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DETERMINATION OF KINETIC PARAMETERS OF PHASE TRANSITION ON THE BASIS OF DTA MEASUREMENTS

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Abstract

A simple method of determination of kinetic parameters by analysis of *DTA*(*t*) function was developed for the case of systems undergoing transitions without mass change and when kinetic equation describing transition rate is known. The presented method also permits the determination of transition rate dα/dt (or $\alpha(t)$) when the kinetic equation of transition is unknown. The developed method was tested using DTA data of crystallization of $2CaO{\cdot}Al_2O_3{\cdot}1.95SiO_2$ glass pure and doped with Cr^{3+} and Nd^{3+}.

Keywords: DTA theory, kinetic equation, phase transition

Introduction

The kinetic analysis of any process usually requires knowledge concerning the time dependence of conversion degree $\alpha(t)$. Determination of $\alpha(t)$ function in the case of thermal analysis methods is easy only when mass of system under reaction changes as a function of time (or temperature) and TG curve can be used for the calculation of the conversion degree α. It is not the case of phase transition, when only DTA signal can be recorded. Theoretical analysis of relations between shape of DTA peak and the conversion degree of a process responsible for the DTA signal is relatively complex and after different necessary simplifications leads to equations poorly describing real dependence $\alpha(t)$. As an example the following equation can be shown [1]:

$$\alpha(t) \approx 1 - \frac{1}{F_0}\left(f(t) - \frac{C_p}{K}\Delta T(t) \right) \tag{1}$$

where:

$$F_0 = \int_0^\infty \Delta T(\tau)\mathrm{d}\tau \quad f(t) = \int_t^\infty \Delta T(\tau)\mathrm{d}\tau \tag{1a}$$

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where C_p – heat capacity of the crucible and sample, K – constant characteristic of the applied apparatus (can be experimentally determined), ΔT – temperature difference between sample and reference at the moment t.

Equation (1) allows the determination of $\alpha(t)$ function using experimental data from the DTA signal. Equation (1) is independent of the kinetic model describing the rate of process responsible for the DTA signal. As a matter of fact, it is the origin of the troubles with description of real $\alpha(t)$ dependencies by simplified Eq. (1), because the shape of DTA peak strongly depends on kinetic equation corresponding to the process leading to heat consumption or production [2]. Moreover, it is illogical to use $\alpha(t)$ calculated on the basis of assumption, that $\alpha(t)$ is independent of the kinetic model, to search kinetic equation corresponding to that model. In the present paper it is shown, that in the case of constant sample mass during reaction, it is possible to find the kinetic parameters of the phase transition responsible for DTA peak by numerical analysis of *DTA*(t) function, taking into account that the shape of a DTA peak depends on the kinetic equation describing rate of this transition.

Analysis of DTA(*t*) function

Let us assume that at the moment t, in a furnace chamber (temperature T_c) of DTA apparatus, two crucibles with sample and reference are placed, the temperatures of which are T_s and T_r respectively. Under non-isothermal conditions – corresponding to DTA technique – temperature T_c as function of time t can be expressed as: $T_c=T_0+\beta t$, where β is heating rate and T_0 is temperature corresponding to t=0. During time dt, quantity of heat exchanged between the furnace chamber and the crucible with reference is equal dQ_r. Simultaneously dQ_s=dQ_p+dQ_t represents heat exchanged between the furnace chamber and the crucible with sample (dQ_p) plus heat either consumed or produced during sample transition (dQ_t). Taking into account heat balance we have:

$$\frac{\mathrm{d}Q_r}{\mathrm{d}t}=(m_r c_r+m_c c_c)\frac{\mathrm{d}T_r}{\mathrm{d}t} \qquad \frac{\mathrm{d}Q_p}{\mathrm{d}t}+\frac{\mathrm{d}Q_t}{\mathrm{d}t}=(m_s c_s+m_c c_c)\frac{\mathrm{d}T_s}{\mathrm{d}t} \tag{2}$$

where m_r, m_s, m_c, c_r, c_s, c_c represent masses and specific heats of reference, sample and crucible, respectively. Of course, the above heat balance needs m_s=*const*., thus validity of developed model is limited to phase transitions or to the reactions like $A_{solid}\rightarrow B_{solid}+C_{solid}$. On the other hand, we have:

$$\frac{\mathrm{d}Q_r}{\mathrm{d}t}=k_{cr}(T_c-T_r) \qquad \frac{\mathrm{d}Q_p}{\mathrm{d}t}=k_{cs}(T_c-T_s) \qquad \frac{\mathrm{d}Q_t}{\mathrm{d}t}=-\Delta H\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{3}$$

