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10-18-94

NASA Technical Memorandum 106447

Ferric Chloride Graphite Intercalation Compounds Prepared From Graphite Fluoride

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Prepared for the
21st Biennial Conference on Carbon
sponsored by the American Carbon Society
Buffalo, New York, June 13-18, 1993



National Aeronautics and
Space Administration

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FERRIC CHLORIDE GRAPHITE INTERCALATION COMPOUNDS PREPARED FROM GRAPHITE FLUORIDE

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ABSTRACT—The reaction between graphite fluoride and ferric chloride was observed in the temperature range of 300 to 400 °C. The graphite fluorides used for this reaction have an sp^3 electronic structure and are electrical insulators. They can be made by fluorinating either carbon fibers or powder having various degrees of graphitization. Reaction is fast and spontaneous and can occur in the presence of air. The ferric chloride does not have to be predried. The products have an sp^2 electronic structure and are electrical conductors. They contain first stage $FeCl_3$ intercalated graphite. Some of the products contain $FeCl_2 \cdot 2H_2O$, others contain FeF_3 , in concentrations that depend on the intercalation condition. The graphite intercalated compounds (GIC) deintercalated slowly in air at room temperature, but deintercalated quickly and completely at 370 °C. Deintercalation is accompanied by the disappearing of iron halides and the formation of rust (hematite) distributed unevenly on the fiber surface. When heated to 400 °C in pure N_2 (99.99 vol %), this new GIC deintercalates without losing its molecular structure. However, when the compounds are heated to 800 °C in quartz tube, they lost most of its halogen atoms and formed iron oxides (other than hematite), distributed evenly in or on the fiber. This iron-oxide-covered fiber may be useful in making carbon-fiber/ceramic-matrix composites with strong bonding at the fiber-ceramic interface.

KEY WORDS: Intercalation, ferric chloride, graphite fluoride defluorination, nongraphitized carbon intercalation, iron halide-carbon composite, iron oxide-carbon composite

1. INTRODUCTION

Graphite fluoride (CF_x) was previously considered to be stable at 400 °C [1]. However, recent studies indicate that CF_x fibers lose fluorine when heated to 300 °C or higher [2]. This phenomenon suggests that the carbon-fluorine bonds in CF_x may not be as strong as previously thought. Thus, CF_x

fibers may be a chemically reactive, especially at 300 °C or higher. For example, can the fluorine in CF_x be replaced by some other chemicals when heated to 300 to 400 °C? Can cross linking occur between adjacent carbon layers as fluorine is driven out of the fibers? The answers to these questions may lead to the development of new materials and new processes. Extensive studies have attempted to answer these questions [3]. In this report, reactions of CF_x with known graphite intercalates were investigated. In particular, the processes and the products of the reactions between CF_x and ferric chloride ($FeCl_3$) are described in detail.

2. EXPERIMENTS

$FeCl_3$ was chosen as a constituent in this study because it is the most studied and best understood of the graphite intercalates. This facilitates the comparison between intercalated graphite and intercalated CF_x . In addition, the intercalation of $FeCl_3$ into graphite is known to occur in the range of 300 to 350 °C, which is also the temperature range where CF_x begins to defluorinate and becomes structurally damaged graphite.

Samples of $CF_{0.68}$ fibers were made by exposing intercalated P-100[†] fibers (previously intercalated with Br_2 and I_2) to cycles of F_2 and N_2 at 350 to 370 °C. The $FeCl_3$ was purchased commercially, and no attempt was made to remove the moisture from it by heating. $FeCl_3$ and a $CF_{0.68}$ fiber sample were placed together in a weighing bottle that was about 2.5 cm in diameter by 5 cm high.

Two covered weighing bottles containing $FeCl_3$, $CF_{0.68}$ fibers, and some air were heated at 300 °C for 5 hr and at 330 to 420 °C for 27 hr, respectively, for the intercalation reaction to proceed. For comparison, a covered weighing bottle containing $FeCl_3$, pristine P-100 fibers, and some air was heated at 310 °C for 4.5 hr.

An additional experiment tested three different kinds of graphite fluorides under reaction with $FeCl_3$. They included two graphite fluorides made from pitch-based carbon fibers, P-55 and P-25, and a commercially available graphite fluoride powder. Their compositions were $CF_{1.0}$, $CF_{0.9}$, and $CF_{0.9}$, respectively. They were intercalated by exposure to distilled $FeCl_3$ in a pyrex glass tube using the experimental apparatus shown in Fig. 1.

[†]P-100, P-55, and P-25 are product numbers of Amoco Performance Products, Inc., Atlanta GA.

The products were then heated at higher temperatures to evaporate FeCl_3 from the fiber surfaces. Pure N_2 (99.99 vol %) was flowed slowly through the glass or quartz tubes during evaporation. Figure 2 illustrates the process sequence for each source of CF_x . Process steps intended to induce intercalation resulted in reaction products A-1 to F-1. Various heat treatments were then used to test the stability of these compounds, resulting in reaction products B-3 and A-2 to E-2.

Before reaction, the interplanar spacing for pristine P-100, P-55, and P-25 was 3.37, 3.42, and 3.45 Å, respectively. Intermediate and final products were examined by x-ray diffraction, energy-dispersive analysis with x-rays (EDS), and weighing.

