

Utilization of DTA in determination of crystallization mechanism in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO(R}_2\text{O)}$ glasses in presence of various nuclei

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Abstract

The effect of various nuclei on crystallization mechanism of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO(R}_2\text{O)}$ glasses were investigated by differential thermal analysis (DTA) through Matusita, Marotta and modified Kissinger methods. The Avrami constant, n , and the activation energy for crystallization of the most promising specimens containing Cr_2O_3 , Fe_2O_3 and TiO_2 in the single, double and triple nuclei series were determined. According to the results the Avrami constants derived from the Marotta method were more consistent with the other experimental observation. While glasses containing TiO_2 as the single nucleant represents surface crystallization and those containing Cr_2O_3 or Fe_2O_3 one-dimensional bulk crystallization, the crystallization mechanism of specimens containing both Cr_2O_3 and Fe_2O_3 and also the glasses containing the triple nuclei, are bulk and two dimensional.

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1. Introduction

Initiation of bulk crystallization is the main difficulty in producing useful glass-ceramics in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO(R}_2\text{O)}$ system. Thus addition of various nuclei, singularly or in combination, to these glasses have been suggested by many investigators to overcome this problem. There seems to how some discrepancies and inconsistencies in the literature on this subject. While Kim et al.¹ introduced Fe_2O_3 (4.6 wt.%) and Cr_2O_3 (0.8 wt.%) as successful nuclei in this system with crystallization activation energy of 695.0 (kJ/ml), Leonelli et al.² reported an activation energy of 506.0 (kJ/ml) with the same nucleant (1.3 wt.% Fe_2O_3). According to results of Barbier et al.³ the activation energy for crystallization of the above-mentioned glasses changes as a function of Cr_2O_3 from 380.4 to 468.2 (kJ/ml), but crystallization mechanism did not change with Cr_2O_3 and was of the surface crystallization type. Surface crystallization mechanism was also the result reported by Ovecoglu et al.⁴ However, they recommended TiO_2 as the

most effective nucleating agent (10 wt.% TiO_2 with crystallization activation energy of 150.0 (kJ/ml) and the Avrami constant, n , of 1.5). Duan et al.⁵ investigated the crystallization of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ glass system by addition of various amounts of TiO_2 as the nucleation agent. According to their results the activation energy for crystallization and the Avrami constant, n , of a specimen containing 5 wt.% TiO_2 were 648.8 (kJ/ml) and 0.7, respectively. The Avrami constant and the activation energy for crystallization of $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO(R}_2\text{O)}$ glasses containing a combination of Cr_2O_3 (0.78 wt.%), Fe_2O_3 (3.71 wt.%) and TiO_2 (0.64 wt.%) nuclei were also determined by Marghussian and Arjomandnia,⁶ respectively, as 2.8 and 280.0 (kJ/ml) for the most promising specimens.

In the present work the crystallization mechanism and activation energy for crystallization of glasses in $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO--MgO}$ system, containing a mixture of Cr_2O_3 , Fe_2O_3 and TiO_2 (in the single, double and triple nucleant series) were investigated by using various routes based on differential thermal analysis.^{7–9} By comparison of the Avrami constants and activation energy of crystallization of glasses in one hand and careful determination of the shifts of crystallization peak temperatures conducted on

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various specimens on the other hand it was tried to give a more clear picture of the mechanism of crystallization in these glasses. The Matusita,^{10,11} modified Kissinger¹² and Marotta methods^{13,14} were adopted for this purpose.

Where x is the volume fraction crystallized at a fixed temperature (T) when heated at a heating rate of α . E , T_c , R and m indicate the activation energy for crystallization, crystallization peak temperature, the gas constant and the dimensionality of crystal growth, respectively.

2. Experimental procedure

The base glass composition was chosen from a previous work⁶ as SiO₂ 55.05, Al₂O₃ 13.61, CaO 24.42, MgO 6.92, Na₂O 2.82 and K₂O 3.02 weight part. The nuclei, Cr₂O₃, Fe₂O₃ and TiO₂ were added to the base glass composition in various combinations. The raw materials used in order to supply this composition were reagent grade silica, α -Al₂O₃, CaCO₃, Mg(OH)₂, Na₂CO₃, Cr₂O₃, Fe₂O₃ and TiO₂. The mixtures of raw material after thorough mixing were transferred to an alumina crucible and melted at 1450 °C for 2 h in an electric furnace. The melts were cast into preheated stainless steel moulds and cooled naturally to room temperature. In order to investigate the thermal behavior of glass samples DTA technique was used employing a model STA-1640 polymer laboratories apparatus.

