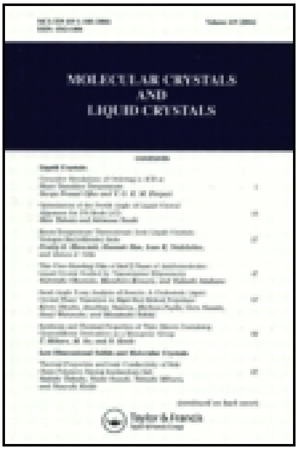
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STUDY OF THE COINTERCALATION OF MAGNESIUM AND COBALT CHLORIDES INTO GRAPHITE

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Abstract The intercalation of magnesium chloride into graphite has been studied as a function of the temperature, in the presence of a chlorine gas. The second stage compound has been obtained at 580°C, the average formula of which is C_9MgCl_2. By cointercalation of $MgCl_2$ and $CoCl_2$, at 600°C, $MgCl_2/CoCl_2$ *ratio equal to* 4.5 *and* during ten days, the first stage compound $C_{5.65}(MgCl_2)_{0.97}(CoCl_2)_{0.03}$ has been obtained. It only contains traces of $CoCl_2$. A theoretical mechanism of this cointercalation is proposed.

INTRODUCTION

Metal halides which are relatively non volatile require higher temperatures and longer reaction times than metal chlorides with high vapour pressure. It is the case with magnesium chloride which is intercalated into graphite in a second stage at about 600°C over a five days period.[1]

It is well known that the apparent volatility of some metal chlorides is increased by the addition of a complexing halide which has the property of generating volatile halide complex species .[2-4]

In order to increase the magnesium chloride content in the GICs, we have decided to intercalate $MgCl_2$ in the presence of $CoCl_2$ which respects several properties :

- easy first stage intercalation compounds when it is used alone at 550°C,
- higher volatility than magnesium chloride,
- finally, about the future application (thermal energy storage), cobalt chloride is not hygroscopic, and its Clapeyron *curve for the ammonia reaction* is close to the $MgCl_2$ one.

After a short recall of experimental conditions for preparing binary GIC-$MgCl_2$, we shall report and discuss here the conditions in which ternary GICs $MgCl_2$-$CoCl_2$ have been prepared.

EXPERIMENTAL

a) Binary $MgCl_2$-GIC

Magnesium chloride intercalation into graphite has already been reported [5-7] A $C_{11}MgCl_2$ first stage compound has been obtained by heating a mixture of graphite powder and dehydrated $MgCl_2$ over a ten days period at 420°C. We have adopted this procedure; but instead of a sealed tube, we have used a quartz non sealed one, crossed by a flow of chlorine gas. Anhydrous magnesium chloride (98%) and Madagascar natural graphite powder (granulommetry Ø < 40µm) have been mixed in a 1:6 molar ratio and redehydrated at 200°C in a stream of nitrogen, then of chlorine during 12 hours. In order to find the optimum intercalation temperature, the reaction has been carried out at different temperatures in 400-700°C range, over seven days; then, to remove the metal chloride excess, the samples have been washed with ethanol. X-ray diffraction, chemical analysis and thermogravimetry have been used for the sample characterization.

b) Ternary $MgCl_2$-$CoCl_2$-GIC

In order to obtain the first stage compound of $MgCl_2$-GICs, powders of $CoCl_2$, $MgCl_2$ and graphite have been mixed in several ratios and then heated at different temperatures to obtain compounds in which $CoCl_2/MgCl_2$ ratio will be minimum.

RESULTS AND DISCUSSION

a) Binary $MgCl_2$-GIC

1) Reaction temperature

In the 400-450°C temperature range and over a period of two weeks, the second stage compound has been only achieved. The $MgCl_2$ richest compound has been obtained at around 580°C [1]. The crystallographic I_c parameter is 12.82 ± 0.03 Å, and the average composition is $C_{9\ 0.5}MgCl_2$ close to the theoretical crystallographic composition $C_{8.8}MgCl_2$.

