CARBONACEOUS MATERIALS CHEMICALLY MODIFIED BY SULFUR AND FLUORINE

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Introduction

Upon heating in vacuum or an inert environment, graphite fluoride (CF_x) decomposes into gaseous fluorocarbons and a solid, soot-like product [1]. Recently, it was observed that if the vacuum or inert environment in this reaction was replaced by an environment of certain reactive chemicals, such as sulfur, the majority of the fluorine atoms appeared to leave the structure of CF_x without reacting with carbon atoms [2]. The carbonaceous product of this reaction had a graphite peak in its x-ray diffraction data, but it was chemically more reactive than graphite [2].

The purposes of this study are to confirm the apparent lack of fluorine-carbon reaction during thermal decomposition of CF_x in sulfur, to further characterize the material resulting from this decomposition, and, from the results of such characterization, to compare these graphite-like products to their graphite precursors.

Experimental

A $CF_{0.9\text{-}1.0}$ powder sample purchased commercially was used for this study. It was treated with two cycles of sulfur and nitrogen exposure at 415°C for the first cycle, and 360°C for the second cycle. It was then heated in nitrogen at 650°C for 30 minutes.

A "Leco" process, named after the company who developed it, was used to measure the bulk carbon and sulfur mass % . In the process, carbon and sulfur in the samples were converted into CO_2 and SO_2, respectively, which were then quantitatively measured using their properties of IR absorption [3]. The masses of carbon in the reactants and products of the reactions were calculated from the sample masses and their carbon mass %. The carbon losses during reactions were then calculated by finding the differences between the carbon mass in the reactant and the carbon mass in the product.

In studying the chemical reactivity, the products were exposed to $FeCl_3$ at 300°C for 3 hours. Their weight before and after such exposures were measured.

The products obtained from CF_x decomposition were further analyzed by a number of different instruments. This includes x-ray photoelectron spectroscopy (XPS) for surface chemical analysis, energy dispersive spectroscopy (EDS) for semi-quantitative bulk chemical composition analysis, inductively coupled plasma mass spectrometry (ICPMS) for quantitative bulk metal content analysis, and x-ray diffraction (XRD) for structure analysis.

Results and discussion

Figure 1 summarizes the $CF_{0.9\text{-}1.0}$ decomposition reactions conducted in this research. The carbon mass data are included in the figure. The carbon loss during these reactions was less than 5%. Fluorine loss during the same reaction, however, was nearly complete. The fluorine peak in the final product's EDS data was barely noticeable. A much lower level of decomposition and much higher carbon loss were observed if the environment was inert or vacuum [1,2,]. It appears sulfur reacts to CF_x in a way that helps carry fluorine atoms out of the carbon structure and prevents C-F reaction.

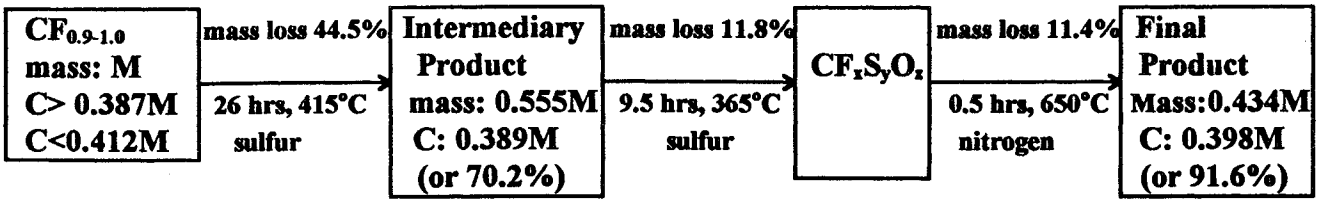
During decomposition of CF_x, some sulfur appeared to replace fluorine and be attach to the carbon structure. The presence of C-S bonds in the products was verified by the XPS data. Table 1 shows the bulk and surface chemical compositions of intermediary and final products described in Figure 1. It was noted that, after 650°C heating, there were still C-F bonds on the surface.

