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INVESTIGATIONS OF DEINTERCALATION PROCESSES IN GRAPHITE INTERCALATION COMPOUNDS WITH $SbCl_5$ AND ICl

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Abstract

Results of the investigations of deintercalation process in intercalation compounds graphite–$SbCl_5$ and graphite–ICl are presented. It was found that sample mass losses have a step character that testifies to the discrete transition from one stage of graphite intercalation compounds to another. The increase in the rate of heating breaks the step character of mass loss dependence on temperature and intensive mass losses occur without stage transitions.

Keywords: graphite, ICl, intercalation compounds, $SbCl_5$, thermogravimetry

Introduction

Practical application of graphite intercalation compounds (GIC) for manufacturing thermoexfoliated graphite and production of composite materials on its basis with various functional characteristics requires detailed investigations in thermal stability of these compounds, conformities of deintercalation process going on in these compounds, i.e. intercalant escape from them. In spite of the wide application of thermoexfoliated graphite in industry a comparatively small number of publications is devoted to investigations of mechanism of intercalant thermodesorption from GIC [1–4].

The aim of this work was to investigate the processes of deintercalation of GIC with $SbCl_5$ and ICl and its dependence on intercalant type and its concentration, heating rate, dispersity of initial graphite (Gr).

Results and discussion

The initial material used for intercalation was natural graphite with particle sizes 160, 300, 315 and 400 μm. The graphite was intercalated with $SbCl_5$ to stage 2 and 3 and with ICl to stage 2 and 5 by a standard method. The mass loss during heating at constant rate in the air was measured on thermogravimetry with the precision of 0.01 mg.

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The number of stage and phase composition of the samples after intercalation and heating were determined by X-ray method.

The influence of intercalant concentration has been investigated for the samples of Gr–$SbCl_5$ of stage 2 and 3 and for the samples of Gr–ICl of stage 2 and 5. Figure 1 shows the mass of the samples as a function of temperature, the rate of heating 2.5 K min^{-1}.

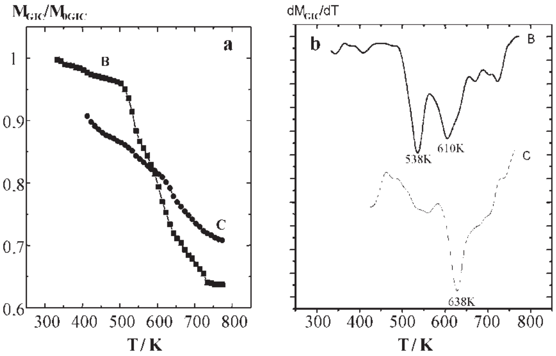

Fig. 1 The change of mass (a) and $dM_{GIC}/dT=f(T)$ (b) for Gr–$SbCl_5$ samples under slow heating to 773 K with constant rate 2.5 K min^{-1}: B – Gr–$SbCl_5$ compound of stage 2; C – Gr–$SbCl_5$ compound of stage 3

The analysis of these data for the above samples has shown that there are several temperature range characterized by intensive mass losses. For the samples of stage 2 the first peak of mass loss is observed at T~540 K. As X-rays studies of Gr–$SbCl_5$ of stage 2 heated to ~600 K show, the reflections corresponding to stage 2 disappear from diffractograms and instead the reflections pattern characteristic of stage 3 appear. This indicates the transition from stage 2 to stage 3 in the samples at T~540 K. On $M_{GIC}/M_{0GIC}=f(T)$ dependence for the samples of stage 3 there are no breaks in this temperature range. The second temperature range where a sharp loss of mass is observed both for the samples of stage 2 and stage 3 is (610–640) K. The peak of mass loss at this temperature is observed. As X-ray studies showed at this temperature the transition from stage 3 to stage 4 takes place. The analysis of absolute values of mass losses and phase composition of the samples heated to 770 K has shown that this temperature leads to complete deintercalation of GIC with $SbCl_5$.