3. RESULTS AND DISCUSSION

3.1. Intercalated Products

Chemical reactions, including intercalation, appear to occur between CF_x and FeCl_3 . These reactions are fast and spontaneous. Table 1 summarizes the data obtained from the FeCl_3 -intercalated graphite fluorides. The empirical formulas of these compounds were obtained with the mass increase data and the EDS data, with pure Fe_2O_3 as the standard for the Fe/O peak ratio, pure FeCl_3 as the standard for the Fe/Cl peak ratio, and pure FeF_3 as the standard for the Fe/F peak ratio.

Figure 3(a) shows the x-ray diffraction data for the FeCl_3 - CF_x reaction product, where the graphite fluoride originated from commercially available $\text{CF}_{0.9}$ powder. This is reaction product F-1 in Fig. 2. Figure 3(b) shows the x-ray diffraction data from reaction product E-1. This product originates from the $\text{CF}_{0.9}$ made from P-25 fibers. The data indicate that E-1 contains FeF_3 [4] and F-1 contains $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ [5]. The samples also contain a well-known, first stage FeCl_3 -GIC (graphite-intercalated compound) whose identity period is 9.3 Å [6].

These results demonstrate three phenomena. First, P-25, a carbon material which has never been successfully intercalated before because of its low degree of graphitization, can be intercalated with FeCl_3 if it is properly pretreated with F_2 . Second, the sp^3 electronic structure of carbon atoms in CF_x can be easily converted to an sp^2 structure. This structural change is accompanied by a decrease of

electrical resistivity from about 10^{12} to less than 10^{-3} Ω -cm, a drop of more than 15 orders of magnitude. Third, FeF_3 and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ were found either in or on reaction products E-1 and F-1 respectively. The EDS analyses presented in Fig. 4 indicate that the sample made from fluorinated P-25 fibers (E-1, Fig. 4(b)) contained a lower fluorine concentration than the sample made from commercially purchased powder (F-1, Fig. 4(a)).

Contrary to previous experiments [7], no reaction occurred between the P-100 fibers and FeCl_3 because air was present in the weighing bottle and the FeCl_3 was wet from a long storage time. However, in the presence of air the same wet FeCl_3 did react and intercalate with $\text{CF}_{0.68}$ made from P-100 fibers. This indicates again that intercalation of FeCl_3 with CF_x is more spontaneous than the intercalation with graphite that has not been pretreated with fluorine.

The concentrations of iron relative to carbon and the halogens for the compound made from P-55 (reaction product D-1) are much higher than that of previously known first-stage FeCl_3 GIC [6]. The magnetic properties of this intercalated compound are not known at this time. However, a regular magnet did not attract the fiber products described in Table 1.

3.2 Deintercalation

No visible change could be observed when the FeCl_3 -intercalated fibers (C-1) were exposed to ambient air for less than 1 month. However, the sample began to turn to dark yellow after 1 month of ambient air exposure. Figure 5 shows a scanning electron micrograph taken after 1 year of ambient air exposure. The white areas on the fibers in this micrograph represent the yellow material observed in the laboratory. This material is thought to be the chemical deintercalated from the fibers. EDS data indicate that the material contains mostly iron, chlorine, and oxygen, with an iron-to-chlorine atomic ratio of about 2:1. The EDS data taken from the "clean" part of the fibers indicate that the carbon fibers also contain iron, chlorine, and oxygen, with an empirical formula of about $\text{C}_n\text{FeCl}_{0.75}\text{O}_{0.18}$. The low chlorine and oxygen concentrations relative to iron suggest the possibility that some iron atoms may be chemically bonded to carbon atoms.

The C-1 intercalated fibers changed significantly when heated in air at 370°C for 16 hr. The x-ray diffraction data in Fig. 6 indicate the presence of hematite (Fe_2O_3), in the form of rust powder [8]. A

small, clean part of this fiber sample was examined by EDS, but the EDS data show nothing but a carbon peak. These results suggest that the fibers were completely deintercalated in the 370 °C air environment, with the formation of hematite unevenly distributed on the fiber surface.

The B-1 intercalated fibers (also made from P-100) were heated in pure N₂ (99.99 vol %) at 400 °C for 16 hr. This treatment drove out a significant fraction of halogen from the fibers. The EDS data indicate that after heating some oxygen was present in the fibers; however, no clear iron oxide peaks are present in the x-ray diffraction data. On the other hand, the intercalation peaks are still present, although they have a lower magnitude.

Heating these intercalated fiber compounds in N₂ (99.99 vol %) at 420 °C for 70 hr, and then at 800 °C for 30 min (B-3) in quartz tube drove most of the halogen out of the fibers. For many selected clean fiber areas, EDS data show large iron peaks and small peaks of chlorine, fluorine, oxygen, and carbon

(Fig. 7). Again, comparing to the Fe/O and Fe/Cl peak ratios from the EDS data obtained from Fe₂O₃ and FeCl₃, respectively, Figure 7 indicates that the amount of iron is so large that some of the iron atoms may be bonded to the carbon. The x-ray diffraction data show large peaks of graphite, small peaks of first stage FeCl₃ intercalated graphite, wuestite (FeO)[9], and another iron oxide which is either magnetite (Fe₃O₄)[10] or maghemite-Q (Fe₂O₃)[11], but no peaks for iron halides and iron metal. The source of oxygen for the iron oxides is believed to be the moisture picked up by the FeCl₃ which was intercalated in the fibers. These results suggest that after 800 °C nitrogen treatment, the fibers lost most halogen atoms, but kept some first stage FeCl₃ intercalated graphite, and a significant amount of iron, some of which in the form of iron oxide. According to the measurement made by the EDS instrument, the iron oxide was evenly distributed either in or on the entire fiber.

