CHEMISTRY LETTERS, pp. 1825-1828, 1986.

Preparation of Graphite Intercalation Compound of Titanium Fluoride in Fluorine Atmosphere

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Graphite intercalation compound(GIC) of titanium fluoride has been prepared in fluorine atmosphere. The GIC's prepared were mainly stage 2 compounds with repeat distance, 11.28-11.59 Å and composition, $C_{11-15}TiF_{4.5-6.2}$. ESCA spectrum indicates that intercalated TiF_6^{2-} anions are in bridged state.

Titanium tetrafluoride is intercalated in graphite only in oxidative atmosphere. Buscarlet et al.[1)] reported that stage 3, $C_{21}TiF_4$ was prepared at 300 °C under chlorine gas of 5-25 atm. However, in fluorine gas of 0.25-1 atm, a stage 2 compound has been easily synthesized. In this paper, we report the preparation, structure and electrical conductivity of GIC with titanium fluoride.

Host materials of GIC are highly oriented pyrolytic graphite(HOPG), natural graphite(NG) and pitch-based carbon fiber(PCF). Titanium fluoride is prepared by fluorinating Ti metal powder at 170-200 °C and successively supplied for the intercalation reaction in the same reactor. Preparation of GIC is as follows. Two nickel vessels containing graphite and Ti powder separately are put in the nickel reactor. After pumping at 200 °C, high purity fluorine gas(Daikin Kogyo Co., purity 99.4-99.7%, N_2 0.3-0.6%, HF<0.01%) is introduced into the reactor to 0.25-1 atm at 170-200 °C, and graphite is allowed to react with titanium fluoride in fluorine atmosphere. After 1-10 d, fluorine gas is replaced with nitrogen gas at the same reaction temperature, and GIC is obtained.

GIC's prepared are mainly stage 2 compounds with repeat distance, 11.28-11.5 Å and composition, $C_{11-15}TiF_{4.5-6.2}$. First stage compound had a repeat distance of 8.33 Å. The color of GIC is blue black or black. Table 1 shows the experimental conditions and analytical data of stage 2 compounds. The repeat distance along $\underline{c}$ axis(d_c) decreases with increasing fluorine pressure and also with increasing reaction time under same pressure. The number of y in C_xTiF_y is usually less than 6, having a trend to increase with increasing fluorine pressure. Figure 1 shows the ESCA spectra of C_xTiF_y prepared from HOPG. They were obtained by cleaving a HOPG sample with knife. It is noted that F_{1s} spectrum has two peaks at 684.8 eV and 683.2 eV corresponding to two kinds of ionic bondings, together with C_{1s} peak at 283.6 eV and Ti_{2p} peaks at 465.2 eV and 459.8 eV which are higher binding energies by more than 4 eV than those for metallic state. Two different ionic bonds shown by ESCA spectrum mean that intercalated titanium fluoride anion TiF_6^{2-} is in bridged state in which fluoride ion is bonded to two titanium cations.

Table 1. Analytical data of 2nd stage C_xTiF_y

Sample	Reaction conditions			d_c/Å	Composition	
	Temp /°C	P_{F_2}/atm	Time/h		a)	b)
PCF-1	200	1	28	11.28	—	—
NG-1	200	0.5	236	11.31	$C_{13.6}TiF_{6.01}$	—
NG-2	200	1	39	11.53	$C_{12.4}TiF_{6.24}$	—
NG-3	200	1	60	11.48	—	—
NG-4	170	1	162	11.45	$C_{12.5}TiF_{4.28}$	—
NG-5	170	0.5	57	11.40	$C_{13.8}TiF_{4.61}$	$C_{15.4}TiF_{5.15}$
NG-6	170	0.5	30	11.52	$C_{13.6}TiF_{4.90}$	$C_{14.5}TiF_{5.25}$
NG-7	170	0.25	52	11.59	$C_{10.5}TiF_{4.52}$	$C_{10.6}TiF_{4.52}$
NG-8	170	0.25	55	11.57	$C_{13.8}TiF_{5.17}$	$C_{12.3}TiF_{4.62}$

a) By elemental analyses of carbon and fluorine.

b) By elemental analyses of carbon, fluorine and titanium.

