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KINETIC STUDIES OF THE CRYSTALLIZATION PROCESS OF GLASS-CERAMICS BASED ON BASALT

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The crystallization kinetic of the basalt glass ceramic of the oxide composition, (%): SiO_2 – 50.82; Al_2O_3 – 12.05; Fe_2O_3 – 9.28; CaO – 15.48; MgO – 11.08; Na_2O+K_2O – 1.14; TiO_2 – 0.15, with addition of 10% TiO_2 as nucleating agent has been studied using thermal analysis under non-isothermal conditions.

In this order, the non-isothermal DTA curves were obtained at different heating rates between 4 and 20°C min^{-1} in the temperature range of 25–1000°C using a Derivatograph-C (MOM, Hungary). The kinetic parameters of the crystallization process were calculated on the basis of Ozawa–Flynn–Wall, Friedman, Budrugeac–Segal and non-parametric kinetic methods.

Keywords: *crystallization kinetics, glass-ceramics, multi-step reaction, non-isothermal kinetics*

Introduction

The glass-ceramics obtained from the melting of basalt rocks develop a high mechanical and abrasion resistance, good chemical stability, special electrical properties and/or wear-resistance. These properties recommend the glass-ceramics for the production of erosion or wear-resistant materials, for fibered glasses and as matrices for nuclear waste inertization [1–4].

The nature and texture of the formed crystalline phases are decisive for the physico-mechanical properties of the glass-ceramics material and these may be influenced in broad limits by the thermal treatment conditions.

The glass ceramics can be obtained in the presence of some adequate nucleation agents which operate upon the crystallization process mechanism, modifying the activation energy, the texture of the obtained glass-ceramic product as well as upon its properties [5–7].

In our paper, the glass-ceramic was obtained using the Şanoviţa basalt (Romania) as raw material. The basalt from Şanoviţa quarry is mainly exploited for construction purposes, as aggregates for concretes and roads and railways embankment. A recent application for the basalt fine fraction is the obtainment of the glass-ceramics products, ceramic glasses and sintered products. Last, but not least, the Şanoviţa basalt has been studied with the view to elaborate a basalt glass designed to immobilize radioactive wastes as incinerator ashes [2, 3, 8, 9].

The main crystalline phase in the glass-ceramic based on basalt is represented by the pyroxene solid solution $Ca(Mg,Fe)SiO_3$ [1, 3, 10, 11].

In the present paper, the crystallization kinetic of the basalt glass-ceramic of the oxide composition, (%): SiO_2 – 50.82; Al_2O_3 – 12.05; Fe_2O_3 – 9.28; CaO – 15.48; MgO – 11.08; Na_2O+K_2O – 1.14; TiO_2 – 0.15, with addition of 10% TiO_2 as nucleating agent has been studied using thermal analysis under non-isothermal conditions.

The kinetic parameters of the crystallization process were calculated on the basis of Flynn–Wall–Ozawa, Friedman, Budrugeac–Segal and non-parametric kinetic methods. The possible crystallization mechanisms were investigated by comparing the obtained kinetic parameters.

Experimental

Sample preparation

The glass-ceramic was obtained by correction of the oxide composition of the natura Şanoviţa basalt by adding $MgCO_3$ and $CaCO_3$. The synthesis method of the glass-ceramic with 10% TiO_2 as nucleating agent (sample BVMT) was presented in our previous paper [5].

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Characterization methods

The samples were subjected to differential thermal analysis (DTA) using a C MOM Hungary derivatograph. The DTA curves were recorded in air in the temperature range 25–1000°C at heating rates: 4, 8, 12, 16, 20°C min^{-1}. The sample mass was 800 mg and the reference substance-aluminum oxide.

Data processing

According to the aim of this paper, the strategy of data processing is of relevance. Therefore, it will be detailed here.

