Thermal Decomposition of Graphite Fluoride. III. Thermal Decomposition of $(CF)_n$ in Oxygen Atmosphere

Nobuatsu WATANABE,* Toshihiko KAWAMURA, and Satoshi KOYAMA
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606
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Thermal decomposition of $(CF)_n$ was carried out under an oxygen atmosphere. The decomposition temperature was found to be a decisive factor to control the decomposition mechanism and the structure of residual substances. The decomposition reaction proceeded faster in oxygen than in a vacuum at temperatures higher than 588 °C. However, it was reversed below 588 °C. The decomposition mechanism in high temperature region was similar to that in a vacuum. The ESCA spectra of residual substances prepared above 588 °C indicated the presence of carbon atoms which were not bonded with fluorine, namely the nuclei comprised of carbon still remained even in oxygen. The rate of the weight decrease was larger in oxygen than in a vacuum because of the reaction of carbon nuclei, which was formed by thermal decomposition, with oxygen. On the other hand, it considerably decreased below 588 °C, where no nuclei was found for any sample.

A high temperature reaction of graphite fluoride with elemental fluorine gives the $(CF)_n$ type graphite fluoride having a layered structure of hexagonal network. The low surface energy is the most characteristic nature of the product.[1] Therefore, while it is useful as a solid lubricant on one hand, it is on the other hand a troublesome substance which brings about the anode effect in the electrolysis of molten fluorides. Currently, there is a necessity of studying the decomposition of $(CF)_n$ in order to produce in good yield and to elucidate the phenomenon of anode effect. Graphite fluoride, $(CF)_n$, decomposes in a vacuum at high temperature to form several kinds of volatile fluorocarbons and amorphous carbon.[2] Previous studies revealed that the Avrami-Erofeyev equation could be applied to the isothermal TG curves for the decomposition of $(CF)_n$ in a vacuum, and that fluorine and carbon atoms were eliminated from $(CF)_n$ in the ratio of 2 to 1 during the decomposition.[3-5] In this study, thermal decomposition of $(CF)_n$ was performed under oxygen atmosphere and comparison was made with the decomposition behavior in a vacuum.

Experimental

The starting material was natural graphite from Madagascar, whose particle size was 46—62 μm, and the purity was 99.5% from ash treatment. Graphite fluoride, $(CF)_n$, was prepared by the fluorination of natural graphite at 600 °C for 10 h (sample I) or for 15 h (sample II) under the stream of mixed gas of fluorine (5.1×10^4 Pa) and argon (5.1×10^4 Pa). Some properties of these samples were summarized in Table 1. Sample I was used for the measurement of TG and DTA, and sample II was used for X-ray diffractometry, elementary analysis, photoelectron and infrared spectroscopy.

Isothermal TG curves for thermal decomposition of $(CF)_n$ were measured with a thermobalance under oxygen flow. The flow rate was between 15 and 20 ml/min. The residual substances were obtained from the partially decomposed $(CF)_n$. They were analyzed with the methods mentioned above. DTA was carried out under reduced pressure of 6.7×10^2 Pa, using α-Al_2O_3 as a reference material. Infrared spectra were taken with the KBr disc method. The fluorine content of residual substance was determined with the oxygen flask method.

Table 1. Samples used for the experiment

Sample	Fluorine content/%	Crystallinity		Color
		d_{001}/Å	β_{001}/°	
I	56.3	6.02	2.40	Gray
II	59.7	5.97	1.67	Gray

Results

Isothermal TG Curves for Thermal Decomposition of $(CF)_n$ in Oxygen. Figure 1 shows isothermal TG curves both in oxygen and in a vacuum at several temperatures. The final weight loss was about 75% in a vacuum, whereas it was almost 100% in oxygen at temperatures above 588 °C. The Arrhenius plot for the TG curves in oxygen is given in Fig. 2. The rate constant was defined to be the slope at the inflexion point of the TG curve. As shown in the figure, it has a distinct break point at 588 °C. This means that the mechanism of thermal decomposition is different from each other in the two regions divided at this tempera-

