Journal of Thermal Analysis, Vol. 41 (1994) 1433-1439

THERMAL BEHAVIOUR OF GRAPHITE INTERCALATION COMPOUNDS WITH OXIDE OF DIFLUORIDE OF PHOSPHORYL

P. Vast

Laboratory of Applied Chemistry, University of Sciences and Technology of Lille France – Bât C4 – Domaine Universitaire Villeneuve d'Ascq, 59655 France

Abstract

We present in this paper the thermal analysis (calorimetry, TG and DSC) of the first stage $P_2O_3F_4$ graphite intercalate compound in atmospheric pressure and high pressure. By heating we obtain always exfoliation phenomenon.

The heating of exfoliated graphite shows an important oxidation resistance in comparison with another exfoliated graphite. This oxidation resistance has been studied also by thermal analysis like TG, in oxygen atmosphere.

Carbon foil rebuilding from exfolied graphite keeps these interesting antioxidation properties.

Keywords: antioxidation treatment of carbon, exfolation, fluorophosphate, graphite intercalate compound

Introduction

Phosphorus compounds don't give intercalation compounds of low stage with graphite. Nevertheless we have shown that the oxide of difluoride of phosphoryl ($P_2O_3F_4$) gives rise to a GIC of first stage [1] with the help of an oxidizer.

This highly intercalated GIC has the formula $C_6P_2O_3F_4$. In dry atmosphere the oxide of difluoride of phosphoryl deintercalates slowly at room temperature to a final first stage intercalation compound with a ratio C/P = 4.

By heating, it is not possible to extract totally the intercalated species without exfoliation of the GIC. This phenomenon depends of the heating speed and begins around at 120°C but it finishes always at 210–220°C.

As we develop in our laboratory the thermal analysis of GIC [2–4], we have studied by thermal analysis the thermal behaviour on the first stage $P_2O_3F_4$ graphite intercalation compound.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

We use a DSC 111 SETARAM and a TG-DTA92 SETARAM for thermogravimetry experiments. For DSC study two kinds of crucible are used: Open crucible in quartz used in argon atmosphere to permit the exhaust of $P_2O_3F_4$, and sealed crucibles in steel to work with a constant quantity of matter and keep the exhausted $P_2O_3F_4$ in high pressure to bring it in contact with graphite. For TG we use alumina crucible in argon atmosphere. In all experiments we have no detected reaction between GIC compound and the crucibles.

We use Madagascar graphite with a granulometry of 0.35 mm. $P_2O_3F_4$ is obtained by dehydration on P_4O_{10}, of HPO_2F_2 obtained itself according to [5].

Results

The Fig. 1 shows characteristic curves in DSC study. With open crucible we observe at the beginning of the heating program a variation of the base line to the endothermic values. This variation is more important for the high heating speed. This curve evolution may be explained by a continuous exhaust of $P_2O_3F_4$. At 150°C, we observe the beginning of an exothermic peak that may better define for the slow heating speed. This exothermic peak has a value of

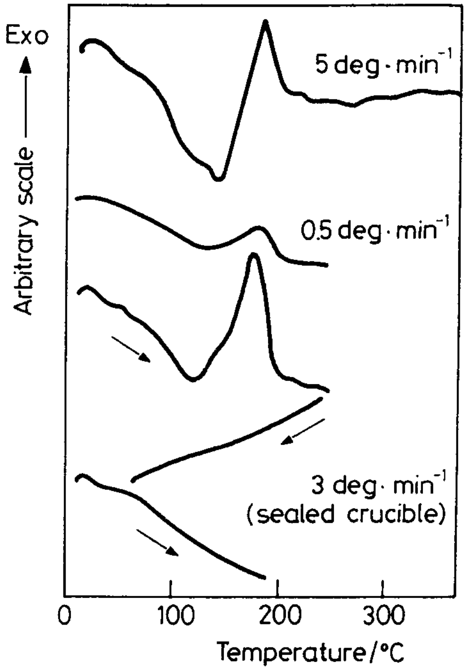

Fig. 1 DSC curves of GIC with $P_2O_3F_4$

−15 Joules by gram of graphite. It cannot be attributed to an exothermic decomposition of $P_2O_3F_4$.

