Journal of Thermal Analysis and Calorimetry, Vol. 88 (2007) 3, 647–652

KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION OF SOME GLASS-CERAMICS BASED ON BASALT

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The crystallization kinetics of some glass-ceramics obtained from Romanian (Şanoviţa) basalt has been studied in non-isothermal conditions using DTA technique. The activation energies of the crystallization processes were calculated using the isoconversional methods Kissinger–Akahira–Sunose and Ozawa–Flynn–Wall. The results obtained show a dependence of the activation energy (E_α) on the crystallized fraction (α) that proves the complex mechanism of the glass-ceramics crystallization process. It has been proved that the Johnson–Mehl–Avrami model cannot be applied for the studied glass-ceramics crystallization process. The effect of 2% TiO_2 as nucleating agent upon the crystallization kinetics and upon the microstructure of the studied glass-ceramics was analyzed.

Keywords: *crystallization kinetics, glass-ceramics, nucleation agents*

Introduction

Glass-ceramics obtained from the melting of basalt rocks have many industrial applications. The good thermal shock resistance, the special electrical properties, chemical inertness, abrasion resistance, mechanical strength and erosion or wear-resistance represent important properties of this materials [1–3].

As result of these properties and the low costs, the glass-ceramics based on basalt, are being used in different industrial fields like: wear resistant balls fort paints and lacquers homogenization, parts for combustion engines, tiles for paving in the chemical industry, replacement for the enamels used in the industrial environments at high temperatures, glazed tiles or matrices for nuclear waste inertization [3–5].

For the production of such materials, different types of basalt rocks were used in Germany, Spanish, Russia, the Czech Republic, Bulgaria, Romania, etc. [3–5].

There are many studies regarding the use of Romanian Şanoviţa (Timiş) basalt for obtaining some glass-ceramics, ceramic glazes and sintered products [2, 3, 6].

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, 6–9].

From the literature data [1, 3, 6, 7] and from our own studies [9, 10] result that, the physico-mechanical and chemical high performances for glass-ceramics involve the choice of the optimum chemical composition for the basalt glass, using the proper nucleation agents and adequate thermal treatment.

In a previous paper [10] we studied the influence of different amounts of CaF_2 as nucleation agent upon the crystallization kinetics of one glass-ceramics obtained from modified Şanoviţa basalt.

In the present paper, the crystallization kinetics of the glass-ceramics obtained from the modified Şanoviţa basalt without nucleation agent respectively with addition of TiO_2 as nucleation agent has been studied under non-isothermal conditions. The activation energies of the crystallization processes were calculated using the isoconversional methods Kissinger–Akahira–Sunose and Ozawa–Flynn–Wall [11, 12]. The validity of the Johnson–Mehl–Avrami model for the non-isothermal crystallization processes of the studied glass-ceramics was also investigated.

For the kinetic studies, a series of non-isothermal DTA measurements were carried out for various heating rates. The effect of nucleation agent upon the microstructure of the studied glass-ceramic was analyzed by means of scanning electron microscopy.

Experimental

Samples preparation

The glass-ceramic was obtained by correction of the oxide composition of the natural Şanoviţa basalt [11] by adding $MgCO_3$ and $CaCO_3$. The composition and the synthesis method of the glass-ceramic

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1388–6150/$20.00

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(sample BD) were presented in a previous paper [10]. Glass-ceramic with 2% TiO_2 as nucleation agent was also prepared.

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 various heating rates: 4, 8, 12, 16, 20°C min^{-1}. The sample mass was 800 mg and the reference substance-aluminum oxide.

The microstructure of the glass-ceramics without nucleation agent (sample BD) and in the presence of 2% TiO_2 as nucleation agent (sample BD-T2) was examined by using a Philips ESEM XL 30 scanning electron microscope.

Kinetic analysis

The general equation of the reaction rate for non-isothermal conditions at constant heating rate is generally written as [11, 12].

$$g(\alpha)=\frac{AE}{R\beta}p(x) \tag{1}$$

where $g(\alpha)$ is the conversion integral, A the pre-exponential factor, E the activation energy, R the general gas constant, β the heating rate and $p(x)$ is the temperature integral, where $x=E/RT$ is the reduced activation energy at the temperature T.

