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A Method to Remove Intercalates From Bromine and Iodine Intercalated Carbon Fibers

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A METHOD TO REMOVE INTERCALATES FROM BROMINE AND IODINE INTERCALATED CARBON FIBERS

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ABSTRACT

Upon exposure to room-temperature fluorine, intercalated carbon fibers (containing either bromine alone or iodine and bromine together) become heavier and less stable. For Amoco P–100 graphitized carbon fibers which were intercalated with 18 percent bromine by weight, 1 hr of fluorine exposure results in a large weight increase, but causes only a small decrease in thermal stability. More than 1 hr of fluorine exposure time results in small additional increases in fiber weight, but significant further decreases in fiber thermal stability. Such phenomena do not occur if the fluorine exposure is at 250 °C. These observations suggest the mechanism that at room temperature, fluorine is absorbed quickly by the intercalated fibers and intercalated slowly into the fibers. Most of the original intercalates are replaced by fluorine in the process of fluorine intercalation. Under an inert environment, the bromine intercalated fibers are much more thermally stable. After 800 °C vacuum heating for two weeks, the brominated fibers lost about 45 percent of their bromine, and their resistivity increased from 64 $\mu\Omega$-cm to a range of 95 to 170 $\mu\Omega$-cm. This is still much lower than the 300 $\mu\Omega$-cm value for pristine P–100. For practical purposes, in order to preserve their thermal stability, brominated fibers need to be protected from exposure to fluorine at room temperature, or to any intercalate at a temperature where, upon direct contact to graphite, an intercalation compound can easily be formed.

Keywords: Deintercalation; Brominated carbon fibers; Iodinated carbon fibers; Fluorine induced deintercalation; Thermal stability

INTRODUCTION

In an experiment to study carbon fiber-fluorine reactions, it was observed that after exposing iodine and bromine intercalated carbon fibers to fluorine, the fibers began to emit smoke, which turned yellow paper to purple in color. This phenomenon is interesting because it suggests deintercalation of an intercalated compound that was thought to be stable. It also raises the possibility that fluorine exposure to other kinds of highly stable graphite intercalated compound (GIC), e.g., brominated carbon fibers, may also result in loss of their stability. This could have some impact on the work which explores the idea of using highly stable brominated carbon fibers to make high-temperature composites for engineering purposes. It could, however, shed light on the fundamentals of deintercalation and GIC stability.

In this research, fluorine-GIC fiber reaction experiments were conducted and examined. The thermal stability of the products of such reactions was also studied. The possible role of fluorine in this reaction and the implications of the findings will then be discussed.

EXPERIMENTS

The reaction described at the beginning of this paper was intercalated P–100, $C_{59}Br_{0.53}I$ (24 percent intercalate weight), reacted with room temperature fluorine for 1 hr to form a product which contained intercalates which were 40 percent of the carbon mass. After 8 hr in ambient air, the intercalates became 32 percent of the carbon mass, and the fibers still emitted smoke. The reactant described here was also placed in direct contact at 250 °C. In this case, no reaction could be detected after 21 hr. With these results, the following experiments were conducted to further study fluorine-GIC fiber reactions and the thermal stability of the fluorine treated products:

(1) Two samples of a bromine and iodine intercalated fiber, $C_{117}Br_{1.5}I$ (17.5 percent intercalate weight), were placed in direct contact with room temperature fluorine for 1 and 12 hr, respectively. The two samples were immediately weighed after the fluorine reaction.

(2) Two fiber samples of the same type as described above were examined. One sample was not treated with fluorine, and the other sample was treated with room temperature fluorine for 4 hr. Both samples were then heated in nitrogen at 450 °C for 24 hr. The two samples were then weighed. In addition, the sample with fluorine pretreatment was examined by x-ray diffraction, SEM, and ESCA.

