

Reaction of Fluorine and Carbon and Properties of Their Compounds

By

Noḡuatsu WATANABE*, Yoshiyuki KOYAMA, Atsuyoshi SHIBUYA
and Kiyoshi KUMON

As the compounds which react with carbon and fluorine possess extremely low surface energies, the formation of the compound on the surface of carbon electrode would cause high overpotential and finally anode effect in fluorine or aluminum cell. Their compounds having the atomic ratio of $C:F=1:1$ are white fine powders and have the properties of good water and oil repellency and lubrication. The present paper is concerned with the reactions of fluorine and six kinds of carbon materials and with the rate determining steps of their reactions. Their properties and structures were studied by means of thermogravimetric and differential thermal analysis, IR and NMR spectra, X-ray diffraction, and the measurements of specific gravity and surface area etc. From these results, there are new compounds containing fluorine atoms between the layers of carbon, where the fluorine atoms are strongly connected to the carbon atoms with covalent bonds, and are very stable to chemicals. Their decomposition temperatures depend upon carbon materials.

1. Introduction

In fluorine¹⁾ or aluminum cell²⁾ with carbon anode, the increase of anode potential in a given current density causes to form inactive materials on the anode surface, which decreases the wettability of the anode surface by electrolyte. The inactive materials³⁾ are graphite fluorides having the atomic ratio of $C:F=1:1$, which are very interesting and important to both fundamental and industrial fields. The compounds are white powders and have many interesting properties e.g. good water and oil repellency,⁴⁾ high lubrication,⁵⁾ and high resistance to most of chemicals and heat. The reactivity of fluorine and carbon and properties of the compounds depend upon carbon materials. As shown in Fig. 1, the compound was a better lubricant than graphite, molybden disulphide, and polytetrafluoroethylene.⁵⁾

In the present paper, the reactions of fluorine and six kinds of carbon materials, the rate determining steps of their reactions, the analysis of their structure, and some properties—decomposition temperature, specific gravity, surface area, lattice constant,

* Department of Industrial Chemistry

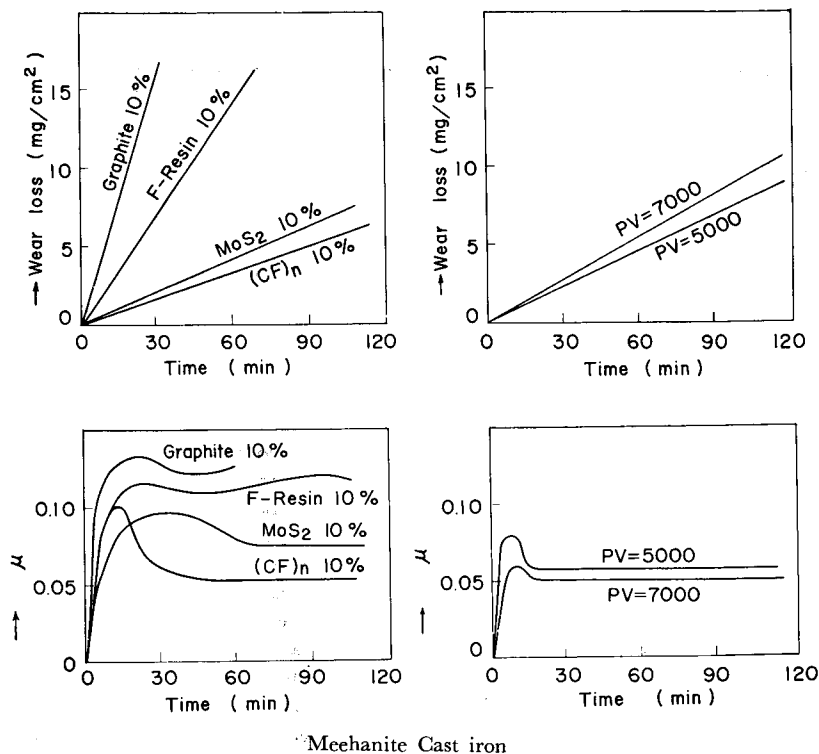


Fig. 1. Wear loss and coefficient of friction of four solid lubricants in phenol resin

and bond energy, etc., are reported by means of thermogravimetric and differential thermal analysis, IR and NMR spectra, X-ray diffractions etc.

