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Thermal Decomposition of Graphite Fluoride. I. Decomposition Products of Graphite Fluoride, $(CF)_n$ in a Vacuum

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The mechanism of thermal decomposition of graphite fluoride, $(CF)_n$ in a vacuum was studied by means of chemical and gas analyses, and the measurement of crystallinity. The crystallinity of $(CF)_n$ was slightly improved in the step of initial decomposition. The fluorine/carbon atomic ratio of initial gaseous product evolved by decomposition was about 2. The product is CF_2 or C_2F_4, and then it gives several compounds by secondary reaction. Every second layers of $(CF)_n$ are decomposed, and the evolved molecules or radicals abstract fluorine atoms which are bonded to the neighboring two layers.

Graphite fluoride $(CF)_n$ is obtained by the direct reaction of elemental fluorine with graphite or other carbon materials, and its atomic ratio F/C is unity.[1] Its crystal structure is shown in Fig. 1. Graphite fluoride retains the layer structure of graphite, but the layer has a zig-zag form because of the formation of C–F bond. The network of carbon atoms is therefore covered with fluorine atoms. Furthermore, the spacing between neighboring two layers is expanded from that of graphite, 3.35 Å to a larger value between 5.8 and 8.9 Å. Carbon atoms which are placed at the edge site of the layer are connected with two or three fluorine atoms.[2] However, the product actually formed is considerably strained,[3] and has a turbostratic structure.[4]

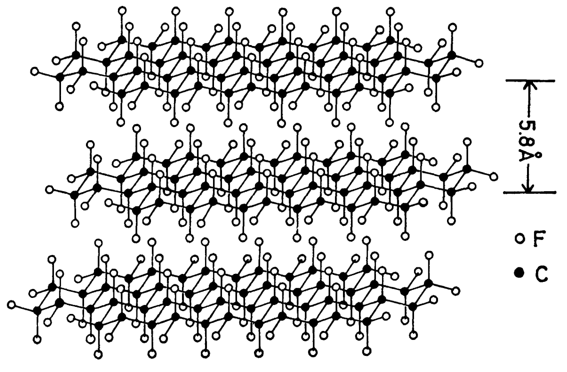

Fig. 1. Crystal structure of $(CF)_n$.
○: Fluorine atom, ●: carbon atom.

Thermal decomposition of graphite fluoride in a vacuum can be represented by:[5]

$$(CF)_n \longrightarrow \text{amorphous carbon} + C_2F_6 + CF_4 + C_3F_8 + C_2F_4 + \text{other perfluorocarbons.} \quad (1)$$

The rate of thermal decomposition is expressed by Avrami-Erofeyev's equation:

$$-\ln(1-\alpha) = (kt)^n, \quad (2)$$

where α is the fraction decomposed, k is the rate constant and n is the dimension of the nucleus growth. Kamarchik and Margrave[6] reported that n was 2 in Eq. 2. This result suggests that the decomposition proceeds two-dimensionally around an active site or a nucleus, and the reaction is auto-catalytic. However, they have not postulated a detailed mechanism for the decomposition.

In this work, the elemental and gas analyses were made in order to reveal the mechanism of the decomposition of $(CF)_n$ in a vacuum. The crystallinity of partially decomposed $(CF)_n$ was also measured.

Experimental

Powdery natural graphite whose grain size was 46—62 μm and flaky natural graphite whose grain size was 279—840 μm were fluorinated with elemental fluorine at 600 °C for 11 h for the former (sample I) and 24 h for the latter (sample II). Samles I and II thus obtained were used as the starting material for decomposition study. Interlayer spacings of samples I and II were 6.00 Å and 5.84 Å, and the F/C ratios were 0.94 and 0.93, respectively. The grain size of $(CF)_n$ is almost the same as that before fluorination.

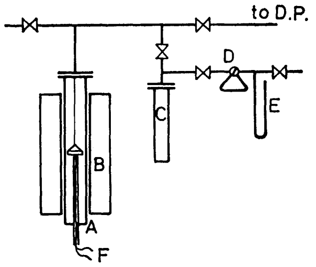

Fig. 2. Schematic diagram of apparatus for thermal decomposition.
A: Reaction tube, B: furnace, C: cold trap, D: gas sampler for gas chromatography, E: Hg manometer, F: thermocouple.

An apparatus made of Monel metal as shown in Fig. 2 was used for gas analysis. The gaseous products evolved by the decomposition were collected in a cold trap kept in liquid N_2. After the decomposition, the trapped gases were evaporated, and the total gas pressure was measured by Hg manometer. The gases were then introduced into a gas sampler, sepa rated and determined by means of gas chromatography. The identification was made by IR spectroscopy.