The fibers containing iron oxide may be useful for making carbon-fiber/ceramic-matrix composite materials. This, however, is beyond the scope of this project.

Figure 8 contains x-ray diffraction data illustrating the change in molecular structure of the P-55 fibers through the entire process of fluorination, intercalation (D-1), and 800 °C heating (D-2).

Part (a) shows x-ray diffraction data from the P-55 fiber starting material. Diffraction measurements

(on the fiber products) were repeated after fluorination (part (b), graphite fluoride), after intercalation (part (c), iron halide- FeCl_3 GIC composite), and finally, after deintercalation (part (d), iron oxide-carbon composite).

4. CONCLUSIONS

Ferric chloride intercalates graphite fluoride easily, resulting in a product containing iron halide crystals and first stage FeCl_3 intercalated GIC. This process enables intercalation with FeCl_3 to take place with carbon materials that have a very low degree of graphitization. Depending on the intercalation condition, the compounds may contain large quantities of iron, large quantities of fluorine, or a small quantity of fluorine.

The graphite-intercalated compound (GIC) deintercalated slowly during 1 year of exposure to ambient air. When heated in air to 370°C , however, this GIC deintercalated completely in 16 hr, and formed hematite (Fe_2O_3) on the fiber surface.

When heated in pure N_2 (99.99 vol %) to 400°C for 16 hr, this GIC deintercalated without losing its molecular structure. When heated to 800°C for 30 min in quartz tube, however, it lost most of its halogen atoms and formed iron oxides (other than hematite) that were detected by energy-dispersive analysis taken from randomly chosen areas. Some iron-carbon chemical bonds may also be formed during this heating process. The iron oxides present on the deintercalated fibers may form strong bonds to both carbon fibers and a ceramic matrix. If so, they will provide superior properties when used in carbon-fiber/ceramic-matrix composites.

5. ACKNOWLEDGMENTS

The author greatly appreciates the efforts of Ralph G. Garlick and Ruth E. Cipicic in collecting the x-ray diffraction data of all samples described in this report, and Dr. Timothy J. Juhlke of Exfluor Research Corporation for his help in fabricating graphite fluoride fibers.

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Table 1.— Intercalated products from reactions in Fig. 2

Label	Original carbon	Empirical formula	Visible x-ray diffraction peak		
			Large iron halide peaks Å	Known FeCl ₃ GIC I _c = 9.3 Å	Graphite peaks
A-1	P-100	C	None	No	Large
B-1	CF _{0.68} from P-100	C _{4.6} FeCl _{2.6} F ₁ *	FeF ₃	Yes	Small
C-1	CF _{0.68} from P-100	†	FeCl ₂ · 2H ₂ O	Yes	Large
D-1	CF _{1.0} from P-55	C _{2.8} FeF _{1.2} Cl _{0.9} O ₁ *	FeF ₃ , FeCl ₂ · 2H ₂ O	Yes	None
E-1	CF _{0.9} from P-25	C ₁₂ FeF ₇ Cl _{3.3} O ₁ *	FeCl ₂ · 2H ₂ O	Yes	Large
F-1	CF _{0.9} powder	C _{7.5} FeF _{4.5} Cl _{0.7}	FeF ₃	Yes	None

*Uncertainty in fluorine and/or oxygen contents is due to small EDS peak heights.

† Weights 132% of the graphite fluoride reactant (CF_{0.68}) weight.

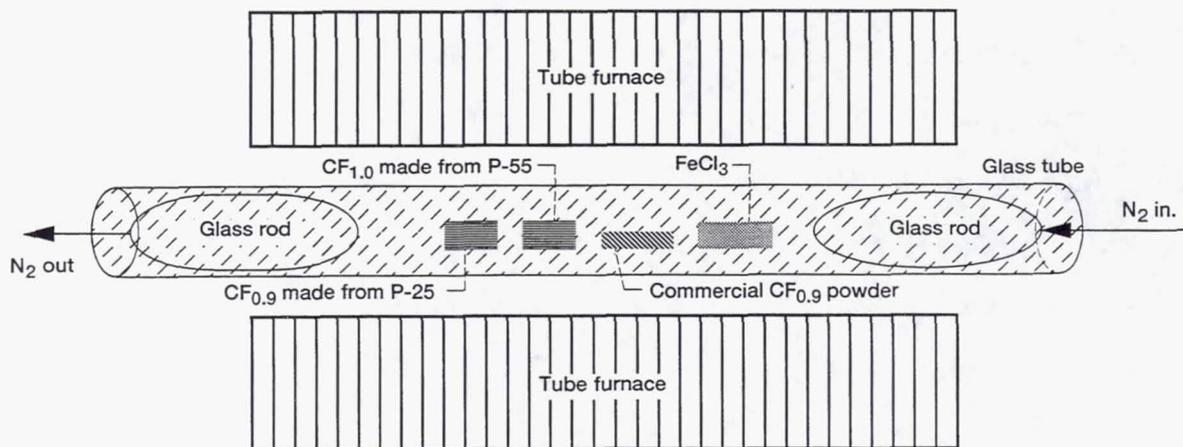


Figure 1.—Experimental apparatus for CF_x-FeCl₃ intercalation.

