

Characterization of CuCl_2 Intercalated Graphite Powders by Thermal Analysis and X-Ray Diffraction

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Introduction

There has been an increasing interest recently in the possibility of using intercalated graphite in practical applications due to its enhanced electrical conductivity and lubricity when compared to the unintercalated material. Recent reports^{1,2} have examined some of the opportunities and problems for various applications of intercalated graphite fibers as conductors and within composites.

To date, no one has reported on the opportunities and problems presented by intercalated graphite in the powder or flake form. Intercalated powders offer opportunities in such areas as conductive coatings, screenable and printable inks, conducting filler for plastics, and lubricants^{3,4}, among others.

Consequently, we have examined CuCl_2 intercalated graphite powders by x-ray powder diffraction, thermal gravimetry (TGA), and differential scanning calorimetry (DSC) with an eye to their suitability as engineering materials in a commercial environment.

Experimental

Natural, high purity (>99% carbon), graphite flake (100-300 microns), of Indian origin was intercalated with commercial grade CuCl_2 in an overpressure of Cl_2 to obtain uniformly staged compounds. The CuCl_2 intercalated compounds were characterized as stages I, II, III, or IV in a powder diffractometer using CuK_α radiation ($\lambda = 1.541 \text{ \AA}$).

Thermal stability was measured for each stage compound (fig 1) using a TGA scanned from room temperature to $\sim 1050^\circ\text{C}$ at $10^\circ\text{C}/\text{min}$ in a dry Ar or N_2 stream in platinum pans.

A DSC scan was run on stage II material as a check against the less sensitive thermal response of the TGA and to monitor the thermodynamics. To eliminate interference from reactions between any chlorine released and the DSC cell, gold pans were used.

Results

The x-ray characterization of the CuCl intercalated powders shows them to be uniformly staged with a small amount of graphite 002 showing at $\sim 26.6^\circ$ in the stages II, III, and IV.

Stoichiometry was calculated from the subsequent weight loss data (Table 1) and compared to previous reports^{5,6,7,8} and that of a unit cell analysis (our thanks to R. Wachnik for this calculation).

The TGA de-intercalation behavior of all samples was qualitatively similar, differing primarily in the total quantity of CuCl_2 lost. Fig 1 shows both weight loss as a function of temperature with the derivative curve showing the rate of weight loss as a function of temperature, both for the stage II compound. The five distinct weight loss regimes designated 1-5 are observed in all stages. Regime 1 is due to absorbed water and is variable. The total weight loss recorded up to 1000°C (excluding regime 1) in stages I through IV are 60%, 50%, 42%, and 33% respectively. De-intercalation of CuCl_2 appears qualitatively similar to evaporation of pure CuCl_2 . All stages appeared stable to temperatures in excess of 200°C . This compares favorably with previous TGA work with the metal chlorides⁹.

DSC results were in good agreement with the TGA results (fig 2) for a sample of stage II material. Endothermic peaks can be observed for regimes 1-5 with heat absorption maxima occurring at 60°C , 280°C , 450°C , 510°C , and 680°C respectively. These values are believed more accurate than those derived from the TGA, in which greater thermal lags are experienced due to slower heat transfer.

In addition to regimes 1-5, a sharp endothermic transition is observed at 400°C for which there is no corresponding weight loss. This implies a phase transition within the intercalate layer. A small endotherm at this temperature can be observed in pure CuCl_2 but in the intercalate it is much larger and increases in value on going from stage IV to stage I. In the TGA the behavior of the high temperature regime at 700°C is also significant in that the absolute magnitude of this weight loss (%) decreases on going from stage IV to stage I, 5%, 3.5%, 3.5%, 1.2%, respectively, and appears to be inversely related to the phase transition at 400°C .

Discussion

The fact that a small graphite peak remains in the x-ray patterns of stages II through IV supports the stoichiometric calculations from the TGA weight loss data (Table 1) in that it shows that the compounds are generally dilute when compared to some previously reported values.

Based on a unit cell analysis, stage I has a formula of $\text{C}_{4.5}\text{CuCl}_2$. If this is indeed the correct stoichiometry then the fractional filling of the galleries obtained from total weight loss are 0.6, 0.81, 0.94, and 0.80 for stages I through IV.