In another experiment, the sample was partially decomposed at 586 °C, and the residual substances were examined by X-ray diffraction and elemental analysis. The fluorine content was determined by a fluoride ion electrode after all fluorine atoms in $(CF)_n$ were allowed to form hydrogen fluoride by the oxygen flask combustion method.

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Results and Discussion

Change in Crystallinity of Graphite Fluoride and Carbon during Decomposition Process. The sample I was partially decomposed at 586 °C in a vacuum. The X-ray diffraction patterns were taken for residual substances.

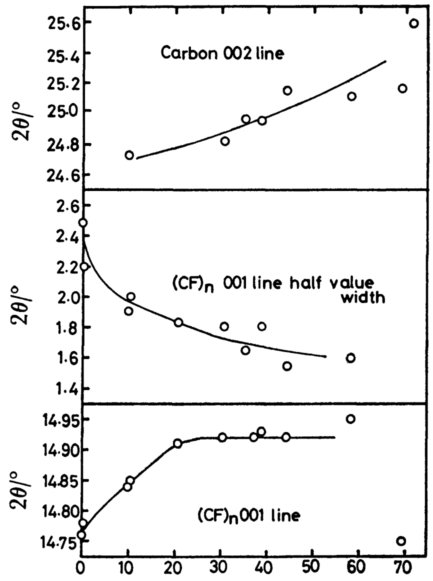

Fig. 3. Change in the crystallinity of graphite fluoride $(CF)_n$ and carbon formed during decomposition. Sample I was used.

Figure 3 shows the change in the position of the 002 line of carbon formed by decomposition, and the position and the half width of the 001 line of $(CF)_n$ during decomposition. The 002 line of carbon shifts to higher angle as the decomposition proceeds. The crystallinity of carbon is improved as the decomposition proceeds. The half width of 001 line of $(CF)_n$ becomes narrower and the position of the line profile shifts to higher angle, namely, the crystallinity of $(CF)_n$ is improved by decomposition, and the shift continues until the weight loss reaches to 20%. From the results, the decomposition is initiated at a strained region distributed in $(CF)_n$ crystal. In this region, a high stress is applied and the interlayer spacing of $(CF)_n$ tends to expand.[3] The strained region is perfectly decomposed within 20% weight loss.

The Composition Change of Graphite Fluoride. Figure 4 shows the composition change of $(CF)_n$ during decomposition at 586 °C. The plot from experiment shows a good agreement with the curve calculated under the assumption that the F/C ratio of gaseous products is 2. Therefore, the initial gaseous product is supposed to be C_2F_4 or CF_2. To confirm this, the decomposition of sample I was carried out in two different apparatus made of either pyrex glass or Monel metal shown in Fig. 2. Figure 5 shows the IR spectra of all gaseous compound by the decomposition. In the former apparatus, the absorption band of SiF_4 was more intense than that of other fluorocarbons (for example, 1250 cm^{-1} for C_2F_6), and the absorption band of CO_2 was observed at 2300 cm^{-1}. They are the reaction products with glass at high temperature. However, Atkinson and Atkinson reported that C_2F_4 did not react with glass below 700 °C.[7] Therefore, the main gaseous product should be an active substance such as CF_2, beside C_2F_4.

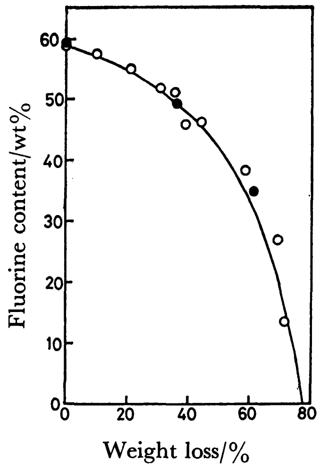

Fig. 4. Change in fluorine contents of solid products decomposed under vacuum.
—○—: Sample I, —●—: Sample II.
Solid line: Calculated under the assumption that the F/C ratio of gaseous products is 2.

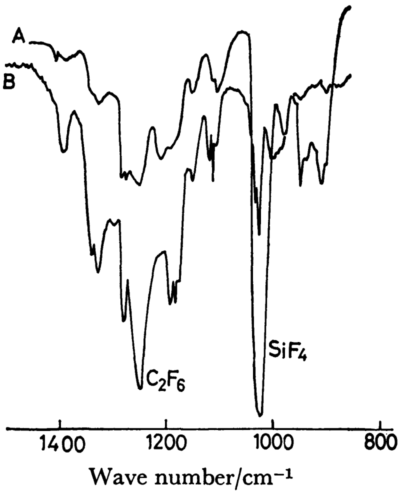

Fig. 5. Infrared spectra of total gases formed during decomposition in a vacuum.
A: Pyrex glass, B: Monel metal.

