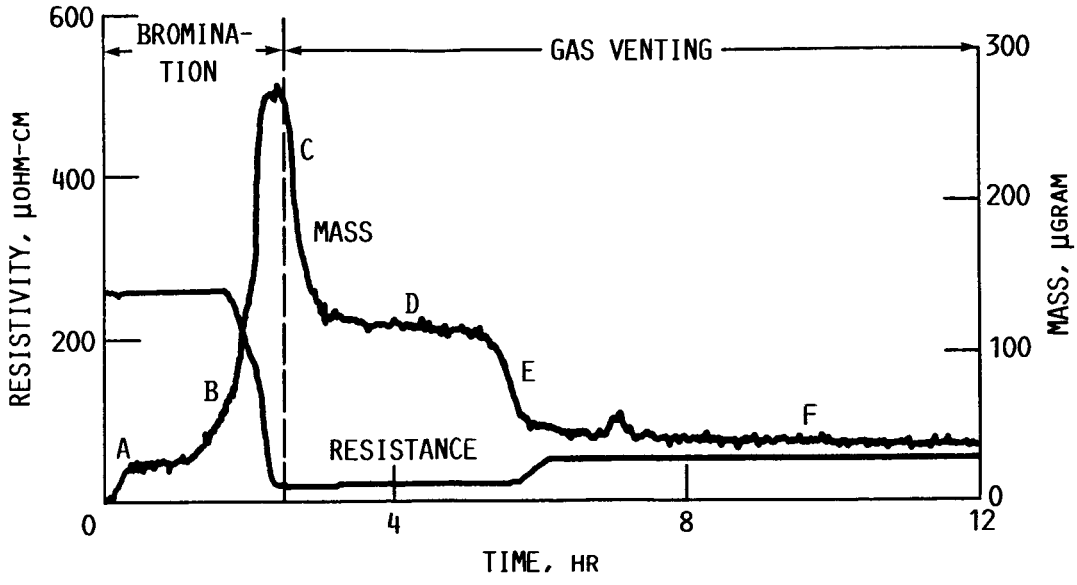

FIGURE 2. - CHANGE IN MASS AND RESISTANCE OF P-100 FIBERS EXPOSED TO BROMINE VAPOR.

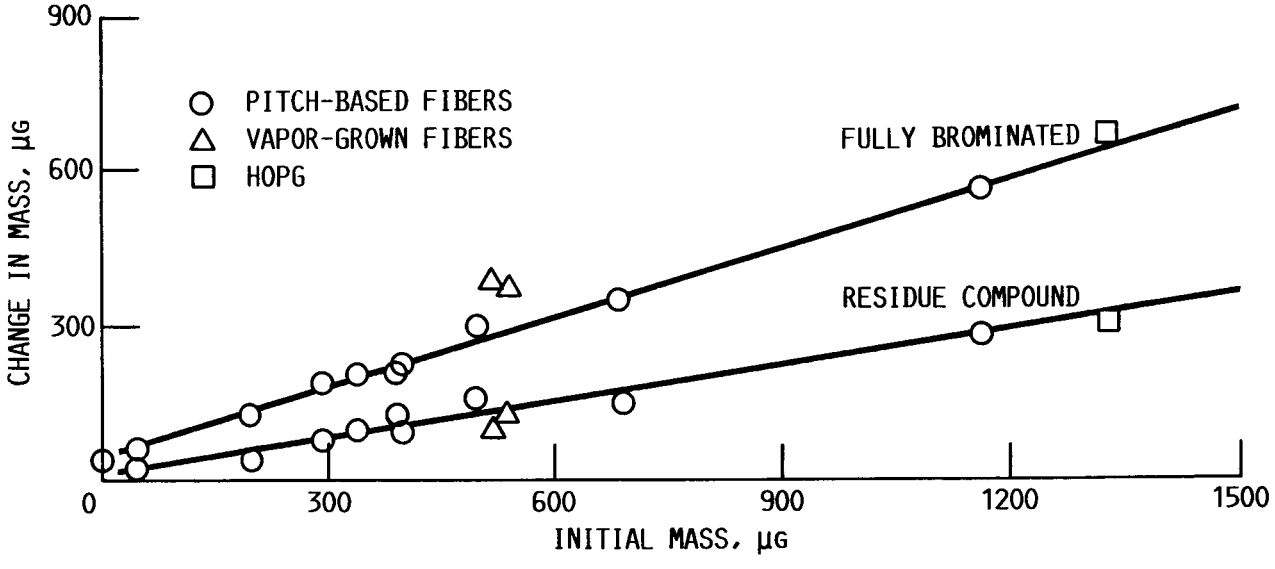

FIGURE 3. - MASS UPTAKE AS A FUNCTION OF INITIAL MASS FOR PITCH-BASED FIBERS, VAPOR-GROWN FIBERS, AND HOPG.

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16. Abstract

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