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Investigation of the Thermoexfoliation Process in Different Acceptor GICs

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The studies of thermoexfoliation process in intercalation compounds Gr-$SbCl_5$, Gr-ICl, and Gr-H_2SO_4 have shown that thermoexfoliation has a vivid non-linear threshold character. Experimental data are discussed within the thermodynamic theory of graphite intercalation compounds. Thermoexfoliation process takes place in the temperature range from T^* to T_{cr} in which intercalant in GIC layers becomes unstable and the transition from the state "intercalant in GIC" into the state of pure intercalant occurs. The maximal effect of thermoexfoliation is obtained at high temperatures of thermal shock T_e, i.e. at large heating rates of the sample.

Keywords: graphite; intercalation compounds; thermoexfoliation; specific surface

INTRODUCTION

It is known that in the process of heat treatment of graphite intercalation compounds (GICs) there occurs intercalant desorption accompanied with essential changes in its micro- and macrostructure, changes in composition and crystalline structure, increase of open porosity, specific surface, decrease of bulk density, etc. The impact of thermal shock on GICs results in formation of highly porous particles with developed surface, the so-called thermoexfoliated graphite (TEG).

The systematically performed studies were aimed at revealing the

influence of the structure of pristine graphite, the type of intercalant, the stage of intercalation and the temperature of thermoexfoliation on such characterictics of TEG as phase composition, bulk density ρ, thermoexfoliation coefficient $K = \frac{\rho_{Gr}}{\rho_{TEG}}$, specific surface, pycnometric density, etc.

EXPERIMENT

The natural graphite of different fractions, from 50 to 400μm has been used for preparation of graphite intercalation compounds (GICs). Intercalation of $SbCl_5$ and ICl was carried out to stage-2 and 3 by single-zone method at the temperatures of 493 and 313 K for intercalation of $SbCl_5$ and ICl respectively. Graphite bisulphate $C_{24}HSO_4 \cdot 2H_2SO_4$ was prepared by the persulphate and bichromate techniques[1]. The stage of produced samples of GIC as well as phase composition of thermoexfoliated graphites was determined by X-ray diffractometer DRON-3M in Co-irradiation. Thermoexfoliation of the samples of GIC was performed in laboratory furnace СШОЛ -1300^{0}C, temperature stability was ±10K.

RESULTS AND DISCUSSION

The studies of thermoexfoliation process in GICs has shown that thermoexfoliation has a vivid non-linear threshold character (Fig.1). At high temperatures (~1000-1100K) **K**(T) dependence that has been studied for Gr-$SbCl_5$ and Gr-H_2SO_4 based on graphite with particle sizes (200-400μm) reached the saturation while for Gr-ICl the thermoexfoliation coefficient has been found to increase until the temperature of thermoexfoliation approached 1573K. The largest thermoexfoliation coefficient **K** in comparison with that for Gr-ICl and Gr-$SbCl_5$ has been found for Gr-H_2SO_4 and was ~ 245 for washed graphite bisulphate of stage-2 at the temperature of thermal shock >1300K. It was found that at the temperature of thermal shock above 873K there occurs

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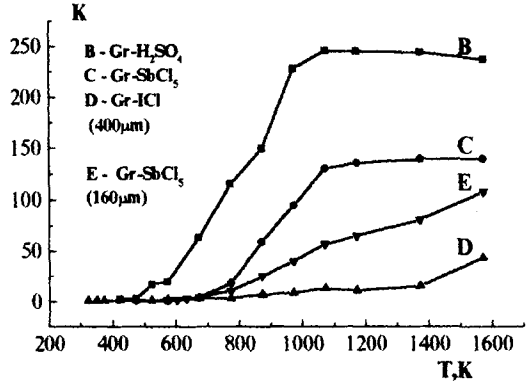

FIGURE 1 Thermoexfoliation coefficient **K** for graphite intercalation compounds: B,C,D, - particle size 400μm, E - particle size 160μm.

complete desorption of intercalant from GIC and thermoexfoliation process is going on so intensively that the mass loss of graphite itself has been observed. It was found that the temperature of the beginning of thermoexfoliation increases with the increase of GIC stage number (decrease of intercalant concentration). The data are presented on Fig.2. As it is seen from Fig.2 the data obtained from

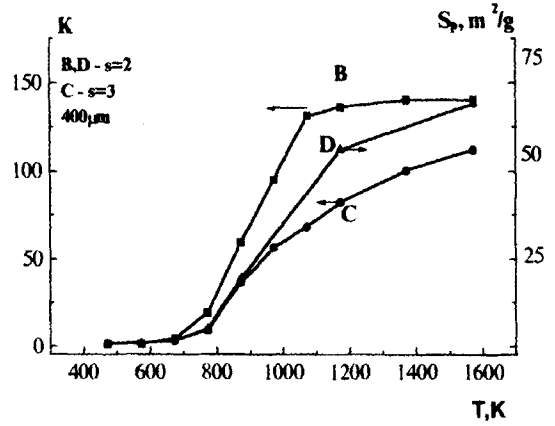

FIGURE 2 Thermoexfoliation coefficient **K** and specific surface area S_p for Gr-$SbCl_5$.

investigations of specific surface and pycnometric density of TEG correlate with data on **K**(T).

