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Fabrication of Iron-Containing Carbon Materials From Graphite Fluoride

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SUMMARY

Carbon materials containing iron alloy, iron metal, iron oxide or iron halide were fabricated. Typical samples of these metals were estimated to contain 1 iron atom per 3.5 to 5 carbon atoms. Those carbon materials containing iron alloy, iron metal, and/or Fe_3O_4 were magnetic. The kinetics of the fabrication process were studied by exposing graphite fluoride ($CF_{0.68}$) to $FeCl_3$ over a 280 to 420 °C temperature range. Between 280 and 295 °C, $FeCl_3$ quickly entered the structure of $CF_{0.68}$, broke the carbon-fluorine bonds, and within 10 to 30 min, completely converted it to carbon made up of graphite planes between which particles of crystalline FeF_3 and noncrystalline $FeCl_2$ were located. Longer reaction times (e.g., 28 hr) or higher reaction temperatures (e.g., 420 °C) produced materials containing graphite, a $FeCl_3$-graphite intercalation compound, $FeCl_2 \cdot 4H_2O$, and $FeCl_2 \cdot 2H_2O$. These products were further heat treated to produce iron-containing carbon materials. When the heating temperature was kept in the 750 to 850 °C range, and the oxygen supply was kept at the optimum level, the iron halides in the carbon structure were converted to iron oxides. Raising the heat to temperatures higher than 900 °C reduced such iron oxides to iron metal. The kinetics of these reactions were used to suggest processes for fabricating carbon materials containing iron alloy. Such processes were then tested experimentally. In one of the successful trial runs, commercially purchased $CF_{0.7}$ powder was used as the reactant, and NiO was added during the final heating to 1200 °C as a source of both nickel and oxygen. The product thus obtained was magnetic and was confirmed to be a nickel-iron alloy in carbon.

INTRODUCTION

In a previous investigation (ref. 1), ferric chloride ($FeCl_3$) was found to react with graphite fluoride (CF_x) between 300 and 400 °C to give a graphite intercalation compound (GIC). The GIC's always contained a large quantity of iron halides, which were either iron chloride or a mixture of iron chloride and iron fluoride. The GIC's could be further heated to change the iron halide component to iron oxide in or on the carbon. The products of these reactions were characterized (see ref. 1) by using x-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS). Reaction kinetics, however, were not studied in the previous investigation.

The graphite fluoride used in these reactions included $CF_{0.68}$ made from highly graphitized P-100 carbon fibers, $CF_{1.0}$ made from less graphitized P-55 carbon fibers, $CF_{0.9}$ made from nongraphitized P-25 fibers, and commercially purchased $CF_{0.9}$ made from crystalline graphite powder. The reactions appeared to occur regardless of the source of the carbon from which CF_x was made or the fluorine-to-carbon ratio of the CF_x reactants, at least when $0.68 \le x \le 1.0$. The main reaction observed can be divided into two subreactions:

In the first, $FeCl_3$ enters the CF_x structure and causes CF_x to defluorinate, which results in a carbon material that contains an iron halide mixture:

$$CF_x + FeCl_3 \xrightarrow[\text{300 to 420 °C}]{} C(\text{iron halides}) \qquad 0.68 \le x \le 1.0 \tag{1}$$

In the second subreaction, the carbon–iron-halide mixture reacts with low concentrations of oxygen at about 800 °C to produce carbon that contains FeO and Fe_3O_4:

$$C\ (\text{iron halides}) \xrightarrow[\text{800 °C}]{\text{low } O_2} C(FeO, Fe_3O_4) \tag{2}$$

The temperature and oxygen concentration are the important parameters in determining the type of products to be obtained in reaction (2). For example, 800 °C and 1-atm air converted all carbon into CO_2, and Fe_2O_3 resulted. On the other hand, the reaction between carbon and 1-atm air at 370 °C was so slow that the reaction products were deintercalated carbon and Fe_2O_3:

$$\text{C (iron halides)} \xrightarrow[370\ ^\circ\text{C}]{1\text{–atm air}} \text{C} + \text{Fe}_2\text{O}_3 \tag{3}$$

In this report, the format C(Y,Z) represents a carbon material that contain the materials Y and Z in the space between the carbon planes.

A study of the reaction kinetics became important when it was found that a product of the aforementioned reactions, Fe_3O_4-containing carbon, was attracted to a magnet (fig. 1). Through a study of the kinetics, the effects of operating conditions (e.g., reaction time, reaction temperature, or reactant quantities) on the product's properties can be understood. Then, it may be possible to optimize the operating conditions and improve the magnetic properties of these products.

In this research, the kinetics of reactions (1) and (2) were constructed from experimental data. The kinetics thus obtained, together with the known chemistry of iron, oxygen, and carbon, were then used to suggest processes that might produce new iron-alloy-bearing carbon products with high permeability values. Experiments were conducted to verify the suggested processes.

EXPERIMENTAL METHODS

Two series of experiments were conducted to investigate reactions (1) and (2). For each reaction, every single experiment was conducted so as to reach a different degree of completeness by choosing a different time-temperature combination for the reaction. The reaction kinetics were then inferred by characterizing, examining, and comparing the products obtained from the individual experiments.

Formation of Iron-Halide Mixtures in Carbon

For the CF_x–$FeCl_3$ reaction, the reactants were placed in a glass tube reactor filled with 99.99-percent nitrogen at room temperature in anticipation of heating them to the reaction temperature of 280 to 350 °C in a tube furnace. The reaction started before the furnace and the reactor reached the reaction temperature. A reaction during heatup may be significant, especially if the reaction time is short. In this research, several reactions were allowed to continue for time intervals ranging from 10 min (0.17 hr) to 28 hr after they reached the desired reaction temperature. The CF_x samples were fibers obtained by several cycles of fluorination (1 atm, 330 to 370 °C fluorine exposure) and defluorination (1 atm, 330 to 370 °C nitrogen exposure) of P-100 carbon fibers that had been preintercalated with bromine and iodine (ref. 2).