In order to predict the crystallization mechanism, in some cases glass powders of two different particle size distributions, $0.45 \times 10^{-3} \mu\text{m}$ to $0.55 \times 10^{-3} \mu\text{m}$ (A) and $<63 \mu\text{m}$ (B), were used in DTA studies. The rates of heating in DTA runs were 5, 10, 12.5 and 25 °C/min and alumina powder was used as an inert reference material. The microstructures of heat-treated samples after polishing and etching in 5% HF solution for 15 s, were characterized in a scanning electron microscope (SEM model leika Cambridge stereo scan 360).

3. Results and discussion

Table 1 shows the chemical composition of some of prepared samples. In this table the base glass composition is denoted as AR. Fig. 1 represents DTA curves of specimens containing various amounts of Cr₂O₃. It can be seen

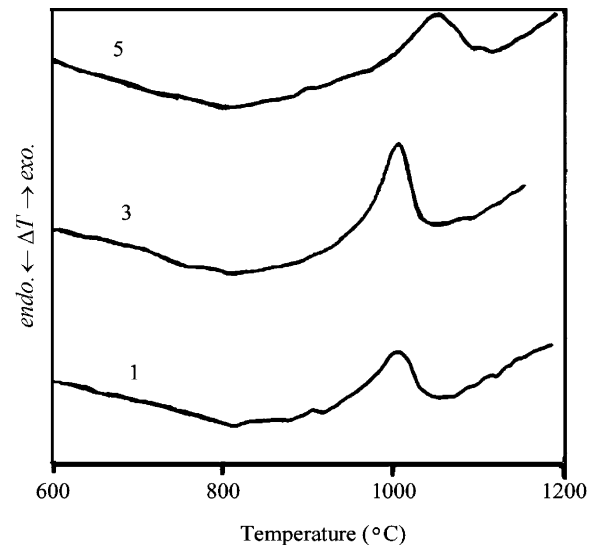


Fig. 1. DTA traces of glasses AR-Cr1 (1), AR-Cr3 (3) and AR-Cr5 (5).

that the specimen containing 3 wt.% Cr₂O₃ was the most promising specimen exhibiting the highest and sharpest DTA peaks with the lowest temperatures in this series. Besides, specimen containing 3 wt.% Cr₂O₃ and 5 wt.% Fe₂O₃ in double nuclei series and 3 wt.% Cr₂O₃, 5 wt.% Fe₂O₃ and 5 wt.% TiO₂ in triple nuclei series were the most promising specimens exhibiting the highest and sharpest crystallization peaks with the lowest temperature (Fig. 2). The crystallization peak temperature of the latter sample was 903 °C. Fig. 3 shows the X-ray diffraction patterns some of the above-mentioned specimens after heat-treatment at their DTA peak crystallization temperatures for 3 h. As it can be seen the main crystalline phase in these specimens is aluminan diopside. Wollastonite can also be observed in AR-Cr3 specimen. Figs. 4 and 5 show the results of variation of $\text{Ln}[-\text{Ln}(1-x)]$ versus $\text{Ln} \alpha$ and $1/T$ for specimen AR-Cr3, derived from the following equation:

$$\text{Ln}[-\text{Ln}(1-x)] = -n \text{Ln} \alpha - \frac{1.052mE}{RT} + \text{constant} \quad (\text{Matusita})$$

where x is the volume fraction crystallized at a fixed temperature (T) when heated at a heating rate of α . E , R , m and n indicate the activation energy for crystallization, the gas con-

Table 1
Chemical composition of glasses (weight percent)

Glass	Oxide								
	SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Cr ₂ O ₃	Fe ₂ O ₃	TiO ₂
AR	52.01	12.86	23.07	6.54	2.66	2.85	–	–	–
AR-Cr3	52.01	12.86	23.07	6.54	2.66	2.85	3	–	–
AR-Fe5	52.01	12.86	23.07	6.54	2.66	2.85	–	5	–
AR-Ti5	52.01	12.86	23.07	6.54	2.66	2.85	–	–	5
AR-Cr3Fe5	52.01	12.86	23.07	6.54	2.66	2.85	3	5	–
AR-Cr3Fe5Ti5	52.01	12.86	23.07	6.54	2.66	2.85	3	5	5