The influence of pristine graphite dispersity on characteristics of deintercalation process has been studied for stage 2 GIC with $SbCl_5$ prepared from graphite powders with particle sizes of 160, 200, 315 and 400 μm. It was found that mass losses when transition from stage 2 to stage 3 takes place, are maximum for the sample with the smallest particle size. This is explained by the fact that the smaller the particles in graphite fraction is, the larger the amount of intercalant absorbed on particle surface is. The intercalant desorption from particle surface results in changes of sample mass on heating to ~500 K, without compound stage being changed, as it has been shown by X-ray studies.

The influence of heating rate on the character of deintercalation process and characteristics of the samples has been studied for Gr–$SbCl_5$ powders of fraction 400 μm at the rates of 2.5, 5 and 20 K min^{-1}. Figure 2 represents the $dM_{GIC}/dT=f(T)$ dependencies for different rates of heating. As it is seen from Fig. 2 the first maximum on $dM_{GIC}/dT=f(T)$ curves characteristic of transition from stage 2 to stage 3 in GIC is observed at the temperatures (535–540) K and does not depend on the heating rate. However, at the increased rate of heating the temperature interval in which this intensive mass loss takes place becomes wider and at the heating rate of 20 K min^{-1} it reaches 630 K. For the sample heated at the rate V_T=20 K min^{-1} the mass loss at 630 K corresponds to the mass loss characteristic of transition from stage 3 to stage 4. The temperature of the second maximum on $dM_{GIC}/dT=f(T)$ curve, which has been shown by X-ray analysis to correspond to transition from stage 3 to stage 4 in the samples heated at low rates (2.5 and 5 K min^{-1}), is practically the same and comprises 670 K.

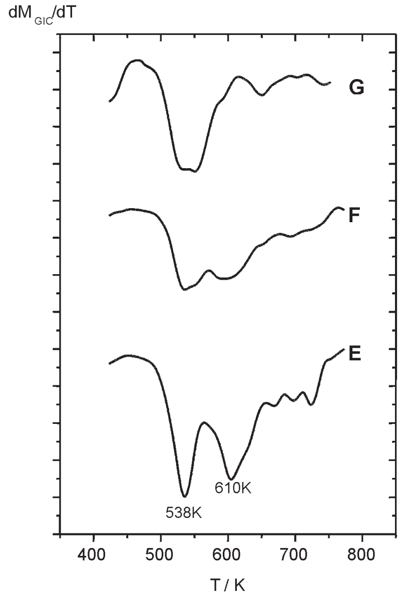

Fig. 2 The $dM_{GIC}/dT=f(T)$ dependence for Gr–$SbCl_5$ samples with particle size 400 μm under heating with constant rate to 773 K: E – 2.5 K min^{-1}, F – 5 K min^{-1}, G – 20 K min^{-1}

At high heating rates which correspond to thermal shock (100–200) K min^{-1} after heat treatment at 800 K the diffractograms of the samples show in addition to intensive lines of pure graphite also the weak intensity reflections only from stage 2 or stage 3, the reflections from higher stages are not present.

Figure 3 shows the results of investigations in thermal desorption that have been carried out for graphite compounds with ICl of stage 2 and 5 heated at the rate of 2.5 K min^{-1}. In contrast with GIC with $SbCl_5$ the several minimums on $dM_{GIC}/dT=f(T)$ dependence that should correspond to successive stage transitions from s=2 to s=3

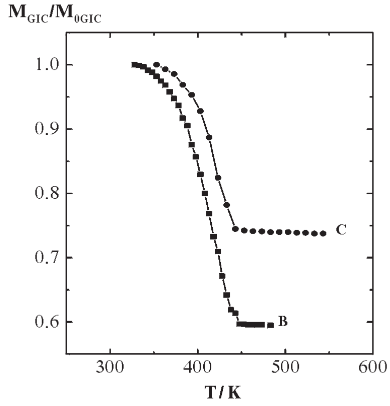

Fig. 3 The change of mass for Gr–ICl samples with particle size 400 μm under heating with constant rate 2.5 K min^{-1} to 773 K: B – Gr–ICl of stage 2; C – Gr–ICl of stage 2; C – GR–ICI of stage 5

