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PREPARATION OF POLY-(DICARBON MONOFLUORIDE), $(C_2F)_n$ FROM EXFOLIATED GRAPHITE

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SUMMARY

New compound Poly-(dicarbon monofluoride), $(C_2F)_n$ was prepared at low temperatures of 335 to 374°C with faster reaction rate from exfoliated graphite than from natural graphite. The fluorination reaction was not controlled by the diffusion of fluorine into graphite layers, but by the reaction of fluorine with graphite, and the activation energy of the reaction was 35.6 Kcal/mol. The product has the interlayer spacing (d_{001}) of 8.8 to 9 Å, half width (β_{001}) of 2.7 to 2.9° and F/C ratio of 0.535 to 0.610. The difference in the reaction rates of exfoliated and natural graphites with fluorine was based on the structure of the starting materials.

INTRODUCTION

Graphite reacts with elemental fluorine at high temperatures giving a kind of intercalation compound, graphite fluoride, with a covalent bond between carbon and fluorine. The products are quite stable in many atmospheres or at high temperatures. They have many good properties as a solid lubricant, a water repellent or an active material of a primary cell in the industrial field [1].

At present time, there are two kinds of stable compounds, $(CF)_n$ and $(C_2F)_n$ [2]. Their preparations depend mainly on the reaction temperature and crystallinity of starting carbon materials. In the case of natural graphite having good

crystallinity, $(CF)_n$ is prepared at around $600^\circ C$, however at relatively low temperatures of 350 to $400^\circ C$ $(C_2F)_n$ is prepared in a high yield. Between the intermediate temperatures, the mixture of these compounds is obtained in various proportions depending on the reaction temperatures. $(CF)_n$ is prepared in short time because of the high reaction rate at high temperatures. At the same time, however, the decomposition of graphite fluoride into gaseous fluorocarbon occurs, which decreases the yield of $(CF)_n$. On the other hand, the yield of $(C_2F)_n$ is almost 100% as accompanied by no decomposition reaction. On preparation of $(C_2F)_n$, there also exists a remarkable difficulty that it takes a long reaction time.

In the present study, exfoliated graphite was used as a starting material to facilitate the reaction between graphite and elemental fluorine at a relatively low temperature, and it was attempted to find out the optimum condition to prepare $(C_2F)_n$.

EXPERIMENTAL

The sample used is exfoliated graphite supplied by CHUO KASEI CO., LTD and natural graphite with particle size of $149 - 279 \mu m$ which is almost the same as that of original natural graphite for preparation of exfoliated graphite. The preparative method of exfoliated graphite is as follows. The intercalation compound is first prepared by the reaction of natural graphite with a mixture of HNO_3 and H_2SO_4 . It was then washed with water, when most of the intercalant is driven out, and the residual compound is treated at $100^\circ C$.

Fig.1 shows the microscopic picture of exfoliated graphite, which is expanded largely along C-axis, though the thickness of original natural graphite is in the range between several μm and several ten μm .

The interlayer spacing of the crystallite (d_0), thickness in C-axis direction (L_c) and lattice strain (η) were obtained of both exfoliated and natural graphite. As shown in Table 1, the crystallite size of exfoliated graphite is smaller, in other words, the lattice strain is larger than that of natural graphite.

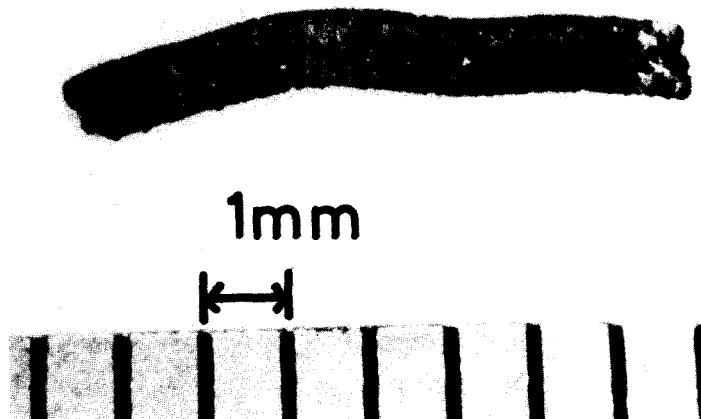


Fig. 1. Exfoliated graphite

TABLE 1

Lattice strain (η) and crystallite size (L_c) of natural and exfoliated graphites

Sample	d Spacing (002) / \AA	η	L_c (002) / \AA	L_c (004) / \AA
Natural graphite	3.35	0.0013	5000	2200
Exfoliated graphite	3.35	0.0037	1800	670

The apparatus used for kinetic study was a thermobalance specially designed for fluorine atmosphere [1]. The weight sensitive portion is a spring balance which is made so as to expand and contract according to the change in weight of a sample, and the expansion and contraction of the spring is detected by the differential transformer. A trace amount of hydrogen fluoride contained in fluorine gas was removed by sodium fluoride pellets heated at 100°C and liquid nitrogen trap. All the reactions were made under fluorine pressure of 200 mmHg for more several days after no weight increase had been detected.