Flynn–Wall–Ozawa integral method [12, 13]

Considering isoconversional conditions, i.e. for the same α_i, the corresponding temperature T_i at different heating rates, the plot of left member of Eq. (1) *vs.* $1/T_i$ give a straight line; from its slope, the activation energy can be calculated.

$$\ln\beta = \ln\left[A\frac{f(\alpha)}{\mathrm{d}\alpha/\mathrm{d}T}\right]_{\alpha} - \frac{E}{RT} \tag{1}$$

From start, the method of Flynn–Wall–Ozawa furnishes the activation energy for each conversion degree, when the data at different heating rates were processed and with this, the question of the variation E *vs.* α is opened.

Friedman differential-isoconversional method [14]

At constant conversion, the differential form of the reaction is:

$$\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha} = f(\alpha)\exp\left(-\frac{E}{RT}\right) \tag{2}$$

or the equivalent

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \tag{3}$$

At a certain conversion, the slope and the intercept of the straight line of $\ln(\beta\mathrm{d}\alpha/\mathrm{d}T)$ *vs.* $1/T$ gives the activation energy and the product $Af(\alpha)$, respectively.

Due to its relative simplicity and independence in respect of the kinetic model, the Friedman's is recommended for obtaining the value of the activation energy. By simple single-step processes, this is usually enough, the obtained E values being invariant in respect of α. A monotonous variation of E *vs.* α is a sign of a complex multi-step processes, and more sophisticated methods are necessary.

Budrugeac–Segal method [15–17]

This method is often useful for description and simulation of complex processes. It is logical a continuation of the Friedman's method and is based on a particular variation of the activation energy obtained with this method:

i) the dependence of E *vs.* α is described by:

$$E=E_0+E_1\ln(1-\alpha) \tag{4}$$

ii) there is a compensation effect, i.e.

$$\ln[Af(\alpha)]=aE+b \tag{5}$$

with Eqs (4) and (5), considering a conversion function

$$\alpha=(1-\alpha)^n \tag{6}$$

and Eq. (3) became:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \left(b + aE_0 - \frac{E_0}{RT}\right) + \\ +\left(aE_1 - \frac{E_1}{RT} + n\right)\ln(1-\alpha) \tag{7}$$

The correct value of n will be the one that gives a correlation coefficient closest to 1 for straight line represented by E *vs.* $\ln(1-\alpha)$, the constants E_0, E_1, a and b being obtained from Eqs (5) and (6), respectively.

Non-parametric kinetic (Sempere and Nomen) method [18–22]

This is a more sophisticated method wich allows the separation of two or more simultaneous processes of a decomposition reaction.

The reaction rates, $r=\mathrm{d}\alpha/\mathrm{d}t$, obtained at different heating rates, are represented in a 3D coordinate system (r, T, α), based on the general hypothesis:

$$r=f(T)g(\alpha) \tag{8}$$

By a proper interpolation algorithm, the obtained experimental points are simulated as a continuous reaction rate surface and then discretized into a square matrix M.

According to Eq. (8), each element of this matrix is:

$$r_{ij}=f(T_i)g(\alpha_j) \tag{9}$$

If the decomposition process is a result of two simultaneous steps 1 and 2, it means that:

$$r=r_1+r_2=f_1(T_i)g_1(\alpha_j)+f_2(T_i)g_2(\alpha_j) \tag{10}$$

respectively the matrix M became:

$$M=M_1+M_2 \tag{11}$$

NPK method uses the singular value decomposition (SVD) algorithm [18] to decompose the matrix M according to:

$$M=U(\mathrm{dg}\ S)V^{T} \quad (12)$$

A vector u_1 given by the first column of the matrix U is analyzed *vs.* α to determine the conversion function. For this we suggest the Šesták–Berggren [23] equation:

$$g(\alpha)=\alpha^{m}(1-\alpha)^{n}[-\ln(1-\alpha)]^{p} \quad (13)$$

A similar vector v_1, corresponding to the matrix V, is searched for an Arrhenius type temperature dependence.

In case of a multi-step process (according to Eqs (10) and (11)), the contribution of each step to the observed process is expressed by the explained variance λ so that $\lambda_1+\lambda_2=100\%$.

By applying this data processing strategy, a separation of complex processes and discrimination between the contributions of the physical (*m*) or the chemical (*n*) phenomenon are expected.