(3) Three samples of brominated P–100 fibers were treated with room temperature fluorine for different periods of time. After fluorine pretreatment, every sample was left in ambient air until the weight decreases reached completion. Every sample was then divided into two parts. Each part was heated in nitrogen by different temperature-time profile. Details of this process are described in Fig. 1. For comparison, a stage-one fluorine intercalated fiber and a brominated P–100 fiber were treated with the same process. Furthermore, two brominated P–100 samples were placed in vacuum ampules and heated to 650 and 800 °C, respectively, for two weeks. Results of all of these experiments are included in Fig. 1.

The electrical conductivity of all fiber samples was measured before and after the reactions, and both the reactants and the products were analyzed by SEM and x-ray diffraction.

RESULTS AND DISCUSSIONS

Since the $C_{59}Br_{0.53}I$ fiber-fluorine reaction described here can be observed only at room temperature, not 250 °C, it is more likely that this reaction is either absorption or intercalation, which is favored at low temperature. The chemical reactions involving covalent bonds is less likely. Otherwise some changes of the properties for the carbon fibers exposed to 250 °C fluorine for 21 hr should be noticeable.

After being exposed to room temperature fluorine for 1 and 12 hr, the halogen-to-carbon weight ratio for $C_{117}Br_{1.5}I$ fibers increased from 17.5 to 33.0 and 39.7 percent, respectively. Compared to room temperature reactions between fluorine and pristine P–100, where no weight change can be observed during the first hour, this reaction is fast. This suggests that, compared to pristine P–100, fluorine is much more easily absorbed by intercalated P–100. This can be an explanation of the phenomenon first observed by Henig: GIC residue compounds are more reactive toward intercalation reaction than the pristine graphite is [1].

Nitrogen heating at 450 °C of $C_{117}Br_{1.5}I$ fibers pretreated with room temperature fluorine for 4 hr drives out most halogen. Weight analysis indicates that the halogen-to-carbon weight ratio decreased from 17.5 to 5 percent. This fiber product has an electrical resistivity value of 680 μΩ-cm. Its EDS data indicate that no bromine or iodine is in the fibers. Its ESCA data indicate that the surface contains 15.5 atomic percent of fluorine but no bromine or iodine. Its x-ray diffraction data indicate that its (002) and (004) graphite peaks are at 3.38 and 1.69 Å, respectively, with the (004) peak intensity being 5 percent of (002) value. In addition, the (002) peak width at half maximum position was 0.85 degree.

The properties of the above-described fluorine-treated and then nitrogen-heated fibers are summarized in Table 1 and compared to the P–100 fibers from which this fiber was made. It can be seen from Table 1 that this fiber product is slightly less ordered than the fiber reactant, probably because of the presence of a small amount of fluorine.

The same heating of the fibers, described in the last paragraph without fluorine pretreatment, drives out only a small amount of halogen. The halogen-to-carbon weight ratio decreased from 17.5 to 15.5 percent. The phenomenon that room temperature fluorine causes the intercalated fibers to lose their thermal stability is clearly demonstrated.

Results of the reaction between fluorine and brominated P–100 fibers are shown in Fig. 1. Here again, brominated P–100 was observed to lose its thermal stability after exposure to room temperature fluorine. However, compared to the bromine and iodine intercalated fibers described above, its deintercalation caused by such fluorine treatment is less complete and much slower. No "fiber smoke" can be seen after fluorine treatment.

The thermal stability of brominated P–100 fibers in an inert environment is also described in Fig. 1. In the 450 to 650 °C range, the fibers lost 26 percent of their bromine and formed a compound $C_{50}Br$, whose electrical conductivity was still very low (less than 90 μΩ-cm). Even at 800 °C, the electrical conductivity of the fibers (95 to 170 μΩ-cm) is still much lower than the pristine value (300 μΩ-cm). This low resistivity value suggests that, in inert environment, the molecular structure of the 800 °C heated fibers was not greatly damaged, and that the bromine-carbon reaction in the brominated P–100 fibers is not significant at a temperature of 800 °C. The increases of the fiber electrical resistivity is believed to be resulted from fiber debromination.

