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THE SYNTHESIS OF $NiCl_2$–$FeCl_3$–GRAPHITE INTERCALATION COMPOUNDS

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Abstract

$NiCl_2$–$FeCl_3$–graphite intercalation compounds have been synthesized by using mixtures of nickel chloride and ferric chloride. With $NiCl_2/FeCl_3$ molar ratios from 1/9 to 6/4, the stage one and stage two compounds were obtained at 400 °C in three days. The stage of the compounds obtained can be controlled by changing the starting graphite/chlorides ratio and also the $NiCl_2/FeCl_3$ ratio. The compounds obtained are very stable in air and even in water.

1. Introduction

The $CuCl_2$–KCl molten salt system has been used successfully to synthesize $CuCl_2$–graphite intercalation compounds (GICs) [1]. In the present work, the $NiCl_2$–$FeCl_3$ system was chosen to prepare acceptor-type compounds. The nickel chloride–graphite intercalation compound has attracted great interest because of its stability in air and also in different kinds of solvent, and it has been used as a cathode in a secondary battery [2, 3]. However, its synthesis required temperatures as high as 600 °C and a certain chlorine gas pressure. On the other hand, the $FeCl_3$–GIC has been studied for many years. Since the melting point of $FeCl_3$ is as low as 303 °C and the Cl_2 gas is given off by itself, the $FeCl_3$–GIC is prepared rather easily. This compound is reported to have relatively high electrical conductivity [4], but usually it is not very stable in air.

By using mixtures of $NiCl_2$ and $FeCl_3$, we have synthesized graphite intercalation compounds of $NiCl_2$ and $FeCl_3$ which are stable in air.

2. Experimental

Natural graphite powder with a particle size of 400 μm was used as the host graphite material. Anhydrous ferric chloride, nickel chloride and graphite powder were mixed in various proportions, graphite/chlorides = 3/1 - 6/1

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and $NiCl_2/FeCl_3$ = 1/9 - 6/4 in mole, and then sealed into a glass tube after drying under vacuum at about 125 °C for two hours. The reaction was carried out at 400 and 420 °C for three days. The reaction products were studied by X-ray diffractometry. X-ray microprobe analysis was also used to probe the distribution of Cl, Ni and Fe in the compound obtained.

3. Results and discussion

3.1. Formation of graphite intercalation compounds

By using a graphite/chlorides ratio of 3/1 and a $NiCl_2/FeCl_3$ ratio of 3/7, the stage one intercalation compound is obtained at 420 °C in three days, of which the X-ray powder pattern is shown in Fig. 1(a). The identity period along the *c*-axis, I_c, for the stage one compound was measured by referring to the internal standard of silicon as 0.946 nm, which agreed with the reported values on $FeCl_3$– [5] and $NiCl_2$–GICs [2]. From the X-ray microprobe analysis, both elements Ni and Fe were detected in the same flakes of the compounds obtained and were found to be distributed homogeneously in the compounds. Therefore, the compounds thus prepared are considered to be intercalation compounds of mixtures of $NiCl_2$ and $FeCl_3$ with graphite, *i.e.*, the $NiCl_2$ and $FeCl_3$ are mixed randomly on a microscopic level in the intercalate layer.

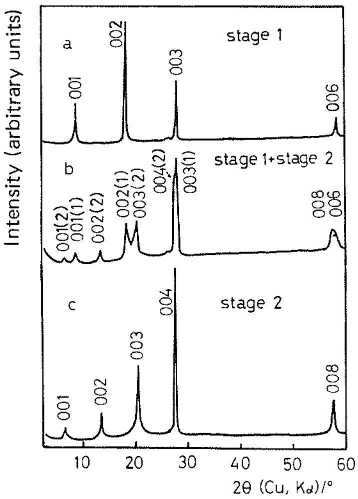

Fig. 1. X-ray powder patterns of the graphite intercalation compounds prepared at 420 °C in three days by using chloride mixtures with different $NiCl_2/FeCl_3$ ratios and the same graphite/chlorides ratio of 3/1. (a) $NiCl_2/FeCl_3$ = 3/7; (b) 5/5; (c) 6/4.

By keeping the starting ratio of graphite/chlorides at 3/1, compounds were synthesized at 420 °C with various $NiCl_2/FeCl_3$ ratios from 1/9 to 6/4. In the cases of 1/9, 2/8 and 3/7, all the products were a single phase of the stage one compound, while a mixture of the stage one and two compounds

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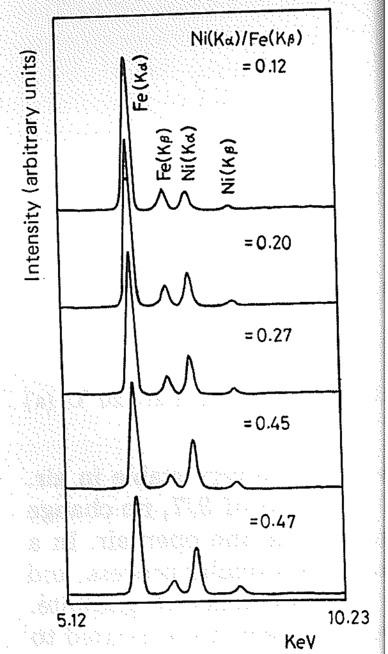

Fig. 2. Energy dispersion spectra
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was obtained in the case of 5/5, and a single phase of stage two in the case of 6/4. The powder patterns of the compounds obtained with the ratios 3/7, 5/5 and 6/4 are shown in Fig. 1. The broad $00l$ peaks of most compounds of the mixtures of different stages, as shown in Fig. 1(b), suggest the existence of stage disorder. On the other hand, the compounds obtained as a single stage usually show sharp $00l$ peaks, whose widths are comparable with instrumental broadening, as shown in Fig. 1(a) and (c).