Results and discussion

Flynn–Wall–Ozawa method

In Fig. 1, a dependence of *E vs.* α is observed.

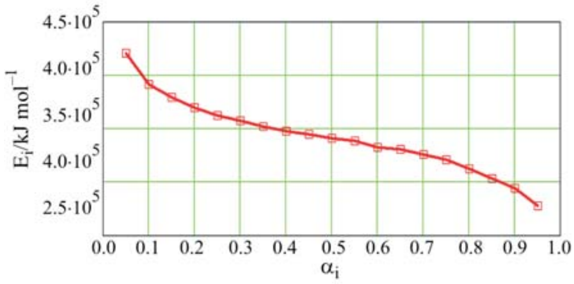

Fig. 1 The variation of activation energy (kJ mol^{-1}) *vs.* conversion degree (Flynn–Wall–Ozawa)

Friedman's methods

The data obtained according to Eq. (3) are summarized in Table 1.

For each isoconversional method, a strong variation of *E vs.* α is observed. That indicated a complex crystallization process for the studied glass-ceramic.

Budrugeac–Segal method

In order to apply the Budrugeac–Segal method, the variation of the activation energy according to Eqs (4) and (5) are checked in Figs 2 and 3.

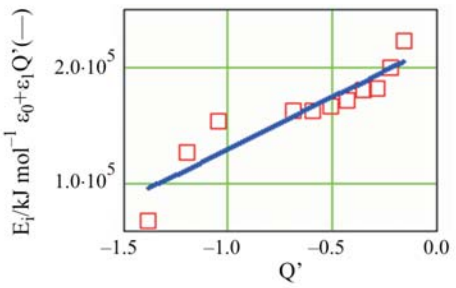

Fig. 2 Dependence E_{i} *vs.* ln(1–α)

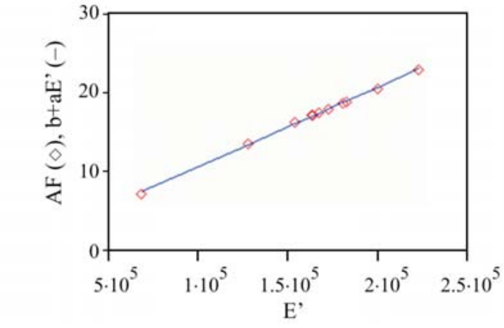

Fig. 3 Compensation effect according to Eq. (5)

The kinetic constants according Eq. (7) are collected in Table 2.

The constants of Budrugeac–Segal method are useful especially for simulations, a few examples depicted in Fig. 4.

NPK method

The experimental reaction rate and the surface obtained by interpolation are presented in Fig. 5.

Table 1 The variation of activation energy (kJ mol^{-1}) *vs.* conversion degree (Friedman)

Sample	α						
	0.2	0.3	0.4	0.5	0.6	0.7	0.8
BVMT	199.4	180.0	166.5	163.1	153.6	68.0	68

Table 2 The kinetic constants by Budrugeac–Segal method

Sample	E_0/kJ mol^{-1}	E_1/kJ mol^{-1}	*a*	*b*	*n*	Corr. coeff.
BVMT	219.3	89.05	$1\cdot10^{-4}$	0.455	0.1	0.9993

