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KINETICS OF CRYSTALLIZATION PROCESSES IN SOME GLASS CERAMIC PRODUCTS

Influence of nucleation agents

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Abstract

The paper presents the kinetic study of the crystallization processes which take place in basalt glasses containing variable amount of nucleation agent (CaF_2, 3÷10%). The activation energies have been calculated using Kissinger’s equation and verified with the Ozawa-Flynn-Wall equation. In this order, the DTA curves have been registered with different heating rates, between 4 and 20 degrees/min. A correlation equation between the activation energy and the amount of nucleation agent (% of CaF_2) was established. By X-ray diffraction it was proved that the crystalline phase formed in the crystallization process represents a pyroxenic solid solution, $Ca(Mg,Fe)SiO_3$.

Keywords: glass ceramics, kinetic study of crystallization processes, nucleation agents

Introduction

Obtaining glass ceramic products implies two stages:

- The realization of the shaped product from the glass melting using technologies similar to those used in the glass industry.
- The application of the adequate thermal treatment for the development of the crystallization processes, to result in a product with high physico-mechanical performances.

The inclusion of the proper nucleation agents in the composition of the initial glass and the application of the adequate thermal treatment has influence upon the texture of the obtained glass ceramic product as well as upon its properties. Generally, in literature a minimum of 85% crystalline phase content and microcrystals dimensions under 1 µm are recommended [1–4]. Among the well studied glass ceramics, those based on basalt (easy accessible raw material) are characterized by very good physico-mechanical properties and chemical stability [1, 2, 5].

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The nucleation agents play the role of crystallization germs sources, conducting the crystallization processes through the heterogeneous nucleation mechanism modifying the activation energy of the process. Among the most popular nucleation agents in this field are: CaF_2, TiO_2, ZrO_2, etc.

The main crystalline phase in the basalt-based glass ceramic is represented by the solid pyroxene solution $Ca(Mg,Fe)SiO_3$ [1–4, 6–10].

In this paper some kinetic studies of the crystallization processes are presented which take place when obtaining basalt based glass ceramics. The activation energies have been calculated using Kissinger's equation and verified with the Ozawa-Flynn-Wall equation.

The crystallization processes have been followed by differential thermal analysis (DTA).

Experimental

The basalt based glasses have been obtained using as raw material the Şanoviţa basalt (Timiş) having the chemical composition presented in Table 1 (sample SB).

Table 1 Oxide composition (% mass) of the studied mixtures

Sample symbol	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O+K_2O	TiO_2	Molar ratio: SiO_2/MO
SB	52.21	12.33	9.55	14.29	10.29	1.18	0.15	1.378
BD	46.39	10.98	8.45	21.00	11.42	1.65	0.11	1.009

Our previous studies [5–10] led to the conclusion that the optimum ratio, crystalline phase/vitreous phase in the basalt based glass ceramic products is obtained for molar ratio $SiO_2/MO \cong 1$ (MO = CaO, MgO, FeO).

The correction of the oxide composition of the studied glasses was made by adding $MgCO_3$ and $CaCO_3$ at the natural basalt (sample BD).

Starting from the BD composition and adding CaF_2 as a nucleation agent, the following samples have been prepared: BD-F3 (with 3% CaF_2), BD-F5 (5% CaF_2), BD-F8 (8% CaF_2) and BD-F10 (10% CaF_2).

After homogenization, the mixtures have been charged in sintered alumina crucibles and melted in an electrical oven having SiC bars, for two hours, at 1350ºC. The obtained melts have been then fritted by pouring in cold water and the resulted glasses have been milled up to a 3% rest on the sieve having the side of the mesh 100 µm.

The obtained samples have been thermally analyzed using a Derivatograph-C (MOM, Budapest). In all the cases the mass of the sample was the same (m= 800 mg) and the heating rate varied between 4 and 20 deg./min. For each heating rate the temperature was determined at which the crystallisation process devolves at the maximum speed.