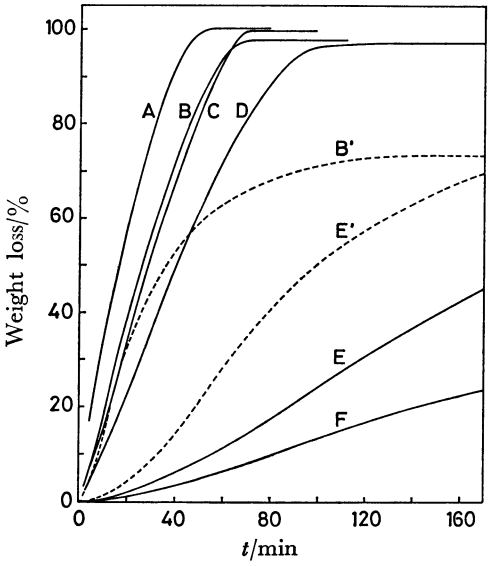

Fig. 1. Isothermal TG curves for thermal decomposition of $(CF)_n$ in oxygen and in a vacuum.
——: Oxygen, ----: vacuum.
A: 623 °C, B,B': 610 °C, C: 602 °C, D: 588 °C, E,E': 575 °C, F: 562 °C.

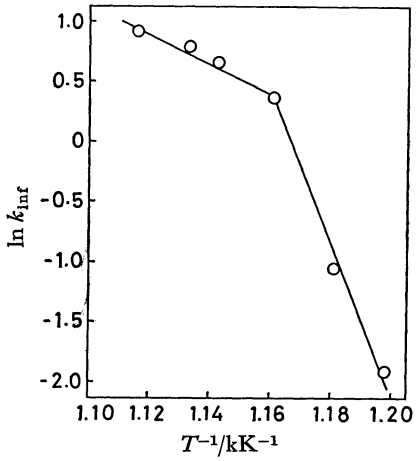

Fig. 2. Arrhenius plot for thermal decomposition of $(CF)_n$ in oxygen.

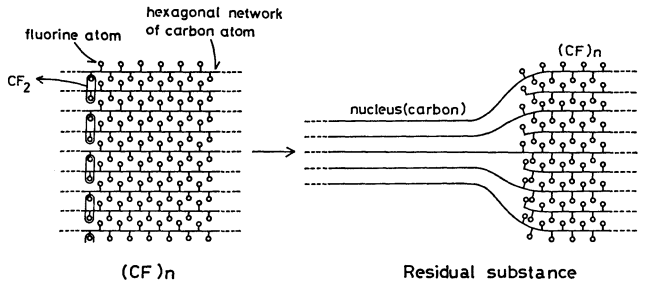

Fig. 3. Schematic illustration of thermal decomposition of $(CF)_n$ in a vacuum.

ture. As seen in Fig. 1, the decomposition proceeds faster in oxygen than in a vacuum at temperatures higher than 588 °C, though the reverse is ture below 588 °C.

The thermal decomposition of $(CF)_n$ has been studied under vacuum previously,[3-5] and the Avrami-Erofeyev equation[6]

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

is applied to the isothermal TG curves. Here α is the fraction decomposed, k is the rate constant and n is the dimension of nucleus growth. The mechanism shown in Fig. 3 is suggested for the structural changes during the decomposition from the facts that n is equal to 2 and $(CF)_n$ has a layered structure.[7] The above equation can also be applied to the isothermal TG curves in oxygen. The result is shown in Fig. 4, where straight lines are obtained at temperatures above 588 °C. This means that the decomposition at higher temperatures is also due to the formation and growth of nuclei. No such plots can be obtained at temperatures below 588 °C, because the decomposition rates are too small to measure the final weight loss.

Structural Analysis of Residual Substance. In order to elucidate the difference in the mechanism of the thermal decomposition due to a temperature, the residual substance was analyzed by several methods. The sample were those prepared by the thermal decomposition of $(CF)_n$ in oxygen at 560 and 610 °C.