2. Experiment

The reactor for the fluorination of carbon sample into which the purified fluorine gas was put through the copper pipe, was made of nickel. The reactor was heated by an electric furnace and the temperature was controlled by an automatic controller with thermocouple. When the reactor was heated to a desired temperature, the fluorine gas was introduced. Unreacted waste fluorine gas was induced to convert to hydrogen fluoride by burning with town gas.⁶⁾ The diluting gas of fluorine is nitrogen or argon. Following six kinds of materials of carbon were reduced to 200 mesh, dried at 120°C.

- A. GRAPHITE FIBER, which was prepared by carbonizing the acrylfiber at about 1500°C.
- B. PETROLEUM COKES, which were prepared by disposing the crude oil at about 1400°C.

C. WOOD CHARCOAL

D. BINDER CARBON, which was prepared by calcinating and carbonizing the mixture of the molasses and coaltar with weight ratio of 7:1 at 850°C.

E. CARBON BLACK, which was prepared by decomposing crude oil of good quality at about 1400°C with 30 atm. steam.

F. NATURAL GRAPHITE (Ceylone)

The degree of fluorination was determined by the increment weight before and after the reaction with fluorine (weight method) and by chemical analysis* of fluorine content in the fluorinated sample (chemical method).

The true specific gravities of carbon materials and fluorides were determined by means of pycnometer using n-butanol as an immersion fluid. The surface area was determined by the adsorption of the nitrogen molecular with B.E.T. method.

3. Results and Discussions

3.1 Some properties of carbon fluorides

The completely fluorinated carbon fluorides are white colored fine powder and their darkness increases with the decrease of the fluorine content. By photomicrographs, particles of them seem transparent (Photo. 2) when they are completely fluorinated, on the other hand, when they are incompletely fluorinated, outer parts of the particles are transparent, but the center of the particles still remains unreactedly black, as seen Photo. 1. All carbon fluorides have the properties of good water and oil repency, and good lubrication.

Some other properties of carbon materials and their fluorides are shown in Table 1.

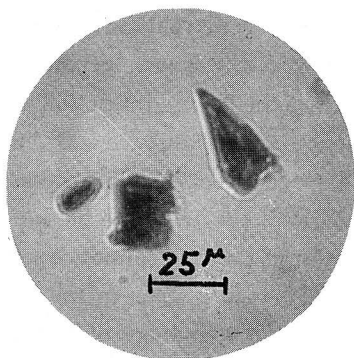


Photo. 1.

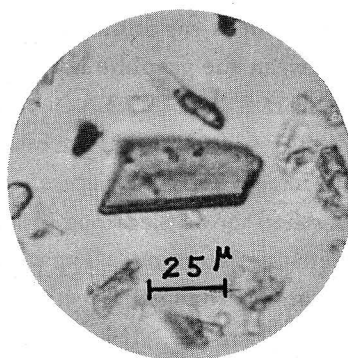


Photo. 2.

* The reaction products were mixed with potassium carbonate and decomposed at 700°C. The carbonate ion and potassium ion were removed and then the fluoride ion was titrated with 0.05 N $\text{Th}(\text{NO}_3)_4$ eq. solution using Alizaline red S as an indicator.

Table 1. Some properties of carbon materials and their fluorides

Material	Material				Fluoride			
	Data of X-ray		True specific gravity	Surface area	Atomic ratio (C:F)	True specific gravity	Surface area	Decomposition temperature
	Half value width	Lattice constant (C)						
Graphite fiber (A)	48	6.88 Å	1.67	2 m ² /g	1:0.96	2.52	340m ² /g	390°C
Petroleum cokes (B)	17	6.88	2.08	4	1:0.98	2.50	290	380
Wood charcoal (C)	—	—	1.68	225	1:0.91	2.35	176	333
Binder carbon (D)	740	7.09	1.64	72	1:0.92	2.34	180	320
Carbon black (E)	225	6.85	1.88	536	1:0.97	2.52	297	392
Natural graphite (F)	1	6.71	2.26	—	1:0.98	2.68	293	485