where k_{cr}, k_{cs} are coefficients of heat transfer between furnace chamber and crucible with reference and sample, respectively. ΔH is total enthalpy change during sample transition and dα/dt is reaction rate. In the case of modern DTA apparatus, we can assume that $k_{cr}=k_{cs}=k_c$, because $m_s<<m_c$. Finally, Eqs (2) and (3) transform to:

$$\frac{\mathrm{d}T_\mathrm{r}}{\mathrm{d}t}=K(T_\mathrm{c}-T_\mathrm{r}) \quad \frac{\mathrm{d}T_\mathrm{s}}{\mathrm{d}t}=K(T_\mathrm{c}-T_\mathrm{s})+H\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{4}$$

where $K=k_\mathrm{c}/m_\mathrm{c}c_\mathrm{c}$ and $H=-\Delta H/m_\mathrm{c}c_\mathrm{c}$.

Because $DTA(t)=T_\mathrm{s}(t)-T_\mathrm{r}(t)$, we can rewrite Eq. (4) in form:

$$\frac{\mathrm{d}DTA(t)}{\mathrm{d}t}+KDTA(t)=H\frac{\mathrm{d}\alpha}{\mathrm{d}t} \tag{5}$$

and after integration we obtain:

$$DTA(t)=H\mathrm{e}^{-\mathrm{Kt}}\int_0^\mathrm{t}\mathrm{e}^{\mathrm{K}\tau}\frac{\mathrm{d}\alpha}{\mathrm{d}\tau}\mathrm{d}\tau \tag{6}$$

Equation (6) describes the DTA signal in the scope of the developed model. It is easy to notice that the shape of the DTA peak depends on kinetic equation describing the transition rate of the sample during heating.

Now let us consider one example. $\alpha(t)$ is expressed by Avrami (Mehl–Johnson) equation for many phase transitions: $\alpha(t)=1-\exp(-kt^\mathrm{n})$, were k and n are parameters. k depends on temperature, and n is independent of, or slightly dependent on temperature. Differentiation of Avrami equation gives:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=nkt^{\mathrm{n}-1}\exp(-kt^\mathrm{n}) \quad \text{or} \quad \frac{\mathrm{d}\alpha}{\mathrm{d}t}=nk^{1/\mathrm{n}}\left[\ln\left(\frac{1}{1-\alpha}\right)\right]^{\frac{\mathrm{n}-1}{\mathrm{n}}}(1-\alpha) \tag{7}$$

Thus the rate constant K_t of transition is given by equation:

$$K_\mathrm{t}=nk^{1/\mathrm{n}}=K_0\exp\left(-\frac{E_\mathrm{a}}{RT_\mathrm{s}}\right) \tag{8}$$

where E_a is activation energy and K_0 is a constant.

After introducing (7) and (8) into (6) we obtain:

$$DTA(t)=nH\mathrm{e}^{-\mathrm{Kt}}\int_0^\mathrm{t}\mathrm{e}^{\mathrm{K}\tau}\,\Xi_0(\tau)\tau^{\mathrm{n}-1}\exp(-\Xi_0(\tau)\tau^\mathrm{n})\mathrm{d}\tau \tag{9}$$

where:

$$\Xi_0(t)=\left(\frac{K_0}{n}\right)^\mathrm{n}\mathrm{e}^{-\frac{\mathrm{nE_a}}{\mathrm{RT_s(t)}}} \tag{10}$$

Equation (9) contains five parameters H, K, E_a, K_0 and n. Parameter K can be easily calculated from the first expression of (4) using experimental temperatures. It is also possible to determine parameter H experimentally but, here, an alternative way will be used. For time t_max corresponding to maximum of DTA peak we have $\mathrm{d}DTA(t_\mathrm{max})/\mathrm{d}t=0$. As a consequence Eq. (5) takes form:

$$KDTA(t_{\max})=H\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{t=t_{\max}} \tag{11}$$

Introducing Eqs (8) and (10) into Eq. (7) we obtain:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=n\Xi_0(t)t^{n-1}\exp(-\Xi_0(t)t^n) \tag{12}$$

For time $t=t_{\max}$ Eq. (12) takes form:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{t=t_{\max}}=n\Xi_0(t_{\max})t_{\max}^{n-1}\exp(-\Xi_0(t_{\max})t_{\max}^{n}) \tag{13}$$

Taking into account Eqs (12) and (13) we can express parameter H as a function of E_a and K_0:

$$H(K_0,E_a)=\frac{KDTA(t_{\max})}{n\Xi_0(t_{\max})t_{\max}^{n-1}\exp(-\Xi_0(t_{\max})t_{\max}^{n})} \tag{14}$$