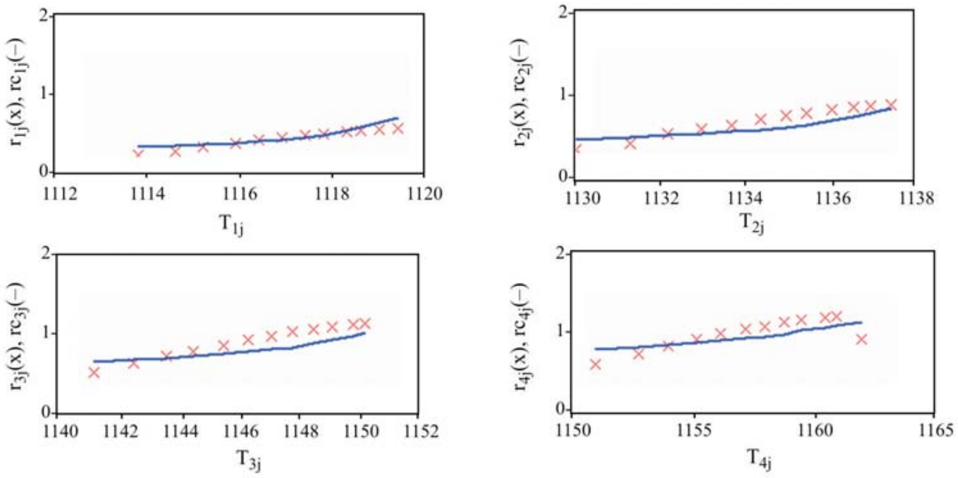

Fig. 4 × – Reactions rate and —– regenerated reactions rate at first 4 heating rates according with Eq. (7) and constants of Table 2

Table 3 Kinetic parameters of NPK method

Sample	Process	λ/%	*E*/kJ mol^{-1}	*A*/min^{-1}	*m*	*n*	*p*
BVMT	1	96.1	82.8	$1.89\cdot10^{3}$	1	1	–
	2	3.4	1057.8	$1.19\cdot10^{47}$	–	1	1

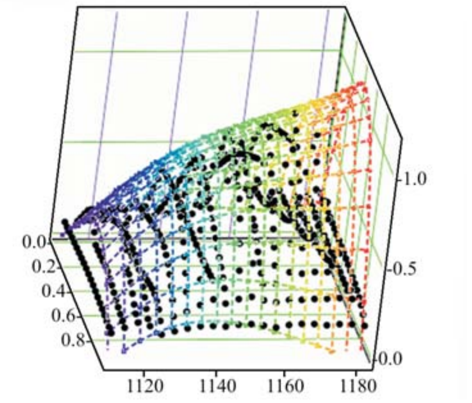

Fig. 5 Interpolated surface and experimental points

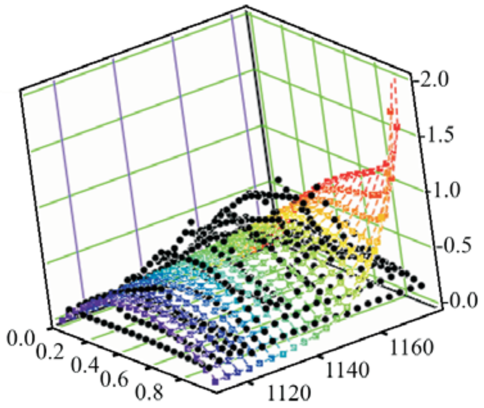

Fig. 6 Recalculated reaction surface according Eq. (14) and experimental points

The results of data processing using NPK method are given in Table 3.

A low contribution of the secondary process was observed. The reaction rate as a function of the conversion degree and temperature is:

$$\begin{aligned} r(\alpha,T) &= (1-\alpha)\alpha A_1 e^{-E_1/RT} s_1 + \\ &+\alpha[-\ln(1-\alpha)]A_2 e^{-E_2/RT} s_2 \end{aligned} \tag{14}$$

where s_1 and s_2 are the first and second value of SVD vectors.

Using Eq. (14) and data of Table 3, the reactions surface was recalculated and represented in comparison with experimental points of reaction rate in Fig. 6. A good agreement is observed.

Conclusions

Budrugeac–Segal method gives a good concordance between calculated and experimental reaction rate in domain of conversion 0.15–0.8. This method is very good for the prediction of thermal behavior, but do not give information about reaction mechanism.

Indifferent of the used method, the activation energy of the crystallization process of the studied glass-ceramics present high values, of the order of hundreds kJ mol^{-1}.

The isoconversional methods (FWO and Friedman) applied to the non-isothermal crystallization of the studied glass-ceramics show a large variation of the activation energy on the conversion degree. This confirms that the crystallization process is complex, multi-step process and the calculated activation energy is an apparent value.

The NPK method furnished a good agreement of recalculated and experimental points and suggested a possible two-step crystallization mechanism involving the nucleation and crystallites growth.

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