Conversion of Iron Halides to Iron Oxides in Carbon

The reactants for the conversion of iron halides to iron oxide in carbon (reaction (2))were the products from two of the experiments in the series for reaction (1). They were placed in a quartz tube filled with 99.99-percent nitrogen and allowed to react over a temperature range of 650 to 1200 °C for periods ranging from 30 min to 3 hr. During this reaction, nitrogen flowed through the quartz tube at a rate of about 0.05 to 0.5 mL/sec.

The reaction products were characterized for noncarbon content by weight analysis, for structure identification by x-ray diffraction (XRD), for chemical element identification by energy-dispersive spectroscopy (EDS), and for morphology by scanning electron microscopy (SEM). It should be noted that the EDS data were obtained with the instrument operated at 25 kV. At this voltage, the electrons penetrated, and therefore examined, only the outer 2 to 3 μm of the samples. The XRD, on the other hand, examined the entire diameter of the fiber samples, typically 10 to 20 μm.

RESULTS AND DISCUSSION

Formation of Iron Halide Mixtures in Carbon

Table I summarizes the experiments conducted to investigate reaction (1). The data in the table reflect four reactions at a constant temperature between 280 and 300 °C, one reaction at 295 to 325 °C for 3.25 hr, and one from reference 1 at 330 to 420 °C. Of the five recent reactions, the 28-hr (285 °C) and the 3.25-hr (295 to 325 °C) ones were conducted by using $CF_{0.68}$ and distilled anhydrous $FeCl_3$ according to the method described in reference 1. The 10-min, 30-min, and 3-hr reactions at 280 to 295 °C were conducted in vials that contained mixtures of $CF_{0.68}$ and commercially purchased anhydrous $FeCl_3$ powder. The vials containing the reactants were exposed to a nitrogen environment in the glass tube reactor for the predetermined time at the predetermined temperature. During the reaction the vials were plugged by glass rods wound with PAN-based carbon fibers.

For comparison, a product obtained from the reaction between $FeCl_3$ and the precursor of the $CF_{0.68}$ (i.e., the pitch-based P-100 carbon fibers described in the previous section) was also included in table I (see test G).

The kinetics of reaction (1) can be inferred from the data shown in table I and are described in the following subsections.

Quick $FeCl_3$ absorption and $CF_{0.68}$ defluorination.—The data in table I show that low reaction temperatures and short reaction times favor the presence of FeF_3 and the absence of crystalline graphite. Exposing $FeCl_3$ to $CF_{0.68}$ fibers at 295 °C for 10 min increased the fiber mass. In addition, most of the $CF_{0.68}$ disappeared, and highly ordered FeF_3 was produced. After 30 min of reaction at 290 °C, the FeF_3 persisted and there were no additional mass changes observed, but the $CF_{0.68}$ disappeared completely. These observations suggest that immediately after direct contact, $FeCl_3$ quickly reacted with all the fluorine in the $CF_{0.68}$ to produce FeF_3.

Formation of FeF_3 in disrupted graphene layers.—After $CF_{0.68}$ was defluorinated and FeF_3 produced, most (if not all) of the covalent bonds between carbon and fluorine had been broken, and the electrical resistance of the fiber product plunged from about 10^{13} Ω/cm to a typical value of 1 to 3 kΩ/cm. This is approximately 4 to 12 times the value for the P-100 graphitized carbon fibers from which the $CF_{0.68}$ was made. The data suggest that the carbon structure changed from sp^3 for the $CF_{0.68}$ to sp^2 for the disrupted graphene layers. However, the XRD shows a broad, barely visible graphite peak, even after 28 hr of reaction at 285 °C. It appears, then, that the FeF_3 formed during this reaction remains in the disrupted graphene layers at 285 °C for at least 28 hr.

State of chlorine in reaction products.—Significant amounts of chlorine were found in the products of all the reactions described in table I. This information was obtained by EDS, which detects the outer 2 to 3 μm of the 10- to 20-μm-diam fibers. The atomic ratio of chlorine to iron was about 1 shortly after the beginning of a 280 to 300 °C reaction. After 3 hr at 280 °C, the atomic ratio increased to a value between 1.5 and 2 (EDS data). However, no chlorine-containing compounds were detected by XRD for any reaction between 280 and 300 °C for up to 28 hr of reaction time. After the 295 to 325 °C reaction, however, $FeCl_2 \cdot 4H_2O$ was identified by XRD analysis of the reaction products (ref. 3). One possible explanation is that during defluorination of $CF_{0.68}$ and formation of FeF_3, the chlorine atoms were in the form of an $FeCl_3$ intercalate that was between the disrupted graphene layers and surrounded the FeF_3 crystals. Higher reaction temperatures caused this intercalate to slowly react with FeF_3 and form $FeCl_2$. Subsequently a hydrate was formed when the products were exposed to the ambient air.

This explanation assumes that the material between the disrupted graphene layers in the reaction product is a mixture of FeF_3 and intercalated $FeCl_3$. If the reaction time is prolonged, this mixture also contains $FeCl_2$.