Applying different approximations for the temperature integral, a wide range of different isoconversional methods can be derived [11–17]. In the present work, two isoconversional methods were used:

Kissinger–Akahira–Sunose method

The Kissinger–Akahira–Sunose (KAS) method, sometimes called the generalized Kissinger method is one of the best isoconversional method. Using the Murray and White approximation [11,12,18] for the temperature integral $p(x)\cong e^{-x}/x^2$ ($20<x<50$), the KAS method is derived. At constant conversion α, this assumption leads to Eq. (2):

$$\ln\frac{\beta}{T_\alpha^2}=-\frac{E_\alpha}{RT_\alpha}+\text{const.} \tag{2}$$

where the subscript α designates values related to a given conversion degree.

The more precise approximation of Coats and Redfern [11, 19]: $p(x)\cong\frac{e^{-x}}{x^2}(1-2/x)$, leads to the same Eq. (2).

Ozawa–Flynn–Wall method

The approximation suggested by Doyle [11, 12, 20] for the temperature integral $p(x)\cong e^{-1.052x-5.330}$, derived to the Ozawa–Flynn–Wall (OFW) method. At constant conversion α, the linear Eq. (3) of Ozawa–Flynn–Wall results:

$$\ln\beta=-1.052\frac{E_\alpha}{RT_\alpha}+\text{const.} \tag{3}$$

Differential thermal analysis (DTA) is very suitable for the kinetic study of the glass-ceramic crystallization under non-isothermal conditions.

The crystallized fraction was determined from the DTA curves using Eq. (4):

$$\alpha(T)=\frac{A_{(\mathrm{T})}}{A_{(\mathrm{Total})}} \tag{4}$$

where $\alpha(T)$ is the crystallized fraction at the temperature T, $A_{(\mathrm{T})}$ the area at the temperature interval ΔT and $A_{(\mathrm{Total})}$ the total area of the crystallization peak.

In order to verify the applicability of the Johnson–Mehl–Avrami (JMA) model for the non-isothermal crystallization processes of the studied glass-ceramics, the Avrami exponent n was calculated using the Ozawa method [13, 14].

Ozawa method

Ozawa proposed an extension of the Avrami [21, 22] Eq. (5) to describe the kinetics of non-isothermal crystallization

$$\alpha=1-\exp(-Kt^{\mathrm{n}}) \tag{5}$$

where K and n are constants with respect to time.

At a given temperature, the equation proposed by Ozawa [14] is expressed as:

$$\log[-\ln(1-\alpha)]=\log\chi(T)-n\log\beta \tag{6}$$

where $\chi(T)$ is a constant.

The Avrami exponent n results from the slope of the plot of $\log[-\ln(1-\alpha)]$ as a function of $\log\beta$ at a given temperature.

Results and discussion

The DTA crystallization curves for the glass-ceramic with 2% TiO_2 as nucleation agent (sample BD-T2) for five different heating rates are presented in Fig. 1.

It is obvious that, with the increase of the heating rate there is a shift of the peak temperature to higher values. This behavior may be explained by the fact that, in non-isothermal conditions, the system state is

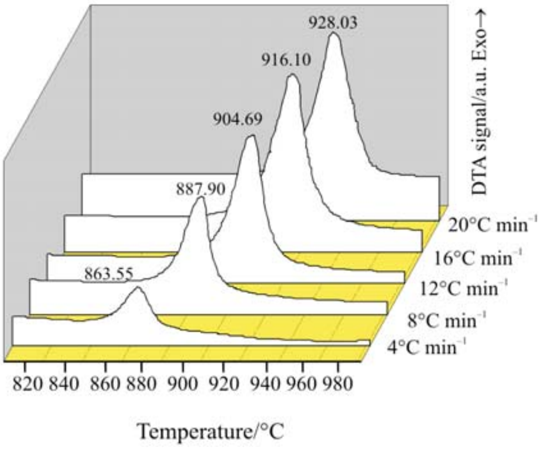

Fig. 1 DTA crystallization curves of BD-T2 sample for different hating rates

Table 1 Temperatures of DTA peaks for different heating rates of the BD sample

Heating rate/°C min^{-1}	4	8	12	16	20
Temperatures of DTA peaks/°C	860.25	884.10	898.80	910.02	917.98

closer to the thermal equilibrium state, the lower the heating rate is.

The temperatures at the maximum crystallization rate (temperatures of DTA peaks) of the BD sample [10] for different heating rates are presented in Table 1.

At the same heating rate for the BD and BD-T2 samples, the temperature of the DTA peak is slightly higher for the glass-ceramics with 2% TiO_2 (sample BD-T2).

The crystallized fraction was determined from the DTA curves using Eq. (4). The dependences of the crystallized fraction on temperature for sample BD-T2 is presented for different heating rates in Fig. 2.