3.2 Structure of the fluorides

The fluorinated samples having the atomic ratio close to $C:F=1:1$ have the true specific gravities of 2.68 in graphite as seen in Table 1. Assuming that the specific gravity of $(CF)_n$, n is 2.68, graphite increases in volume by 6.28 cc/g. atom with introduction of 1 g. atom of fluorine atom into the graphite lattice. Assuming that this volume increase was due to the swelling of graphite only in the direction of c-axis, the spacing of graphite layers increased from 3.35 Å to 7.34 Å, and this value agreed with the X-ray diffraction data.⁷⁾ Therefore, it seems that the fluorine atoms enter between the graphite layers, and the spacings of the layers increase on the average from 3.35 Å to 7.3 Å in view of the fact that the X-ray diffraction patterns were diffusive, it seems that the increase in the spacing is not uniform and the layers come to have a zigzag structure. The infrared spectrum of graphite fluoride by nujol method shows the strong absorption ($1,215\text{ cm}^{-1}$) considered to be due to the $C-F$ stretching vibration. The stretching vibration of the compounds, having the fluorine atoms attached directly to benzene ring, mostly appear in the range of $1,100\sim 1,300\text{ cm}^{-1}$.⁸⁾ It is presumed that each carbon layer of graphite is a rigid body and each carbon atom is attached to a fluorine atom. Because each carbon layer has an infinite mass compared with a fluorine atom, it may be assumed that the layers are fixed and only the fluorine atoms vibrate with the frequency corresponding to $1,215\text{ cm}^{-1}$. On these assumptions the force constant of $C-F$ bond is

calculated to be $16.6 \text{ md}/\text{\AA}$. Thus the force constant of the stretching vibration of $C-F$ bond in CF_4 is $9.15 \text{ md}/\text{\AA}$. As it seems impossible that the $C-F$ bonds in graphite fluoride are stronger than those of CF_4 , it is presumed that the carbon atoms in graphite fluoride vibrate in zigzag structure like cyclohexane.

The NMR spectrum of F^{19} nucleus in graphite fluoride was compared with that of sodium fluoride and polytrifluorochloroethylene, which are the representative compounds having the fluorine atoms with ionic and covalent bonds, respectively. No definite differences between these spectra can be observed and therefore it is found that there are no fluorine molecules or weakly bonded fluorine atoms in graphite fluorides.

3.3 Calorimetric properties of the fluorides

When heated, the graphite fluoride suddenly decomposed at about 600°C by an exothermic disproportionation reaction into carbons and fluorocarbons of low molecular weight such as CF_4 , C_2F_6 , etc. The carbon is sooty and completely amorphous in view of X-ray diffraction. The results of D.T.A. and thermogravimetric analysis of the pyrolysis of graphite fluoride are shown in Figs. 2 and 3.

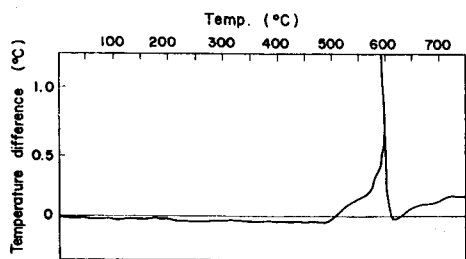


Fig. 2. D.T.A. curve of pyrolysis of graphite fluoride

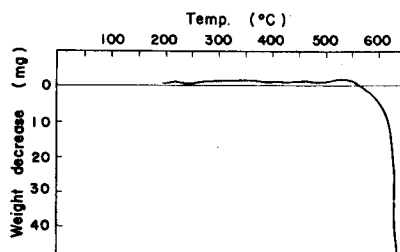
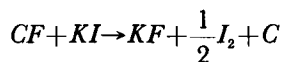


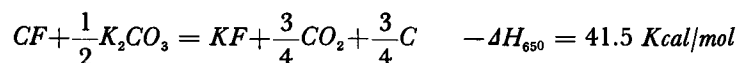
Fig. 3. Thermogravimetric curve of graphite fluoride pyrolysis

When graphite fluoride was heated with alkali halide such as KI , KBr , KCl , NaI , $NaBr$, and $NaCl$, it reacted with them to form halogen gases and alkali fluorides. For example, the reaction with potassium iodide occurs as the following exothermic reaction in the temperature range of $360\sim 500^\circ\text{C}$.