The products were analyzed by X-ray diffractometry and elemental analysis.

RESULTS AND DISCUSSION

Reaction kinetics for the fluorination of exfoliated graphite

Fig.2 shows the weight increase of a sample as a function of reaction time. Weight increase was first observed at around 330°C, below which the reaction proceeded so slowly that no weight change was detected. The reaction of exfoliated graphite was much faster than that for natural graphite at 400°C. The times which were taken for complete fluorination of exfoliated graphite were 10 hours at 400°C and 80 hours at 335°C; whereas more than a hundred hours was necessary for the fluorination of natural graphite at 400°C.

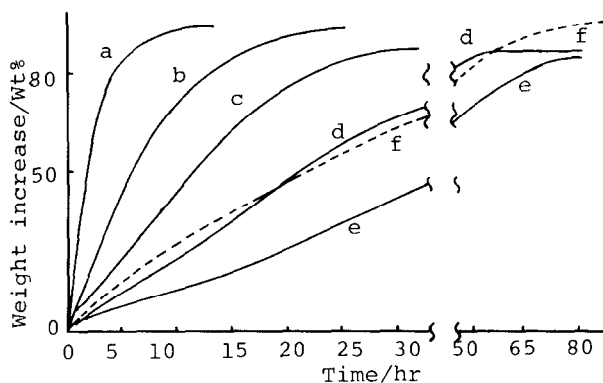


Fig. 2. Weight increase vs. time curves for fluorination of exfoliated (E.G.) and natural (N.G.) graphites

		(F ₂ pressure; 200mmHg)
a.	E.G.	400°C
b.	"	380
c.	"	360
d.	E.G.	347°C
e.	"	335
f.	N.G.	400

Fig.3 shows the Arrhenius plot obtained from the logarithm of reaction rate of exfoliated graphite vs. reciprocal temperature. From the gradient of this plot, the activation energy is calculated to be 35.6 Kcal/mol, which is approximately consistent with 37.7 Kcal/mol of the dissociation energy of fluorine molecule.

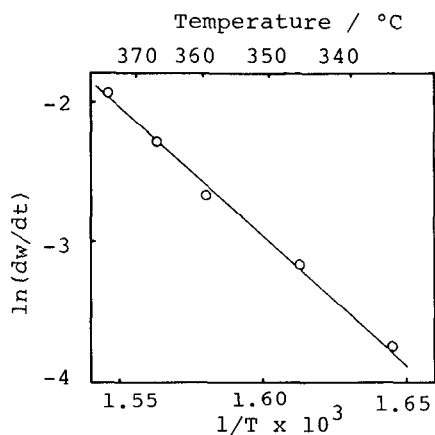


Fig. 3. Relation between logarithm of reaction rate and reciprocal temperature

The results were analysed by using Jander equation for the reaction of gas with solid [3]. There are two possible rate determining steps for the reaction. One is the diffusion of fluorine between graphite layers (equ.1) and another is the reaction of graphite with fluorine (equ.2) [3].

$$[1-(1-x)^{1/2}]^2 = k_1 t \quad (1)$$

$$[1-(1-x)^{1/2}] = k_2 t \quad (2)$$

x : ratio of reacted graphite to original one

$k_{1,2}$: reaction rate constant

t : reaction time

Plot of $\log[1-(1-x)^{1/2}]$ vs. $\log t$ gave the gradient of unity which means that the reaction rate of exfoliated graphite is controlled by the reaction of graphite with fluorine.

Analysis of the product

Fig.4 shows the interlayer spacing d_{001} and half width of 001 diffraction peak β_{001} of $(C_2F)_n$ produced from exfoliated graphite as a function of reaction temperature. The interlayer spacing of $(C_2F)_n$ and $(CF)_n$ are known to be about 9 and 6 Å, respectively [2]. Both of the interlayer spacing and half width decreased with decreasing temperature, which shows that the crystallinity and purity of the products become higher with

decreasing temperature. The amount of $(CF)_n$ mixed in a product increased with increasing temperature, especially over $380^\circ C$, where the interlayer spacing has a smaller value between 9 and 6 \AA , and the half width increases gradually having a maximum point because of the overlap of two peaks corresponding to $(C_2F)_n$ and $(CF)_n$ [2]. In fact, d_{001} was 7.82 \AA and β_{001} was 5.1° for a sample prepared at $480^\circ C$.