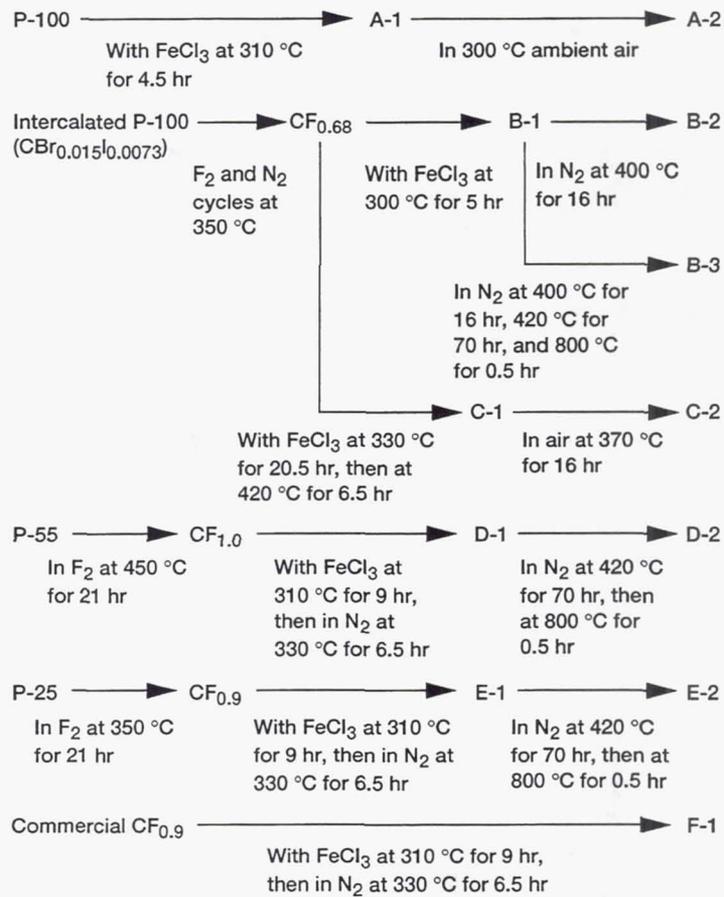


Figure 2.—Experiments conducted in this study.