High iron concentration.—The amount of iron in this product was estimated by heating the products in air at 370 °C, slowly increasing the temperature to 500 °C over a 1-week duration, and then measuring the weight of Fe_2O_3 thus obtained. This method produced an error due to the evaporation of a small amount of iron halide during heating. Therefore, the true iron concentration is believed to be slightly higher than the values obtained from this method.

If all the fluorine in $CF_{0.68}$ reacted to form FeF_3, the ratio of FeF_3 to carbon would be 0.68/3, or 0.23, and the atomic ratio of total iron to carbon in this product would be 0.23 plus the remaining iron contribution from the intercalated $FeCl_3$. This compares to the estimated experimental values of at least 0.18 and 0.22 for the products of the 10- and 30-min reactions (table I), respectively. This reasoning explains the high iron concentration in the carbon product obtained in this research.

Distortion and/or disappearance of FeF_3 crystals.—Table II shows the XRD peak for FeF_3 in the carbon products formed after 30 min and 28 hr of $FeCl_3$–$CF_{0.68}$ reaction. For comparison, standard XRD data for a pure FeF_3 crystal (ref. 4) are also included in this table. Note that the XRD for the FeF_3 produced in the 30-min reaction

is very close to that for standard rhombohedral FeF_3. The data from the 28-hr reaction, however, deviate somewhat from the standard values.

Another observation, which cannot be ascertained from tables I and II, was made: The FeF_3 XRD peaks obtained from the product of the longest reaction (28 hr) are much lower and broader than other FeF_3 XRD peaks obtained from the product of the 30-min reaction.

The data shown in table II suggest that immediately after the reaction, the FeF_3 produced has the structure of a pure crystal. Longer reaction times allow more $FeCl_3$ intercalation, which causes the structure of FeF_3 to change. This may be due to either the diffusion of chlorine into the FeF_3 structure, or the increasing external mechanical pressure that results from the continuous influx of $FeCl_3$ into the carbon structure.

Removal of FeF_3 at high reaction temperature.—Test F in table I indicates that if the $CF_{0.68}$–$FeCl_3$ reaction is conducted at a much higher temperature (330 to 420 °C), the fiber product becomes very different. Its XRD shows a large graphite peak, small first-stage $FeCl_3$ GIC peaks (identity period, I_c = 9.3 Å), and the presence of $FeCl_2 \cdot 2H_2O$ (see ref. 5). No trace of fluorine in or on the carbon fibers was detected, either by XRD or by EDS.

These data suggest that, at a high temperature and over a long time, the fluorine atoms produced from FeF_3 at an early stage of the reaction between $CF_{0.68}$ and $FeCl_3$ are removed from the carbon structure while the $FeCl_3$ continues to enter the carbon structure. A probable mechanism of fluorine removal is the reaction of FeF_3 and the nearby $FeCl_3$ intercalate, causing production and evaporation of either mixed iron halides ($FeCl_xF_y$) or chlorine fluoride (ClF). This may result in a product which, upon exposure to ambient air, has XRD peaks of $FeCl_3$–GIC, graphite, and $FeCl_2 \cdot 2H_2O$.

From this analysis, the formation of an iron halide mixture in carbon can be described as follows:

$$CF_x + FeCl_3 \xrightarrow[\text{280 to 325 °C}]{N_2} C(FeF_3, Fe, Cl) \tag{4}$$

$$C(FeF_3, Fe, Cl) + FeCl_3 \xrightarrow[\text{295 to 325 °C}]{N_2} C(FeF_3, FeCl_2, Fe, Cl) \tag{5}$$

$$C(FeF_3, FeCl_2, Fe, Cl) + FeCl_3 \xrightarrow[\text{420 °C, 6.5 hr}]{N_2} C(FeCl_2, Fe, Cl) \tag{6}$$

$$FeCl_2 + \text{ambient air} \xrightarrow[\text{25 °C}]{} FeCl_2 \cdot 2H_2O \tag{7}$$

$$FeCl_2 + \text{ambient air} \xrightarrow[\text{25 °C}]{} FeCl_2 \cdot 4H_2O \tag{8}$$

In the remainder of this report, $C(FeF_3, FeCl_2, Fe, Cl)$ and $C(FeCl_2, Fe, Cl)$ will be abbreviated by using $C(FeX_n)$, where X represents a halogen.

Oxidation of $C(FeX_n)$ in a High Temperature, Low-Oxygen Environment

When the products of reactions (5) and (6) were treated at 800 °C in nitrogen in a quartz reactor for 30 min, the products became FeO and Fe_3O_4 contained in carbon (ref.1). The source of oxygen was believed to be the water that had been adsorbed on the carbon before the heating was begun (ref.1). Note that the oxygen supply had to be low enough to keep carbon consumption and CO and CO_2 formation from being significant, and to prevent Fe_2O_3 from being produced.

The oxidation of $C(FeX_n)$ in a high-temperature, low-oxygen environment was further studied experimentally and is described in the following subsections.

Effects of heating temperature in the 750 to 1200 °C range.—Five samples of the $C(FeX_n)$ product from reaction D (see table I) were heated in a quartz reactor in a nitrogen environment at 650 to 750, 850, 900, 950, and 1200 °C, respectively. Another $C(FeX_n)$ sample obtained from reaction E (table I) was similarly tested at 1180 °C.

The heating time and heating products are described in table III. The chemicals produced were identified by XRD (refs. 6 to 9).