Results described in Fig. 1 also indicate the differences between room temperature fluorine treatments on the sample for 1 hr and those for 90 hr. Even though these two treatments resulted in similar weight gain immediately after the fluorine treatment, their effect on the bromine content in the fibers were very different. After the fibers were exposed to fluorine for 1 hr of room temperature fluorination and then to ambient air for long time of room temperature deintercalation, the bromine-to-carbon atomic ratio decreased only slightly, from 0.027 to 0.025. The same bromine-to-carbon ratio changed significantly, from 0.027 to 0.010, if the room temperature fluorination became 90 hr.

Data in Fig. 1 also show that the 1-hr fluorine treated fibers are more thermally stable than the 90-hr fluorine treated sample, which, according to x-ray diffraction data, contains stage-one fluorine intercalated GIC.

Based on the observations described above, it is reasonable to suggest the following fluorine-fiber reaction mechanism. During the first hour of fluorine exposure, large amounts of fluorine can be absorbed by the fibers without driving bromine out of the fibers. Desorption of fluorine could happen if the fibers are removed from the fluorine surrounding them; however, the absorbed fluorine can be slowly intercalated into the fibers if their surroundings continue to be fluorine. In this case, the originally intercalated bromine may be replaced by fluorine and either becomes merely absorbed by the carbon atoms or is driven out of the fibers. Heating these fibers in nitrogen at 450 °C drives out most halogen except the fraction of bromine which is still intercalated in the fibers.

The process of the 90-hr-fluorine intercalation into brominated fibers resulted in structural damage to the brominated fibers. This is suggested by its x-ray diffraction peak, which is broader than those from either bromine intercalated fibers or fluorine intercalated fibers.

CONCLUSIONS

After heating brominated P–100 in an inert environment at 400, 450, 650, and 800 °C, the electrical resistivity values for these fibers became approximately 80, 90, 90, and 130 μΩ-cm, respectively. For comparison, pristine and regular brominated P–100 have resistivity values of approximately 300 and 65 μΩ-cm, respectively. Damages of molecular structure due to such heating appears to be small, and the changes of the fiber electrical resistivity during such heating are believed to be mostly the results of debromination.

Fibers intercalated with bromine and fibers intercalated with both bromine and iodine can deintercalate and lose their thermal stability if they are exposed to room temperature fluorine. It is believed that, compared to pristine carbon fibers, intercalated fibers can absorb fluorine much easier. If the fluorine exposure is long enough, fluorine can be intercalated into the fibers and drive out the original intercalates. For practical purposes, in order to preserve their thermal stability, brominated fibers need to be protected from exposure to fluorine at room temperature, or to any intercalate at a temperature where, upon direct contact to graphite, an intercalation compound can be easily be formed.

