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THEORETICAL MODEL AND EXPERIMENTAL STUDY OF PORE GROWTH DURING THERMAL EXPANSION OF GRAPHITE INTERCALATION COMPOUNDS

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A new technique, which allows one to simultaneously follow the mass and volume of graphite intercalation compounds (GICs) during thermal transformation into expanded graphite, was developed. This enabled us to elucidate the mechanism for the thermal expansion of GICs and formulate a quantitative model for the process. Effective activation parameters of the thermal decomposition of new GICs were obtained by using non-isothermal kinetics procedure. Thermal decomposition was described as a break of intermolecular bonds followed by diffusion.

Keywords: *graphite intercalation compounds, micro-pores, thermal decomposition, thermal expansion*

Introduction

Graphite intercalation compounds (GICs) have a unique ability of huge expansion under heating. Several mechanisms for expansion were proposed [1–7], but some of them need to be substantiated by more detailed studies. Some authors suggested expansion to begin through formation of penny-shaped micro-cavities, which undergo further expansion [4–6]. Islands of intercalant, as suggested by Daumas and Herold, are likely to be nucleation centers [8].

The most advanced mechanism for the thermal expansion of GICs was proposed by Martin and Brocklehurst, who elaborated the description based on the Griffith crack [6]. In the present study, we will describe thermal expansion of GICs made from graphite nitrate. Graphite nitrate is known to be unstable even at room temperature. Its stabilized forms were obtained by treating it with some kinds of organic compounds [9]. For all these compounds made from natural flake graphite, expansion is obviously 3 dimensional, unlike 1D expansion of residual pyrographite bromide studied in [6]. Consequently, our final results will differ from those of [6].

Traditional experimental methods of thermal analysis were rarely used for studying the GICs decomposition. Some examples are known for the GICs with metal chlorides, e.g. [10], but no extensive literature on the decomposition of GICs with Brønsted acids is available. Described below is a method of thermal analysis especially tailored to GICs that allows one to simultaneously determine both the mass and the volume of the GIC sample.

Experimental

Compounds, which were selected as modifiers for graphite nitrate, are listed in Table 1. The detailed description of the synthesis of the corresponding GICs can be found in [9].

Table 1 Activation parameters of thermal decomposition of modified graphite nitrates

Modifier	A/K^{-1} c^{-1}	E/kJ mol^{-1}
Dioxane	2.45	53.3
Ethylene glycol dimethyl ether	1440	76.1
Ethyl formate	852	74.3
Formic acid	1235	75.3
Methylacetate	429	73.2
Ethylacetate	247	69.3
Pentylacetate	0.1	41.4

A typical sample of 20 mg was chosen to provide an equal temperature distribution inside the bulk of material and also a nearly uniform pressure upon flakes in all the parts of the sample. We call such process ‘free expansion’.

The experimental set-up, which allows one to simultaneously measure the mass loss and volume, includes the balance connected to the cylindrical glass

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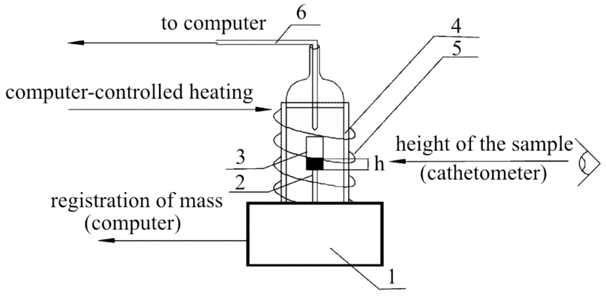

Fig. 1 Set-up for simultaneously measuring the volume and mass loss of the GIC sample under heating; 1 – balance, 2 – sample holder, 3 – cylindrical glasstest-tube, 4 – tubular glass furnace, 5 – nichrome wire, 6 – thermocouple

test-tube by the sample holder (Fig. 1). The sample holder is placed into the tubular glass furnace heated with a nichrome wire. The temperature inside the furnace is monitored with the thermocouple, which was connected to the ADC card inside the computer. Control over the heating was performed by a specially written computer program. The computer also registered the mass of the sample. An experimental error of mass determination was 0.05 mg. The volume of the sample was followed by visual inspection of the sample height using the cathetometer with an accuracy of 0.05 mm.

We used a constant heating rate of 2K min^{-1}. Preliminary tests showed this rate to be sufficiently low for achieving quasi-stationary conditions, so activation energy measured is not influenced by the heating rate. The temperature interval used was 20 to 400°C, which is sufficient for deintercalation reactions to be completed. Side reactions, for instance oxidative destruction of GICs by air, usually take place at much higher temperatures.