By examining and comparing the reactants and the products in table III, one can determine that heating at 750 °C

- transforms the FeF_3 structure from rhombohedral to cubic
- reduces part of the cubic FeF_3 in carbon to FeF_2
- oxidizes part of the FeF_2 to FeO
- reduces part of the $FeCl_3$ intercalate in carbon to $FeCl_2$
- oxidizes the $FeCl_2$ to FeO
- oxidizes part of the FeO to Fe_3O_4

The EDS data indicated the presence of carbon, iron, and chlorine in the sample, but no fluorine. However, the XRD shows the presence of fluorine in the form of FeF_3 crystals. This suggests that most, if not all, fluorine is located at the interior, more than 2 to 3 μm from the sample surface, where the x-ray can reach, but the 25-kV electron beam used for EDS examination cannot.

Oxidation of FeF_2 and FeO to Fe_3O_4 reached completion after 1 hr of heating at 800 °C in nitrogen. Further oxidation was not observed at this low-oxygen condition. On the other hand, the Fe_3O_4 began to be reduced to Fe at 900 °C, when the reducing power of carbon intensified. It is believed that CO (produced by carbon reacting with Fe_3O_4, O_2, or CO_2) was also an important reducing agent in this reaction.

Effects of oxygen.—The quantity of oxygen supplied to reaction (2) appears to have been a key parameter in determining the products. Too little oxygen caused incomplete oxidation, which resulted in evaporation of unreacted iron halides at the reaction temperature and a low iron concentration in the carbon product. With too much oxygen, on the other hand, the carbon host was consumed, and a structurally damaged carbon product resulted. In addition, the oxygen could have completely oxidized the FeX_n and produced Fe_2O_3.

The oxygen for this reaction was originally thought to have come from water adsorbed by the reactant of reaction (2) (i.e.,$C(FeX_n)$) when it was temporarily stored in ambient air (ref. 1). However, results from recent experiments indicate that the oxygen supply may depend more on the quartz (SiO_2) sample holder and the quartz tubular reactor and less on the water adsorbed by the samples in air.

In one such recent experiment, a relatively large sample of $C(FeX_n)$ powder was exposed to ambient air for more than 10 min to allow moisture adsorption; then, together with sections of thin quartz rods, it was placed on a piece of nickel foil and heated to 1100 °C in a quartz reactor containing nitrogen. In this case, even though the powder sample picked up some moisture during the ambient air exposure, the oxygen from all available sources was not sufficient to convert most of the iron halides into iron oxides. Most of the product contained little iron and was not attracted to a regular magnet. Only the small fraction of the sample that was in direct contact with the quartz rods was magnetic.

It is believed that the fluorine emitted from the sample attacked the SiO_2, which released oxygen and initiated the oxidation of some metal halides. Other possible oxygen sources include the diffusion of water vapor from ambient air through the quartz tube reactor at 1000 °C, impurity (0.01 percent) of the “inert” nitrogen environment, or the oxygen and water that remained in the residual air or on the reactor's inner wall after the nitrogen purging.

When enough oxygen was supplied, carbon could be completely oxidized, Fe_3O_4 could be completely reduced by the CO thus produced, and pure iron would be produced. Figure 2(a) is an SEM micrograph showing iron fibers thus produced by heating sample D (see table I) at 1200 °C in nitrogen. Figure 2(b) is an SEM photo of iron-containing carbon fibers produced by heating sample E (table I) at 1180 °C in nitrogen. This product has an estimated Fe/C atomic ratio of 1:3.6. The oxygen quantity necessary for carbon oxidation was apparently different for the two tests heated at approximately 1200 °C. The reason for such differences cannot be positively identified at this time. However, a possible reason is that, at 1180 to 1200 °C, atmospheric water vapor may diffuse into the quartz reactor at different rates because of different ambient humidity during these two runs.

Location of iron in carbon.—The surface of the fiber sample in figure 2(b), which has an Fe/C atomic ratio of 1:3.6, does not appear to have a large quantity of iron coating. This suggests that the iron particles were located in the fiber interior. To confirm this, one of the fibers shown in figure 2(b) was fractured, and the central 1- by 1-μm region of the fractured cross section was examined by EDS. The results indicated that the central region contained as much iron as the surface region of the fibers. It is not clear whether the iron and/or iron oxide particles were located

between the graphene layers or at the grain boundaries. The XRD does not give clear evidence; it shows large graphite peaks for some of these samples and small graphite peaks for others.

The reactions described in this section can be summarized by the following equations:

$$C(FeX_n) \xrightarrow[\text{650 to 750 °C}]{} C(FeF_2, FeF_3, FeCl_3) \tag{9}$$

where FeF_3 is in a recently discovered (see ref. 6) cubic structure, FeF_2 is crystalline, and $FeCl_3$ is an intercalate.

$$C(FeF_2FeF_3, FeCl_3) \xrightarrow[\text{650 to 750 °C}]{\text{low } O_2} C(FeO, Fe_3O_4) \tag{10}$$

$$C(FeO, Fe_3, O_4) \xrightarrow[\text{750 to 850 °C}]{\text{low } O_2} C(Fe_3O_4) \tag{11}$$

$$C(Fe_3O_4) \xrightarrow[\text{900 to 1200 °C}]{} C(Fe) + CO + CO_2 \tag{12}$$

$$C(Fe_3O_4) \xrightarrow[\text{1200 °C}]{\text{low } O_2} Fe + CO + CO_2 \tag{13}$$

$$2C + O_2 \longrightarrow 2CO \tag{14}$$

$$2CO + O_2 \longrightarrow 2CO_2 \tag{15}$$

$$CO_2 + C \xrightarrow[\text{>800 °C}]{} 2CO \tag{16}$$

$$C(Fe) \xrightarrow[\text{500 °C}]{\text{1−atm air}} Fe_2O_3 + CO_2 \tag{17}$$

Oxidation of $C(FeX_n)$ in 1-atm Air

It has been shown that at 370 °C in 1-atm air, oxygen reacts with the products of reactions (5) and (6) to form small Fe_2O_3 particles that migrate to the carbon surface (ref. 1). The Fe_2O_3 thus formed was a powder that covered the carbon surface unevenly (ref. 1). This oxidation reaction occurred at an upper limit of below 420 °C; above this, carbon oxidation in air becomes significant (ref. 10). Recent experiments indicated that this reaction occurred at as low as 200 °C for a C(iron halide) sample made from a P-75-pitch-based $CF_{0.75}$.

