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THERMAL ANALYSIS OF GRAPHITE INTERCALATION COMPOUND WITH $CuCl_2$

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ABSTRACT

The behaviour of graphite intercalation compound $C_{7,73}CuCl_2$ composition has been investigated under high temperature conditions, the mechanism, kinetics and thermodynamics of its linear pyrolisis have been characterized, the thermal expansion coefficients of the pressed material samples have been estimated and the presence of their dependence on thermal and baric compound prehistory has been revealed.

INTRODUCTION

Problems of optimization of artificial diamonds synthesis as well as thermally exfoliated graphite and carbon fibres intercalation productions determine the necessity of graphite intercalation compounds (GIC's) behaviour physico-chemical study at high temperatures.

The aim of this paper is to continue the investigation of graphite intercalation compounds with chlorides d-elements as intercalation components (among them with copper dichloride). Previously we have studied in details the properties of the following compositions GIC's: $C_{6,35}CuCl_2$, $C_{6,97}CoCl_2$, $C_{16,8}CoCl_2$, $C_{7,7}FeCl_3$ and $C_{11,83}FeCl_3$/1-6/.

MEASURING METHODS

The GIC under study was synthesized (using Zavalievsk location graphite) and identified as previously in /7/: $C_{7,73}CuCl_2$ contained 59,15 weight % $CuCl_2$ and represented GIC (according to X-ray phase analysis) of the first stage with admixture (8-10%) of the second stage.

The material study was carried out up to 1300 K using dynamic thermogravimetry (TG), quantitative differential thermal analysis (DTA), thermodilatometry and X-ray phase analysis with experimental features of application had been reported previously in (2-6). It should be noted that the thermodilatometry of the pressed $C_{7,73}CuCl_2$ samples was done in 5-10 minutes after their formation.

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RESULTS AND DISCUSSION

As it follows from the TG results obtained, when GIC-$CuCl_2$ powder-form samples (with dispersion less 0,25 mm) were heated (with rate of 5 K/min) under vacuum their mass change was fixed at the temperature greater than 460-480 K. As the temperature rises a decomposition degree (α) and the decomposion rate ($\frac{d\alpha}{dT}$) increase sharply: the full removal of $CuCl_2$ from GIC is reached to 1200 K and $\frac{d\alpha}{dT}$ at 720-730 K reaches its maximum (0,23%/K). During the experiments a deposit appearance was observed in the cold part of the reaction container, as the experiments progressed this deposit increased in intensity and its colour changed from light gray to yellow and then to brown. X-ray analysis of the carbon residue showed the presence of graphite only and in sublimation there were copper di- and monochlorides (their ratio changed depending on a temperature stage of the pyrolisis process and ambient experimental conditions).

$C_{7,73}CuCl_2$ DTA curves corresponding heating to 1300 K under vacuum are characterized by presence of three endothermic effects: an endopeak near $T_1=590\pm15$ K extending along the temperature scale and also two sharply expressed endopeaks with T_2 at 748±1 K and with T_3 at 976±2 K. The presence of the T_1 endopeak may be caused apparently by the removal of chloride boundary molecules as well as water and HCl (which are present in the material by virtuous of its synthesis features /7/). Endoeffect with T_2 (this value is in agreement with the temperature at which $\frac{d\alpha}{dT}$ is maximum) is caused by the basic thermodestruction process and the T_3 endoeffect is connected probably with the solid phase transformation in the pyrolisised graphite residue (which can be reproduced at the repeated heating of the substance).

A variation of ambient experimental conditions (a transfer from vacuum to inert medium, a change of the heating rate, sample weighed amount and its dispersion) does not lead to changes in the form of TG and DTA curves, though their characteristics are changed in the direction having been previously pointed out for GIC's-$FeCl_3$ thermodestruction /3/.