Graphite fluoride reacts with potassium carbonate to form KF and CO_2 .

The heat of the reaction was calculated from the peak area in D.T.A., compared with that of sodium nitrate fusion which occurred approximately at the same temperature (m.p. 310°C) as the reaction and of which latent heat was known (3.80 Kcal/mol).



The heat of formation of CF has been calculated from this heat of reaction.

	$-\Delta H_{298}$	$-\Delta H_{650}$
$CF + \frac{1}{2}K_2CO_3 = KF + \frac{3}{4}CO_2 + \frac{3}{4}C$	-----	41.5
$2K + C + \frac{3}{2}O_2 = K_2CO_3$	281.1	266.9
$K + \frac{1}{2}F_2 = KF$	134.5	135.1
$C + O_2 = CO_2$	94.2	94.5
$C + \frac{1}{2}F_2 = CF$		31.0

When graphite fluoride was heated to 450~500°C in hydrogen atmosphere, it formed carbon and hydrogen fluoride. Comparing the area of the peak of D.T.A. with that of fusion of potassium bichromate (m.p. 398°C), the heat of reduction was calculated by means of latent heat of fusion of potassium bichromate (8.5 Kcal/mol).



The heat of formation of CF was obtained from the equation as above.

	$-\Delta H_{298}$	$-\Delta H_{780}(\text{Kcal/mol})$
$CF + \frac{1}{2}H_2 = C + HF$	-----	16.3
$\frac{1}{2}H_2 + \frac{1}{2}F_2 = HF$	64.5	64.2
$C + \frac{1}{2}F_2 = CF$		47.9

With these values and dissociation energy of fluorine molecule, the



bond energy of $C-F$ in graphite fluoride was calculated, assuming that $C-C$ bond energy in graphite did not vary. The values of 68.5 and 85.4 Kcal/mol were obtained from the calculations. These values are relatively small compared with

the C-F bond energy of other fluorocarbon.

According to C.A. Coulson¹⁾ the C-C bond energy in the carbon network of graphite layers lies between those of benzen and single C-C bond, the order of bond is 1.53 and the bond energy is greater than single bond by 21.9 Kcal/mol. If the C-C bond of graphite becomes a single bond at the fluorination, the C-F bond energy of graphite fluoride would be larger by the energy change of C-C bond, and hence the above values would become 90.4 Kcal/mol and 107.3 Kcal/mol, respectively. The latter value agrees approximately with C-F bond energies of other fluorocarbon.

From these results it might be concluded that graphite fluoride has a structure in which a fluorine atom is connected strongly with covalent bond to each carbon atom linked together with single bonds to form hexagonal network, and the planes of the network are arranged in parallel with one another.

The bond energies of the other carbon fluorides seem to be smaller than those of graphite fluoride, but they are not determined.

3.4 Reactivities of carbon and fluorine

Six kinds of carbon materials in Table 1 were reacted in $\frac{1}{3}$ atm. of fluorine partial pressure for one hour. The relations between the degree of the fluorination of carbon and the reaction temperature are shown in Fig. 4. Each curve has a maximum value, temperature of which is called "maximum temperature". Fig. 4 shows the degree of the fluorination determined by chemical analysis with temperature. For graphite fiber, petroleum cokes and carbon black, the value of the maximum temperature by chemical analysis is the same as that from increment

