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Note

THERMAL ANALYSIS OF GRAPHITE INTERCALATION COMPOUNDS WITH DICHLORIDES OF SOME *d*-ELEMENTS

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A prospect of the practical usage of graphite intercalation compounds (GICs) dictates the necessity of studying their physico-chemical characteristics, which are also of certain scientific interest. For GICs with *d*-element dichlorides, however, such information is scarce in the literature.

The aim of this paper is to carry out the thermal analysis (TA) for GIC–$MeCl_2$ (Me=Mn, Fe, Co, Ni, Cu) up to 1300 K.

EXPERIMENTAL

GIC–$MeCl_2$ synthesis and identification was performed as in ref. 1. The substances obtained were of the second (Me=Fe, Co, Ni, Cu) and first stage (Me=Mn, Co, Cu) compounds [2]. GIC–$CuCl_2$, which was a 2nd (8–10%) and 1st stage mixture, was also studied [3]. Note that, according to the form of the X-ray diffractograms, GIC–$FeCl_2$ was characterized by an unordered structure of the intercalated layer.

Thermal analysis of the GICs was carried out using thermogravimetric (TG), differential thermal (DTA) and thermodilatometric (TDA) analysis methods, as well as by means of the triple-heat-bridge method along with X-ray and chemical analyses [4,5]. Reproducibility errors for the characteristics measured are given in Table 1 at the assigned statistical reliability of 0.95.

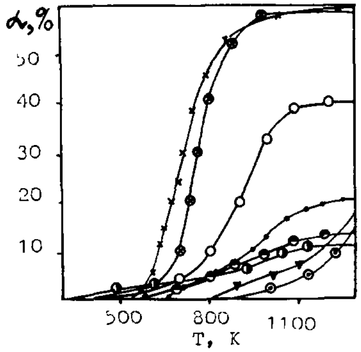
RESULTS AND DISCUSSION

TA results obtained are given in Figs. 1–3 and in Table 1. As it follows from the TG curves (Fig. 1), heating of GIC samples up to 1300 K at 5 K min^{-1} and 1.2–1.5 Pa leads to their thermodestruction.

TABLE 1

Physico-chemical properties of GIC–$MeCl_2$ at high temperature with Mn (1), Co (7), Cu (8) (1st stage), Ni (4), Co (3), Fe (2), Cu (5) (2nd stage) and Cu (6) (1st + 2nd stage mixture)

GIC	$C_p = a\times10^{-2} + b\times10^{-5}T - c\times10^{4}T^{-2}$ ($J\,g^{-1}\,K^{-1}$) (±2.5%)			ΔT (K)	$\beta\times10^{6}$ (K^{-1}) (±5%)	ΔT (K)
	a	*b*	*c*			
1	−32.3501	218.667	−3.15134	350–400	58.8	300–470
	96.9003	6.80034	4.26992	480–600	361	470–530
					1550	530–570
2	47.3592	94.5870	0.581162	350–540	106	300–500
					635	510–620
					250	630–670
					67	680–720
3 [4]	73.8357	63.1693	2.57635	350–600	102	300–580
					311	590–820
4	71.7404	56.6343	2.23673	350–600	46	450–570
5	91.5743	42.7127	3.68015	380–550	–	–
6 [3]	83.8986	−16.2856	2.50269	370–500	86	290–475
					504	485–800
7 [4]	60.9833	45.5410	1.04695	350–600	117	290–540
					265	550–590
					80	600–820
8 [4]	34.6357	57.7184	−0.475346	370–520	99	290–440
					135	450–520
					700	530–590
					197	600–820



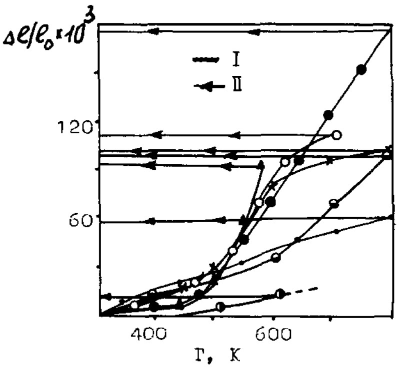


Fig. 1. TG curves for heating to 1300 K (rate, 5 K min^{-1}: vacuum) of the 1st stage GIC–$MeCl_2$ compounds with Mn (4), Co (5), Cu (8), 2nd stage compounds with Ni (1), Fe (2), Co (3), Cu (6), and (1st + 2nd) stage with Cu (7).

Fig. 2. Relative elongation of the pressed cylindrical samples of the 1st stage GIC–$MeCl_2$ compounds with Mn (4), Co (3), Cu (5), 2nd stage compounds with Ni (1), Co (2), Fe (6), and (1st + 2nd) stage with Cu (7) vs. temperature. (I) Heating, (II) cooling.