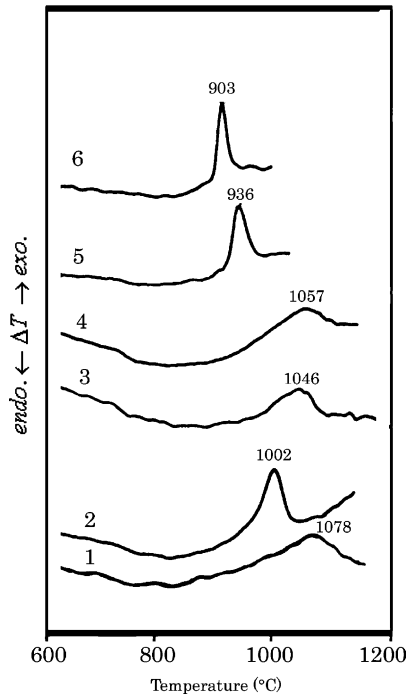


Fig. 2. DTA curves of the most promising glasses AR (1), AR-Cr3 (2), AR-Fe5 (3), AR-Ti5 (4), AR-Cr3Fe5 (5) and AR-Cr3Fe5Ti5 (6).

stant and the dimensionality of crystal growth and Avrami constant, respectively. According to Matusita’s method the above-mentioned plots should be linear, the slopes of which represent the Avrami constant and crystallization activation energy, respectively. Figs. 6 and 7 show the results of variation of $\text{Ln } \alpha$ versus $1/Tp$ and $\text{Ln } \Delta T$ versus $1/T$ for this

Table 2

Avrami exponent and crystallization activation energy determined by various methods

Glass	Avrami constant, n		Activation energy (kJ/mol)		
	Matusita	Marotta	Matusita	Marotta	Modified Kissinger
AR-Cr3	2.8	1.9	366.4	314.0	334.4
AR-Fe5	2.7	2.0	399.0	343.7	378.1
AR-Ti5	1.7	1.5	494.3	440.7	489.4
AR-Cr3Fe5	3.0	2.6	356.3	321.5	341.4
AR-Cr3Fe5Ti5	3.2	3.0	254.0	207.5	183.2

specimen derived from the Marotta’s method:

$$\begin{cases} \text{Ln } \Delta T = \frac{-nE}{RT} + \text{constant} \\ \text{Ln } \alpha = \frac{-E}{RT_c} + \text{constant} \end{cases} \quad (\text{Marotta})$$

where ΔT and T_c indicate deviation from baseline and crystallization peak temperature. Also Fig. 8 represent the results of variation of $\text{Ln } \alpha^n / Tp^2$ versus $1/Tp$ for specimen AR-Cr3, which named modified Kissinger method:

$$\text{Ln} \left(\frac{\alpha^n}{T_c^2} \right) = \frac{-mE}{RT_c} + \text{constant} \quad (\text{modified Kissinger})$$

Table 2 summarizes the crystallization activation energy and the Avrami constant determined by the above-mentioned methods. According to Table 2, in each method specimens containing 3 weight part Cr_2O_3 exhibit the minimum crystallization activation energy within the single nuclei containing series. But in the specimens containing a mixture of