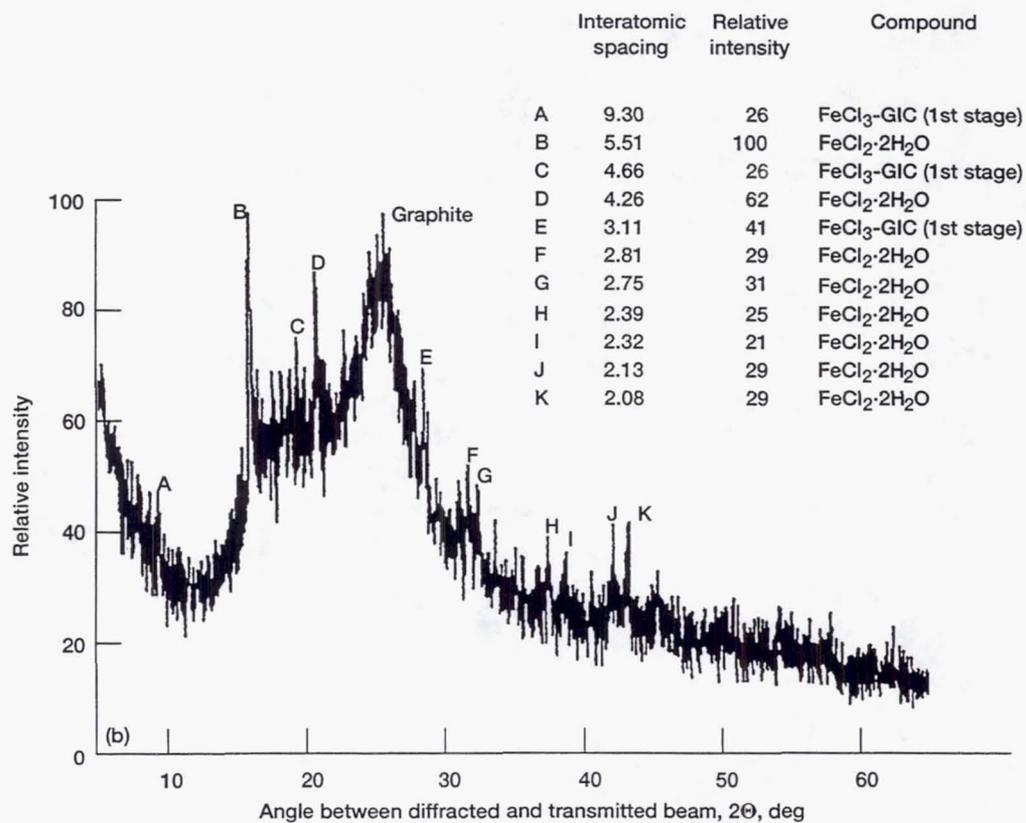
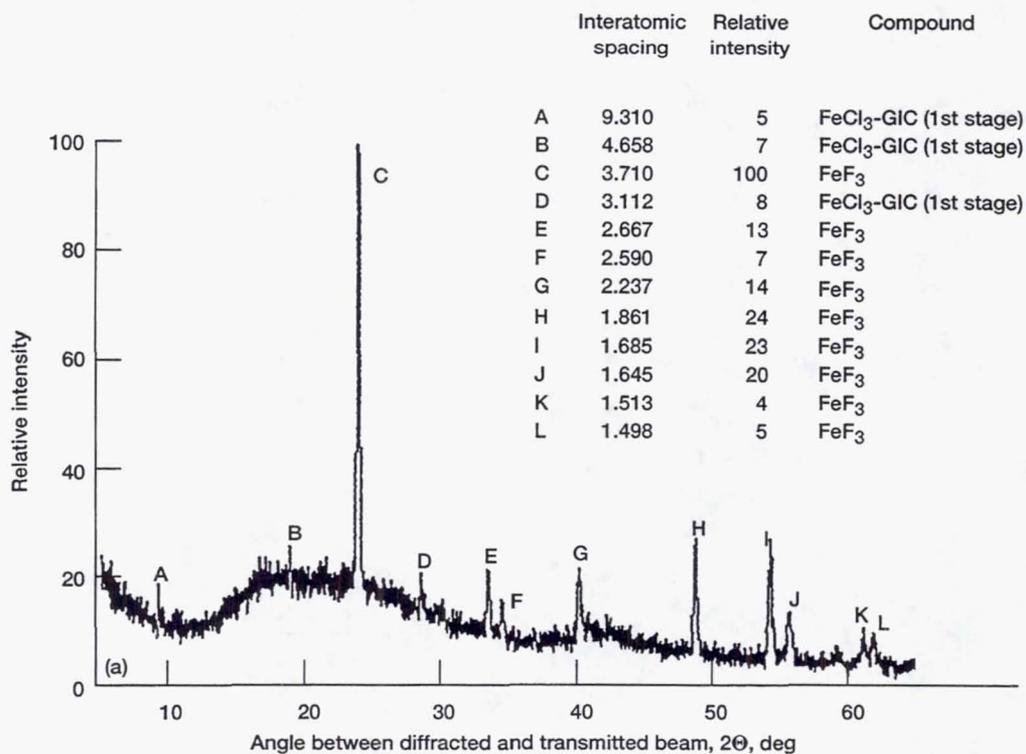


Figure 3.—X-ray diffraction data for FeCl₃-graphite fluoride reaction products. (a) Reaction product F-1 made from commercially available CF_{0.9} powder. (b) Reaction product E-1 made from fluorinated P-25 fibers (CF_{0.9}).