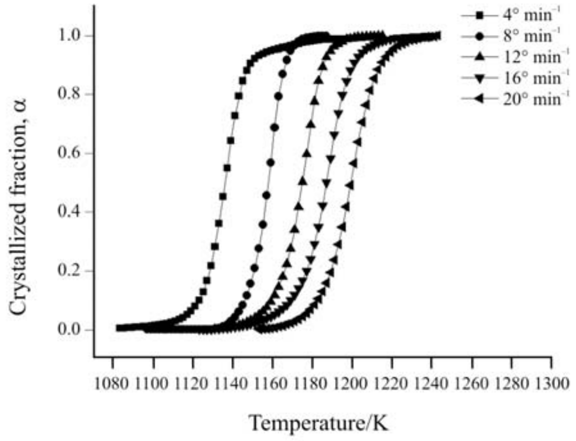

Fig. 2 Crystallized fraction (α), as a function of temperature for sample BD-T2 at different heating rate

Kissinger–Akahira–Sunose method

The activation energies for the crystallization processes were calculated from the slope of the linear fitted function of $\ln(\beta/T_\alpha^2)$ *vs.* T_α^{-1}(Eq. (2)), for several crystallized fractions. The KAS plots are shown in Fig. 3 for sample BD.

Figure 4 shows the variation of E_α, calculated with the KAS method, with the crystallized fraction α, for sample BD (without nucleation agent) respectively for sample BD-T2 (with 2% nucleation agent).

As it may be seen in Fig. 4, the E_α values monotonously decrease with α, which reveals a complex crystallization process for both samples, without and with nucleation agent. Also, the E_α values vary depending on whether the nucleation agent is used or not, being smaller when 2% TiO_2 was used as nucleation agent (sample BD-T2).

Ozawa–Flynn–Wall method

The activation energies of the crystallization processes were also estimated by using the OFW

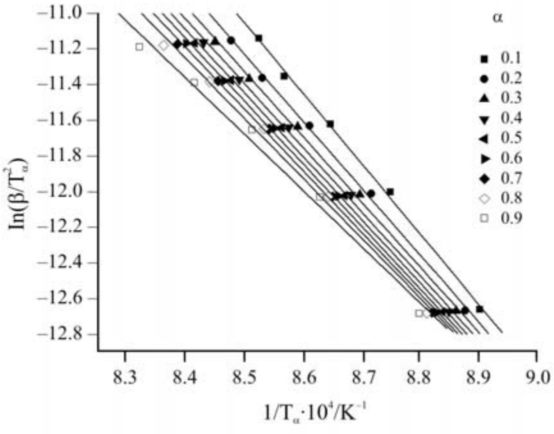

Fig. 3 Plots of $\ln(\beta/T_\alpha^2)$ as a function T_α^{-1} for sample BD at different crystallized fractions

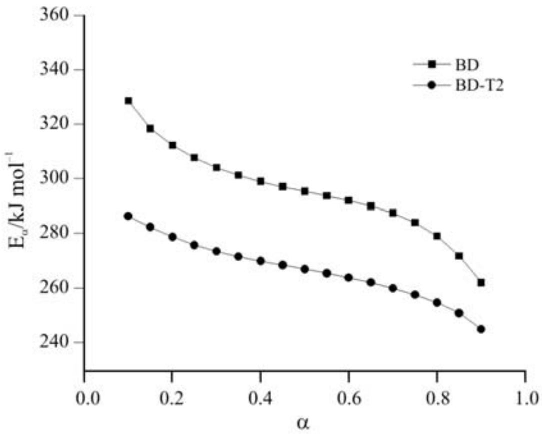

Fig. 4 Variation of E_α, calculated with the KAS method, with α for samples BD and BD-T2

Table 2 Avrami exponents *n* and the correlation coefficients r^2 at different temperatures for samples BD and BD-T2

BD			BD-T2		
T/°C	n	r^2	T/°C	n	r^2
880	5.64	1.0000	890	5.32	0.9887
882	5.64	0.9992	892	5.27	0.9924
884	5.33	0.9923	894	5.20	0.9948
886	5.39	0.9856	896	5.14	0.9964
888	5.32	0.9900	898	5.08	0.9975
890	5.25	0.9917	900	5.00	0.9979
892	5.16	0.9938	902	4.93	0.9977
894	5.06	0.9954	904	5.39	0.9977
896	5.08	0.9853	906	5.47	0.9985
898	5.45	0.9862	908	5.50	0.9988
900	5.78	0.9877	910	5.51	0.9987
902	5.74	0.9918	912	5.46	0.9982
904	5.68	0.9954	914	5.30	0.9966
906	5.57	0.9983	916	5.10	0.9937
908	5.40	0.9999	918	4.85	0.9909
910	5.19	0.9981	920	4.60	0.9879