With a sealed crucible, we obtain the same curve with the same exothermic peak. In this latter case, since all part of $P_2O_3F_4$ is kept in contact with graphite, a possible new intercalation reaction which be possible when the temperature is again decreased. However no thermic reaction is observed (Fig. 1) and the same when the temperature is again increased. This last results shows that, even under a high pressure of $P_2O_3F_4$, it is not possible to intercalate again the graphite.

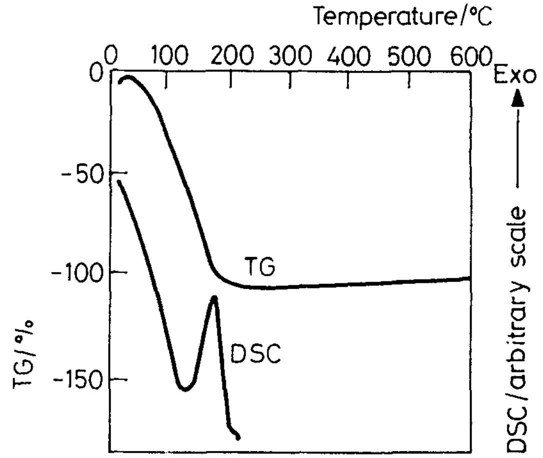

Fig. 2 TG curve of GIC with $P_2O_3F_4$ comparaison with DSC curve

The Fig. 2 shows the thermogravimetry analysis curve. We observe a quick loss of intercalate which is achieved at 200°C. We have drawn on the same figure, the DSC curve obtained with the same heating speed (3 deg·min^{-1}). We see that the exothermic peak begins at the last part of the mass loss, and it is maximal at the end of desintercalation.

Discussion

The exfoliation phenomenon needs energy to turn to vapor the intercalate compound and separate the graphene planars – see general references [6]. Our results may be explained if we suppose a reaction with graphite and $P_2O_3F_4$ between of 150–200°C, because $P_2O_3F_4$ is stable in this temperature.

As we obtain an exothermic peak at the end of desintercalation, we can explain this amazing result by a reaction between $P_2O_3F_4$ and graphene planars. This reaction is possible between active sites of carbon and $P_2O_3F_4$ considering the high reactivity of $P_2O_3F_4$ [7]. So if this assumption holds true, an important evolution of the graphitic network shall be detected. So we have studied by Raman microprobe the graphite at two stages of the desintercalation at the beginning of the exothermic peak, i.e. 150°C, and i.e. at the end 220°C. At the beginning of exfoliation we have the more important peak at 1582 cm^{-1} and a weak peak at 1355 cm^{-1}. So we obtain the spectrum of graphitic compound, but at 220°C, the second peak at 1350 cm^{-1} increases without shift for the peak at 1582 cm^{-1} and without appearance of a peak at 1500 cm^{-1} characteristic of amorphous carbon [8] (Fig. 3). This shows an evolution of the graphitic network. This result in agreement with new graphite structure has to involve new properties of graphite materials.

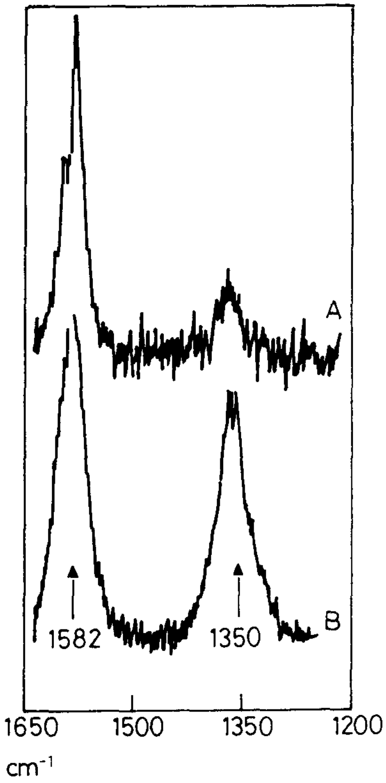

Fig. 3 Raman spectra of GIC heated at 150°C (A) - 200°C (B)

In fact if we have reaction between graphite active site and $P_2O_3F_4$, we can hope to obtain graft of $P_2O_3F_4$ on the active sites and obtain an inhibition of these active sites [9]. So we have studied the thermogravimetric evolution of first stage graphite $P_2O_3F_4$ intercalate in oxygen atmosphere.