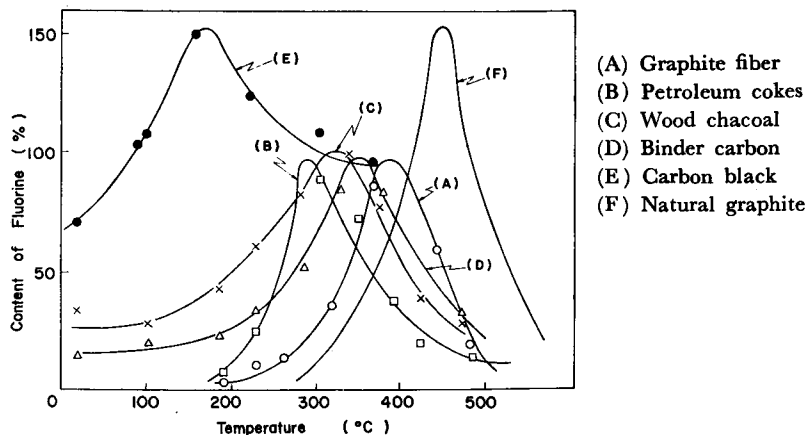


Fig. 4. Temperature dependence of fluorine content in some carbons
 F_2 press.; $1/3$ atm. Time; 1hr

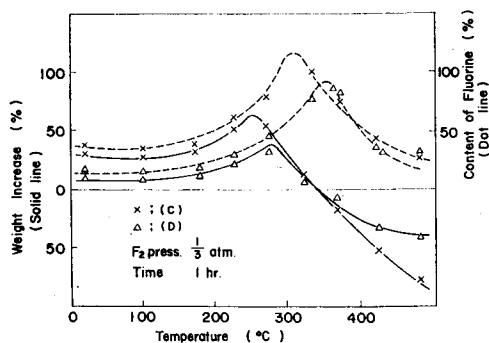


Fig. 5. Temperature dependence of fluorine content by chemical method and weight method

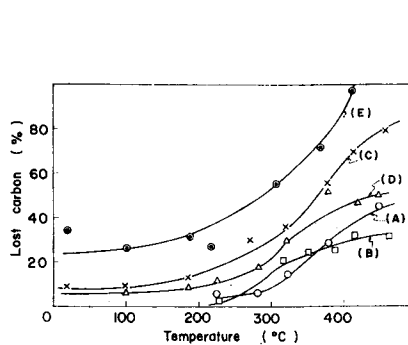


Fig. 6. Percentages of carbon

of sample weight by fluorination, but for wood charcoal and binder carbon, the former is different from the latter, as shown in Fig. 5. By chemical analysis, 260°C is obtained for wood charcoal, and 300°C for binder carbon, while 320°C is obtained for wood charcoal and 370°C for binder carbon by weight increment. 390°C is obtained for graphite fiber, 290°C for petroleum cokes, 190°C for carbon black, and 420°C for natural graphite by both methods.

Considering the difference between the content of fluorine in sample by weight increment and that by chemical analysis, the carbon materials may be burned down in the reaction with fluorine or by the decomposition of fluoride, to be lost.¹¹⁾ Amount of the lost carbon (by) temperature is shown in Fig. 6. The amount is constant in the region of low temperature, and suddenly increases near the maximum temperature of the weight method.

When the products, prepared at low temperature, from carbon black, wood charcoal, and binder carbon, which have large surface area, are reacted with potassium iodide solution, the iodine is isolated¹²⁾. The active fluorine adsorbed on carbon may oxidize iodides ion of potassium iodide. Fig. 7 shows the adsorbed fluorine calculated from the isolated iodine with the reaction temperature. In Fig. 8 their dependence on fluorine partial pressure and in Fig. 9 their reaction time are shown. In 1/3 atm. of fluorine partial pressure and at the temperature of 20°C, 32%, 38%, and 30% of total fluorine content are obtained as absorbed fluorine volumes of carbon black, wood charcoal, and binder carbon, respectively.

In X-ray diffraction patterns, the "half-value-width" means the values divided half width of peak by height, and it is compared with natural graphite. The maximum temperature may depend much more upon surface area than on crystallinity of carbon materials. The fluoride of wood charcoal and binder carbon would be different from the other three fluorides.