Analysis of Gaseous Products. Reaction conditions and the amounts of each gas evolved by decomposition of 100 mg of $(CF)_n$ are shown in Table 1. C_2F_6, C_3F_8, and other saturated fluorocarbons were observed in addition to C_2F_4. They would be produced by the secondary reaction of C_2F_4 or CF_2. It is noteworthy that the amounts of unsaturated fluorocarbons, C_2F_4 and C_3F_6, formed in the experiment without trapping the gas during the reaction (run 6) are small compared with those formed in the experiment with trapping them (run 4). Moreover, the amounts of CF_4 and C_2F_6 are

TABLE 1. ANALYSIS OF GASEOUS PRODUCTS EVOLVED FROM GRAPHITE FLUORIDE DURING THERMAL DECOMPOSITION

Run	Sample	Temp/°C	t/min	Weight loss/%	Total gas/ 10^{-5} mol/100 mg	Gaseous products				
						/10^{-5} mol/100 mg(%)			/1000 counts/100 mg	
						CF_4	C_2F_6	C_2F_4	C_3F_8	C_3F_6
1	I	663	34	73.7	37.0	9.09 (24.6)	14.64 (40.0)	3.81 (10.3)	767	264
2	I	661	10	72.5	35.8	10.14 (28.4)	13.58 (38.0)	4.16 (11.6)	729	289
3	I	611	119	72.0	28.6	6.23 (21.8)	10.10 (35.3)	3.19 (11.2)	631	291
4	I	618	82	70.1	26.9	7.58 (28.2)	10.07 (37.5)	3.10 (11.5)	625	288
5	I	618	10	13.5	4.64	1.49 (32.0)	1.70 (36.7)	0.71 (15.3)	88	22
6[a)]	I	619	82	70.1	31.8	9.11 (28.6)	11.38 (35.7)	0.01 (0.03)	729	59
7	II	616	338	74.4	34.1	7.76 (22.7)	12.49 (36.6)	2.75 (8.10)	861	180
8	I	569	920	74.4	30.7	9.20 (29.9)	8.56 (27.8)	3.10 (10.0)	387	269
9	I	569	411	53.9	24.8	9.42 (38.0)	7.68 (31.0)	3.08 (12.4)		
10	I	567	189	46.8	19.1	5.97 (33.7)	6.21 (35.0)	2.28 (12.9)	270	153

a) Without trapping the gases during the decomposition.

almost the same in both runs 4 and 6. From the result, it is clear that C_2F_4 and C_3F_6 do not form CF_4 or C_2F_6 but such compounds which have higher molecular weight. In fact, Atkinson and Atkinson[7)] have reported that C_2F_4 cannot be decomposed into CF_4 at temperatures below 700 °C. Therefore, thermal decomposition of $(CF)_n$ should be expressed by the following equation,

$$2(CF)_n \longrightarrow nC^* + XCF_2 + YC_2F_4, \quad (X+2Y=n) \qquad (3)$$

where C* is amorphous carbon. Kamarchik and Margrave[6)] have concluded that the initial gaseous product in the decomposition of $(CF)_n$ is only C_2F_4, and that it changes to various gaseous products by secondary reactions. Their conclusion is inconsistent with the present results and those obtained by Atkinson and Atkinson.[7)]

Other Products. In the decomposition of $(CF)_n$, a tarry product[8)] and carbon have been found on the wall of the reaction tube in addition to the gaseous compounds. C_2F_4 or CF_2[9)] formed by the initial reaction reacts with each other on the wall of apparatus or in the gas phase to form the tarry product, carbon deposit and perfluorocarbons of low molecular weight.

Process of Thermal Decomposition of Graphite Fluoride. Since the F/C ratio of gaseous compounds formed by thermal decomposition of $(CF)_n$ is 2, the remaining carbon atoms in $(CF)_n$ must be formed as perfectly amorphous carbon, and its crystallinity will never be improved even if the decomposition proceeds. However, the X-ray diffraction pattern of the residual carbon shows the improvement of the crystallinity, and moreover, the residual carbon obtained by complete decomposition has almost the same shape as that before decomposition. From these facts, every layer of $(CF)_n$ does not necessarily decompose, namely, C–C bonds in every second layer of $(CF)_n$ are ruptured by decomposition to form radicals, which abstract fluorine atoms bonded to the neighboring two layers to form CF_2 or C_2F_4 as shown in Fig. 6A.

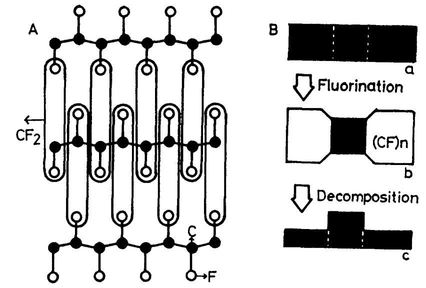

Fig. 6. Schematic illustration of thermal decomposition of graphite fluoride $(CF)_n$ (A) and thermal decomposition of partially fluorinated graphite (B).
a: Original graphite, b: partially fluorinated graphite, c: residual carbon after perfect decomposition.