Introducing Eq. (14) into Eq. (9) we obtain finally:

$$DTA(t)=nH(K_0,E_a)e^{-Kt}\int_0^t e^{k\tau}\,\Xi_0(\tau)\tau^{n-1}\exp(-\Xi_0(\tau)\tau^n)\mathrm{d}\tau \tag{15}$$

This equation contains only three kinetic parameters: n, K_0 and E_a (K has to be determined experimentally). By fitting Eq. (15) to experimental DTA signal, $DTA^{\exp}(t)$, using condition: $\sum_{i=1}^{N}[DTA^{\exp}(t_i)-DTA(t_i)]^2\rightarrow \min$, these parameters can be found.

The above described way can be adapted for other kinetic models. Replacing Eq. (7) by adequate kinetic equation a new form of Eq. (15), corresponding to chosen kinetic model, can be derived. Thus the presented method has a general meaning.

Example: Crystallization of $2CaO{\cdot}Al_2O_3{\cdot}1.95SiO_2$ glass pure and doped with Nd(III) and Cr(III)

Crystallization of pure and doped with different cations glass belonging to $CaO–Al_2O_3–SiO_2$ system was studied earlier due to the importance of this process from the point of view of laser materials production [3–7]. The glass of composition $2CaO{\cdot}Al_2O_3{\cdot}xSiO_2$ crystallizes in one stage for $1<x<2.5$ (Fig. 1). The composition of crystals obtained as a result of crystallization is the same as the composition of the initial glass [3, 4]. In papers cited kinetic analysis of glass crystallization was performed on the basis of a simplified method, which considered only changes of DTA peak temperature with heating rate. Simplified methods allow the determination mainly of activation energy but the values obtained discussed in detail in [2] are doubtful.

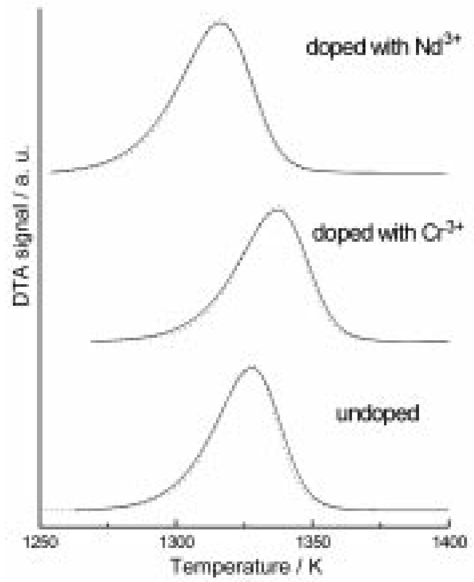

Fig. 1 Fitting of Eq. (15) to experimental DTA line of $2CaO \cdot Al_2O_3 \cdot 1.95SiO_2$ glass crystallization, pure and doped with chromium and neodymium (solid lines represent experimental DTA peak and dotted lines represent DTA curve calculated from Eq. (15) using fitted parameters from Table 1)

Table 1 Kinetic parameters of crystallization of $2CaO \cdot Al_2O_3 \cdot 1.95SiO_2$ glass pure and doped with Cr^{3+} and Nd^{3+}

Glass composition	Dopant	Kinetic parameters	
		K_0	E_a/kJ mol^{-1}
$2CaO \cdot Al_2O_3 \cdot 1.95SiO_2$	–	$(6.10 \pm 7) \cdot 10^{26}$	749 ± 26
	Cr^{3+}	$(1.94 \pm 6) \cdot 10^{28}$	793 ± 28
	Nd^{3+}	$(4.36 \pm 4) \cdot 10^{22}$	638 ± 18

The developed method has been applied for the detailed description of the crystallization rate of $2CaO \cdot Al_2O_3 \cdot 1.95SiO_2$ glass pure and doped with Nd(III) and Cr(III). Figure 1 shows the quality of fitting Eq. (15) to experimental data when the assumption was made that the crystallization rate of the discussed glasses is described by Avrami equation with n=1.5 and Table 1 contains fitted kinetic parameters. Activation energies presented in Table 1 are consistent with those obtained for crystallization of glasses ($2CaO \cdot Al_2O_3 \cdot 2SiO_2$) [7].

Conclusions

The developed method of determination of kinetic parameters by numerical analysis of DTA peak can be applied for the systems in which the sample transition is not connected with mass change. Derived Eq. (5) permits the determination of the reaction rate when the kinetic equation is unknown. Thus the introduced method can be helpful in searching a kinetic model or an equation describing transition processes.

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