Table 2 shows the fluorine contents and color of the residual substance. The fluorine contents are

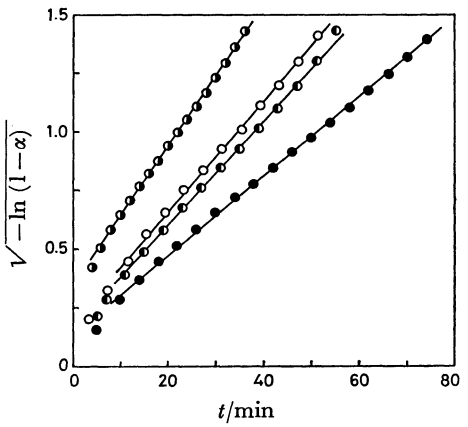

Fig. 4. $\sqrt{-\ln(1-\alpha)}$ *vs.* t for thermal decomposition of $(CF)_n$ in oxygen.
◑: 623 °C, ○: 610 °C, ◐: 602 °C, ●: 588 °C.

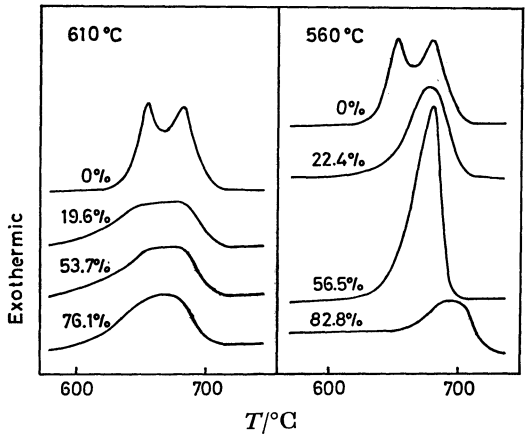

Fig. 5. DTA curves for residual substance formed in oxygen. Numerical value for each curve indicates the weight loss of residual substance.

Table 2. Fluorine content and color of residual substance

T / °C	Weight loss / %	Fluorine content / %	Color
560	15.4	57.6	Gray
	31.1	59.5	White
	59.3	59.9	White
	62.6	57.9	White
610	12.2	58.6	Black
	28.7	59.3	Black
	42.2	57.8	Black
	59.4	57.9	Black
Before decomposition		59.7	Gray

almost constant and independent of decomposition temperature or weight loss. This fact indicates that fluorine and carbon atoms are eliminated in the ratio of 1 to 1 during the decomposition in oxygen. In addition, it was observed that $(CF)_n$ turned black as soon as the decomposition started at 610 °C and this color did not change during the decomposition as observed in a vacuum.[4] On the other hand, $(CF)_n$ gradually turned white at 560 °C as the decomposition

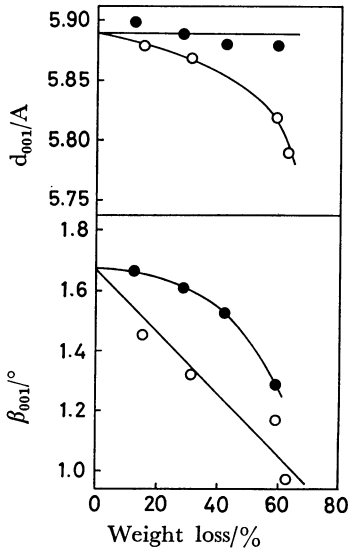

Fig. 6. Change in crystallinity of residual substance formed in oxygen.
●: 610 °C, ○: 560 °C.

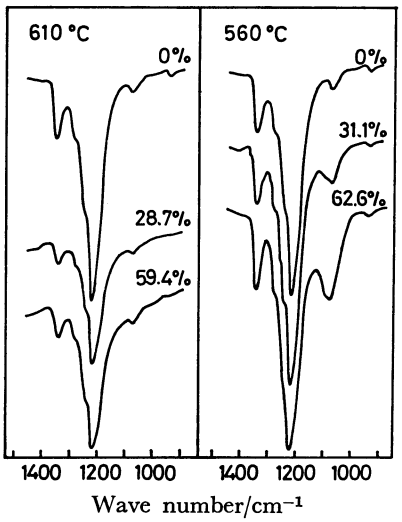

Fig. 7. IR spectra of residual substance formed in oxygen. Numerical value for each spectrum indicates the weight loss of residual substance.

proceeded.

The DTA curves are shown in Fig. 5, where the residual substance formed at 610 °C is thermally less stable than that formed at 560 °C.