Results and discussion

Model for GICs expansion

The typical temperature dependences both of the volume and of the mass loss are expressed by sigmoid curves where four successive steps in thermal decomposition can be distinguished (Fig. 2). Initially, the mass loss is not accompanied by the volume change of the sample. We attribute this to the removal of surface and edge bounded species. The 2$^{\text{nd}}$ step, which could be related to the formation of isolated pores, is characterized by an abrupt increase in the sample volume with the mass loss being moderate. The most rapid mass loss arises during the 3$^{\text{rd}}$ step, the slope of the expansion curve becoming almost constant. Isolated pores turn into interconnected channels with opened edges. The last step is the removal of the rest of gaseous products, while the volume remains constant.

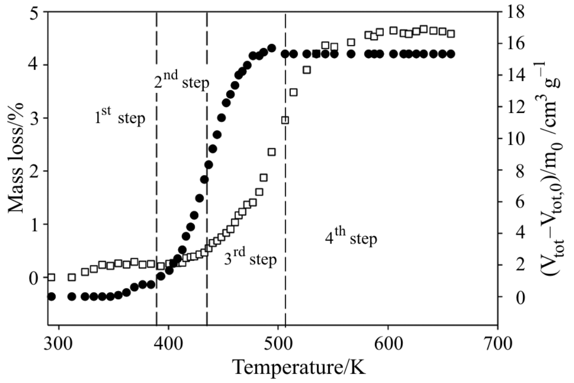

Fig. 2 Successive steps in thermal decomposition of the graphite nitrate based GICs (sample modified by formic acid); □ – mass loss dependence on temperature, ● – volume change *vs.* temperature

Peculiarities of the curves can be explained on the basis of a physical model giving a quantitative description to the process. For this, we proceed from some initial points. As showed by Inagaki [11], the cavity in exfoliated graphite looks like a body of rotation whose form closely resembles an ellipsoid. This is quite natural because of the two-dimensional isotropy of the layer of intercalated species. We make an assumption that the ratio γ of semi-axes a and c of this body remains unchanged during thermal expansion, i.e.

$$a/c=\gamma=\text{const} \qquad (1)$$

According to [11], at the end of expansion under thermal shock conditions, a and c values range from 10 to 16 μm and from 6 to 8 μm, respectively. We have also assumed that

- the gas in the cavity obeys the ideal gas law

$$PV=\nu RT \qquad (2)$$

- the pressure P inside the cavity, which is similar to the Griffith crack, is expressed by Eq. (3) [12]

$$P=\beta/\sqrt{a} \qquad (3)$$

where β depends on elastic properties of GICs.

Although Eq. (3) was established for a cylindrical cavity [12], we assume it to be valid for an arbitrary body of rotation as well. Note that an explicit expression for β is unnecessary for our purposes. The volume of the cavity V is expressed by

$$V=gca^2 \qquad (4)$$

where g is the geometrical factor, e.g. for an ellipsoid g=4/3π. It is of crucial importance that the number of moles of gas in the cavity ν is not constant and increases rapidly due to instant evaporation of intercalant from the layer region captured by the cavity:

$$\nu=n\pi a^2 \qquad (5)$$

where n is the number of moles vaporized from the unit surface, πa^2 is the circle area. After substitution of Eqs (1), (3)–(5) into Eq. (2) one obtains the following expression for c:

$$c=\gamma(\pi nRT/g\beta)^2 \tag{6}$$

Substitution of Eq. (6) into (4) on account of Eq. (1) gives the expression for the volume of the cavity:

$$V=(\gamma^5\pi^6/g^5)(nRT/\beta)^6 \tag{7}$$

Note the unusual high-power dependence of the volume on temperature.

To accommodate the model to the description of the experimental data, it is necessary to turn from the cavity volume to the sample volume. Supposing that the cavities do not coalesce, the change in the sample volume is determined by the total volume of the cavities.

$$V_{\text{tot}}-V_{\text{tot},0}=(g^5\pi^6/g^5)N(nR/\beta)^6(T^6-T_0^6) \tag{8}$$

where V_{tot}, $V_{\text{tot},0}$ are the sample volumes at the current and initial temperatures, respectively; N – is the number of cavities in the sample. The calculation of the difference in Eq. (8) allows us to exclude the volume not related to cavities. The constant factor in Eq. (8), which includes unknown quantities such as β, n, N, γ, was found from the fitting of experimental points.