The preceding phenomenon can be described as follows:

$$C(FeX_n) \xrightarrow[\text{200 to 420 °C}]{\text{1−atm air}} C + Fe_2O_3 \tag{18}$$

Iron Alloy in or on Carbon

Previous sections described the formation of iron and/or iron oxide particles in or on carbon materials. These materials can be attracted to a magnet. Their magnetic properties have been examined and reported elsewhere (ref. 11). In the research reported herein, experiments were conducted to test if the iron and/or iron oxide particles can be replaced by an iron alloy having higher permeability values. Since nickel-iron alloys (NiFe and Ni_3Fe) are known to have permeability values more than one order of magnitude higher than pure iron (ref.12), a decision was made to attempt to put a nickel-iron alloy into carbon. Three different approaches were used. They are described in the following paragraphs.

First approach: Reaction between CF_x and $NiCl_2$–$FeCl_3$ mixture.—An attempt was made to form a mixed-metal halide in the carbon lattice and then treat it according to the process described in this report to produce a nickel-iron alloy in carbon. Toward this end, a $CF_{0.75}$ sample made from P-75 was treated with a $NiCl_2$–$FeCl_3$ mixture for 2 hr. However, the $CF_{0.75}$ selectively reacted with the $FeCl_3$, so the product contained no nickel.

Second approach: Dissolution between iron/iron compound and NiO in carbon.—Another approach was based on the hope that NiO would be able to diffuse into carbon and dissolve or react with either the iron or the iron compounds. In this scenario, the NiO could serve the dual function of supplying the oxygen for CO formation and iron oxide reduction and supplying the nickel for nickel-iron alloy formation. In the experiment, a sample of $CF_{0.7}$ powder made from graphite was treated with $FeCl_3$ at about 300 °C for 80 min and then at 380 °C for 45 min. The product was mixed with an excess of NiO, placed in sections of small quartz tubes, and heated to 1200 °C for 45 min in a reactor that had been purged by 99.99-percent nitrogen at a high flow rate for 16 hr. The resulting product was magnetic, and its EDS showed the presence of iron, nickel, and carbon (fig. 3). A more detailed EDS analysis indicated that the chemical composition of the product was not uniform: A small part of it had only nickel peaks, but most of it was carbon with nonuniform concentrations of both nickel and iron. The average Ni:Fe atomic ratio for this product was estimated to be 2.8:1. The XRD of the product shows high, sharp nickel peaks (ref. 3) in the proximity of the low, broad nickel-iron peaks. In figure 4 the XRD of this product is compared to an XRD of nickel powder obtained from the same machine. According to the XRD of nickel-iron obtained from the literature (ref. 14), the broad nickel-iron peaks suggest a wide range of Fe:Ni atomic ratios.

This experiment demonstrated that a nickel-iron alloy can be made at 1200 °C from NiO, even though pure NiO has a higher melting point (1990 °C).

Third approach: Dissolution between iron/iron compound and $NiCl_2$ in carbon.—The third approach was based on the hope that $NiCl_2$ would either melt (at 1001 °C) or sublimate (at 973 °C), diffuse into the carbon, and dissolve the iron or the iron compounds. A $C(FeX_n)$ sample produced from the reaction between CF_x and a $NiCl_2$–$FeCl_3$ mixture (see *First approach*) was exposed to an excess of $NiCl_2$ at 1100 °C in nitrogen for 30 min. A quartz tube was again used as the reactor. The XRD of the resulting product showed large graphite peaks and small nickel-iron peaks (ref. 14). The relatively small peaks suggest a low alloy concentration. This was confirmed by the EDS data, which detected iron and nickel atoms in the outer 2 μm of the carbon fibers. The EDS data, however, also indicated that chlorine was present. A semiquantitative analysis of the EDS data determined that the atomic ratios of Cl, Fe, and Ni were 32, 21, and 47 percent, respectively. The low alloy concentration and the presence of chlorine atoms in the product probably explain why the product was barely attracted to a magnet. These results demonstrate that a nickel-iron alloy can be made at 1100 °C in carbon according to the method just described.

The reactions described in this section can be summarized in the following equations:

$$C(FeX_n) + NiO \xrightarrow[1100\ °C]{N_2} C(Ni, Ni-Fe\ alloy) \tag{19}$$

$$C(FeX_n) + NiCl_2 \xrightarrow[1100\ °C]{N_2\ \text{in quartz tube}} C(Ni-Fe\ alloy, Cl) \tag{20}$$

CONCLUDING REMARKS

The kinetics of the reaction between $FeCl_3$ and graphite fluoride ($CF_{0.68}$) were examined. Analyses indicated that $FeCl_3$ quickly entered the carbon structure of $CF_{0.68}$ and reacted with the fluorine. This reaction produced carbon with disrupted graphene planes between which crystalline FeF_3 and noncrystalline $FeCl_3$ were located. Long reaction times between CF_x and $FeCl_3$ appeared to allow slow graphite intercalation compound (GIC) formation, FeF_3 struc-tural distortion, and FeF_3–$FeCl_3$ reactions. This resulted in products that had XRD peaks indicating graphite, $FeCl_3$–GIC, $FeCl_2 \cdot 4H_2O$, and $FeCl_2 \cdot 2H_2O$.