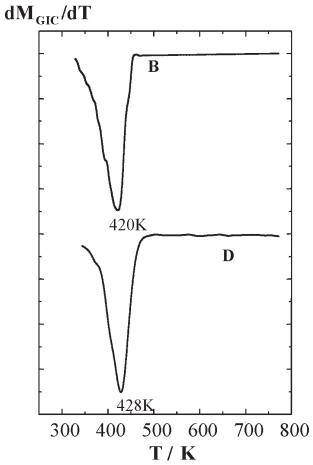

Fig. 4 The dM_{GIC}/dT=f(T) dependence for Gr–ICl of stage 2 with particle size 400 μm under heating with constant rate to 773 K: B – 2.5 K min^{-1}, D – 10 K min^{-1}

and to s=4 have not been found for GIC with ICl. In this case we observed only one essential minimum on dM_{GIC}/dT=f(T) dependence the position of which depends on the stage of initial graphite. The lower the stage of GIC is, the lower the temperature is, at which the value of dM_{GIC}/dT=f(T) is minimal. At the smallest rate of heating of 2.5 K min^{-1} we observed only the extension of this single minimum, which may be considered as the fusion of the three minimums (corresponding to stage transitions) into a single one (Fig. 4). As it has been found in previous investigations, GIC with ICl are non-stable beginning practically from T_{room}. In contrast with GIC Gr–SbCl$_5$ the rate of ICl evaporation from GIC at these rates of heating V_T is large and exceeds the rate of stage-to-stage transition V_S [4]. Therefore, the step-like behavior of $M_{GIC}/M_{0GIC}=f(T)$ dependencies and several successive stage transitions in GIC with ICl may be experimentally found only at very small rates of heating. As it is seen from Fig. 4 the increase at the rates of heating V_T to 10 K min^{-1} leads to a slight shift of the minimum into the region of higher temperatures and makes it more abrupt.

All obtained data are in agreement with the theory of thermodynamic stability of GIC [5]. According to this theory the following inequality is valid: $T_1^* < T_2^* < T_3^*$ where T_s^* is the temperature of thermal stability of stage S. The experimental temperatures of minimums on dependencies of first derivative of mass with respect to temperature for graphite intercalation compounds with $SbCl_5$ and ICl correlate with theoretically calculated values of T_s^*.

Conclusions

The investigations of thermodesorption in intercalation compounds Gr–$SbCl_5$ of stage 2 and 3 have shown that the mass losses have the step character: there are a few ranges of intensive mass losses. According to the thermodynamic theory of stability for each stage of the compound there exists T_s^* temperature and the heating above this temperature causes the compound to pass into unstable state and intercalant transits from the ‘state between the layers’ into the state of pure substance.

In GIC of stage S at the large rates of heating after the temperature reaches $T>T_s^*$ the intercalant between the layers passes into a metastable state with a strong tendency to become stable, i.e. into the compound of stage S+1 and the excess of intercalant diffuses and evaporates from GIC.

If the rate of temperature increases, it exceeds the finite rate of transition V_S from stage S into stage (S+1), the transition from stage S into stage S+1 cannot be completed. The increase in rate of heating breaks the step character of mass losses dependence on temperature.

Under thermal shock the time required for increasing the temperature to T_C (T_C is the ternary temperature) becomes considerably less than the time necessary for stage transition of intercalant and for its diffusion toward the sample’s boundaries. The escape of intercalant mass takes place in the whole volume of the sample resulting in its exfoliation.

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References

1 D. D. L. Chung, Carbon, 25 (1987) 361.
2 C. T. Ho and D. D. L. Chung, Carbon, 28 (1990) 825.
3 G. Mazieres, G. Colin, J. Jegoudez and R. Setton, Carbon, 14 (1978) 176.
4 S. H. Anderson and D. D. L. Chung, Carbon, 25 (1987) 377.
5 E. I. Kharkov, V. I. Lysov, L. Yu. Matzui and L. L. Vovchenko, 9th CIMTEC – World Forum on New Materials, Symposium 1, P. Vincenzini, A. Dogli Esposti (Eds). Techna Srl. 199 (1999).