Indicated thermostimulated processes leave trace on the GIC-$CuCl_2$ pressed samples thermal expansion. The heating of $C_{7,73}CuCl_2$ up to 523 K bring to increasing the relative elongation in the axial direction ($\frac{\Delta l}{l}$) by 1,9% and this elongation being remained at the material cooling down to 300 K. It was noted the diameter of cold samples has increased by 0,7% and the mass loss has been found to be 0,1-0,2 weight%. Noted features in the material thermal expansion character are fully displayed when the GIC heating is continued up to 823 K. The sample height increases irreversible (by 18,6%) exceeding the corresponding value in the radial direction (4,6%), in addition, essentially greater mass loss of the samples than has been indicated (2,3 weight%). It has been noted that experimental $\frac{\Delta l}{l_o}$ values for GIC-$CuCl_2$ are considerably greater than that of additive values calculated from $\frac{\Delta l}{l_o}$ of Zavalievsk graphite pressed cylindrical samples as well as copper dichloride. Non reversibility of the material thermal expansion and its superadditivity can be apparently explaind by the removal of water, hydrogen chloride and copper chloride from the material. Anisotropy indicated in $\frac{\Delta l}{l_o}$ for $C_{7,73}CuCl_2$ was present in other GIC's investigated by us and was caused apparently by a predominanted orientation of material crystals at their solid-phase compaction during the investigated samples formation process.

So as we had established earlier /4/ the GIC's $\frac{\Delta l}{l_o}$ depend on thermal and baric prehistory of the material than for $C_{7,73}CuCl_2$ we studied the influence of these factors on its $\frac{\Delta l}{l_o}=f(T)$.

Repeated dilatometric investigations of GIC-$CuCl_2$ which had been previously thermally treated up to 523 K (to the temperature at which the basic thermodestruction process has been not initiated yet) in the process of its thermomechanical analysis brought to the $\frac{\Delta l}{l_o}$ results, which considerably differed from the results for the first heating. The second cycle "heating up to 523 K - cooling up to 300 K" gives the second series of experimental data: the heating leads to the further increasing $\frac{\Delta l}{l_o}$ (up to 3%), residues $\frac{\Delta l}{l_o}$ rise up to 2,2% (for the axial direction) and up to 1,3% (for the radial direction). The third cycle gives data, which differ from data of the second cycle along "heating branch" and coincide with the data along "cooling branch" (the further size growth of the samples has not been observed after their cooling). Subsequent experiments have given the same pattern of temperature change in $\frac{\Delta l}{l_o}$ as it is in case of the third cycle, i.e. the hysteresis is realized in $\frac{\Delta l}{l_o}=f(T)$. We have payed attention to the fact that the thermal expansion of $C_{7,73}CuCl_2$ becomes comparable (in the range of a mesurement error and calculations) with the corresponding values for $7,73C_{graphite}+CuCl_2$ mechanical mixture. An application of the "heating up to 523 K - cooling up to 300 K - compacting up to initial dimentions" cycle leads to the third series of data in $\frac{\Delta l}{l_o}$ for

$C_{7,73}CuCl_2$: a baric treatment of GIC-$CuCl_2$ in manner as in /4/ gives higher values of $\frac{\Delta l}{l_o}$ in comparison with the first heating and than greater is a cycle number, the higher is $\frac{\Delta l}{l_o}$ values. It should be noted that by using the electronic scanning microscopy we have identified new phases in the thermal-baric treated samples. The above mentioned phases were the size of 1 mkm and had octahedronal form.

In order to determine the hysterises realization reasons in $\frac{\Delta l}{l_o}=f(T)$ and of the substance baric treatment influence on $\frac{\Delta l}{l_o}$ it is necessary to carry out additional investigation, in particular it is required to clear out a mechanism of the possible mechanochemical processes, taking place in the material during its cold solidstate compacting.

The evaluation of the apparent activation energy for main thermodestruction process of the $C_{7,73}CuCl_2$ in manner as in /3/ has been done using TG analysis data which is equal to 30±2 kJ/mol (for the heating rate of 5K/min in the temperature range of 500-850 K).

According to DTA data the values of decomposition heat (for main thermodestruction process) have been estimated which are equal to 170±10, 115±10 and 75±7 kJ/mol for vacuum, air and a sealed steel ampule.

Mathematical data processing of GIC-$CuCl_2$ thermal expansion has shown that in the temperature range of 300-515 K and 525-820 K the linear expansion coefficient of $C_{7,73}CuCl_2$ takes the values of 86 and 504 ($10^6 K^{-1}$) respectively.

The indicated features in the thermal behaviour of $C_{7,73}CuCl_2$ graphite intercalation compound allow to draw a conclusion, using obtained by us data for 1-st pure stage GIC-$CuCl_2$ of $C_{6,35}CuCl_2$ composition that the presence of the second stage in the graphite material increases in some extend its thermal stability and changes considerably the character of its thermal expansion for baric treated GIC.

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