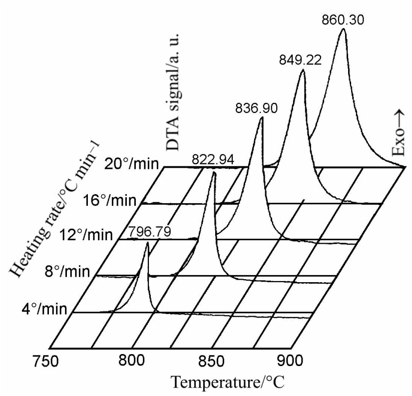

Fig. 1 The DTA curves of the BD-F8 sample for different heating rates

In Fig. 1, the DTA curves of the BD-F8 sample for different heating rates are presented.

For all the samples (BD, BD-F3, BD-F5, BD-F8, BD-F10) the peak temperatures of crystallization for different heating rates are presented in Table 2.

Table 2 The peak temperatures of crystallization for different heating rates, for the samples BD, BD-F3, BD-F5, BD-F8, BD-F10

Heating rate/ °C min^{-1}	BD	BD-F3	BD-F5	BD-F8	BD-F10
	Temperatures/°C				
4	860.25	841.88	825.87	796.79	788.16
8	884.10	867.75	849.93	822.94	812.23
12	898.80	883.45	867.43	836.90	828.84
16	910.02	895.98	878.40	849.22	840.47
20	917.98	906.64	889.87	860.30	851.10

In order to make the comparison possible between the samples with different nucleation agent content, in Fig. 2 the DTA curves for samples BD, BD-F3, BD-F5, BD-F8, BD-F10, at the same heating rate (12 deg min^{-1}) are presented.

The activation energies of the crystallization processes have been calculated based on the Kissinger's equation [11, 12] as well as with the Ozawa-Flynn-Wall's equation [13, 14].

The identification of the crystalline phase formed after the thermal treatment has been made by X-ray diffraction, using a DRON 3 diffractometer (CuK$_\alpha$).

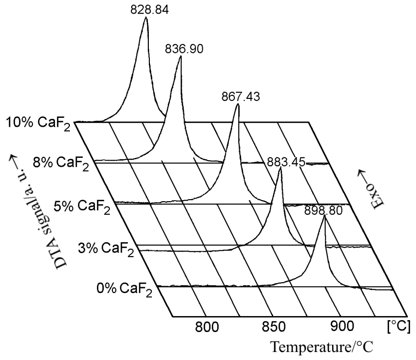

Fig. 2 The DTA curves for samples BD, BD-F3, BD-F5, BD-F8, BD-F10, for the same heating rate (12 deg min^{-1})

Results and discussion

From Table 2 it follows that the peak temperatures of the crystallization process decreases with increasing CaF_2 content for the same heating rate. This phenomenon is obvious in Fig. 2, at a heating rate of 12 deg min^{-1}. This behaviour is explained by the action of CaF_2, which lies at the basis of the heterogeneous nucleation resulting in crystallization germs formation. The crystals of the pyroxene solid solution ($Ca(Mg,Fe)SiO_3$) develop afterwards on these germs.

The activation energies of the crystallization processes have been calculated based on Kissinger's equation [11, 12]:

$$\ln\left(\frac{a}{T^2}\right) = const. - \frac{E}{RT} \tag{1}$$

where: α – heating rate (K min^{-1}); T – temperature at the peak maximum (K); E – activation energy (J mol^{-1}); R – general constant of gases (J $\text{mol}^{-1}\text{K}^{-1}$);

In Figs 3 and 4 $\ln(a/T^2)=f(1/T)$ dependences for the BD-F3, BD-F5, BD-F8 and BD-F10 samples are presented. The calculated values of the activation energies for all the studied samples, as well as the correlation coefficients (ρ), are presented in Table 3.