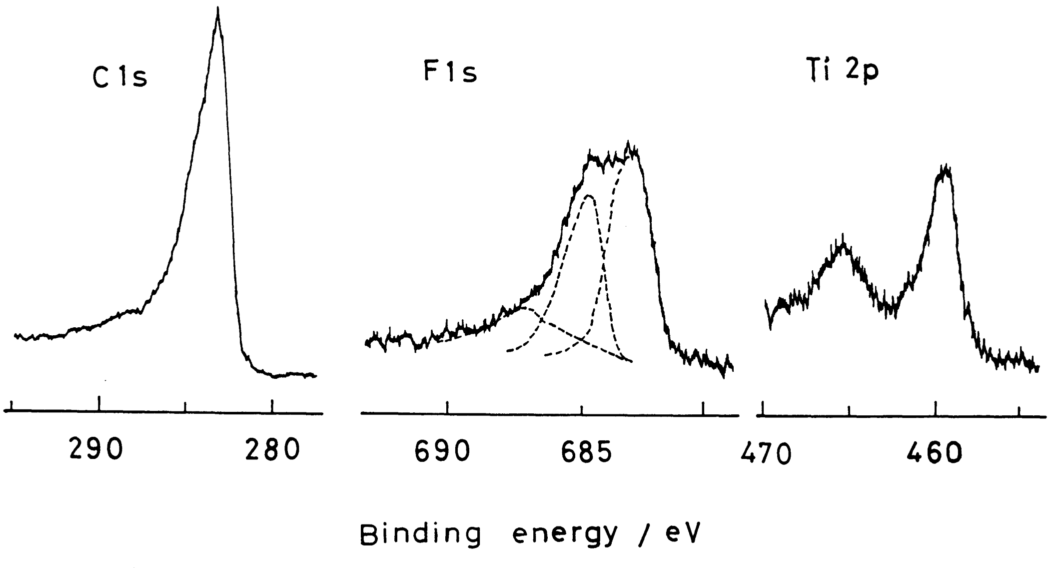

Fig.1. ESCA spectra of C_xTiF_y prepared from HOPG.

The F_{1s} peak at a lower energy position, 683.2 eV corresponding to a bridging fluorine and that at 684.8 eV a non-bridging fluorine. The latter is close to the position of F_{1s} peak of K_2TiF_6, 685.3 eV. This is consistent with that the number of y in C_xTiF_y is usually less than 6, namely around 5.

With increasing fluorine pressure, the bridged TiF_6^{2-} anions are expected to decrease, accompanied by increase in non-bridged TiF_6^{2-} anion. It was recently shown by Okino and Bartlett$^{2)}$ that an octahedral MF_6 anion is easily nestled into benzene ring of carbon layer. This effect brings about the decrease in d spacing along c axis by 0.2 Å. If close-packed fluoride ions of MF_6 between carbon layers are completely nestled into benzene rings of carbon layers above and below intercalated MF_6 anion, the decrease in d spacing is 0.4 Å. The experimental data in Table 1 indicate that the repeat distance(d_c) decreases by 0.3 Å with increasing fluorine pressure and with increasing reaction time. This shows that the nestling of fluoride ions with increase in the non-bridged TiF_6^{2-} anion.

Table 2 is the X-ray powder diffraction data for stage 2, C_xTiF_y. The most characteristic feature is that (100) diffraction line indicating the presence of superlattice is observed, and all (h00) and (hk0) lines are sharp. This corresponds to the high regularity in orientation of intercalated species between carbon layers, which would be brought about by the bridging of TiF_6^{2-} anions. On the other hand, (001) and (h01) lines are broad, indicating that stacking of carbon layer is somewhat disordered. This superlattice along ab axis is observed in all the samples , whose compositions are in the range of $C_{11-15}TiF_{4.5-5.2}$.

Figure 2 shows the structure model for C_xTiF_y. Large fluoride anions are oriented in close-packed octahedron between carbon layers and a small titanium cation occupies the center of the octahedron of fluoride ions. The orientation of fluoride ions would be responsible for the scattering of incident X-ray because the number of titanium ions is much smaller than that of fluoride ions. When most of intercalated TiF_6^{2-} anions are bridged in chain structure, there are still some vacant positions which are not occupied by fluoride and titanium ions. However, the vacant positions for fluoride ions are much fewer than those for titanium ions. This may be the reason why the superlattice is observed. With increasing fluorine pressure, the number of non-bridging TiF_6^{2-} anion increases and the nestling of TiF_6^{2-} anion occurs. The nestling is further facilitated with increasing reaction time. The stacking of carbon layer would therefore be A/BA/BA/B···(A,B: carbon layer, /: intercalate).