The products of the $CF_{0.68}$–FeX_n reaction were further heat treated to produce iron-containing carbon materials. When the oxygen supply was kept at the optimum level, the FeX_n evaporation was kept to a minimum, and the iron halide in or on the carbon was converted to iron oxide. The iron oxide was eventually reduced to iron metal at temperatures higher than 900 °C. During such a heat treatment, NiO or NiCl could be added to the reaction to produce a carbon material containing a nickel-iron alloy, a highly ferromagnetic material.

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TABLE I.—REACTION CONDITIONS AND PRODUCT CHARACTERIZATION FOR $FeCl_3$–$CF_{0.68}$ REACTION

Sample	Reaction conditions		Noncarbon-to-carbon weight ratio	Atomic ratio		X-ray diffraction peaks			
	Temperature, °C	Time, hr		Fe/C[a]	Cl/Fe[b]	C (graphite)	FeF_3	$FeCl_2 \cdot nH_2O$	CF_x
A	295	[c]0.17	3.08	0.18	1.2	Very small	Sharp, high	None	Very small
B	290	[c]0.5	3.01	.22	.95	Very small	Sharp, high	None	None
C	280	3	2.99	– – –	1.7	Very small	Sharp, high	None	None
D	285	28	3.18	– – –	1.5	None	Medium	None	None
E[d]	295 to 325	3.25	1.88	– – –	1.25	Small	Sharp, high	n = 4	None
F	330 then 420	20 6.5	1.75	– – –	– – –	Large	None	n = 2	None
G[e]	300	5	1.28	– – –	4	Large	None	n = 4	None

[a]Ratio estimated by comparing the sample weight before and after treatment at 500 °C air, which converted sample to pure Fe_2O_3.
[b]Cl/Fe ratio estimated by EDS from SEM operated at 25 kV; therefore, only outer 2- to 3-µm depth of sample was examined.
[c]Because of short reaction times, length of heatup (sample A = 7 min; sample B = 20 min) may have significant effect on product properties.
[d]Sample post-heated in nitrogen at 350 °C for 7 hr.
[e]Sample obtained from reaction between $FeCl_3$ and precursor of $CF_{0.68}$ (i.e., P-100 carbon fibers). It was post-heated in nitrogen at 350 °C for 0.35 hours

TABLE II.—X-RAY DIFFRACTION DATA FOR THE PRODUCTS OF $FeCl_3$–$CF_{0.68}$ REACTION

Standard pure rhombohedral FeF_3		Reaction product 290 °C, 30 min.		Reaction product 285 °C, 28 hr	
Interatomic spacing,[a] Å	Relative intensity, percent	Interatomic spacing,[b] Å	Relative intensity, percent	Interatomic spacing,[b] Å	Relative intensity, percent
3.731	100	3.725	100	3.631	100
		[c]3.393	7	2.958(?)	12
2.678	15	2.675	8	2.594	12
2.602	7	2.601	3	– – – – –	– –
2.244	14	2.243	8	2.162	30
2.133	2	– – –	– –	2.104	21
				2.016(?)	12
1.866	21	1.869	17	1.847	52
				1.719(?)	16
1.689	21	1.691	9	1.674	37
1.649	10	1.649	4	1.636	21
1.562	3	– – –	– –	1.534	16
1.516	6	1.519	2	1.503	15
1.501	5	– – –	– –	– – – – –	– –
1.339	5	1.341	1	1.332	15
1.300	2	– – –	– –	– – – – –	– –
1.278	3	– – –	– –	– – – – –	– –
1.243	2	1.247	1	1.233	12
1.228	5	1.229	1		

[a].Includes all FeF_3 peaks with relative intensity values ≥2 percent.
[b]Includes all peaks that can be observed from the diffractogram for the product.
[c]Graphite peak

TABLE III.—PRODUCTS OF C $F_{0.68}$ .FECL$_3$ REACTIONS DESCRIBED IN TABLE I AFTER SUBSEQUENT FINAL HEATING

[Heated in a quartz tube containing 99.99-percent nitrogen.]

Reactants from reaction–	Time to each final temperature, hr	Final temperature, °C	Heating time, hr	Surface observed by SEM	X-ray diffraction peaks of heated products				
					Graphite	Fe	FeO	Fe_3O_4	Others
D	0.75	650 then 750	0.5 .25	Clean	Large	None	Small	Small	Cubic FeF_3, FeF_2
D	2.25	850	1	Big particles	Small	None	None	Large	None
D	3.25	900	3	Heavy coating	Large	Small	None	None	None
D	1.20	950	1.23	Clean	Small	Large	None	None	None
D	2.10	1200	.67	(b)	Very small or none	Large	None	None	None
E	1.8	1180	.33	Small particles	Medium	Large	None	None	None

[a]Reactants are products of $CF_{0.68}$-$FeCl_3$ reactions described in table II.

[b]After 1200 °C heating, this sample became mostly fibers of pure α iron and some carbon powder with high iron content.