2) Reaction time

Chemical analyses within different reaction times, show that only six hours are needed for the intercalation of 85% of the total $MgCl_2$ necessary to prepare the second stage compound [1]. The magnesium chloride content in the GICs is higher at 580°C than at 600°C, because of the thermodynamical limit which is higher at 580°C than at 600°C. The reaction is complete after five days.

The magnesium chloride content in C_9MgCl_2 obtained here was not high enough to allow the chemical storage of thermal energy. Then, we have proceeded via the cointercalation of $MgCl_2$ and $CoCl_2$ into graphite.

b) Ternary $MgCl_2$-$CoCl_2$-GIC

The influence of several parameters : temperature of intercalation, $MgCl_2/CoCl_2$ ratio, reaction time.... have been studied.

1) Influence of the $MgCl_2/CoCl_2$ ratio

The reaction duration has been set to four days, the temperature at 580°C and the initial chlorides ratio varied in the 1-8 range. Figure 1a shows the variation of $MgCl_2$ molar percentage as a function of the $MgCl_2/CoCl_2$ ratio. One can notice that $MgCl_2$ content is increased with this ratio, and the GIC stage also depends of it (figure 1b) : the stage 1 compounds are only obtained for $MgCl_2/CoCl_2$ values in the 1-5 range. Thus, we decided to keep this ratio between 4 and 5 in order to obtain the first stage compounds containing more $MgCl_2$ and chose to work above and below 580°C for a few days.

2) Reaction at a temperature below 580°C

Mixtures of $MgCl_2$ and $CoCl_2$ ($MgCl_2/CoCl_2$ = 4) have been mixed with natural graphite in a chlorine atmosphere and heated at 570°C for four days. Figure 2a shows that 72% of the total chloride intercalated are $CoCl_2$ at the beginning of the reaction. The $CoCl_2$ content decreases while $MgCl_2$ content increases in the GICs. The richest compound obtained after four days has the average formula of $C_{6.72}(MgCl_2)_{0.5}(CoCl_2)_{0.5}$.

3) Reaction at a temperature above 580°C

We hoped to increase the $MgCl_2$ content in the first stage compounds obtained for the $MgCl_2/CoCl_2$ ratio equal to 4.5 by increasing the temperature at 585 and 600°C, and the time reaction to ten days. Figure 2b shows the $MgCl_2/(MgCl_2+CoCl_2)$ and $CoCl_2/(MgCl_2+CoCl_2)$ molar percentages obtained from chemical analyses, in the GICs prepared at 585°C. One can observe that $CoCl_2$ which is the most volatile chloride intercalates into the graphite better than $MgCl_2$ during the reaction first hours; but the $CoCl_2$ content decreases while the $MgCl_2$ content increases with time. In a ten days period, the first stage compound $C_{5.81}(MgCl_2)_{0.65}(CoCl_2)_{0.35}$ has been obtained. Figure 2c shows the molar percentages in the GICs prepared at 600°C. More than 75% of the metal chloride intercalated during the reaction first hours are $MgCl_2$. The $CoCl_2$ content intercalated into graphite in these conditions is low, and the average formula is $C_{5.65}(MgCl_2)_{0.97}(CoCl_2)_{0.03}$. Finally, these last conditions are the best ones to prepare the first stage $MgCl_2$-GICs.