Table 3 The values of the activation energies and of the correlation coefficients (ρ) obtained based on the Kissinger and Ozawa-Flynn-Wall equations

Sample	Kissinger method		Ozawa-Flynn-Wall method		Average value of the activation energy
	E/kJ mol^{-1}	ρ	E/kJ mol^{-1}	ρ	E_{av}/kJ mol^{-1}
BD	292	0.9999	296	0.9999	294
BD-F3	254	0.9994	260	0.9995	257
BD-F5	249	0.9986	255	0.9988	252
BD-F8	240	0.9989	246	0.9991	243
BD-F10	236	0.9990	242	0.9992	239

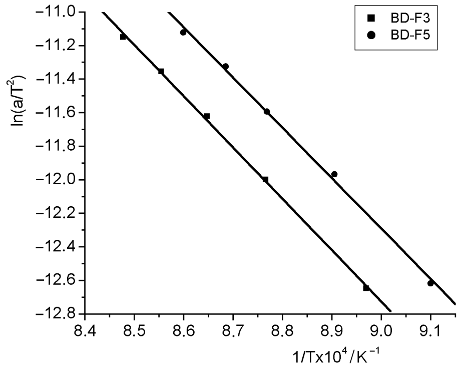

Fig. 3 The $\ln(a/T^2)=f(1/T)$ dependence for the BD-F3 and BD-F5 samples

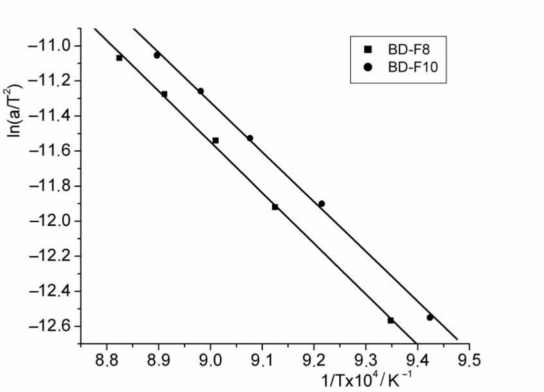

Fig. 4 The $\ln(a/T^2)=f(1/T)$ dependence for the BD-F8 and BD-F10 samples

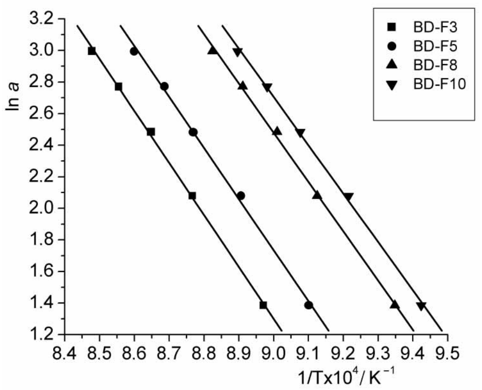

Fig. 5 The $\ln a=f(1/T)$ dependences for the samples BD-F3, BD-F5, BD-F8, BD-F10

The activation energies of the crystallization processes have also been calculated based on the Ozawa-Flynn-Wall equation [13–15]:

$$\ln a = const. - 1.052\frac{E}{RT} \qquad (2)$$

where: a – heating rate (K min^{-1}); T – temperature at the peak maximum (K); E – activation energy (J mol^{-1}); R – general constant of gases (J mol^{-1} K^{-1});

In Fig. 5 the $\ln a = f(1/T)$ dependences for the samples BD-F3, BD-F5, BD-F8 BD-F10 are presented.

The values of the obtained activation energies as well as the corresponding correlation coefficients are also shown in Table 3.

It may be noticed that the values of the activation energies obtained by the Ozawa-Flynn-Wall method are close to the values obtained by the Kissinger method (for the samples having the same composition). We specify that the activation energies in the case of the Ozawa-Flynn-Wall method were computed only at the peak maximum corresponding to a given conversion degree (= 50%). The literature considers the Kissinger method (valid for any conversion degree) better for the calculation of the activation energies of the crystallization processes of the glasses [12, 15].