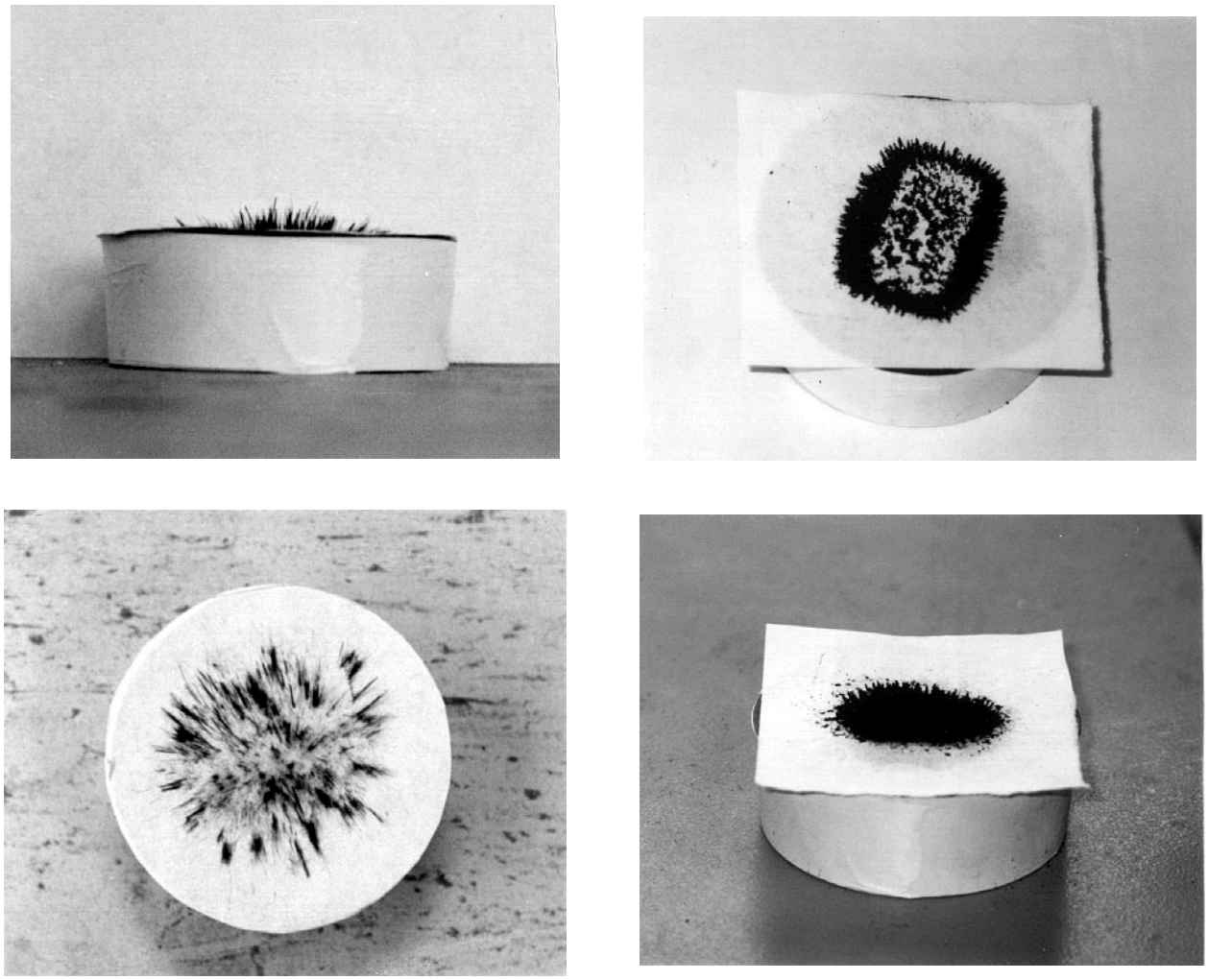


Figure 1.—Iron-containing carbon materials on magnets.

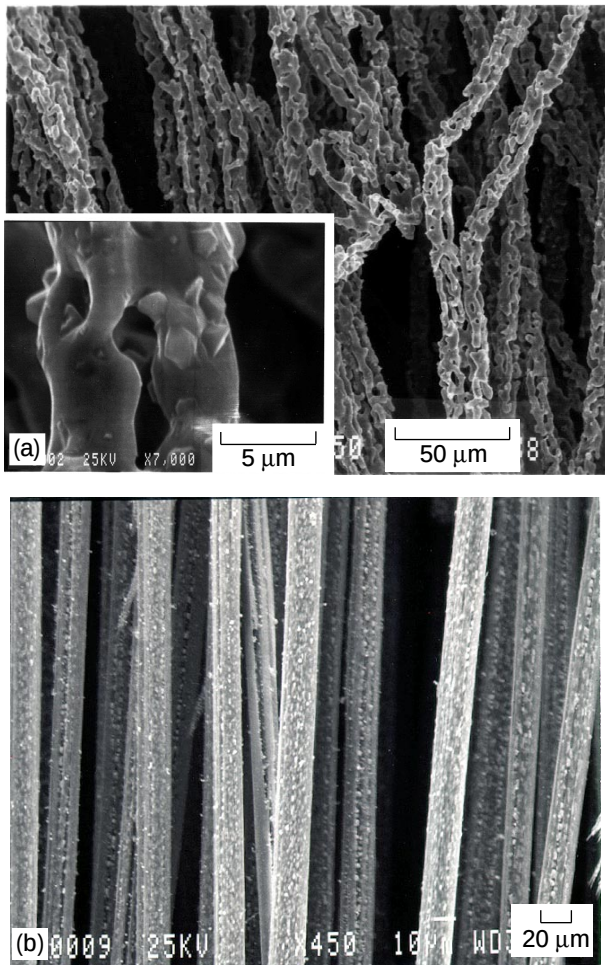
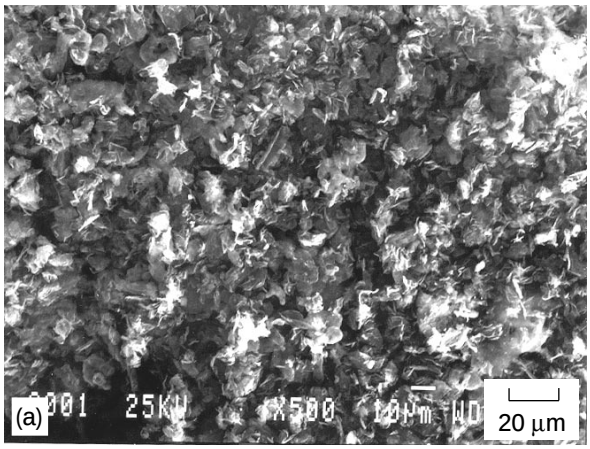