The reaction at 400 °C with the graphite/chlorides ratio of 4/1 gave a single phase of the stage one compound, but the ratio 6/1 led to a mixture of the stage two compound with a small amount of stage one when the $NiCl_2/FeCl_3$ ratio was kept at 3/7. These results show that both the graphite/chlorides and $NiCl_2/FeCl_3$ ratios have a strong influence on the stage of intercalation compounds obtained.

Other factors such as reaction temperature are also considered to be important for controlling the stage. One of the advantages of the present molten salt method is synthesis at a low temperature in a short period; however, the effect of reaction temperature on the stage of the resultant GICs was not studied.

Energy dispersion spectra were measured on a flake of the compounds prepared with different starting $NiCl_2/FeCl_3$ ratios from 1/9 to 6/4. The relative intensity of the Kα line of Ni to that of Fe in the GIC increases with the increase in the starting $NiCl_2/FeCl_3$ ratio, as shown in Fig. 2. Thus, by

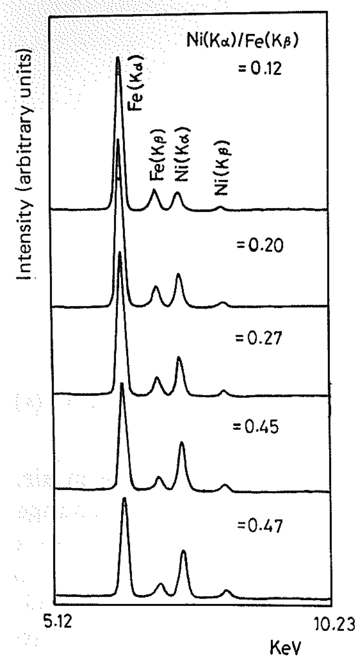

Fig. 2. Energy dispersion spectra on the intercalation compounds prepared from different $NiCl_2/FeCl_3$ ratios. (a) 1/9; (b) 2/8; (c) 3/7; (d) 5/5 and (e) 6/4.

changing the starting ratio of $NiCl_2/FeCl_3$, the composition of the intercalated chlorides also changes.

The present result indicates that $NiCl_2$ can intercalate into graphite together with $FeCl_3$ at as low a temperature as 400 °C. In order to intercalate the $NiCl_2$ alone into graphite, a temperature of 600 °C and more than 600 Torr of Cl_2 gas pressure were necessary [2]. In the present system, $FeCl_3$ lowers the melting point of the system and also gives off Cl_2 gas by its decomposition. Therefore, it may be possible to prepare at low temperatures compounds in which $NiCl_2$ occupies a large percentage in the intercalates by adding a small amount of $FeCl_3$.

3.2. Stability of the compounds

After reaction, the unreacted chlorides were washed out by cold water. In most cases, an appreciable decomposition of the compounds was not detected from the X-ray powder patterns. When washed by boiling water, however, the amount of stage two compound relative to stage one seems to increase, as shown in Fig. 3. It was not clear whether this was caused by the decomposition of the stage one compound to stage two or from inhomogeneity of the mixture of the compounds with two different stages. Nevertheless, the 002 line of the graphite was not detected, as can be seen from Fig. 3.

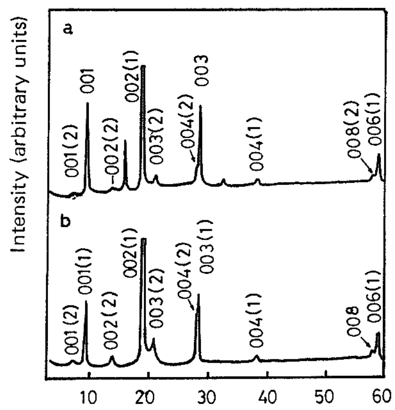

Fig. 3. X-ray powder patterns of the sample formed with $NiCl_2/FeCl_3$ = 2/8 at 420 °C. (a) Before washing and (b) after washing in boiling water.

The compounds prepared in the present work were very stable in air. On the sample obtained with a starting $NiCl_2/FeCl_3$ ratio of 3/7, no change in the powder pattern was observed after two months in the open air. In a previous paper, air-stable $CuCl_2$–GICs were prepared by a similar process, and their high stability was supposed to be due to the coexistence of graphite. However, the high stability of the present compounds seems to be related to the presence of $NiCl_2$. The stability mechanism of the compounds containing $NiCl_2$ must be studied in detail.

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