Kamarchik and Margrave proposed the following mechanism as the thermal decomposition of $(CF)_n$. Fluorine atoms migrate from the interior of the particle to the edge, from which C_2F_4 is released.[6)] According to their suggestion, the area of layer plane of residual carbon should become a half that of undecomposed one, and the thickness in the direction of c-axis should be the same as that of original graphite.

To confirm this, the change of the shape in the decomposition of flaky $(CF)_n$ having unreacted graphite in the sample[10)] was observed by a microscope. The shape of the sample (Fig. 7) after decomposition was almost the same as that of the original one. The decomposed $(CF)_n$ region becomes thinner than the unreacted graphite. This process is shown by Fig. 6B. The mechanism of thermal decomposition of $(CF)_n$ postu-

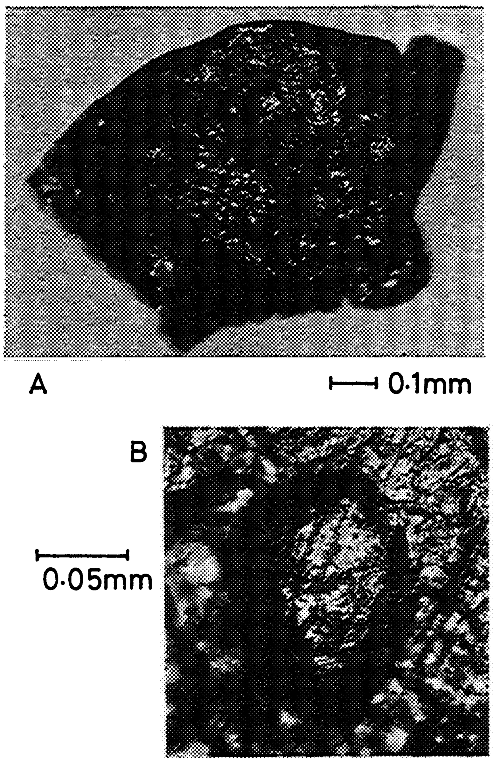

Fig. 7. Residual carbon formed from graphite fluoride having unreacted graphite.
A part of A is enlarged and shown in B.

lated by Kamarchik and Margrave cannot explain this phenomenon.

This reaction is similar to the mechanism of the decomposition of other graphite intercalation compounds.[11] In the case of thermal decomposition of $(CF)_n$, every second layers can be regarded as intercalants and the other layers as graphite layers. After releasing the intercalants, the interlayer spacing of the residual graphite decreases to that of original graphite. Owing to the decomposition of $(CF)_n$, the thickness of the particle in the direction of c-axis decreases to a half that of the original graphite. On the other hand, since the layer of unbonded carbon atoms with fluorine in $(CF)_n$ does not take part in decomposition, it maintains the original thickness.

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References

1) The presence of a new type of graphite fluoride was confirmed by the authors, and its composition was found to be $(C_2F)_n$; Y. Kita, N. Watanabe, and Y. Fujii, *J. Am. Chem. Soc.*, **101**, 3832 (1979). In the present work, however, only $(CF)_n$ was dealt with.

2) N. Watanabe and H. Takenaka, 5th European Symposium on Fluorine Chemistry, Aviemore Scotland, 16—20 th September (1974).

3) N. Watanabe and H. Takenaka, *Tanso*, **92**, 2 (1978).

4) N. Watanabe, Y. Koyama, and S. Yoshizawa, *Denki Kagaku*, **31**, 756 (1963).

5) N. Watanabe and Y. Kita, *Nippon Kagaku Kaishi*, **1975**, 1896.

6) P. Kamarchik, Jr., and J. L. Margrave, *J. Therm. Anal.*, **11**, 259 (1977).

7) B. Atkinson and V. A. Atkinson, *J. Chem. Soc.*, **1957**, 2086.

8) The F/C ratio of this substance is unity, and it is similar to the compound reported by Atkinson and Atkinson.[7] Namely, it is polymeric substance having a chain of conjugated double bond.

9) The decomposition of $(CF)_n$ is an exothermic reaction. Provided that the initial product of decomposition is only CF_2, the reaction becomes endothermic. Therefore, either the formation of C_2F_4 or the reaction of the active species in the particle should be also taken into account.

10) The sample was prepared from natural graphite of 279—840 μm at 600 °C under 26.6 kPa fluorine.

11) M. Inagaki, *Carbon*, **4**, 137 (1966).