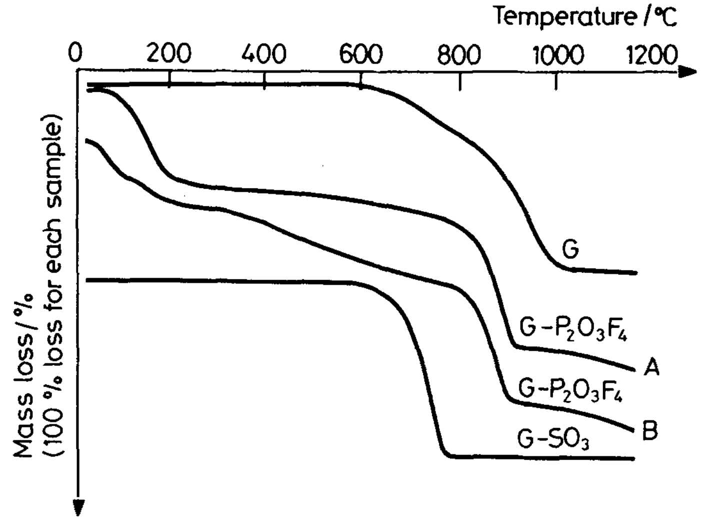

Fig. 4 Thermogravimetric analysis of GIC with $P_2O_3F_4$ in oxygen atmosphere. Comparaison with graphite and another exfoliated graphite

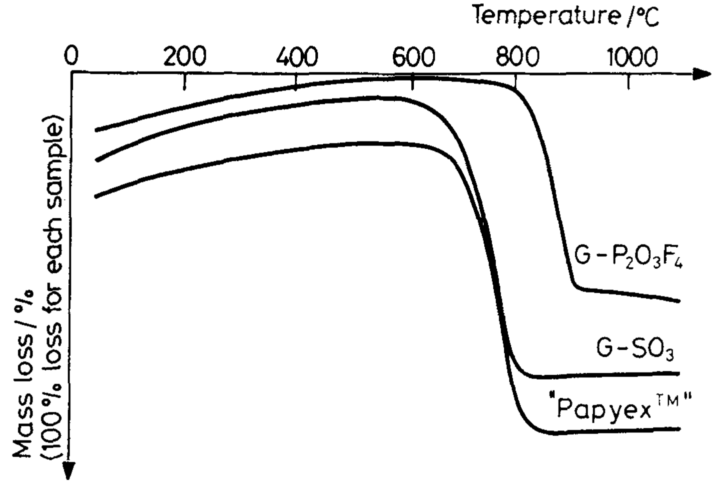

Fig. 5 Thermogravimetric analysis in oxygen atmosphere of rebuilding graphite foils obtained from GIC with $P_2O_3F_4$, SO_3, and commercial graphite foil. Heating speed 5 deg·min^{-1}

The Fig. 4 shows the result. In the first stage, we observe the same desintercalation curve than with an argon atmosphere. The carbon burning off appears in higher temperature (curve A) than the initial graphite of Madagascar. We obtain the same result with a GIC after 24 h in wet atmosphere at room temperature (curve B). So we have studied also in the same condition exfoliated graphite obtained from graphite intercalated with SO_3. It begins to burn off before the exfolied graphite obtained with $P_2O_3F_4$. The heating of exfoliated graphite shows an important oxidation resistance in comparison with another exfoliated graphite, obtained for example from intercalated compounds with sulfuric acid or anhydrid sulfuric acid.