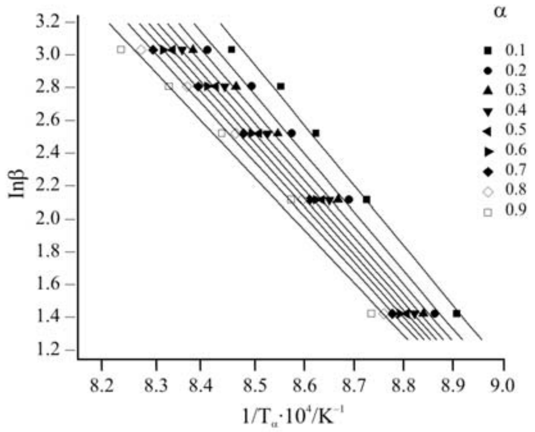

Fig. 5 Plots of ln β as a function of T_α^{-1} for sample BD-T2 at different crystallized fractions

method. For constant crystallized fraction, the value of E_α was calculated from the slope of the linear fitted function of lnβ vs. T_α^{-1}(Eq. (3)). The OFW plots are presented in Fig. 5 for sample BD-T2.

Figure 6 presents the variation of E_α, calculated with the OFW method, with decrystallized fraction α, for sample BD (without nucleation agent) respectively for sample BD-T2 (with 2% nucleation agent).

As it may be noticed, the activation energies values calculated using the OFW method too, decrease with the crystallized fraction for both samples, without and with nucleation agent. This behavior confirms the complex mechanism of the glass-ceramics crystallization process, involving probably an autoacceleration effect. As result, the calculated activation energies are apparent values, depending on the elementary processes activation energies (nucleation and growth) involved in the crystallization process.

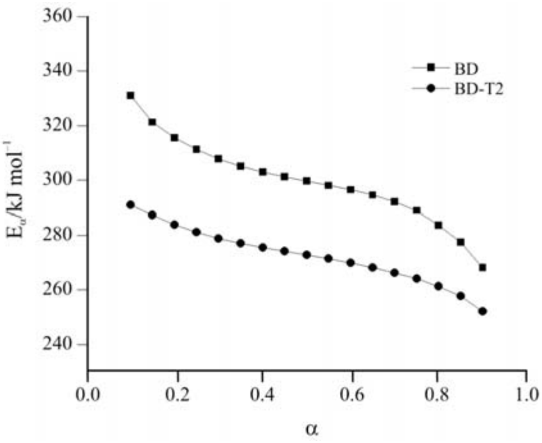

Fig. 6 Variation of E_α, calculated with the OFW method, with α for samples BD and BD-T2

Comparing Figs 4 and 6, it can be observed the slightly smaller values obtained with KAS method than those calculated with OFW method for both samples.

Starink [11, 23] considers the Ozawa–Flynn–Wall method more inaccurate than the Kissinger–Akahira–Sunose method.

The decrease of the activation energy for the sample BD-T2 (with 2% TiO_2 as nucleation agent) can be explained by the modification of the crystallization mechanism comparatively with sample BD (without nucleation agent); for sample BD the crystallization mechanism is based on homogeneous nucleation, different from the heterogeneous nucleation mechanism for the sample BD-T2.

The effect of 2% TiO_2 as nucleation agent upon the microstructure of the studied glass-ceramics was analyzed by scanning electron microscopy (SEM). Figures 7 and 8 present the SEM photomicrographs of sample BD respectively BD-T2.

As it can be observed from Fig. 7, the sample without nucleation agent (sample BD) exhibit irregular elongated faceted crystals with large dimensions and inhomogeneously distributed. As against Fig. 7, the micrograph of sample BD-T2 with 2% TiO_2 as nucleation agent (Fig. 8) exhibit small crystals with a very uniform dimensional distribution.

The favorable effect of the TiO_2 as nucleation agent can be associated with the possibility of titanium inclusion in the pyroxene crystalline lattice, this fact determining an increase of the pyroxenic phase crystallization trend, in agreement with the literature data [24].