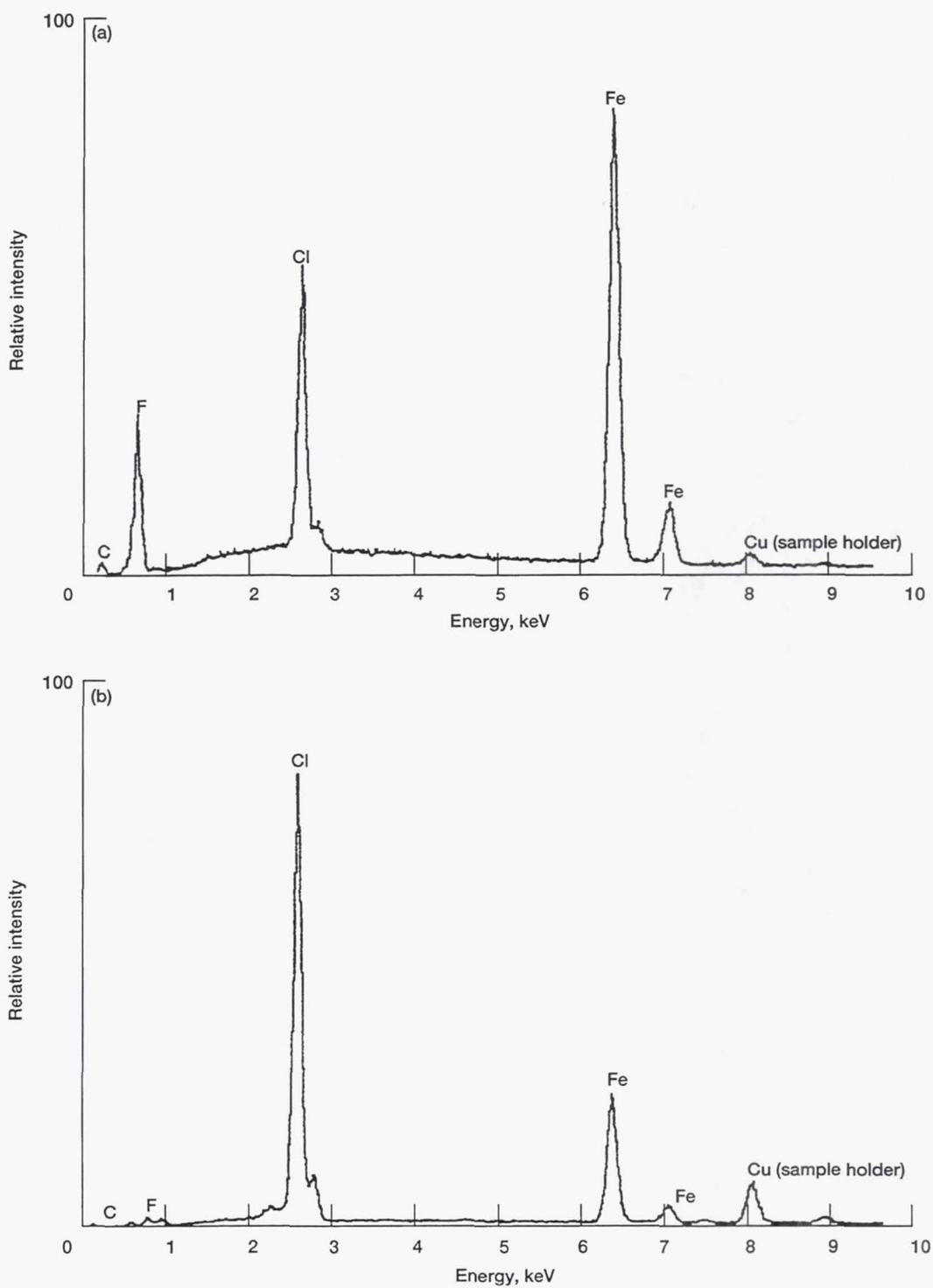


Figure 4.—Energy-dispersive spectrum for FeCl₃-graphite fluoride reaction products. (a) Reaction product F-1 made from commercially available CF_{0.9} powder. (b) Reaction product E-1 made from fluorinated P-25 fibers (CF_{0.9}).

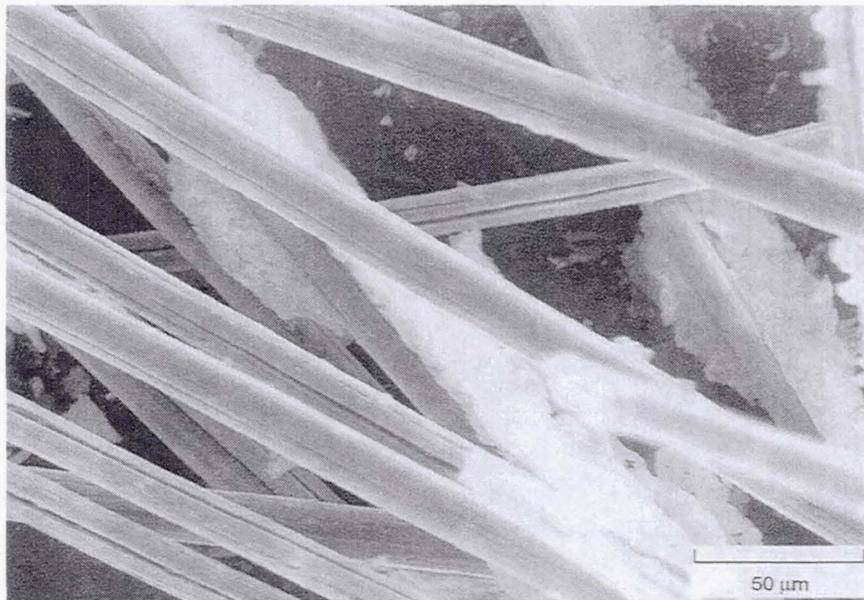


Figure 5.—Scanning electron micrograph of FeCl_3 graphite fluoride reaction product made from fluorinated P-100 fibers ($\text{CF}_{0.68}$). Data were taken after 1 year of ambient air deintercalation (reaction product A-2).

