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THERMAL ANALYSIS OF FLUORATION PRODUCTS OF GRAPHITE INTERCALATION COMPOUND WITH CAESIUM

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ABSTRACT

A set of thermal analysis methods are used to characterize for the first time physicochemical peculiarities of graphite intercalation compounds with caesium fluoration products behaviour (which differ by initial graphite matrix, time-temperature conditions of graphite intercalation compound receiving and fluorine agents). We define temperature parameters of the malerials obtained linear pyrolysis, peculiarities of compacted samples thermal expansion and their heat capacities. On the results obtained basis we made an assumption on the chemical composition of the products and provide recomendation on temperature conditions to be followed when using the materials.

INTRODUCTION

In order to reveal the exploitation regimes of a material under heat influence we must have data on its physicochemical behaviour under high temperatures. In addition to this such data gives us the representation about the interparticle interactions in the substance, thus having a substantial scientific importance as well. Utilization of graphite intercalation compounds with alkali metals fluoration products as catalysts for industrial organic synthesis reactions called the necessity of detailed physicochemical study of the above products, under the thermal influence including.

MEASURING METHODS

In this paper we report the thermal analysis results under up to 1300K of graphite intercalation compound C_8Cs fluoration product (GICFP) taken as model material, synthesized and identified as described in /1/; note, that the above material consists mainly of graphite and caesium fluoride as well as other components in negligible quantities which may be referred to graphite fluoride

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and C_8CsF.

Investigations of the graphite material were performed using the methods of dynamic termogravimetry (TG), differential thermal analysis (DTA), dilatometry, by means of triple heat bridge thermographic set up for heat capacity (C_p) determination, as well as using X-ray and chemical analyses in the manner suggested in /2-5/.

All experiments were repeatedly performed and repeatability error for reliability level 0.95 was found to be: for dilatometric determination of relative elongation ($\Delta l/l_o$) -3.5%, for C_p determination - 2%, for TG measurements - 5%.

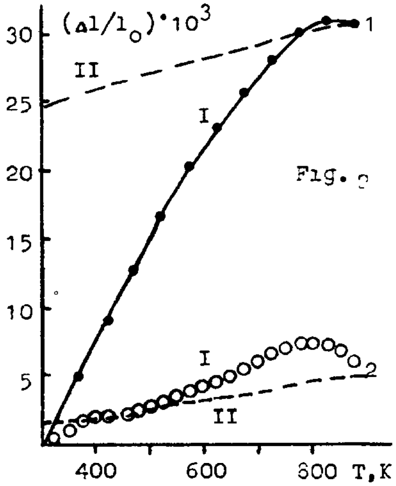
RESULTS AND DISCUSSION

TG experiment results show that the least registrated mass loss of the testing material in vacuum with the heating rate of 3 K/min was observed at 320-330K; with the temperature rise up to 620-625K the relative mass loss (α,%) rises insignificantly (up to 6 mass%); the mass loss rate ($d\alpha/dT$) in this temperature interval is maximum (0.04%/K) at 350K. The above peculiarities can be related with the removing process of physically and chemically bonded water out of the material. With the further temperature growth a more rapid α (up to 25 mass% at 1220K) and $d\alpha/dT$ rise (with maximum 0.055%/K at 740K) was observed, as may be supposed by caesium fluoride removal as well as by graphite fluoride decomposition /6/.

Presence of oxygen in gas surroundings (air ambient) during the sample heating leads to superimposing on the above processes of the oxidation stage which seems to be caused by higher α and $d\alpha/dT$ values compared to vacuum and argon ambient.

DTA results coincide with TG data: under vacuum there are a distinct endopeak at 375K and a temperature scale stretched endopeak at 500K on the DTA curve. Thermal effect absence at higher temperatures seems to be due to low material decomposition degree, that leads to larger endopeak stretching along the temperature scale.

Further investigations of the graphite residue - a product of GICFP thermally treated showed that full fluoride components removal from GICFP did not take place, as after heating was over the graphite material contained up to 36% of other components.



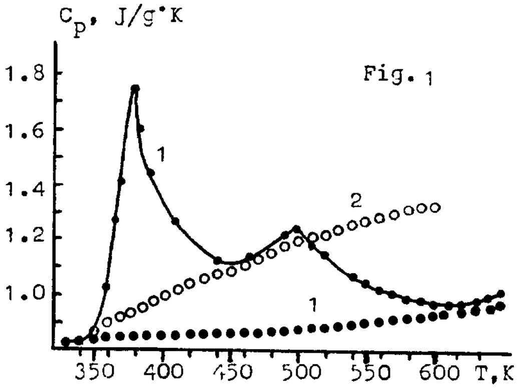


Fig.1. Heat capacity temperature dependence for GICFP (1) and electrolytical graphite (2).

Fig.2. Relative elongation for axial (1) and radial (2) temperature dependence of pressed (density 2 g/cm^3) GICFP (I-heating,II-cooling).

Heat capacity data analysis (Fig.1) showed, that C_p versus temperature curve marked two endopeak with T_f at 375 and 500K, which approves DTA and TG results. Product mass loss after heating to 640K was 4.2%. During repetitive heat capacity measurements endopeak value decrease is observed, which is due to further material-dehydratation (mass loss after each further measurement did not exceed 0.2%) till the monotonous and reproducible C_p growth was achieved.

Dilatometric results (Fig.2) of pressed cylindrical material samples (density 2 g/cm^3) show that heating up to 770K leads to axial elongation on 3.1%, while radial growth was only 0.75%, i.e. thermal expansion is anisotropic, which is caused probably as mentioned before for graphite substances /4,7,8/ by their texturing during pressing. Existence of several intervals on $\Delta l/l_0$ curve may be explained by the fact, that the process of thermal expansion is superimposed by the removal process of the volatile components. While heating over 770K $\Delta l/l_0$ value decreases marking the start of sample thermomechanical destruction, although their complete destruction was not observed. As the curve trace indicated the tested material being cooled down 900K is characterized by residual elongation.

Mathematical treatment of experimental results shower that $\Delta l/l_o=f(T)$ dependence in the temperature interval 320-750K in axial and radial directions is well approximated (mean deviation of experimental values against analytical ones is no more than 2%) by the following equation:

$$(\Delta l/l_o)\cdot 10^3_{(axial)} = -28.0 + 0.10T - 3.53\cdot 10^{-5}T^2$$

$$(\Delta l/l_o)\cdot 10^3(radial) = -4.9 + 2.62\cdot 10^{-2}T - 3.55\cdot 10^{-5}T^2 + 2.95\cdot 10^{-8}T^3$$

Thus DTA, TG, C_p and dilatometry data showed that the material synthesized by fluoration (using fluorine-argon mixture) C_8Cs (obtained on the electrolytical graphite matrix) adsorb some water and must be utilized at temperatures not higher than 750K. Thermally treated graphite residue contains up to 36% of other components, indicating on strong interparticle interaction in it.

Similar study was performed on C_8Cs fluoration products, obtained from various graphites (oil coke, technical carbon, Zaval'ievsk location natural graphite, electrolytical graphite) under different C_8Cs synthesis temperature (without heating, at 425K, at 725K) and with the help of a number of fluoration agents (fluorine-argon mixture, $(C_3F_7)N$, $CCl_2F\text{-}CClF_2$). Substantial differense of the above data against corresponding results, detained for samples synthesized by freon-113 interaction with C_8Cs (oil coke matrix) gave us possibility to suppose presence of CsCl in graphite composition material obtained. Further detail study showed the absence of CsF in GICFP and formation of CsCl in it.

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