Figure 6 shows the results obtained from X-ray diffractometry. Only the lines correspond to $(CF)_n$ can be observed and those of carbon are not observed at both temperatures. The interlayer spacing and half width were calculated from the diffraction profile of the 001 line of $(CF)_n$. The decrease in the half width means that the strain of $(CF)_n$ is removed. The rate at 560 °C is larger than that at 610 °C.

Figure 7 shows the IR spectra of residual substances. The pattern of the peak at 1075 cm^{-1} for the sample prepared at 560 °C varies with the decrease in weight, whereas the pattern is hardly changed by heating at 610 °C. However, there is no peak for carbonyl group as observed in graphitic oxide.[8]

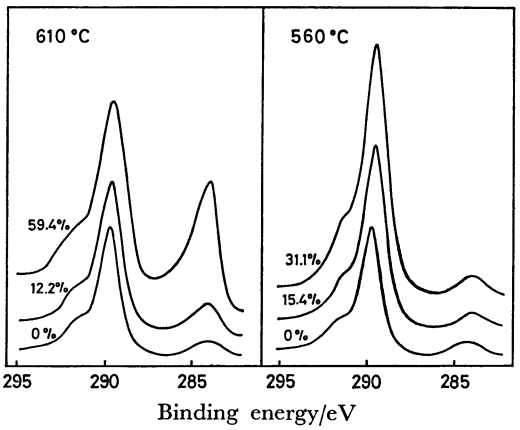

Fig. 8. C_{1s} ESCA spectra of residual substance formed in oxygen. Numerical value for each spectrum indicates the weight loss of residual substance.

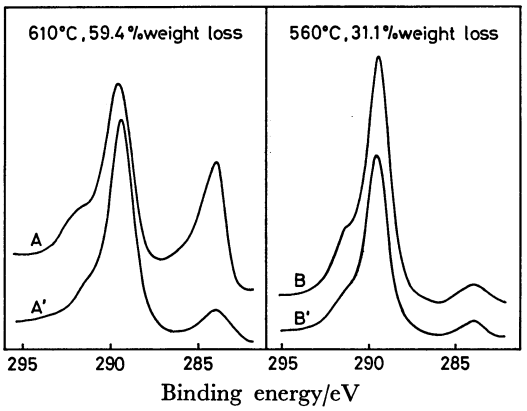

Fig. 9. C_{1s} ESCA spectra of residual substance formed in oxygen.
A,B: Before grinding, A′,B′: after grinding.

The ESCA spectra of the residual substances are shown in Fig. 8, where two peaks are observed at 284 and 289.5 eV. The former is due to C_{1s} electrons of graphite or hydrocarbons, and the latter is due to those of tertiary C–F group.[9,10] No changes are observed in the spectra of the residual substances formed at low temperature, whereas in the case of the sample prepared at high temperature, the intensity of the peak at 284 eV increases as the decomposition proceeds. Figure 9 shows the change in the C_{1s} ESCA spectra for samples ground with an agate mortar. For the sample prepared at 610 °C, there is a decrease in the intensity of the peak at 284 eV. In general, the information obtained from ESCA is limited to the surface layer of the sample. Therefore, the ESCA spectra show that carbon atoms having no bond with fluorine atoms are present only on the surface of the residual substance formed at 610 °C. However, since the amount of such carbon atoms is regarded to be negligible compared with that of carbon bonded with fluorine, the fluorine contents are not dependent on the weight loss, as shown in Table 2. For the sample formed at 560 °C, no such carbon atoms are found. This is consistent with the result of the elementary analysis.

All the evidences shown above indicate that the

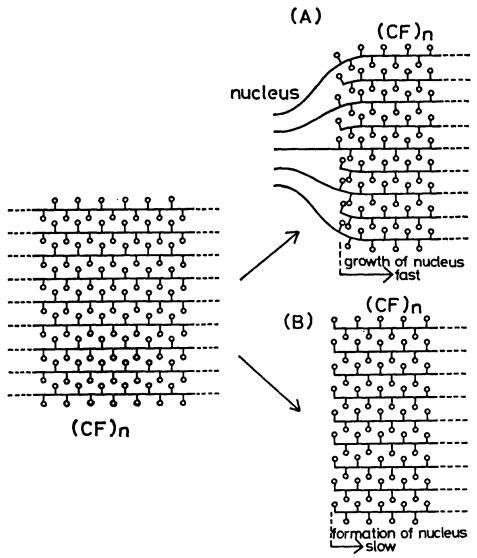

Fig. 10. Schematic illustration of thermal decomposition of $(CF)_n$ in oxygen.
(A): Residual substance formed in high temperature region, (B): residual substance formed in low temperature region.

