

HIGH TEMPERATURE STABILITY OF BROMINE INTERCALATED GRAPHITE FIBERS

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Introduction

Composites of intercalated graphite fibers show promise to significantly reduce the weight of electromagnetic interference shielding in spacecraft and aircraft.¹ Bromine intercalated pitch-based fibers have been among the most heavily studied systems because of their attractive electrical and thermal conductivities, and their high stability over a wide range of environmental conditions.² Studies have found that the resistivity of bromine intercalated P-100 fibers, for example, does not increase when the fibers were exposed temperatures of 200 °C in air for several years. If the temperature was as high at 450 °C, however, the resistivity increased dramatically within a few hours.² It remained unclear, however, whether the resistivity increase was due to deintercalation, migration of the bromine to pores and defects, or air oxidation of the fibers. Thus, this study was undertaken to distinguish among those alternatives.

Methods and Materials

The fibers used in this study were Thornel P-55, P-75, P-100, and K-1100 pitch-based graphite fibers (BP-Amoco). The structure of these fibers is similar, but varies in the extent of graphitization, the P-55 being the least graphitized and the K-1100 the most. The fibers were intercalated with bromine for 24-72 hr using either a room temperature or 0 °C vapor phase reaction. Intercalation was verified using resistivity measurements and x-ray diffraction.

A computer controlled Perkin-Elmer TGS-2 Thermogravimetric Analyzer (TGA) was used to monitor the mass as 10-35 mg samples as they were heated from 20 to 960 °C in a He or N₂ atmosphere using a heating rate of 20 °C/min. Diffraction patterns were measured using a Huber Precession Camera with Mo K x-rays generated by a Rigaku Rotaflex rotating anode generator. The temperature coefficient of the resistance was measured using the four-point technique. Individual fibers were mounted on alumina substrates with silver paint and cooled using an Air Products Displex Helium Refrigerator. The temperature was lowered in 10 K increments and allowed to equilibrate before the measurement was taken.

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Results and Discussion

When pristine pitch-based fibers were heated to 960 °C in the presence of an inert gas (either He or N₂) there was a steady decline in the sample mass above 800 °C of 2-6 percent. This is attributed to oxidation of the fibers by small amounts of oxygen which were not purged from the TGA apparatus. This is supported by the observation that if fibers are ramped up to temperature a second time, immediately following the first, there is an additional, steady decline in the sample mass above 800 °C of 2-4 percent. There was no apparent trend in mass loss with the graphitization evidenced by comparison of the behavior of P-55, P-75, P-100, and K-1100 fibers.

TGA of bromine intercalated P-100 fibers under the same conditions yielded data virtually identical with that of the pristine fibers. The same was true of P-55, P-75, and K-1100 fibers. There were no cases where the samples experienced an abrupt mass loss, so it was concluded that significant amounts of bromine are not lost from the fibers even at temperatures as high as 960 °C.

Although these results indicate that significant amounts of bromine are not lost from the fibers, it is possible that after heating the bromine may be arranged differently within the fibers. At the extreme, bromine could be covalently bonded to the graphite lattice, perhaps similar to the graphite fluoride structure. A sensitive indication of the bromine arrangement is its x-ray diffraction pattern, and the $h0l$ zone, in particular. The in-plane structure of bromine has been reported to be chain-like, and misregistries of the chains give rise to rod structures at room temperature.³ These are clearly visible in the normal incident x-ray photograph of bromine intercalated P-100 fibers, which is shown in Figure 1a. The same structures are also visible in Figure 1b, which shows the diffraction pattern of the bromine intercalated fibers which have been heated to 900 °C for 60 min under nitrogen. Clearly there are no large changes in the arrangement of the bromine within the graphite lattice. The same results were found for bromine intercalated, and intercalated then heated K-1100 and P-75 fibers. However, the rod structures in bromine intercalated P-55 fibers disappeared when the fibers were heated, even though the mass loss on heating was not significantly different than that which occurred with the pristine fibers.

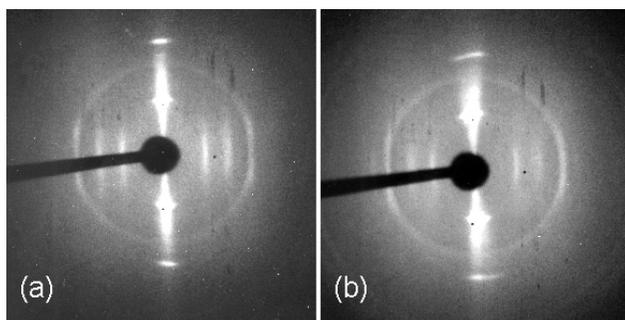


Figure 1 – Normal-incident x-ray photograph of a bundle of bromine intercalated P-100 fibers (a) before and (b) after being heated to 900 °C in nitrogen.

