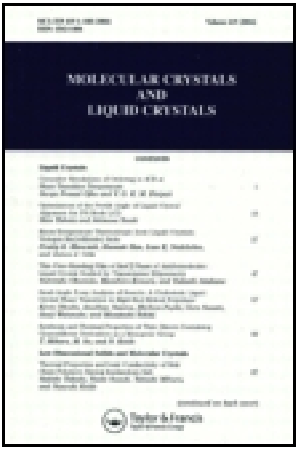

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FORMATION AND STRUCTURE OF TERNARY GRAPHITE INTERCALATION COMPOUNDS WITH TWO METAL CHLORIDES

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Abstract The formation processes of the "bi-intercalation" type compounds in the systems of $AlCl_3$-$FeCl_3$-graphite and $AlCl_3$-$CuCl_2$-graphite were studied by using three different reaction paths. By structural refinement the "mixed" type compounds were found to have more defective intercalate layers than the "bi-intercalation" type.

INTRODUCTION

Studies of graphite intercalation compounds(GIC's) with two different metal chlorides have been carried out by different authors[1-5]. These ternary GIC's can be divided into two types on the basis of the structure of the intercalate layers; "mixed" and "bi-intercalation" types. In the present work, the formation processes of the "bi-intercalation" type graphite intercalation compounds(GIC's) in the systems of $AlCl_3$-$FeCl_3$- and $AlCl_3$-$CuCl_2$-graphite were studied through different reaction paths and the crystallographic characterization was carried out on the GIC's obtained.

EXPERIMENTAL

Ternary $AlCl_3$-$FeCl_3$- and $AlCl_3$-$CuCl_2$-GIC's were synthesized through the following three reaction paths; 1) the reactions of the stage-1 $FeCl_3$-GIC and $CuCl_2$-GIC with $AlCl_3$, 2) the reactions of the stage-2 $FeCl_3$-GIC and $CuCl_2$-GIC with $AlCl_3$, and 3) the reactions of the host graphite with an equi-molar mixture of either $FeCl_3$ or $CuCl_2$ and $AlCl_3$. The host graphite used was a natural graphite powder with an average flake size of 400 µm.

The reaction was carried out in a sealed glass tube at 150°C. The weight change in the products was measured to determine the total amount of metal chlorides intercalated. On different flakes of the GIC's obtained, the atomic ratio of Al to either Fe or Cu was determined by energy dispersive X-ray spectroscopy (EDS). From these data, the relative concentrations of $AlCl_3$, $FeCl_3$ or $CuCl_2$ in the product GIC's were calculated. On cleaved surfaces of the reaction products, the line analyses of Al, Fe and Cu by EDS were also carried out, in order to know the distribution of the metals. The stage structure of the product GIC's were determined from X-ray powder patterns.

X-ray powder patterns over a wide range of l-indices of the GIC's were also measured using a step-scanning technique with a step-width of 0.02° in 2θ and an accumulation period of 10 sec. From the integrated intensities of the 00l lines, the structure amplitudes and then the distribution of charge density, $\rho(z)$, projected onto the c-axis were calculated by using the Fourier summation technique. The relative positions of the constituent atoms and their densities in the layer were determined by a procedure called pattern-fitting structure refinement[5].

RESULTS AND DISCUSSION

Reaction of Stage-1 GIC's with $AlCl_3$

In the reaction systems, the intercalation of $AlCl_3$ was reasonably supposed to proceed through the exchange of either $FeCl_3$ or $CuCl_2$ intercalated in the starting GIC's, because it was experimentally proved no de-intercalation of $FeCl_3$ and $CuCl_2$ from the starting stage-1 compounds at 150°C in the sealed tube. The weight contents of each metal chloride in the reaction products are plotted against heating time in Fig. 1a) and b).

The contents of $FeCl_3$ and $CuCl_2$ in the compounds decrease with the reaction time, in good correspondence to the increase in $AlCl_3$ content. The X-ray powder pattern showed that the stage-1 structure was retained during the whole reaction process and no occurrence of bi-intercalation in this system.

In Fig. 1, the de-intercalated amounts of $FeCl_3$ and $CuCl_2$ multiplied by 1.5 and 1.2, respectively, are plotted by cross marks for each reaction time. Good agreement between the values expressed by the cross marks and the experimentally determined amount of $AlCl_3$ makes it possible to estimate the amount of intercalated $AlCl_3$ through the exchange of the metal chlorides intercalated.