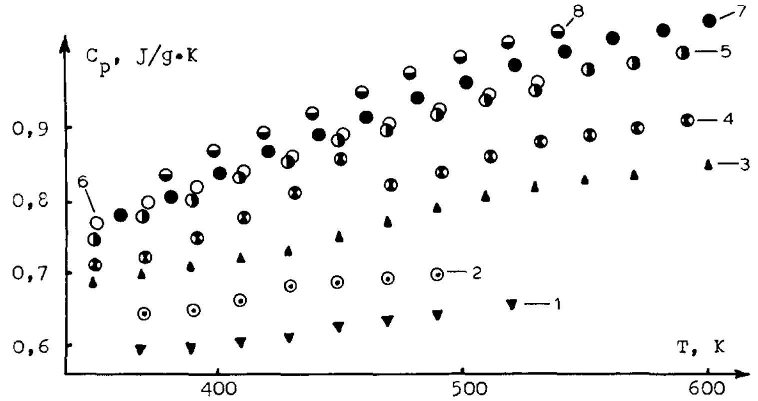


Fig. 3. Heat capacities of the 1st stage GIC–MeCl$_2$ compounds with Cu (1), Co (3), Mn (4), 2nd stage compounds with Ni (5), Fe (6), Co (7), Cu (8), and (1st + 2nd) stage with Cu (2) vs. temperature.

One can see that the temperatures of the beginning of the samples' mass loss and their decomposition degree (α) essentially differ for the GICs investigated. One should note that the complete removal of an intercalant up to 1300 K evidently takes place only for GIC–CuCl$_2$, but in all other cases, mainly the edge chloride molecules are removed. Mass loss rate curves are characterized by a monotonous temperature dependency for GIC–Ni(Fe)Cl$_2$ and the existence of extremum sections for GIC–Co(Mn, Cu)Cl$_2$. By means of X-ray and chemical analyses it was noted that when GICs were heated in vacuum the intercalant was removed as MeCl$_2$, only for GICs–CuCl$_2$ at higher temperatures was the appearence of Cu^{1+} noted.

DTA and TDA results agree with TG data. Endothermal peaks on DTA curves (or baseline deviations from "zero position", which is the beginning of the endothermal peak forming) correspond to temperature intervals of the main mass loss by GIC samples. A sharp increase in relative elongations in the axial direction ($\Delta l/l_0$) of the compacted samples observed within the same temperature intervals also agrees with the above results (Fig. 2).

Note that, with the same stage, GIC–Mn(Ni, Fe, Cu)Cl$_2$ thermal expansion, as a whole, has the same characteristics as we observed earlier for GIC–CoCl$_2$ [4]: irreversibility, anisotropy, possibility of hysteresis implementation, dependence on thermal and pressure prehistory of samples, greater linear thermal expansion coefficient values (β) in comparison with those for the corresponding graphite and salt mixtures, though there are specific features and essential differences, and the thermal expansion for different stage GICs with the same guests is different [4].

In the case of (1st + 2nd) stage GIC–CuCl$_2$ compounds, for which a practically complete CuCl$_2$ removal was observed during pyrolysis, by means of quantitative DTA we evaluated a heat of decomposition of 170 ± 10 (at 1.2–1.5 Pa) and 115 ± 10 kJ mol^{-1} in air; in a sealed stainlesssteel ampoule, where the processes of removing the introduced component from the sample do not take place, the value obtained: (75 ± 7) evidently characterizes the heat necessary for the fracture of the C–salt bond (one can suppose that in this case the mechanism of the thermodestruction process will differ from that discussed above in vacuum).

Data on the heat capacity (C_p) of GIC–$MeCl_2$ show (Fig. 3) that within the temperature range 350–600 K, C_p monotonously rises with the temperature increase. Only for GIC–$MnCl_2$ does an anomaly take place within the range 410–470 K, and this is evidently due to the thermostimulated structure rearrangement of the intercalant layer. This anomaly is reversible and similar to that observed earlier for other GICs, particularly in ref. 5 for GIC–$FeCl_3$. Enthalpy and entropy values of the above transition, evaluated on the basis of $C_p(T)$ data, give about 1.3 J g^{-1} and 0.003 J g^{-1} K^{-1}, respectively.

Results of the mathematical treatment of $\Delta l/l_0$ and C_p temperature dependencies are given in Table 1.

Thus, on the basis of GIC–$MeCl_2$ (Me=Mn, Fe, Co, Ni, Cu) TA data one can conclude that of the investigated compounds GIC–$NiCl_2$ is the most thermostable, and the least stable ones are GIC–$CuCl_2$ compounds. For one and the same intercalant $MeCl_2$ the second stage GICs are more stable and characterized by greater thermal expansion coefficients in comparison with the first stage compounds [3,4,6].

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