Fiber resistivity should be sensitive both to the amount of bromine within the fiber and its bonding. Bromine could conceivably be in the fibers in at least three states. If the bromine is intercalated, charge would be transferred to the graphite lattice, and the additional (hole) carriers would be expected to lower the resistivity. If the bromine is found in pores and along the grain boundaries it is not expected that the resistivity would change significantly. If the bromine is covalently bound to the graphene sheets in a graphite fluoride-type structure, the π -electron network would be disrupted and the resistivity would increase.

TABLE I – Graphite fiber sample resistivity

Fiber	ρ_{pristine} $\mu\Omega\text{-cm}$	ρ_{bromine} $\mu\Omega\text{-cm}$	$\rho_{\text{heated Br}}$ $\mu\Omega\text{-cm}$
P-55	975	394	382
P-75	750	243	286
P-100	306	63	84
K-1100	128	22	41

Table I shows the resistivity of pristine, bromine intercalated, and bromine intercalated and then heated, for several grades of fibers. The resistivity values are calculated assuming a fiber diameter of 10 μm . The resistivity increases upon heating, and the relative magnitude of the effect increases as the graphitization of the fiber increases. Perhaps some of the bromine is migrating from the galleries between the graphene planes to pores and defect sites. These results are consistent with earlier work which showed that lower resistivity intercalated fibers are less stable to high temperatures than higher resistivity, but seems to contradict the x-ray diffraction evidence above. It is especially noteworthy that on heating P-55 lost the diffraction lines indicating intercalation, but retained its low resistivity.

Perhaps a more sensitive measure of the bonding interactions is the temperature coefficient of the resistivity (TCR). As is evident from Figure 2, pristine P-100 fibers have a semiconductor-like negative TCR, whereas bromine intercalated P-100 fibers have a nearly neutral or slightly

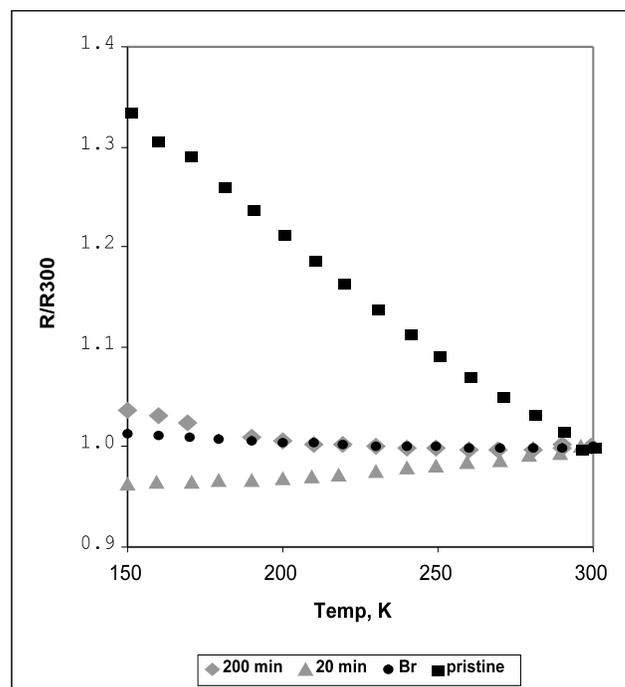


Figure 2 – Temperature dependence of the resistivity of pristine P-100 fibers, Br intercalated P-100 fibers unheated, and heated to 900 °C for 20 and 200 min.

metal-like positive TCR. Bromine intercalated P-100 fibers that had been heated in an inert atmosphere to 900 °C for 20 min and for 200 min exhibited little change. The implication is that there is no change in the conduction mechanism and so also the bonding of bromine intercalated P-100 fibers heated to high temperatures in an inert atmosphere.

When bromine intercalated graphite fibers are heated to 900 °C in an inert atmosphere, TGA shows that there is no appreciable mass loss, x-ray diffraction indicates there are no gross structural changes (with the exception of the bromine intercalated P-55 sample), and the temperature dependence of resistivity indicates that there are no gross changes in the bonding. Fiber resistivity does, however, increase slightly on heating, with the effect being greater for lower resistivity fibers, which may indicate the migration of some bromine. These results show that bromine intercalated fibers may be suitable for application at temperatures at least as high as 900 °C, provided oxygen is excluded. This may enable their use in carbon-ceramic, or even carbon-carbon composites.

References

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