Reaction of Stage-2 GIC's with $AlCl_3$

The content of $AlCl_3$ in the products increases with heating time in the systems, as shown in Fig. 2a) and b). The measured $AlCl_3$ content can be divided into two components; $AlCl_3$ exchanged with intercalated $FeCl_3$ and $CuCl_2$, which can be estimated from the de-intercalated amounts of respective metal chloride on the basis of the result described above (the cross marks in the figure), and that intercalated into un-occupied galleries.

In the X-ray powder pattern of the products, new lines appeared, which could be indexed according to the structure of "bi-intercalation" type GIC's. Consequently, the intercalation of $AlCl_3$ into un-occupied graphite gallery proceeded, associated with the exchange of $FeCl_3$ and $CuCl_2$ in the starting stage-2 GIC flakes for $AlCl_3$. The main reaction products were the "bi-intercalation" type compounds.

Reaction of Graphite with Metal Chloride Mixture

In two systems, $AlCl_3$ was preferentially intercalated even during heating process up to 150^{o}C and so the "mixed" type GIC's were formed by co-intercalation of two chlorides. After the formation of a single phase with the stage-1 structure, the content of $AlCl_3$ started to decrease and those of $FeCl_3$ and $CuCl_2$ to increase with heating time, which was due to a gradual exchange of intercalated $AlCl_3$ for $FeCl_3$ and $CuCl_2$ through gaseous complexes. The formation of "mixed" type GIC's was proved by the X-ray powder patterns. However, the sample obtained after heating for 7 days revealed the segregation of this "mixed" type compound into a bi-phasic product which consisted of either stage-1 $FeCl_3$- or $CuCl_2$-GIC's and $AlCl_3$-GIC. In these systems, Al_2Cl_6, $FeAlCl_6$ and $CuAl_2Cl_8$ species seem to take part in the formation of ternary GIC's.

Crystallographic Characterization of Resulting GIC's

The charge density distributions along the c-axis was calculated on the "mixed" and "bi-intercalation" type compounds. For the "mixed" type GIC, the relative heights of the peaks in the charge density distribution were in good agreement with the coexistence of two metal chlorides in the same graphite gallery. For the "bi-intercalation" type GIC, on the other hand, the peak heights for each atom coincided with the "bi-intercalation" structure.

The relative positions for each atom and its relative atomic density as determined by the refinement procedure are summarized in Table 1, together with the over-all composition of GIC, reliability factor R of the calculated intensities from the observed ones and the effective Debye-Waller parameter B in the temperature factor. The refinements show that the atomic ratios of Cl/Al, Cl/Fe and Cl/Cu for each intercalate layers in the "bi-intercalation" types are approximately 3 and 2, respectively. On the other hand, both ratios Cl/Al and Cl/Fe for the "mixed" type $AlCl_3$-$FeCl_3$-GIC are 3.7, and the ratios Cl/Al and Cl/Cu for the "mixed" type $AlCl_3$-$CuCl_2$-GIC are 3.6 and 2.4, respectively. These results suggest the presence of a metal-deficient intercalate layer in these "mixed" type compounds.

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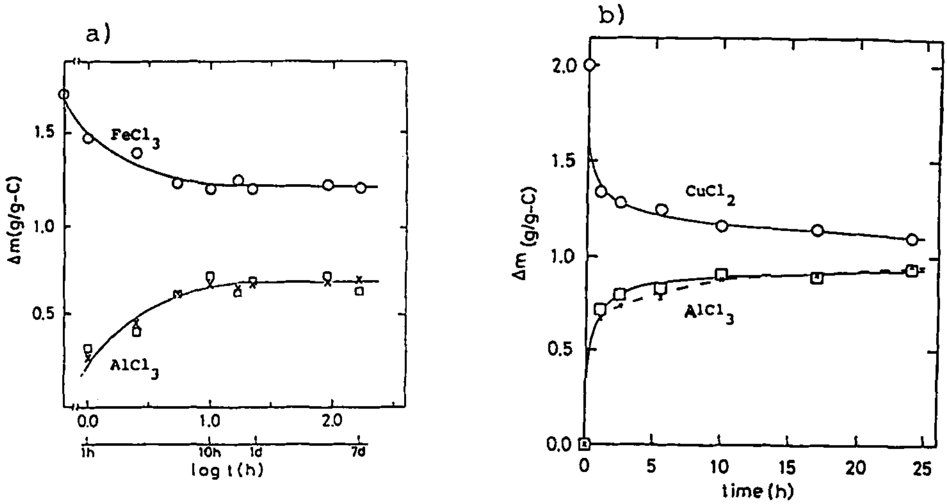

FIGURE 1 Changes of contents of metal chlorides in the products during the reaction between stage-1 GIC's and $AlCl_3$ at 150°C.

a) $AlCl_3$-$FeCl_3$-system, b) $AlCl_3$-$CuCl_2$-system.