To reveal the character of changes in GICs composition and structure arising under thermoexfoliation we have performed X-rays studies of GICs that had been subjected to thermal shock at different temperatures. As it is seen from Fig. 3 the intercalant is still available in TEG samples produced from

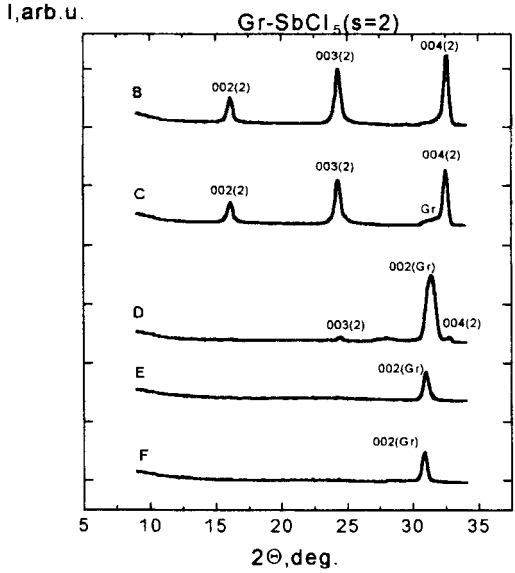

FIGURE 3 Diffraction patterns for Gr-$SbCl_5$ (s=2) thermoexfoliated at different temperatures (particle size ~400μm): B - 473K, C - 573K, D - 673K, E - 773K and F - 1573K

Gr-$SbCl_5$(s=2) at low temperatures of thermoexfoliation: as the temperature of thermal shock increases the diffraction patterns show the growing intensity of reflections from pure graphite and lower intensity of reflections from intercalant layers (B,C,D diffractogramms). The presence of the reflections only from intercalant corresponding to stage-2 indicates a sharp desorption of intercalant without any structural rearrangement in GIC (i.e.,

without transitions from one stage to another (2→3, 3→4 and so on)) due to thermal shock. Similar results have been obtained by authors[2] in their studies of thermoexfoliated Gr-$FeCl_3$ of stage-1. At higher temperatures of thermoexfoliation the complete desorption of intercalant from TEG takes place and at the temperatures T>773K the diffraction pattern shows only the reflections corresponding to pure graphite.

All the obtained experimental data are in agreement with the predictions of thermodynamic theory of GICs, based on the concepts of partial thermodynamic functions of intercalant in GIC[3]. According to this theory there is a certain critical temperature T*(different for different intercalants and GIC stages) above which GIC cannot exist:

$$T_s^*(C_2) = \frac{\Delta H_{12}(C_2) - \Delta H_{12}(C_2 = 1)}{\Delta S_2^0(C_2) - \Delta S_{02}^0(C_2 = 1)} \qquad (1)$$

where C_2 is intercalant concentration, $\Delta H_{12}(C_2)$ and $\Delta H_{12}(C_2=1)$ are entalpies of intercalant evaporation from GIC and from intercalant substances in free state, respectively; $\Delta S^0_2(C_2)$ and $\Delta S^0_{02}(C_2=1)$ are the changes of entropy in standard state, i.e. under P_0=1atm. and T_0 corresponding to P=1 atm.

It should be noted that $T_1^* < T_2^* < T_3^* \ldots$ and at $T>T_s^*$ the chemical potential of intercalant in GIC $\mu_2(T,C_2)$ is larger than that of intercalant in free state $\mu_{20}(T)$ and $\Delta\mu_2(T)>0$, i.e. intercalant at $T>T_s^*$ is in non-equilibrium (metastable) state and tends to make a transition from the state in GIC layers into the state of pure intercalant when the temperature is increased. Under the thermal shock this transition (that can be compared with some restrictions to melting) is going on throughout the whole volume of the substance in the closed space (at $\Delta V>0$) and creates high pressure on graphite layers that causes thermoexfoliation. In Gr-ICl sublimation (evaporation) takes place on the substance surfaces (in our case on the surface of intercalant layers in GIC) and so the excessive pressure does not arise within the layers in GIC and thermoexfoliation is not

observed. As it has been shown in [3], T* estimated by (1) for Gr-$SbCl_5$ is 630K and 690K for stage-2 and stage-3 respectively, which is in good agreement with the temperature of the beginning of thermoexfoliation obtained for these compounds experimentally (Fig.2).

The major conformities of thermoexfoliation process can be formulated as follows:

1. The process of thermoexfoliation occurs in GIC systems characterized by T* temperature above which in terms of thermodynamics the intercalant in GIC layers becomes unstable in relation to pure intercalant.
2. At the temperatures T<T* thermoexfoliation does not occur at any heating rates dT/dt of the sample.
3. Thermoexfoliation process takes place in the temperature range from T* to T_{cr} in which the transition from the state "intercalant in GIC" into the state of pure intercalant occurs.
4. The maximal effect of thermoexfoliation is obtained at high temperatures of thermal shock T_e, i.e. at large heating rates of the sample.

Acknowledgments

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