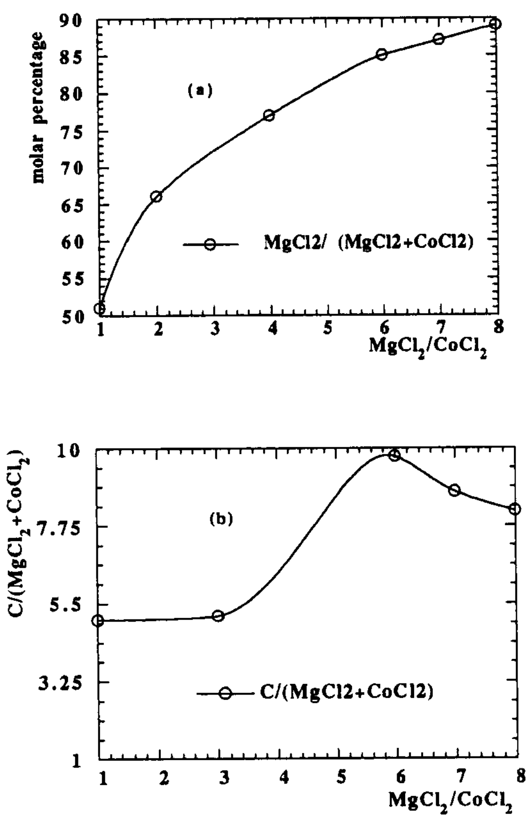

Figure 1a Evolution of the molar ratio in the GIC as function of the initial $MgCl_2/CoCl_2$ ratio.

b Evolution of n = $C/(MgCl_2+CoCl_2)$ molar ratio as a function of the initial $MgCl_2/CoCl_2$ ratio. (n = 5 ; 1st stage, n = 8-9 ; 2nd stage)

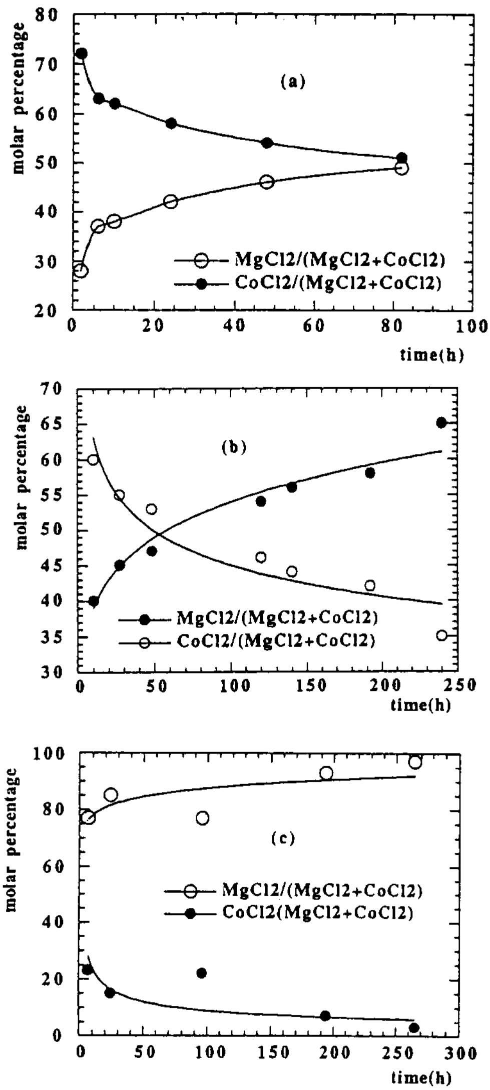

Figure 2 Evolution of the metal chlorides molar ratio as a function of the reaction time in the GICs prepared at :

a : 570°C, b : 585°C, c = 600°C.

4) Reaction mechanism

The reaction mechanism consists of two steps : $CoCl_2$ is first intercalated in stage 1, while the second step consists of the desintercalation of $CoCl_2$ and the intercalation of $MgCl_2$ in stage 1 according to :

$$\langle C_nCoCl_2\rangle + [MgCl_2] \rightleftharpoons \langle C_nMgCl_2\rangle + [CoCl_2]$$

The enthalpy of this exchange reaction has been estimated at -28kJ.

CONCLUSION

Results of our work have shown that compound of stage 2 (C_9MgCl_2) richer than the one which is reported in the literature ($C_{11}MgCl_2$) can be prepared at 580°C over a five days period.

At 600°C, mixtures of $CoCl_2$ and $MgCl_2$ in a ratio equal to 4.5 give a cointercalation compound of stage 1 with a crystallographic parameter I_c equal to 9.51Å, which contains only traces of cobalt. The richest compound average formula prepared in these conditions is $C_{5.65}(MgCl_2)_{0.97}(CoCl_2)_{0.03}$.

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