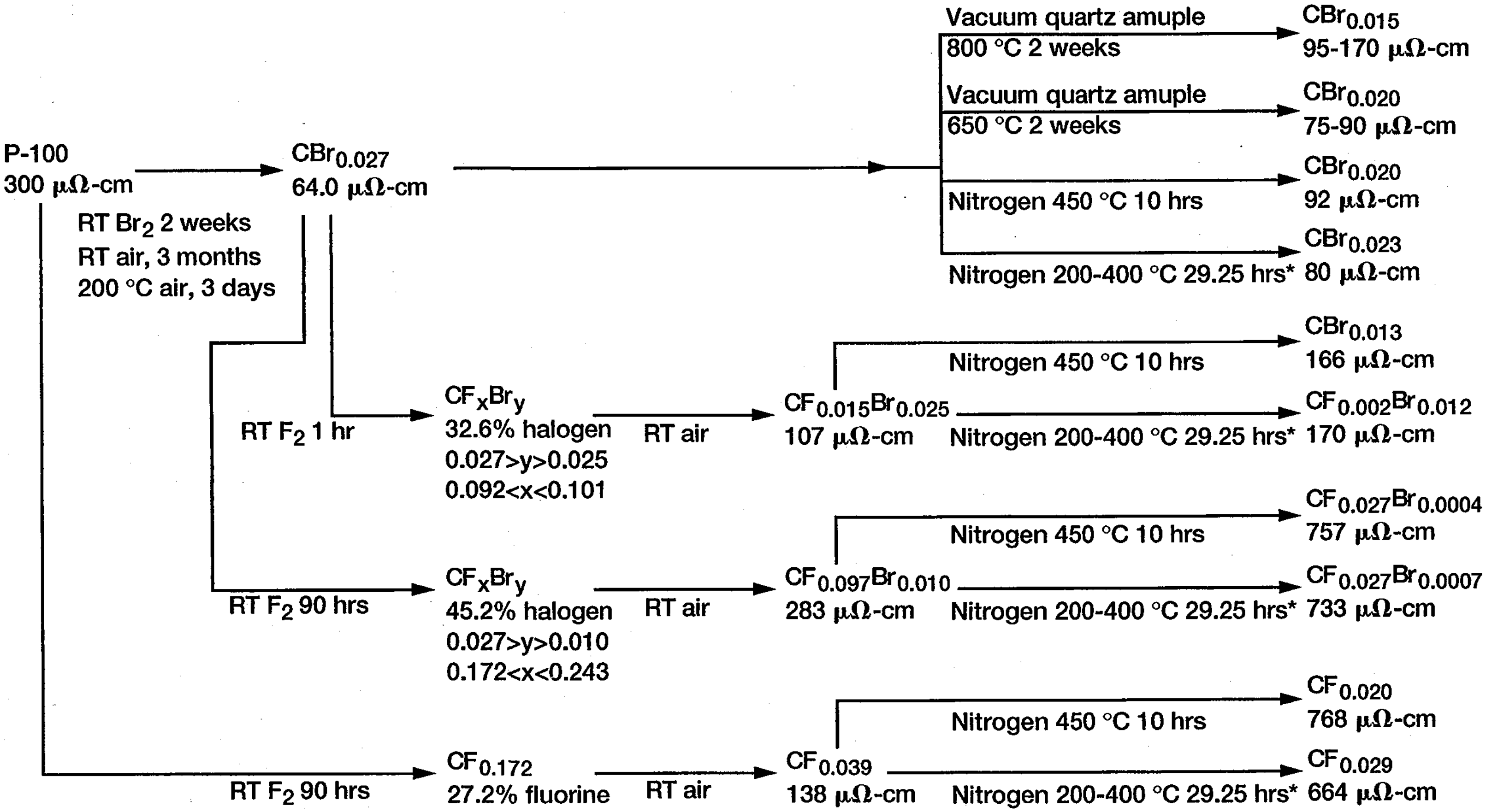
REFERENCE

1. G. Henig, The Journal of Chemical Physics, **20**, (9), 1438, 1952.

TABLE 1.—PROPERTIES OF THE REACTANT AND THE PRODUCT OF THE FOLLOWING REACTION

$$\text{P–100} \xrightarrow[\substack{\text{Then 130 °C}\\ \text{iodination}}]{\substack{\text{Room temperature}\\ \text{brominaton}}} C_{117}Br_{1.5}I \xrightarrow[\substack{\text{Room temperature}\\ \text{4 hours}}]{\text{Fluorine}} CF_xBr_yI_z \xrightarrow[\substack{\text{450 °C}\\ \text{24 hours}}]{\text{Nitrogen}} CF_{0.03}$$

	Reactant (Amoco P–100)		Product ($CF_{0.03}$)	
Electrical resistivity, µm-cm	440		680	
X-ray diffraction peaks	(002)	(004)	(002)	(004)
Position, Å	3.37	1.69	3.38	1.69
Relative intensity, percent	100	3	100	5
Width at half maximum height, °	0.45	----	0.85	----
Weight ratio to the reactant	1.00		1.05	
Surface chemical composition	Carbon (100%)		Carbon (83%) Fluorine (15.5%) Oxygen (1.5%)	



RT: Room temperature.

*: Heating in nitrogen at 250 °C for eight hours, then at 300 °C for 0.75 hours, then at 350 °C for 10.5 hours, then at 400 °C for 10 hours.

Figure 1.—Procedure and products of the brominated fibers-fluorine reactions.

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