Preliminary powder density determination agrees with this stoichiometry. It is possible that the regime at 700°C is associated with the fraction of the intercalated layer which is ionized, i.e. CuCl_3^- . If so, the fractional ionization in each stage will be proportional to this weight loss and is 0.02, 0.07, 0.08, and 0.15 in stages I through IV. According to Wertheim^{10,11} and Flandrois¹², transition metal chlorides form islands bounded by ionized states. Our results imply that as a stage number increases the island diameter decreases. If this is true, then the variation in magnitude of the phase transition at 400°C may be inversely proportional to the extent of fractional ionization. The smaller the island, the lower the probability of the phase transition taking place in the neutral CuCl_2 phase within the island.

The fractional ionization estimated from the high temperature weight loss data are in qualitative agreement with conductivity measurements. Stage I conductivity is several times lower than stage II or III which are of similar magnitude. The apparent low levels of ionization in stages II and III, 0.07-0.08, are also consistent with the fact that CuCl_2 intercalated graphite has a conductivity approximately three times lower than in AsF_5 intercalated graphite¹³.

Our conductivity values for CuCl_2 intercalated graphite compare favorably with previously reported values for other intercalated metal chlorides^{14,15}. In addition, these fractional ionization values are consistent with conductivities one might expect based on the work by Moran, et al.,¹⁶. Further experiments are in progress to verify these proposals.

Conclusions

DSC and TGA coupled with x-ray diffraction appears to be a powerful combination of techniques which, in conjunction with other physical measurements, may lead to a better understanding of the processes occurring in transition metal chloride intercalated graphites. Further, the stability exhibited by these compounds appears to make them good candidates for commercial use.

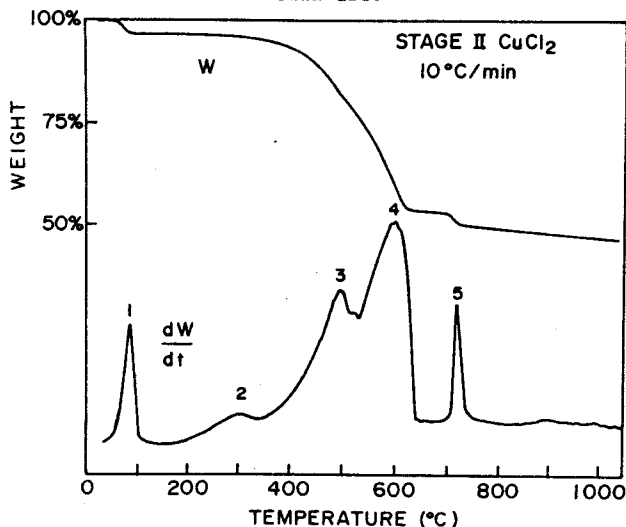


Figure 1

Weight loss and rate of weight loss (derivative) as a function of temperature for stage II CuCl_2 intercalated graphite at a heating rate of 10°C/min under argon.

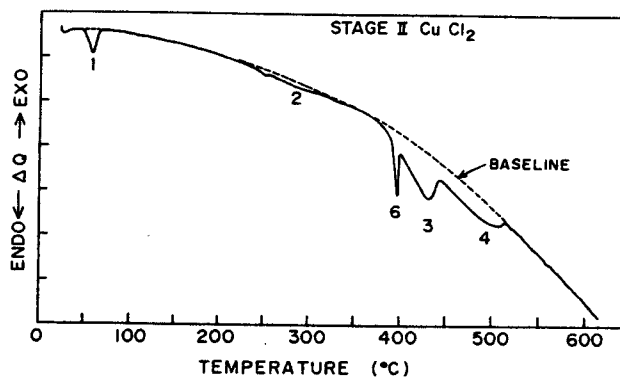


Figure 2

DSC curve for stage II CuCl_2 intercalated graphite at a heating rate of 10°C/min under argon.

Table 1

Stoichi- ometry	Stage	Method	Ref.
$\text{C}_{4.5}\text{nCuCl}_2$	n	Unit cell anal.	This report
$\text{C}_{4.9}\text{nCuCl}_2$	n		5
$\text{C}_{6\text{n}}\text{CuCl}_2$	n	Wt. uptake, e^- diffraction	6,7
$\text{C}_{6.35}\text{CuCl}_2$	I	TGA	8
$\text{C}_{7.5}\text{CuCl}_2$	I	TGA wt. loss	This report
$\text{C}_{11.5}\text{CuCl}_2$	II	TGA wt. loss	This report
$\text{C}_{15.2}\text{CuCl}_2$	III	TGA wt. loss	This report
$\text{C}_{22.8}\text{CuCl}_2$	IV	TGA wt. loss	This report

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