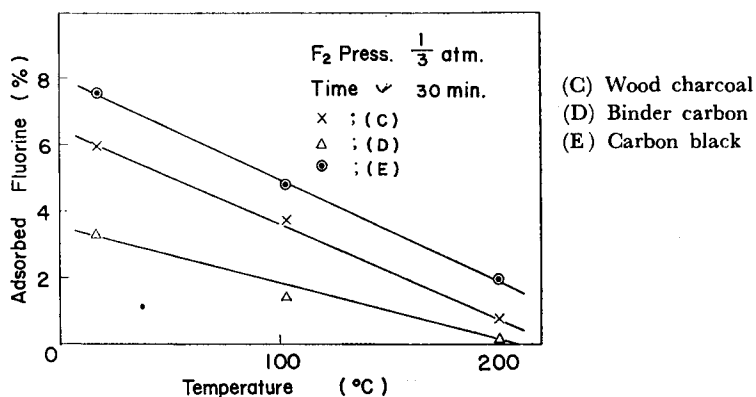


Fig. 7. The temperature dependence of adsorbed fluorine

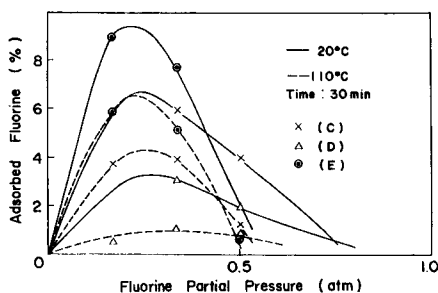


Fig. 8. Fluorine partial pressure dependence of adsorbed fluorine

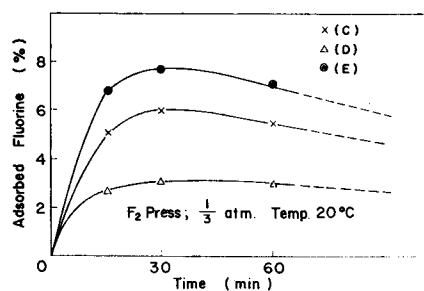


Fig. 9. Time dependence of adsorbed fluorine

3.5 The rate determining steps of graphite fluoride formation

The reactions of fluorine and graphite powder above 200 mesh is represented by wt% of fluorine absorbed in graphite powder; if graphite is completely changed into $(CF)_n$, the percentage of its increment weight is theoretically 158%.

The reactions are shown in Fig. 10 with the curves, plotted for temperature and fluorine pressure with time. In low fluorine pressure such as 0.2 atm., the graphite particles were only partially fluorinated even at the high temperature above 400°C. In high fluorine pressure, such as 0.8 atm., they were highly reacted and the reaction rate was much increased with temperature as shown in Fig. 11. At low temperature, such as 280°C, the larger particles gave the higher percentage of the increment weight. At 420°C, each percentage of the increment weight is almost the same independently of the particle size. At 450°C, the smaller particles gave the higher percentage.

Increment weight percentage in the reaction with diluting gases, argon and nitrogen gases, in the same fluorine partial pressure, are shown in Figs. 12 and 13. In dilution, fluorine partial pressure was arranged to be 0.2 atm., while the whole