The model proposed is in good agreement with the experimental data on the thermal expansion of the GICs studied. It corresponds to the 2nd step in thermal decomposition when the mass loss is still small. The examples below confirm the validity of the model (Figs 3 and 4), with correlation coefficients being typically about 0.98–0.99.

As can be seen from the figures, the second step, which is characterized by the 6th power temperature dependence of the volume, is followed by the approximately linear dependence. This may be caused by several reasons. The first reason for the linearity is the mass loss, which is characteristic of the 3rd step. On the other hand, the linearity can be connected with the spreading of the expanding cavity in a region with no intercalant. If this is the case, the number of moles becomes constant, unlike Eq. (5). Instead, we have

$$\nu=\nu_1=\text{const.} \tag{9}$$

and further

$$c=[(\nu_1RT/\beta g)^2/\gamma^3]^{1/5} \tag{10}$$

$$V=(\gamma/g)^{1/5}(\nu_1RT/\beta)^{6/5} \tag{11}$$

As is evident from the last formula, the temperature dependence of the volume is almost linear. Thus, the presence of the step of the linear dependence of the volume on temperature may be considered as an implicit indication of the island-like structure of the GICs corresponding to the Daumas–Herold model [8].

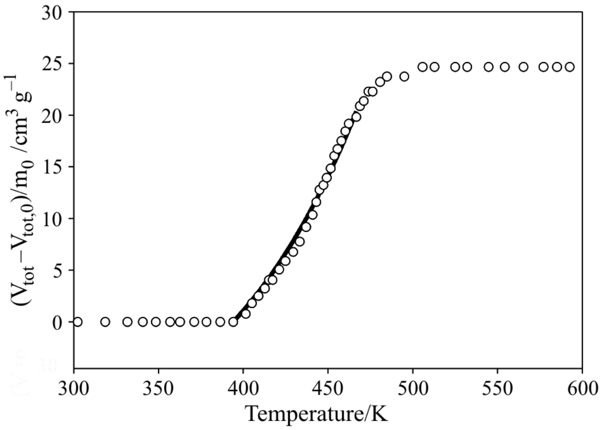

Fig. 3 Comparison between the experimental data and the model proposed for the pore growth inside the GIC sample modified by dioxane; ○ – temperature dependence of the volume per 1 g of initial sample, —– calculated curve by using Eq. (8)

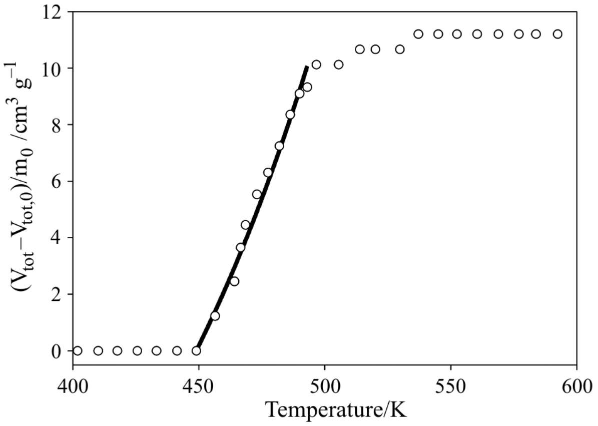

Fig. 4 Comparison between the experimental data and the model proposed for the pore growth inside the GIC sample modified by glacial acetic acid; ○ – temperature dependence of the volume per 1 g of initial sample, —– calculated curve by using Eq. (8)

Non-isothermal kinetics of GICs expansion

Since our method is also able of providing us with the data on the mass, we used these conventional thermogravimetric data to obtain kinetic parameters as this could shed light on chemical transformations connected with thermal decomposition.

For the mentioned purpose, a non-isothermal kinetic approach was chosen. This approach has an advantage of giving the kinetic parameters in a single continuous experiment, provided that the description is valid over the whole range of transformation temperatures [13]. In contrast, the isothermal procedure is frequently incapable of describing the process at higher temperatures, most of the sample decomposing significantly before the needed temperature is reached.