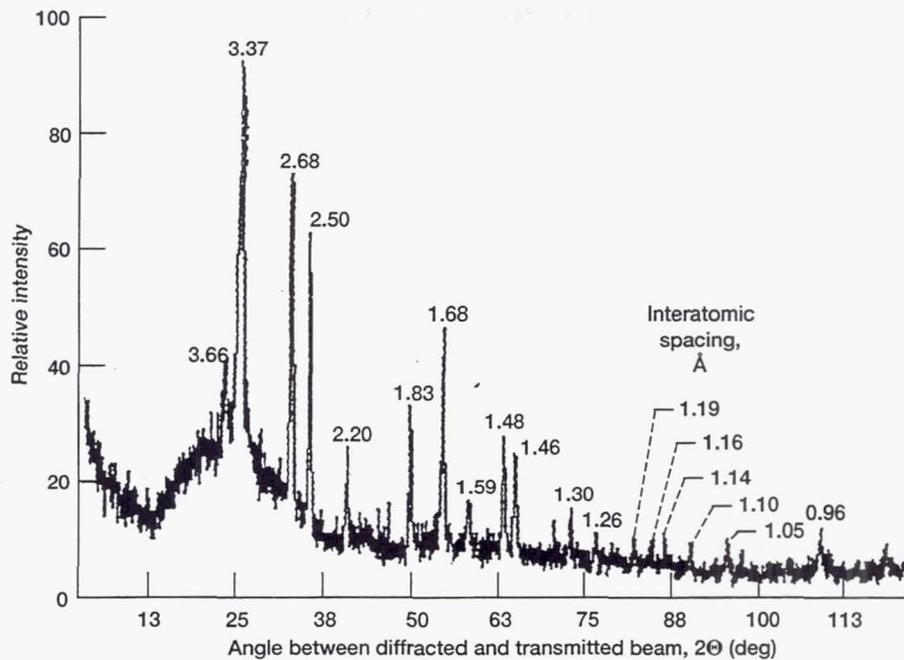


Figure 6.—X-ray diffraction data for FeCl_3 graphite fluoride reaction product made from fluorinated P-100 fibers ($\text{CF}_{0.68}$). Data were taken after this product was treated with 370°C air exposure for 16 hr (reaction product C-1). Interplanar spacings indicate that all these diffraction peaks are of hematite (Fe_2O_3).

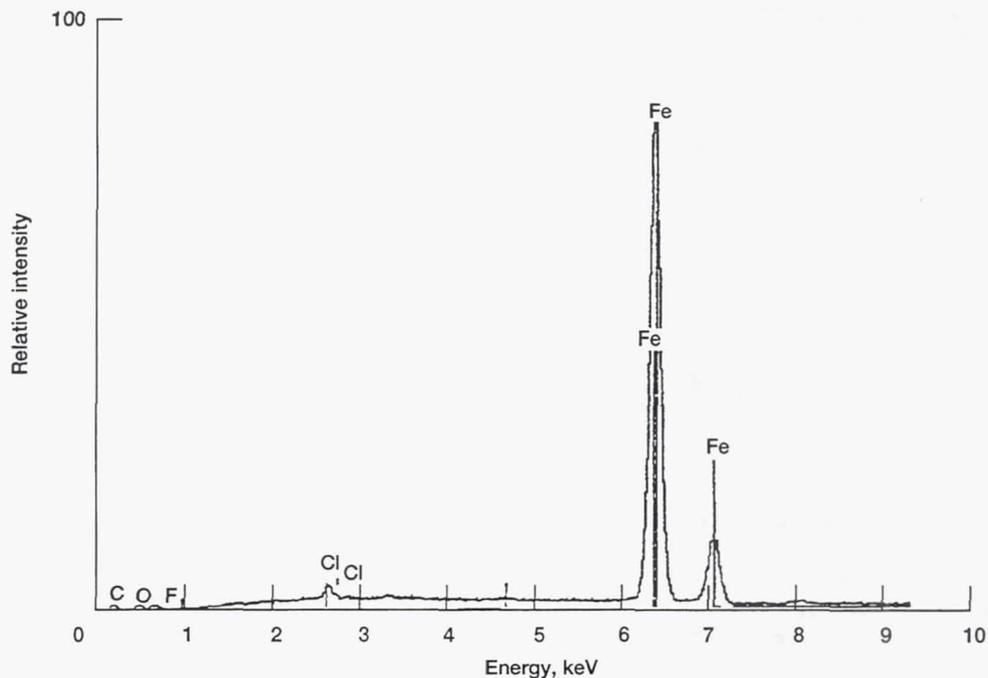


Figure 7.—Energy-dispersive spectrum for FeCl_3 -graphite fluoride reaction product made from fluorinated P-100 fibers ($\text{CF}_{0.68}$). Data were taken after this product was treated with N_2 exposure at 420°C for 70 hr and at 800°C in quartz tube for 30 min (reaction product B-3).