The adhesion force of this decomposed product to metals as well as among themselves was found to be very low [4]. This may be the combined results of the C-S and C-F bonding on the surface, presumably at the defect sites and the grain boundaries of the carbon structure.

The XRD data of the intermediary and final products described in Figure 1 shows graphite peaks. However, their intensities are very low. They are in fact lower than the graphite peaks similarly obtained from activated carbon (Table 2). Therefore, these products are considered amorphous.

However, unlike regular amorphous carbon, the carbonaceous product decomposed from CF_x in sulfur were reactive to some intercalates for graphite. After

Figure 1. Reactions and Carbon Mass Content During $CF_{0.9\text{-}1.0}$ Decomposition in Sulfur



being exposed to $FeCl_3$ at 300°C for 3 hours, this product gained 186% weight. The product was analyzed and found to be $C_9FeCl_3O_4S_{0.14}$. The source of oxygen is not clear, but is believed to come from water absorbed by $FeCl_3$. Data from XPS analysis showed that its surface had similar chemical composition as the bulk. Such composition suggests a first stage graphite intercalation compound (GIC). However, its XRD data show no peaks, suggesting an amorphous structure. (Figure 2).

Conclusions

Thermal decomposition of $CF_{0.9\text{-}1.0}$ powder in sulfur at 365-410°C resulted in near-complete removal of fluorine and a carbonaceous product that contains sulfur. The carbon loss during this reaction was found to be less than 5%. In this product, the sulfur atoms were covalently bonded to carbon, possibly at the grain boundary and the active sites. The decomposed product has a very low adhesion force to metal or to itself. It was amorphous, but was reactive to $FeCl_3$ at 300°C. The reaction resulted in a product whose Fe : C atomic ratio was about 1:9. This product, however, was amorphous, not a 1st stage graphite intercalation compound.

References

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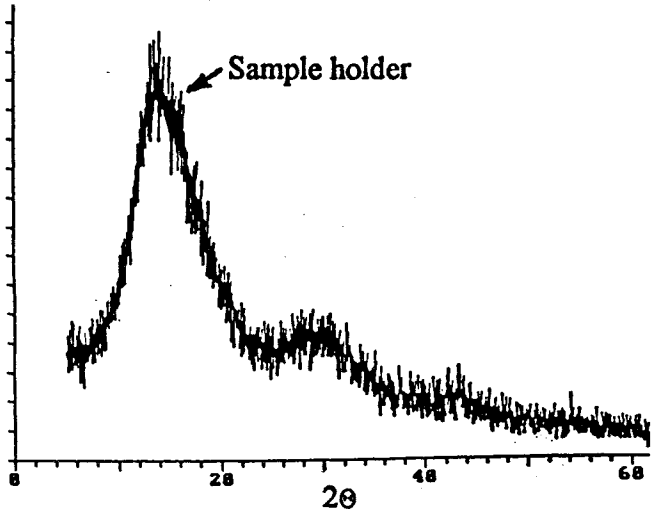

Figure 2. X-ray Diffraction Data of $C_9FeCl_3O_4S_{0.14}$ Show an Amorphous Product, Not a 1st Stage GIC.

Table 1 Chemical Composition (Wt. %) of the Intermediary Product Described in Figure 1

	Intermediary Product				Final Product			
	C	S	F	O	C	S	F	O
Surface	59.3	2.5	35.2	3.1	89.2	3.1	5.7	2.0
Bulk	70.2	3.8	26 (balance)		91.6	4.46	3.9 (balance)	

Table 2. X-ray Diffraction Peaks [Graphite (002)] for Different Carbon Materials

	Scan rate (2θ/s)	Peak position (Å)	Height (counts)	Width at half height (2θ)
Crystalline Graphite	0.04	3.35	70000	0.18
P-100 Carbon Fiber	0.04	3.37	15000	0.36
Activated Carbon	0.04	3.36	3500	1.0
Final Product in Figure 1	0.05	3.35	1000	0.6