The observed parameter of thermal decomposition is a degree of transformation α

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \tag{12}$$

where m – the current mass, m_0 and m_∞ – the initial and residual masses. While there are numerous models for describing thermal decomposition of solids, we use an approach consisting in formally applying the homogeneous kinetic model

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(1-\alpha)^{\mathrm{n}} \tag{13}$$

where k is the rate constant, n is the reaction order. The heating rate b does not depend on the reaction time t.

$$T=\mathrm{bt}+T_0 \tag{14}$$

where T and T_0 – the current and initial temperatures, respectively. In what follows we will use the temperature dependence of k, similar to the Arrhenius equation, with the pre-exponential factor proportional to T

$$k = AT\exp\left(-\frac{E}{RT}\right) \tag{15}$$

The solution of Eq. (13) on account of Eqs (14) and (15) is given by

$$g_{\mathrm{n},\alpha_0}(\alpha) = \int_{\alpha_0}^{\alpha} \frac{\mathrm{d}\alpha}{(1-\alpha)^{\mathrm{n}}} = \frac{A}{b}\int_{\mathrm{T}_0}^{\mathrm{T}} T\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \tag{16}$$

Integration over α is easily performed, while the right-hand side of Eq. (16) is a special function depending on the parameter E called 'apparent activation energy'. As usual, partial integration leads to asymptotic expansion, in which we keep three terms only

$$g_{\mathrm{n},\alpha_0}(\alpha) = I(T) - I(T_0) \tag{17}$$

$$I(T) = \frac{AR}{bE}T^3\exp\left(-\frac{E}{RT}\right)\left[1 - 3\frac{R}{E}T + 12\left(\frac{R}{E}\right)^2 T^2\right] \tag{18}$$

Despite various methods for determining parameters A and E, which are mainly aimed at overcoming the calculation difficulties (e.g. [14–18]), at present A and E can be obtained using numerous computer programs directly from Eqs (17), (18).

The experimental $g(\alpha)$ curves were established to be best fitted by Eqs (17), (18) with n=2. Final results are given in Table 1. To demonstrate the adequacy of the calculations, we give a typical kinetic curve in Fig. 5.

As is evident, the correspondence between the theoretical and experimental curves is sufficiently good. It is important that the equations chosen describe the experimental data practically over the whole range of the degree of transformation (from 0.02 to 0.98), with the non-linear regression correlation coefficients being within the limits of 0.997–0.998. Relative errors of A and E determination are typically 4 and 0.2%, respectively.

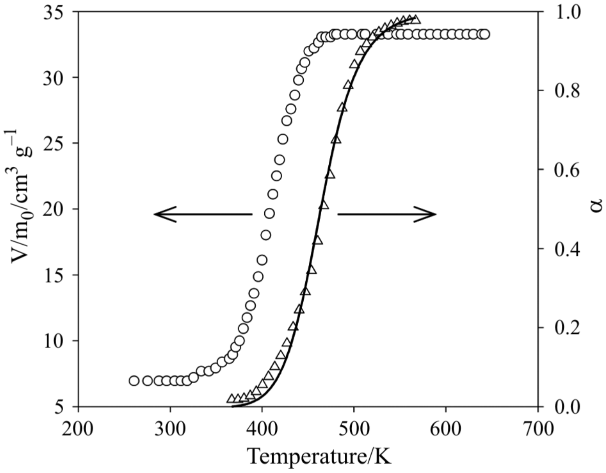

Fig. 5 Thermal decomposition of graphite nitrate modified by ethyl formate; ○ – temperature dependence of the volume per 1 g of initial sample, △ – temperature dependence of the experimental degree of transformation, — – calculated curve by using Eq. (17)

While the real meaning of E is controversial as regards the solid-state reactions [19], it is noteworthy that the apparent activation energies are somewhat higher than those inherent in the processes limited by diffusion [20]. This may partially be ascribed to the rupture of relatively strong intermolecular bonds. The E values are close to the energies of the strong hydrogen bonds formed by charged species, which are supposed to exist for this kind of GICs [21]. Thus, the measured kinetic parameters are mean values that reflect both the thermal decomposition of GICs and the outflow of gaseous products of decomposition.

Conclusions

An experimental method is proposed for studying the thermal expansion of GICs under quasi-stationary conditions. The experimental set-up allows one to simultaneously measure the volume and mass of the sample under heating. The data obtained are analyzed by means of the theoretical model elaborated.

According to the model, a unique property of GICs to increase their volume under heating is explained by Eq. (8), with its 6th power of temperature. This is due to three synergetic factors: the accumulation of gaseous phase in the cavity, the increase in temperature, and the decrease in the pressure limiting the development of the cavity with its growth. The model is in good agreement with the experimental data.

The activation parameters of thermal decomposition of the new GICs produced from graphite nitrate are obtained from non-isothermal kinetic calculations. The *E* values evidence the duality of the process, most likely being a break of hydrogen bonds followed by diffusion.

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