

FABRICATION OF IRON-CONTAINING CARBON MATERIALS FROM GRAPHITE FLUORIDE

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INTRODUCTION

In a previous investigation, ferric chloride (FeCl_3) was found to react to graphite fluoride (CF_x) in the temperature range of 300-400 C, resulting in a graphite intercalated compound (GIC). The GIC product could be further heated to produce iron oxide in or on carbon. The products of these reactions were characterized using x-ray diffraction (XRD) and energy dispersive spectrum (EDS)-[1]. However, the reaction kinetics was not studied.

The need for studying kinetics became apparent when a product of the above reactions, Fe_3O_4 -containing carbon, was found to be picked up by a magnet. Through the study of the kinetics, the above reaction could be modified to enhance the magnetic properties of the carbon products.

The objective of this research is to develop a kinetic theory for the above reactions, and to use the developed theory to make iron-containing carbon having desired magnetic properties.

KINETICS STUDY

FeCl_3 - CF_x reaction at 300-400°C

Products of this reaction have XRD peaks of FeCl_3 -GIC, FeF_3 and/or $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, but only some of them have graphite peaks [1]. Recent experiments concluded that the presence of FeF_3 and the absence of graphite peaks are favored if the temperature is low and the reaction time is short. The absence of FeF_3 and the presence of graphite and $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ are favored if otherwise.

The above observations suggest that, immediately after direct contact of FeCl_3 and CF_x , FeCl_3 quickly enters the carbon structure and reacts to fluorine, producing FeF_3 with a small amount of FeCl_3 impurity, or FeX_3 . The product has a theoretical Fe/C atomic ratio of slightly above 0.33x, where x is the F/C ratio for the reactant CF_x . This explains the high iron content in the product of this reaction. The fluorination of FeCl_3 happens between the carbon layers of the CF_x , where the reaction product (i.e., FeX_3) is located. Continuous FeCl_3 exposure at high temperature allows GIC formation, FeX_3 migration, and FeX_3 - FeCl_3 reactions, which result in products having

XRD peaks of FeCl_3 -GIC, $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$, and graphite.

Oxidation of FeCl_3 - CF_x reaction products in 1 atm air (<420°C)

This reaction produces Fe_2O_3 powder on carbon material. This reaction is best carried out at a temperature lower than 420°C, above which carbon oxidation in air becomes significant [2], and iron loss in the form of iron halide evaporation becomes important. Recent experiments indicated that this reaction can be conducted satisfactorily at a temperature as low as 200°C.

Oxidation of FeCl_3 - CF_x reaction product under limited oxygen supply at 800°C

For this reaction, limited reaction time and oxygen supply at 800°C causes less oxidation on carbon but more on iron halides, resulting in FeO and Fe_3O_4 , but no Fe_2O_3 , in or on carbon material.

The quantity of oxygen supplied in this reaction appears to be a key parameter in determining the magnetic properties of the products. Too little oxygen causes incomplete oxidation. This results in evaporation of unreacted iron halides, and therefore low iron concentration in the carbon product. Too much oxygen would consume the carbon host at 800°C, and results in Fe_2O_3 on the surface of the structurally damaged carbon material.

It was thought that oxygen in this reaction came from water adsorbed by the reactant when it was temporarily stored in ambient air [1]. However, recent experiments indicated that the quartz (SiO_2) sample holder is also an important source of oxygen. Fluorine or fluoride leaving the sample during this reaction attacks SiO_2 , causes the SiO_2 to release oxygen, and therefore initiates the oxidation of the metal halides.

PROCESS DESIGN AND EXPERIMENTS

Based on the above kinetics study, a process to manufacture iron-containing carbon with desirable properties could be designed. In this research, processes were designed to illustrate the above-described kinetics and its applications. The permeability values of the materials obtained by

similar processes are described in a separate report [3].

Iron in or on carbon

Process: Let the FeCl_3 react to CF_x until the FeX_3 formation is at least near completion. Let the FeX_3 -containing carbon product be reduced, producing iron or iron oxide in or on carbon.

In the experiment which followed the above process design, a $\text{CF}_{0.68}$ fiber sample was treated with saturated FeCl_3 vapor at 285°C for 28 hours and then post-heated in 330°C nitrogen for 22 minutes. The XRD, SEM, and EDS data suggest that this product has unpure FeF_3 crystals on the surface, contains FeCl_2 , but does not have a graphite's 3.35\AA interlayer spacing. The product was then divided into five samples, which were placed in quartz sample holders and heated in N_2 (99.99 vol.%) to $750, 850, 900, 950,$ and 1200°C , respectively. Different final heating temperatures resulted in different materials, which are described in Table 1.

Iron-nickel alloy in or on carbon

This product is desirable because iron-nickel alloy has a much higher permeability than pure iron [4].

Process: Let FeCl_3 react to CF_x until the FeX_3 formation is near completion, but before FeX_3 migration and GIC formation become significant. Let the product be mixed with NiO at room temperature and heated in a quartz tube to a temperature where FeX_3 is converted to oxides and then reduced and form an alloy with nickel. The NiO serves the dual functions of iron oxidation and iron-nickel alloy formation.

In the experiment which followed the above process design, a sample of $\text{CF}_{0.7}$ powder was treated with FeCl_3 at $300\text{--}380^\circ\text{C}$ for 125 minutes. The resulted product was then mixed with excess quantity of NiO , placed in small quartz tubes, and heated to 1200°C for 45 minutes in

nitrogen (99.99 vol.%). This process resulted in a mixture of Ni and Ni_3Fe alloy on carbon powder (XRD and EDS data).

CONCLUSIONS

The kinetics of the reaction between FeCl_3 and graphite fluoride (CF_x) was developed. It was concluded that FeCl_3 can quickly enter the carbon structure of CF_x and react to fluorine. This reaction produces carbon having graphite planes between which iron halide FeX_3 (FeF_3 with some impurity of FeCl_3) is located. Long time reaction between CF_x and FeCl_3 allows GIC formation, FeX_3 migration, and $\text{FeX}_3\text{--FeCl}_3$ reactions, resulting in products having XRD peaks of $\text{FeCl}_3\text{--GIC}$, $\text{FeCl}_2\cdot 2\text{H}_2\text{O}$, and graphite.

Products of the above reaction can be further heat treated to produce iron-containing carbon materials. If the oxygen supply is kept at an optimum level, then the carbon oxidation and FeX_3 evaporation can be kept at minimum, and the FeX_3 in or on carbon can be converted to iron oxide and eventually reduced to iron metal at a temperature higher than 900°C . In such heat treatment, NiO could be added to the reactor to produce a carbon material containing Ni_3Fe , a highly ferromagnetic material.

REFERENCES

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Table 1. Materials From $\text{CF}_{0.68}\text{--FeCl}_3$ Reaction and Subsequent Final Heating

Final Heating * Time and Temperature	X-ray Diffraction Peaks				
	Graphite	Intercalation (I_c)	FeO	Fe_3O_4	Iron Metal
0.5 hr at 650°C , then 0.25 hr at 750°C	large	$9.3+3.35(N-1)\text{\AA}$, $N=1,2,3$	small	small	none
1 hr at 850°C	small and broad	none	none	large	none
3 hr at 900°C	large	none	none	none	small
1.25 hr at 950°C	small and broad	none	none	none	large
0.67 hr at 1200°C	very smal or none	none	none	none	large

* The final heating was conducted in nitrogen (99.99 vol.%) using quartz sample holder