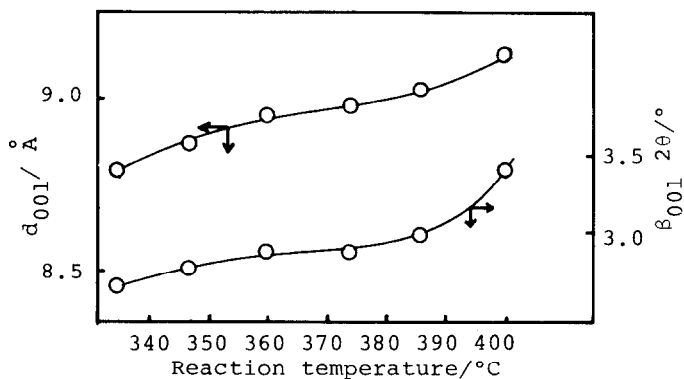


Fig. 4. Variation of d_{001} and β_{001} of graphite fluoride (F_2 pressure; 200mmHg)

Table 2 is the results of elemental analysis for fluorine and carbon, F/C ratios calculated from these values and the content of $(C_2F)_n$. The content of $(C_2F)_n$ was calculated on the assumption that the product contains only $(CF)_n$ as an impurity. By representing the amounts of $(C_2F)_n$ and $(CF)_n$ as x and $1-x$ respectively, F/C ratio is given by the following equation.

$$F / C = 1 - (1/2)x \quad (3)$$

It is known by ESCA measurement that $-CF_2$ and $-CF_3$ groups are formed on the surface of edge plane of graphite [2], and at the first stage of fluorination a thin film composed of $(CF)_n$ is prepared on the surface layer of a graphite sample, followed by the formation of $(C_2F)_n$ [2]. Since it is very difficult to obtain pure $(C_2F)_n$ without $(CF)_n$ or $-CF_2$ and $-CF_3$ groups, the F/C ratio of $(C_2F)_n$ is slightly larger than the theoretical value of 0.5. When the calculation of the purity was made, the presence of $-CF_2$ and $-CF_3$ groups was neglected, then the purity

TABLE 2

Composition, F/C ratios and $(C_2F)_n$ content in graphite fluoride prepared from exfoliated graphite

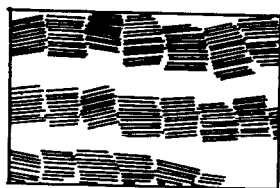
reaction temperature /°C	F/Wt%	C/Wt%	F/C ratio	$(C_2F)_n$ content /%
400	50.63	49.20	0.650	70
386	48.54	50.03	0.613	77
374	48.64	50.38	0.610	78
360	47.74	52.02	0.580	84
347	46.51	53.33	0.551	90
335	44.86	52.95	0.535	93
Natural graphite 400	50.00	48.57	0.650	70

of $(C_2F)_n$ should be slightly higher than the values listed in Table 2. It is also understandable from Table 2 that the fluorination has to be performed at temperatures between 335 and 370°C to prepare $(C_2F)_n$ with fairly high purity. This temperature range of 335-370°C is somewhat lower than that of 350-400°C for natural graphite.

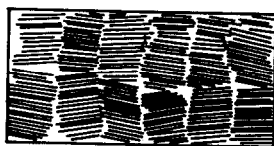
Graphite fluoride prepared at 347°C was treated at 600°C under fluorine atmosphere of 1 atm. Both of F/C ratio and peak position of 001 diffraction line were not changed after heat treatment. Only color was changed from black to white.

Difference in the reaction rates between exfoliated and natural graphite

There are two possible explanations for the result that the reaction rate is much faster for exfoliated graphite than for natural graphite. The arrangement of crystallite of both graphites is shown schematically in Fig.5a. As shown in the lattice strain and crystallite size in Table 1, exfoliated graphite is more expanded than natural graphite in the direction of C-axis, which enables it easier to supply fluorine gas to reaction interface through graphite particles. Another factor is the difference in the magnitude of stress applied to graphite network along C-axis. Fig.5b shows the illustration for the



Exfoliated graphite



Natural graphite

Fig.5a. Illustration of the crystallite arrangement of exfoliated graphite and natural graphite

graphite graphite fluoride

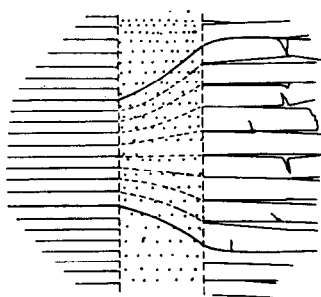


Fig.5b. Illustration of the fluorinated layers near the reaction interface

process of fluorination of graphite [4]. In order to make up a covalent bond between carbon and fluorine, graphite layers must be expanded by about 2.6 \AA in the direction of C-axis against the stress. Since the stress applied depends on the thickness of crystallite size (L_c) of each starting material, it is reasonable that exfoliated graphite is fluorinated more easily than natural graphite.

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