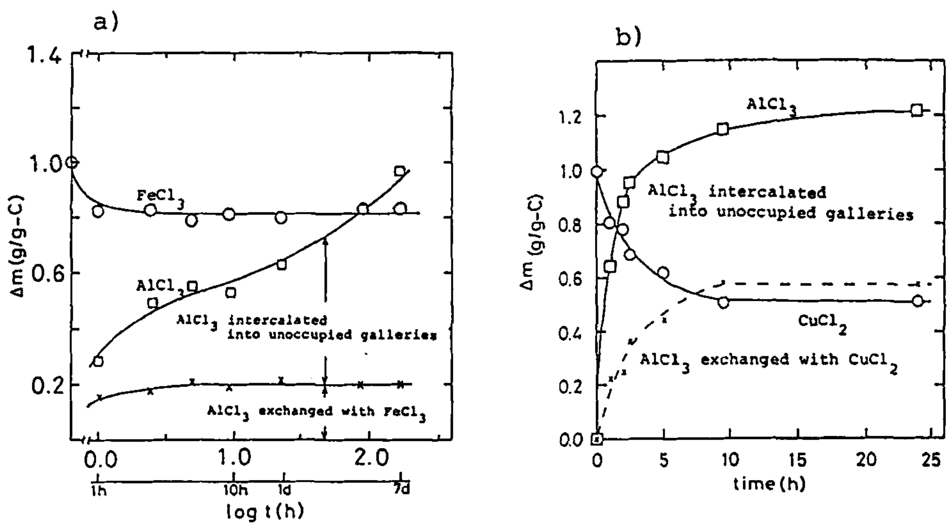

FIGURE 2 Changes of contents of metal chlorides in the products during the reaction between stage-2 GIC's and $AlCl_3$ at 150°C.

a) $AlCl_3$-$FeCl_3$-system, b) $AlCl_3$-$CuCl_2$-system.

Table 1 The refined structure parameters, relative position and density of atoms, derived by the pattern-fitting technique.

(a)"Mixed" type ternary GIC's

$AlCl_3$-$FeCl_3$-GIC

Atom	Relative position	Atomic density
C	1.000	4.00
Cl	0.661	1.59
Al+Fe	0.500	0.425[Al] +0.425[Fe]
Cl	0.339	1.59
C	0.000	4.00

Composition:
$C_{9.41}(AlCl_{3.74})_{0.50}(FeCl_{3.74})_{0.50}$
Reliability R = 6.8 %
Effective Debye-Waller parameter B = 10 Å^2

$AlCl_3$-$CuCl_2$-GIC

Atom	Relative position	Atomic density
C	1.000	3.60
Cl	0.647	1.42
Al+Cu	0.500	0.60[Al] +0.28[Cu]
Cl	0.351	1.42
C	0.000	3.60

$C_{8.52}(AlCl_{3.59})_{0.71}(CuCl_{2.38})_{0.29}$
R = 2.7 %
B = 9 Å^2

(b) "Bi-intercalation" type ternary GIC's

$AlCl_3$-$FeCl_3$-GIC

Atom	Relative position	Atomic density
Fe	1.000	0.235
Cl	0.930	0.705
C	0.752	3.10
Cl	0.573	0.795
Al	0.500	0.53
Cl	0.427	0.795
C	0.248	3.10
Cl	0.070	0.705
Fe	0.000	0.235

Composition:
$C_{6.20}(AlCl_{3.00})_{0.53}(FeCl_{3.00})_{0.47}$
Reliability R = 6.7 %
Effective Debye-Waller parameter B = 5 Å^2

$AlCl_3$-$CuCl_2$-GIC

Atom	Relative Position	Atomic density
Cu	1.000	0.270
Cl	0.925	0.540
C	0.751	2.95
Cl	0.578	0.720
Al	0.500	0.460
Cl	0.422	0.720
C	0.249	2.95
Cl	0.075	0.540
Cu	0.000	0.270

$C_{5.90}(AlCl_{3.13})_{0.46}(CuCl_{2.00})_{0.54}$
R = 12.6 %
B = 7 Å^2