The activation energies of the crystallization processes decrease with the increase of the nucleation agent (CaF_2) content.

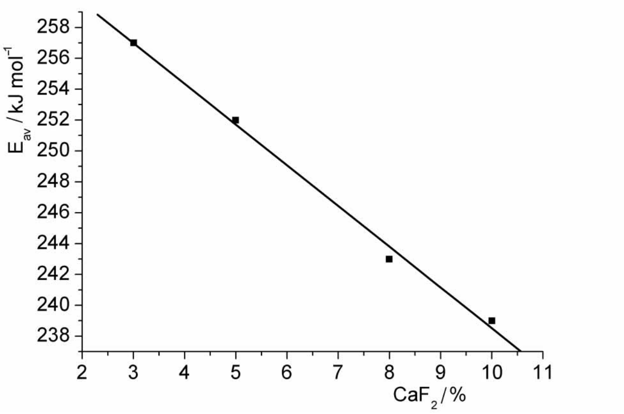

Fig. 6 The $E_{av} = f(\% \; CaF_2)$ dependence

According to the representation in Fig. 6, between the average value of the activation energy and the CaF_2 content exists a linear relationship described by the equation:

$$y = 264.89 - 2.64x \qquad (3)$$

where: y – represents the average value of the activation energy; x – represents the CaF_2 content (%).

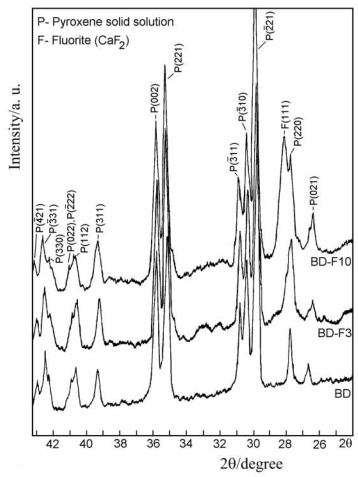

Fig. 7 XRD spectra of the samples BD, BD-F3 and BD-F10

It may be noticed that the average activation energy of sample BD (294 kJ mol^{-1}) does not correspond to the linear relationship shown in Fig. 6, for 0% CaF_2 content, but is significantly higher.

This suggests a completely different crystallization mechanism in the case of sample BD based on homogeneous nucleation, which takes place in a more difficult way than the heterogeneous nucleation mechanism in samples containing nucleation agents.

The nature of the crystalline phase resulted from the studied crystallization process has been established by X-Ray diffraction. The X-Ray diffraction spectra in Fig. 7 prove the existence of the same main crystalline phase in all the samples meaning the pyroxene solid solution $Ca(Mg,Fe)SiO_3$.

The pyroxene phase has been identified based on the JCPDS files numbers 41-1370 [16] and 41-1372 [17].

Together with the pyroxene solution, in sample BD-F10, CaF_2 crystals have also been noticed.

The obtained results allow an observation of the effect of the nucleation agent (CaF_2) upon the activation energy in the crystallization processes and also the establishing of the optimum temperatures for the thermal treatment in order to obtain this particular type of glass ceramics.

It has to be said that between the activation energies of the crystallization processes and the physico-mechanical properties of the obtained glass ceramics there is no direct proportionality.

Concerning this aspect, the formation of some microcrystals smaller than 1 μm, uniformly distributed in the volume of the sample, which do not lead to internal tensions, is essential to obtain high physico-mechanical performances.

Conclusions

- The utilization of the thermal analysis (DTA) allows the calculus with a good precision of the activation energies of the crystallization processes which take place in the basalt-based glass ceramic using CaF_2 as a nucleation agent.
- The increase of the nucleation agent content, 3–10% CaF_2, determines a linear decrease of the activation energy of the crystallization processes.

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