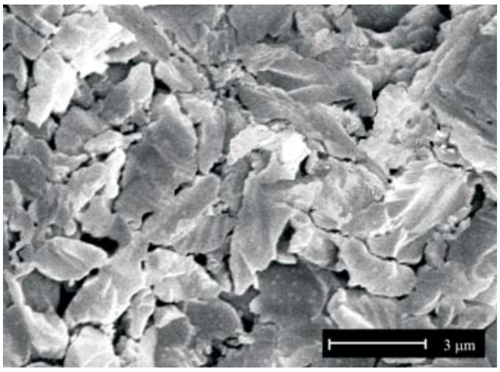

Fig. 7 SEM photomicrograph of sample BD

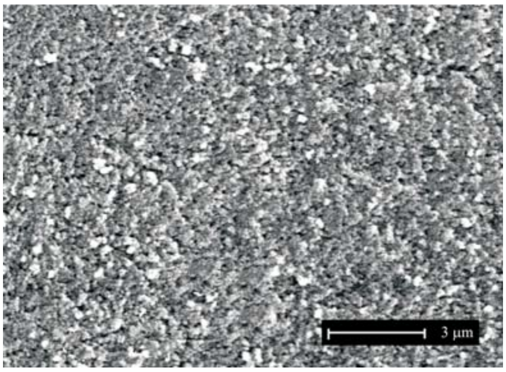

Fig. 8 SEM photomicrograph of sample BD-T2

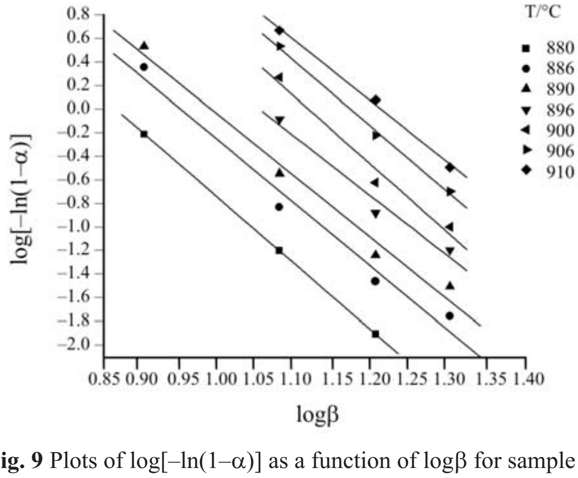

Fig. 9 Plots of log[–ln(1–α)] as a function of logβ for sample BD at different temperatures

In order to confirm the complex mechanism of the crystallization process and the validity of the JMA model for the studied glass-ceramics, the Avrami exponent n was determined using Ozawa method (Eq. (6)). The plots of $\log[-\ln(1-\alpha)]$ *vs.* $\log\beta$ at different temperatures for sample BD are presented in Fig. 9. Table 2 summarizes the Avrami exponent values calculated by using Ozawa method, for sample BD and BD-T2 at different temperatures.

As can be seen from the data in Table 2, for both samples, the Avrami exponent has values greater than four (n>4.0). These high values for n indicate that the studied glass-ceramics crystallization cannot be described by the Johnson–Mehl–Avrami (JMA) model.

Recent theories regarding the crystallization kinetics [25–27] demonstrate the necessity of the JMA model extension, taking into account the finite size effect and non-uniform nucleation, the non-spherical, anisotropic particles formation during the crystallization process and the transient nucleation effect.

Conclusions

The activation energies of the studied glass-ceramics (sample BD and BD-T2), calculated with the isoconversional KAS and OFW methods show high values, of the order of hundreds kJ mol^{-1}, being slightly reduced when the KAS method was used.

The addition of 2% TiO_2 as nucleation agent (sample BD-T2) at the initial glass-ceramic (sample BD) determines a decrease of the activation energy and the modification of the shape and dimension of the crystals too.

The isoconversional analysis applied to the non-isothermal crystallization of the studied glass-ceramics shows the dependence of the activation energy on the crystallized fraction which confirms that the crystallization mechanism is complex and the calculated activation energies are apparent values, depending on the activation energies of nucleation and crystallites growth.

The Avrami exponent calculated with Ozawa method has high values (n>4) indicating that the JMA model cannot be used for the crystallization of the studied glass-ceramics. For clearing the glass-ceramics complex crystallization process, a lot of effects have to be considered like the time-dependent nucleation and growth of crystallites, the inhomogeneous nucleation and finite sample size effect and also the non-spherical, anisotropic particles formation.

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DOI: 10.1007/s10973-006-8024-1