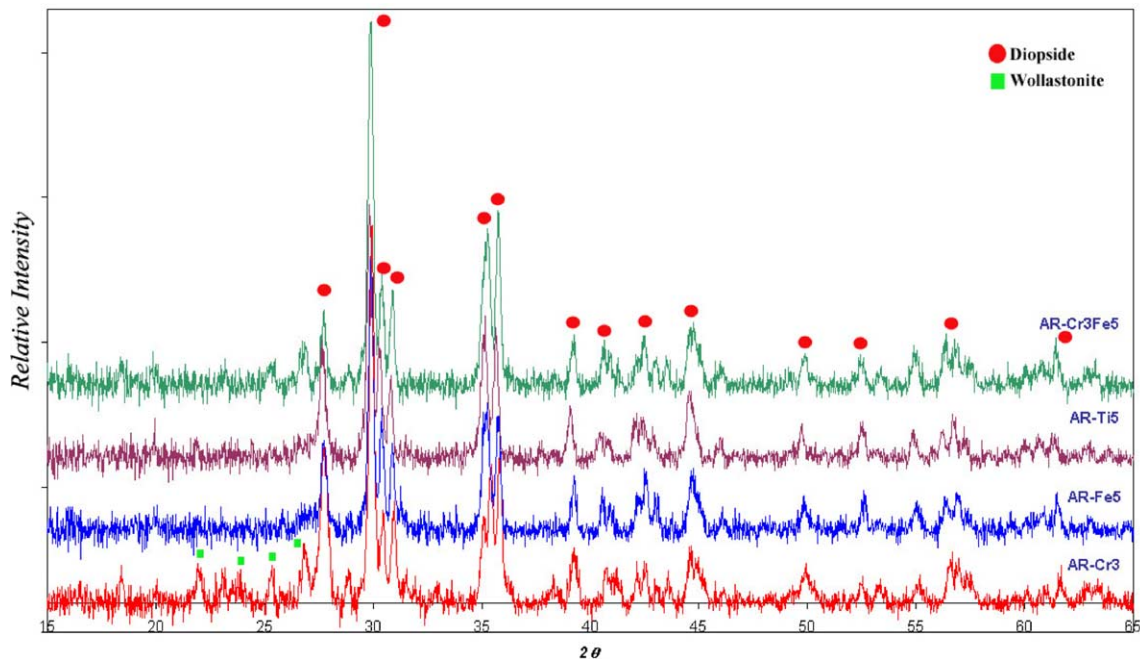


Fig. 3. XRD patterns of heat-treated glasses AR-Cr3, AR-Fe5, AR-Ti5 and AR-Cr3Fe5 at their DTA peak crystallization temperature for 3 h.

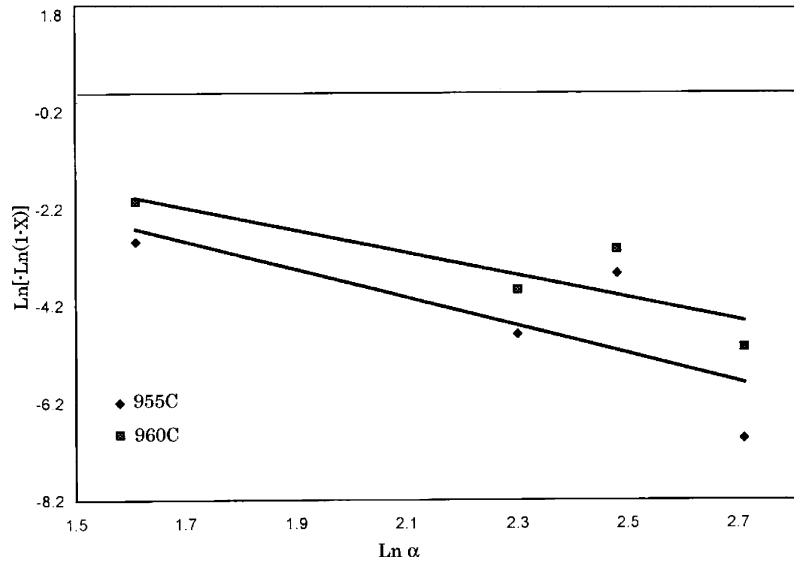


Fig. 4. Variation of $\text{Ln}[-\text{Ln}(1-x)]$ vs. heating rate ($\text{Ln } \alpha$) in AR-Cr3 for determination of the Avrami exponent according to Matusita method.

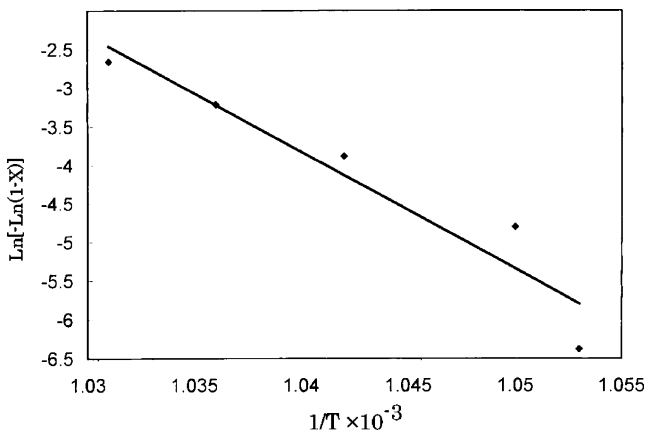


Fig. 5. Determination of crystallization activation energy for AR-Cr3 by Matusita method.