mechanism of the thermal decomposition of $(CF)_n$ in oxygen at temperatures higher than 588 °C is different from that below this temperature as suggested from the Arrhenius plot.

Discussion

Mechanism of Thermal Decomposition of $(CF)_n$ in Oxygen. From the results described above, the mechanism shown in Fig. 10 is suggested for the thermal decomposition in oxygen. The decomposition is initiated by the nucleus formation at the edge plane or strained regions of $(CF)_n$ as is discussed in the study under vacuum.[4] The result of X-ray diffractometry supports the above view. The nucleus consists of carbon atoms. Since fluorine and carbon atoms are eliminated in the ratio of 2 to 1 during the decomposition in a vacuum, the ratio of carbon atoms in the residual substance increases as the decomposition proceeds. In the presence of oxygen, it is expected that the decomposition rate in oxygen is larger than that in a vacuum because of the reaction of carbon with oxygen. This inference seems to be reasonable because no peak due to carbonyl group is observed in the IR spectra and fluorine and carbon atoms are eliminated in the ratio of 1 to 1. However, since the decomposition in a vacuum proceeds faster than that in oxygen at 575 °C as shown in Fig. 1, the inference is not valid for the decomposition at low temperatures.

In the case of the thermal decomposition in oxygen at high temperatures, the mechanism is considered to be similar to that in a vacuum from the following results; (i) the decomposition proceeds faster in oxygen than in a vacuum, (ii) the isothermal TG curves are fit to the Avrami-Erofeyev equation, (iii) the change in the color of residual substances in oxygen is similar to that in a vacuum and (iv) carbonaceous parts are present on the surface of residual substances. If the nuclei grow at a rate larger than that of the reaction of carbon with oxygen, they will still remain even in the presence of oxygen. Therefore, the weight loss in oxygen is almost equal to a sum of that in a vacuum and that by the elimination of carbon dioxide. and the rate of the weight loss in oxygen is larger than that in a vacuum.

On the other hand, in the low temperature region, the nuclei grow at a rate smaller than that of the reaction of carbon with oxygen. That is, since the nuclei are consumed as soon as they are formed, the rate of weight loss is smaller than that in a vacuum. From this reason, the ESCA spectra of residual substances formed at 560 °C show no peak corresponding to the carbon atoms which are not bonded with fluorine atoms.

Structural Aspect of Residual Substance. The differences in the properties of the residual substances formed at 560 °C and 610 °C are discussed in relation to the nucleus described above. The residual substances formed at 610 °C have carbonaceous parts which can change to nuclei, whereas those formed at 560 °C have no such parts. The strain energy produced by the difference in the crystal structure between reactant and product is one of the sources for the activation of nucleus in the thermal decomposition of solids.[11] Since the residual substances formed at 610 °C have such strain energy in the particle, their crystallinity is inferior to that of the residual substances formed at 560 °C, and the former is thermally less stable than the latter.

References

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6) The Avrami-Erofeyev equation is derived on the assumption that the reaction in question is initiated by the formation of nucleus which grows either n-dimensionally or $(n-1)$-dimensionally. The nucleus is the fragment of the product.
7) Nuclei are formed at the edge of layers or at the strained parts of $(CF)_n$ when the rupture of C–C bond occurs, and at the same time, fluorocarbon radical (*i.e.* CF_2) or fluorocarbon molecule (*i.e.* C_2F_4) are formed. The nuclei mainly consist of carbon atoms. Since the interface between $(CF)_n$ and nuclei is more reactive than the bulk of $(CF)_n$, it is more likely that the decomposition proceeds by two dimensional growth of the nuclei in the layers. From another experiment, it was found that the rupture of C–C bond takes place at every second layer of $(CF)_n$.
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