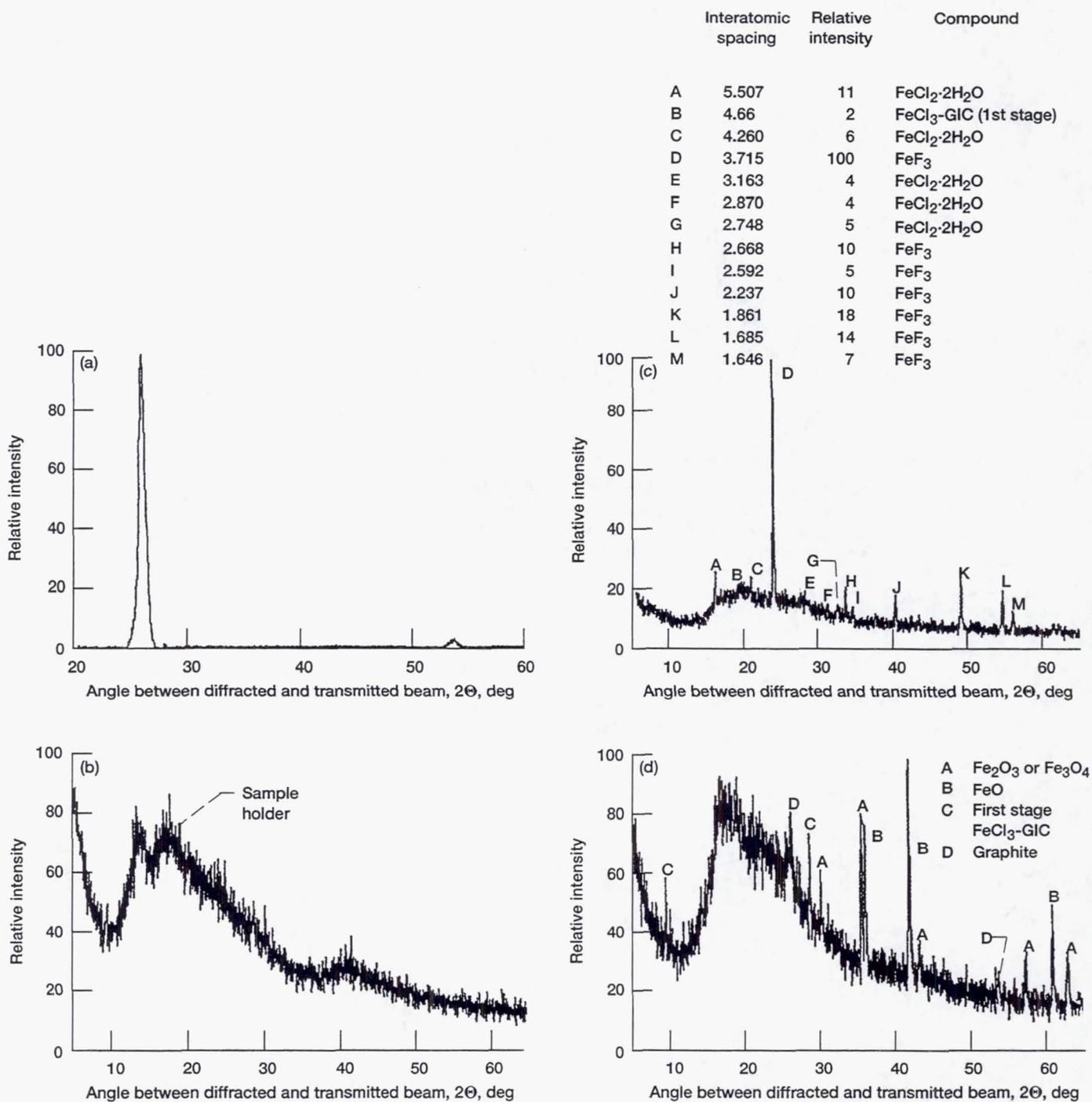


Figure 8.—X-ray diffraction data for the carbon-based materials at different stages of the entire process. (a) P-55 before reaction. (b) After 450 °C fluorination in pure F₂ (CF_{1.0}). (c) After exposure to FeCl₃ at 310 °C for 9 hr, then in N₂ at 330 °C for 6.5 hr. (d) After heating in N₂ at 420 °C for 70 hr, then at 800 °C in quartz tube for 0.5 hr.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 1994	3. REPORT TYPE AND DATES COVERED Technical Memorandum		
4. TITLE AND SUBTITLE Ferric Chloride Graphite Intercalation Compounds Prepared From Graphite Fluoride			5. FUNDING NUMBERS WU-506-41-41	
6. AUTHOR(S) Ching-cheh Hung				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135-3191			8. PERFORMING ORGANIZATION REPORT NUMBER E-8299-1	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Aeronautics and Space Administration Washington, D.C. 20546-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER NASA TM-106447 Corrected Copy	
11. SUPPLEMENTARY NOTES Prepared for the 21st Biennial Conference on Carbon sponsored by the American Carbon Society, Buffalo, New York, June 13-18, 1993. Responsible person, Ching-cheh Hung, (216) 433-2302.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Unclassified - Unlimited Subject Category 23			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The reaction between graphite fluoride and ferric chloride was observed in the temperature range of 300 to 400 °C. The graphite fluorides used for this reaction have an sp ³ electronic structure and are electrical insulators. They can be made by fluorinating either carbon fibers or powder having various degrees of graphitization. Reaction is fast and spontaneous and can occur in the presence of air. The ferric chloride does not have to be predried. The products have an sp ² electronic structure and are electrical conductors. They contain first stage FeCl ₃ intercalated graphite. Some of the products contain FeCl ₂ ·2H ₂ O, others contain FeF ₃ in concentrations that depend on the intercalation condition. The graphite intercalated compounds (GIC) deintercalated slowly in air at room temperature, but deintercalated quickly and completely at 370 °C. Deintercalation is accompanied by the disappearing of iron halides and the formation of rust (hematite) distributed unevenly on the fiber surface. When heated to 400 °C in pure N ₂ (99.99 vol %), this new GIC deintercalates without losing its molecular structure. However, when the compounds are heated to 800 °C in quartz tube, they lost most of its halogen atoms and formed iron oxides (other than hematite), distributed evenly in or on the fiber. This iron-oxide-covered fiber may be useful in making carbon-fiber/ceramic-matrix composites with strong bonding at the fiber-ceramic interface.				
14. SUBJECT TERMS Intercalation; Ferric chloride; Graphite fluoride defluorination; Nongraphitized carbon intercalation; Iron halide-carbon composite; Iron oxide-carbon composite			15. NUMBER OF PAGES 16	
			16. PRICE CODE A03	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT	

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