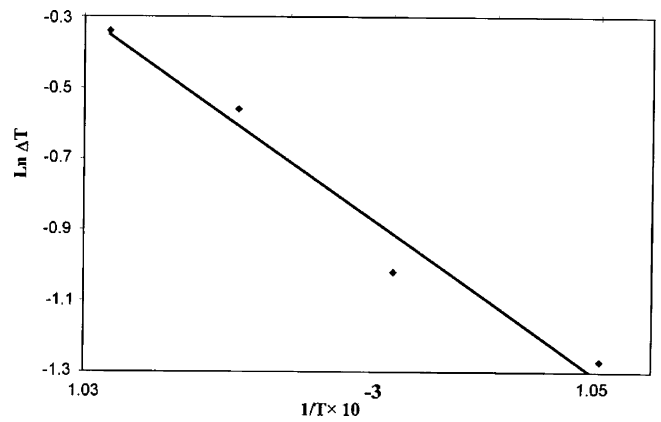


Fig. 7. Variation of $\text{Ln } \Delta T$ vs. $1/T$ in AR-Cr3 for determination of the Avrami exponent by Marotta method.

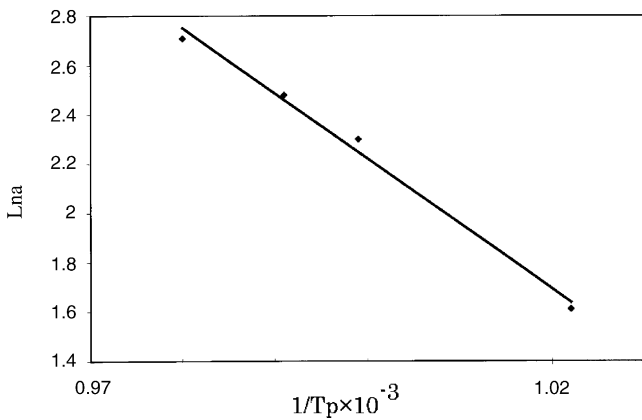


Fig. 6. Determination of crystallization activation energy for AR-Cr3 by Marotta method.

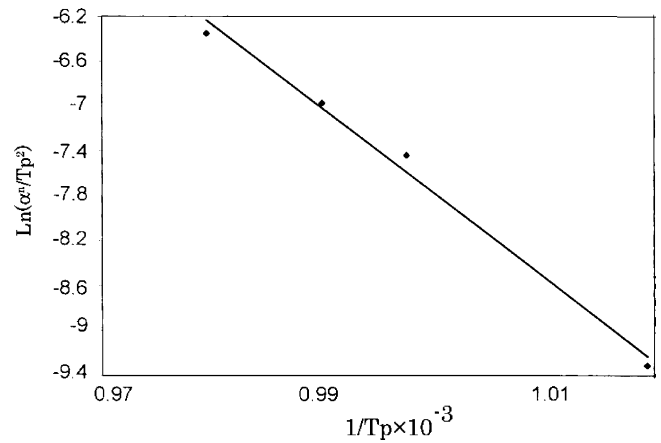


Fig. 8. Variation of $\text{Ln } \alpha^n / T_p^2$ vs. $1/T_p$ in AR-Cr3 for determination of crystallization activation energy by modified Kissinger method.

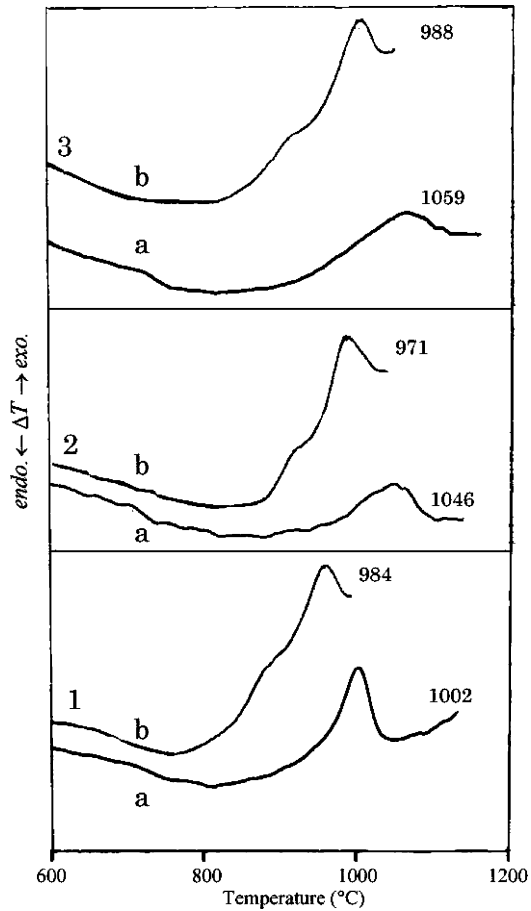


Fig. 9. DTA traces of glasses AR-Cr3 (1), AR-Fe5 (2) and AR-Ti5 (3) with different (a) coarse particles (0.45–0.55 mm) and (b) fine particles (<63 μm).