Figure 2.—Scanning electron micrograph of fibers from reaction of $FeCl_3$-$CF_{0.68}$ subsequently heated to 1200 °C. (a) Iron produced by reduction of iron oxides in presence of carbon. (b) Iron particles in carbon fibers produced when carbon is not completely consumed in reduction of iron oxide.



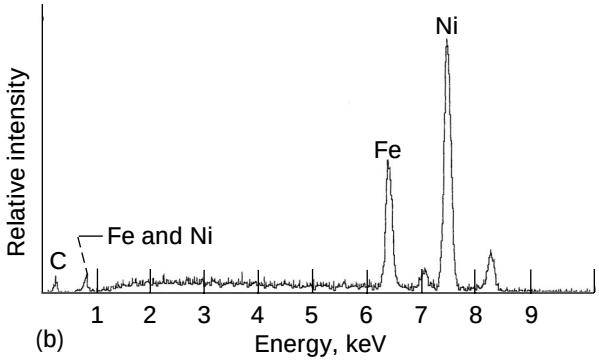


Figure 3.—Product obtained from reaction of $CF_{0.7}$ powder and $FeCl_3$ at 300 to 380 °C, followed by heating to 1200 °C with NiO in a quartz tube containing nitrogen. (a) Scanning electron micrograph. (b) Energy-dispersive spectrum.

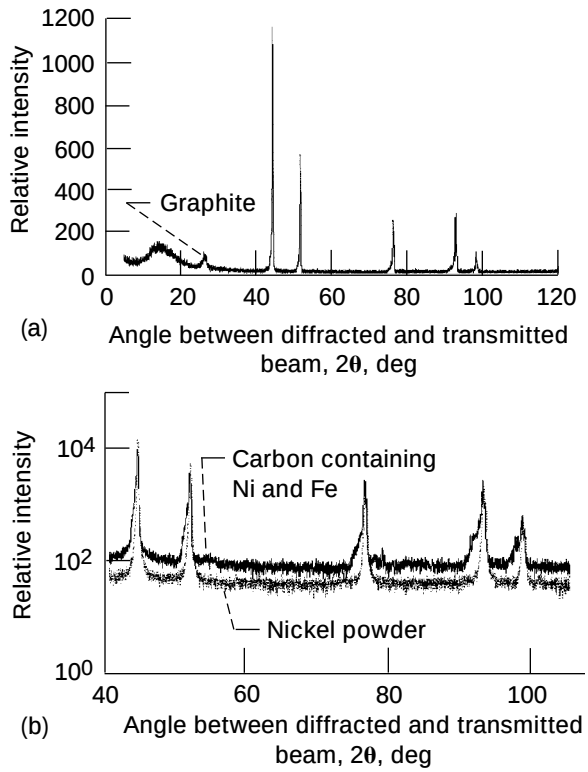


Figure 4.—X-ray diffraction data of product obtained from reaction of $CF_{0.7}$ powder and $FeCl_3$ at 300 to 380 °C, followed by heating to 1200 °C with NiO in a quartz tube containing nitrogen. (a) X-ray count in linear scale. (b) Comparison between this product and nickel powder; x-ray count in log scale.

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13. ABSTRACT ***(Maximum 200 words)***

Carbon materials containing iron alloy, iron metal, iron oxide or iron halide were fabricated. Typical samples of these metals were estimated to contain 1 iron atom per 3.5 to 5 carbon atoms. Those carbon materials containing iron alloy, iron metal, and/or Fe_3O_4 were magnetic. The kinetics of the fabrication process were studied by exposing graphite fluoride ($CF_{0.68}$) to $FeCl_3$ over a 280 to 420 °C temperature range. Between 280 and 295 °C, $FeCl_3$ quickly entered the structure of $CF_{0.68}$, broke the carbon-fluorine bonds, and within 10 to 30 min, completely converted it to carbon made up of graphite planes between which particles of crystalline FeF_3 and noncrystalline $FeCl_3$ were located. Longer reaction times (e.g., 28 hr) or higher reaction temperatures (e.g., 420 °C) produced materials containing graphite, a $FeCl_3$-graphite intercalation compound, $FeCl_2 \cdot 4H_2O$, and $FeCl_2 \cdot 2H_2O$. These products were further heat treated to produce iron-containing carbon materials. When the heating temperature was kept in the 750 to 850 °C range, and the oxygen supply was kept at the optimum level, the iron halides in the carbon structure were converted to iron oxides. Raising the heat to temperatures higher than 900 °C reduced such iron oxides to iron metal. The kinetics of these reactions were used to suggest processes for fabricating carbon materials containing iron alloy. Such processes were then tested experimentally. In one of the successful trial runs, commercially purchased $CF_{0.7}$ powder was used as the reactant, and NiO was added during the final heating to 1200 °C as a source of both nickel and oxygen. The product thus obtained was magnetic and was confirmed to be a nickel-iron alloy in carbon.

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