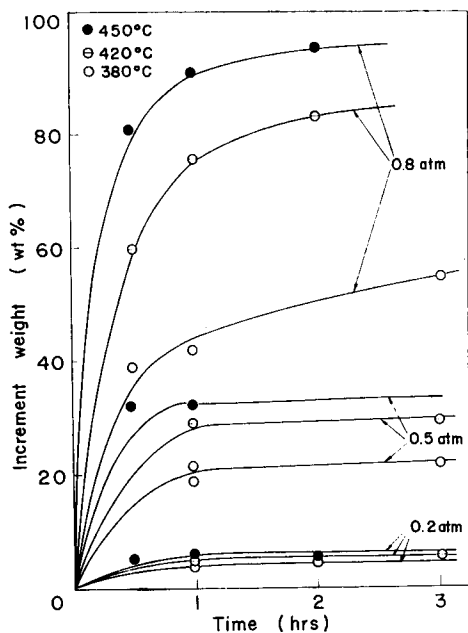


Fig. 10. Dependence of increment weight on fluorine pressure and reaction time

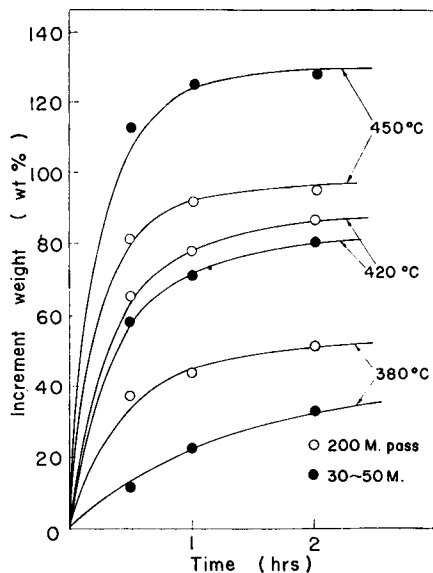


Fig. 11. Dependence of increment weight on particle size, temperature, and reaction time

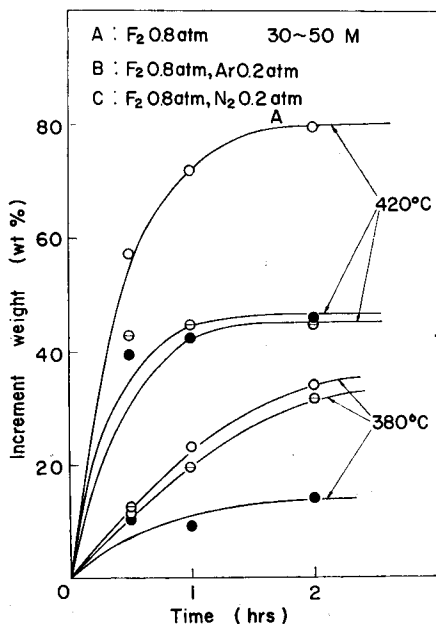


Fig. 12. Dependence of increment weight on temperature, kinds of diluting gas, and reaction time

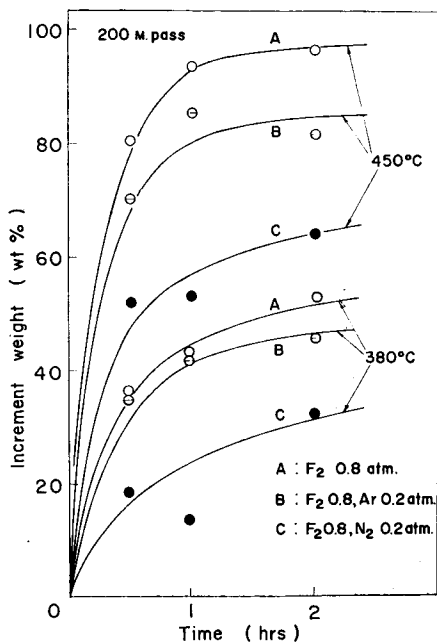


Fig. 13. Dependence of increment weight on temperature, kinds of diluting gas, and reaction time

pressure was kept to be 1 atm. The weight increment of graphite in the reaction with following gases of the same fluorine partial pressure are shown in Fig. 12.

Reaction gas A: Fluorine undiluted

B: Fluorine diluted with argon gas

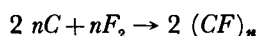
C: Fluorine diluted with nitrogen gas

At the same temperature, the percentage of graphite increment weight with A is the highest and that with C is the lowest. Each percentage of the weight has the same increasing tendency with temperature.