Cr_2O_3 , Fe_2O_3 and TiO_2 generally a reduction of E and an increase of n value is observed. Considering the Avrami constants in each method and the differences of crystallization peak shift for fine and coarse particles of different composition (Fig. 9), it can be deduced that the n values determined from the Marotta method should be more reasonable than another.

Therefore, considering the amounts of the Avrami constants calculated from the Marotta method it can be deduced that in AR-Cr3 and AR-Fe5 specimens, the crystallization mechanism were one-dimensional bulk type while in the AR-Ti5 specimen surface crystallization was possibly operative. In the case of TiO_2 this is consistent with the findings of other investigators⁴ on the same glass system and crystallization phase.

The comparison of n values of AR-Cr3Fe5 and AR-Cr3Fe5Ti5 glasses indicates that the same crystallization mechanism predominates in both glasses. However, it can be seen that the added TiO_2 reduced the activation energy of crystallization of AR-Cr3Fe5 more than 100 (kJ/mol). This issue would probably leads to increasing of crystallization rate of AR-Cr3Fe5Ti5 glass. It seems that TiO_2 reduces the glass viscosity and helps in this regard.

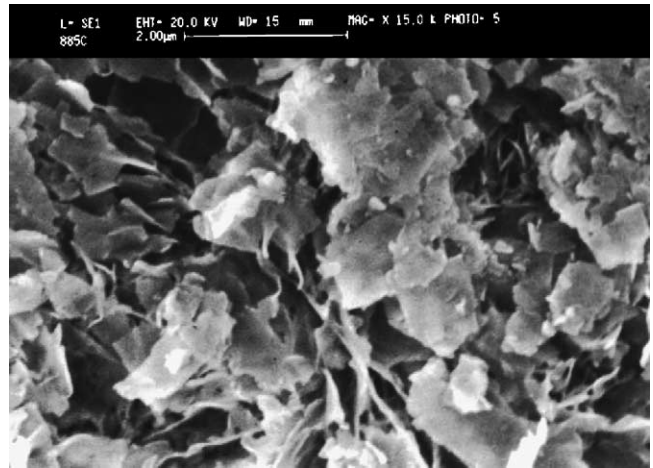


Fig. 10. SEM micrograph of AR-Cr3Fe5Ti5 glass nucleated at 740 °C for 3 h and then crystallized at 885 °C for 3 h.

According to a previous work¹⁵ the most suitable nucleation temperature for AR-Cr3Fe5Ti5 specimen was 740 °C. The DTA curve of the samples nucleated at 740 °C for 3 h showed 885 °C as the crystallization temperature. Fig. 10 is a SEM micrograph taken from a polished and etched specimen after a two stage heat treatment at 740 °C and 885 °C for 3 h, respectively. The presence of platelet-shaped crystalline particles in the microstructure is again an evidence for a two-dimensional bulk crystallization mechanism.

It should be noted that the E value determined in this work is the lowest reported so far for this system. Therefore it can be concluded that by using a mixture of Cr_2O_3 , Fe_2O_3 and TiO_2 nuclei in SiO_2 – Al_2O_3 – CaO – MgO and related systems very effective bulk nucleation may be achieved.

4. Conclusions

1. According to DTA results obtained by various methods such as Matusita, Marotta and modified Kissinger effective bulk nucleation may be initiated in SiO_2 – Al_2O_3 – CaO – MgO system by using a mixture of Cr_2O_3 , Fe_2O_3 and TiO_2 nuclei. The minimum crystallization activation energy and maximum Avrami constant were obtained by combination of Cr_2O_3 , Fe_2O_3 and TiO_2 nucleating agent with amounts of 3, 5 and 5 wight part, respectively. In this case a two-dimensional bulk crystallization mechanism is operative which was confirmed by SEM analyses of microstructure.
2. The Avrami constants derived from the Marotta method were more compatible with the amount of crystallization peak shifts than the Matusita method.
3. Although titanium dioxide has no effect on the crystallization mechanism but it can reduces the activation energy of crystallization through the reduction of glass viscosity.

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