The in-plane electrical conductivity at 20 °C increases rapidly with increasing intercalate. The highest conductivity was obtained at a stage 3 compound $C_{27}TiF_5$, being 2.4×10^5 S cm^{-1} which is 13 times that of pristine HOPG(1.7×10^4 S cm^{-1}). Afterwards the conductivity gradually decreased. C_xTiF_y prepared from HOPG showed high stability in air. The electrical conductivity decreased from 2×10^5 S cm^{-1} to 1.5×10^5 S cm^{-1} in air during 50 d. It would be due to the slight exfoliation of HOPG sample by absorption of moisture. The (003) and (004) diffraction lines at 23.6° and 31.4° (by Cu Kα) for stage 2, C_xTiF_y were unchanged during 90 d.

Table 2. X-Ray powder diffraction data for 2nd stage C_xTiF_y

Peak	Intensity[a]	$1/d^2$ (obsd, $Å^{-2}$)	$1/d^2$ (calcd, $Å^{-2}$)	(hkl)
1	vw, br	0.0294	0.0301	002
2	vw	0.0557	0.0556	100
3	vs, br	0.0670	0.0678	003
4	vw, br	0.0815	0.0858	102
5	m, br	0.1221	0.1206	004
6	w	0.2236	0.2226	200
7	vvw	0.2339	0.2348	113
8	vw, br	0.2499	0.2527	202
9	vw, br	0.3046	0.2904	203
10	vvw, br	0.3247	0.3270	106
11	vvw, br	0.3722	0.3693	007
12	vw, br	0.4102	0.4110	205
13	vvw	0.4906	0.5008	300
14	m	0.6647	0.6677	220
15	vvw, br	0.7097	0.7049	208
16	vw	0.7526	0.7535	312
17	vvw	1.5435	1.5581	420

a) s:strong, m:medium, w:weak, v:very, br:broad

Hexagonal, a_0=4.89505, c_0=11.51887 Å.

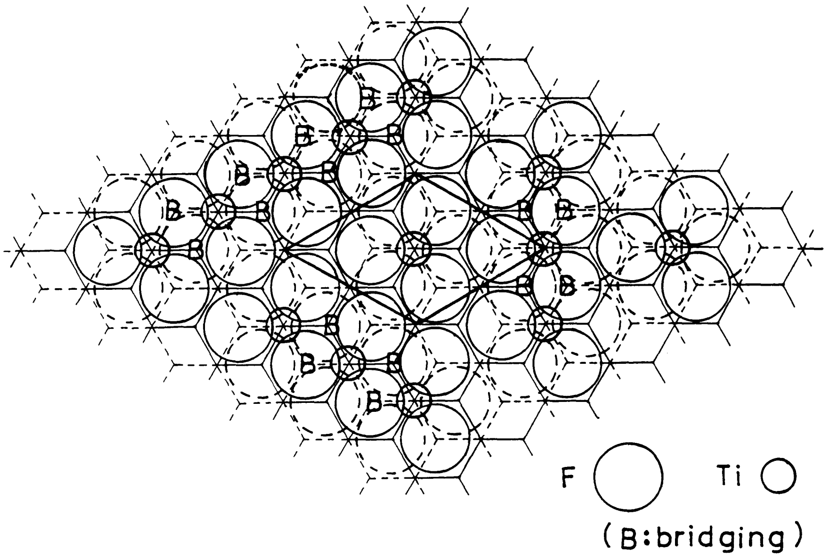

Fig.2. Structure model of C_xTiF_y -Bridging Model- .

References

1) E. Buscarlet, Ph. Touzain, and L. Bonnetain, Carbon, 14, 75(1976).

2) F. Okino, Ph.D. Thesis, University of California at Berkeley, U.S.A., 1984, Chap. 3.

(Received June 5, 1986)