Carbon foils rebuilding from exfoliated graphite keep these interesting antioxidation properties. The Fig. 5 shows the various behavior of rebuilding graphite foils obtained from GIC with SO_3, and $P_2O_3F_4$, after exfoliation.

The burning off curve is the same for a commercial graphite foil (Papyex^{TM}) and one obtained from GIC intercaled with SO_3. On the other hand we observe a better behaviour of foil obtained from GIC with $P_2O_3F_4$.

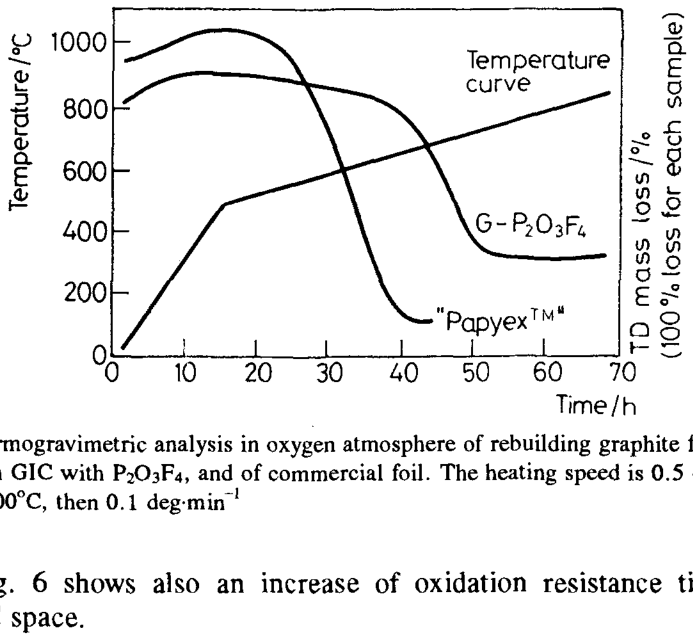

Fig. 6 Thermogravimetric analysis in oxygen atmosphere of rebuilding graphite foil obtained from GIC with $P_2O_3F_4$, and of commercial foil. The heating speed is 0.5 deg·cm^{-1} up to 500°C, then 0.1 deg·min^{-1}

The Fig. 6 shows also an increase of oxidation resistance time in the 500–700°C space.

In conclusion thermal analysis has showed that this $P_2O_3F_4$ GIC may be an interesting precursor for exfoliated graphite which may be used as rebuilding graphite foil in industrial applications where antioxidation properties are required.

References

1 B. Iskander and P. Vast, Carbon, 18 (1980) 299.
2 F. Beguin and P. Vast, Synt. Met., 23 (1988) 427.
3 P. Vast and G. Palavit, Calorim. Anal. Therm., 15 (1986) 146.
4 P. Vast, Calorim. Anal. Therm., 23 (1992) 335.

5 P. Vast, A Semmoud and A. Addou, J. Fluor. Chem., 27 (1985) 319.
6 D. Petitjean thesis Nancy 1992.
7 P. Vast and A. Semmoud, J. Fluor. Chem., 3 (1987) 297.
8 P. Lespade, thesis Bordeaux 1982.
9 D. W. McKee, C. L. Spiro and E. J. Lamby, Carbon, 22 (1985) 285.

Zusammenfassung — Vorliegend wird eine bei Normaldruck und unter Hochdruck durchgeführte Thermoanalyse (Kalorimetrie, TG und DSC) einer $P_2O_3F_4$-Graphit-Einlagerungsverbindung ersten Grades dargelegt. Während des Erhitzens konnte auch ein Abblättern beobachtet werden.

Das Erhitzen abgeblätterten Graphits zeigt eine bedeutende Oxidationsbeständigkeit im Vergleich zu anderem abgeblätterten Graphit. Diese Oxidationsbeständigkeit wurde auch mittels Thermoanalyse, wie z.B. TG in einer Sauerstoffatmosphäre untersucht.

Aus abgeblättertem Graphit wieder angelagerter Kohlenstoff behält diese interessanten antioxidativen Eigenschaften bei.