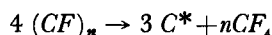
Relation between percentage of graphite increment weight and fluorine pressure was not linear. The higher pressure gave the higher increment weight percentage, as shown in Fig. 10. According to the figure, the following equation is obtained¹³⁾

$$\frac{dw}{dt} = KP^m$$

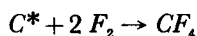
where, $\frac{dw}{dt}$ is reaction rate, P is fluorine pressure, K is constant value of reaction rate, m is reaction order, which was observed to be 1.6–2.0. Assuming that the reaction of fluorine and carbon is represented by the following equation:



The rate of reaction should be proportional to fluorine pressure, P , and the percentage of the increment weight should be linearly increased. Experimental value of m was 1.6–2.0, because CF_4 would be formed from a part of $(CF)_n$ in the following reaction:



Carbon C^* formed by the reaction is more active than graphite to react with fluorine, to form CF_4 .



By the reactions mentioned above, the mixing of CF_4 in the fluorine gas causes decrease in fluorine partial pressure.

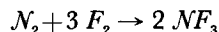
Rate of $(CF)_n$ formation reaction would not have linear relations with apparent fluorine pressure, because the above reactions proceed at the same time. The reaction rate would depend upon the particle size. In practice, the larger the surface area, the more successfully the reaction proceeds, the fluorine gas should be supplied to the particle surface as fast as the reaction proceeds, and so the following two steps would be considered to determine reaction rate.

- (A) Supplying of fluorine gas to the particles
- (B) Graphite fluoride formation reaction in the process of the reaction of graphite and fluorine

At low reaction temperature, the rate of the step (B) is slower than that of the step (A), therefore the step (B) determines the over-all reaction rate. The rate of step (B) is proportional to the surface area of graphite particles, so that the smaller particles make the over-all reaction proceed more rapidly.

At the higher reaction temperature, the rate of the step (B) becomes so rapid that the step (A) could not proceed without delay, and moreover, the rate of CF_4 formation is increased, so that fluorine partial pressure on the graphite particle surface is decreased, therefore, the step (A) determines the over-all reaction rate. The larger particles make fluorine diffusion through the particles proceed more readily. Therefore, the large particles make to over-all reaction proceed more rapidly.

Comparing the two diluting gases, argon gas gives higher percentage of graphite increment weight than nitrogen gas. This would be due to the following reaction:



Therefore, it would have to take account of the decrease of activity of fluorine.

4. Conclusion

The reactions of carbons and fluorine, and properties of the compounds were discussed. The reactivity and the properties depended upon original carbon materials. Each of the compounds has good water and oil repellency and lubrication.

Literature

- 1) N. Watanabe, M. Ishii and S. Yoshizawa: *Denkikagaku*, **29**, 492, 497 (1961), **30**, 171 (1962).
- 2) N. Watanabe and N. Ooba: *Denkikagaku*, **35**, 178 (1967).
- 3) O. Ruff and O. Bretschneider: *Z. anorg. allgem. Chem.* **217**, 1 (1934), W. Rudorff and G. Rudorff: *Z. anorg. allgem. Chem.* **253**, 281 (1947).
- 4) K. Horita and N. Watanabe: *Denkikagaku*, **37**, 848 (1969).
- 5) T. Ishikawa and T. Shimada: Fifth international fluorine symposium (Moscow) 1969.
- 6) S.G. Turnbull and A.F. Bennig, et. al.: *Ind. Eng. Chem.* **39**, 286 (1947).
- 7) N. Watanabe, Y. Koyama and S. Yoshizawa: *Denkikagaku*, **31**, 756 (1963).
- 8) H.W. Thompson and R.B. Temple: *J. Chem. Soc.*, **1948**, 1423, E.E. Ferguson and J.R. Nielson, et. al.: *J. Phys.* **31**, 1457 (1953).
- 9) G. Hergberg: "Infrared and Raman Spectra of Polyatomic Molecules", (1945), Van Nostrand, New York.
- 10) C.A. Coulson: *Proc. Roy. Soc.*, **A169**, 413 (1939).
- 11) A.K. Kuriakose and J.L. Margrave: *Inorg. Chem.*, **4**, 1639 (1965).
- 12) N. Watanabe and A. Shibuya: *Kogyo Kagaku Zasshi*, **71**, 963 (1968).
- 13) N. Watanabe and K. Kumon: *Denkikagaku*, **35**, 19 (1967).