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Crystallization Kinetics of Basalt Glass

Şenol Yılmaz,[a] Osman T. Özkan[b,c] & Volkan Günay[b,d]*

[a]Sakarya University, Engineering Faculty, Metallurgy Department, Adapazari, Türkiye
[b]TÜBITAK, Marmara Research Centre, Materials Department, Gebze 41470, Türkiye
[c]Istanbul University, Engineering Faculty, Metallurgy Department, Avcilar-Istanbul, Türkiye
[d]Istanbul Technical University, Faculty of Chemistry and Metallurgy, Metallurgy Department, Maslak-istanbul, Türkiye

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Abstract: The crystallization behaviour of basalt glass at elevated temperatures was studied using glass samples prepared by melting the natural basalt rock from the Thrace region of Türkiye. DTA and XRD analysis revealed the crystallization of augite [(Ca Fe Mg) SiO_3 at 800°C. The kinetics of crystallization of augite were studied by applying the DTA measurements carried out at different heating rates and the activation energies of crystallization and viscous flow were measured as 238 kJ mol^{-1} and 413 kJ mol^{-1}, respectively. The resultant basalt glass-ceramic revealed very fine and homogeneous microstructure. © 1996 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Basalt is a grey to black, fine grained volcanic rock which is the major constituent of oceanic islands and a common component of the continental masses as well. Chemically it is composed of major oxides: silica, alumina, iron oxide, calcia, magnesia, and of lesser importance, soda, potassia, titania and manganese and phosphorus oxides, as well as trace amounts of other species. Plagioclase feldspar and monoclinic pyroxene, normally augite, are two major minerals, with magnetite, olivine and certain other accessory minerals often present.[1]

Volcanic basalt rocks are widely available in various regions of Türkiye. Detailed information about their occurrence and chemical compositions are given elsewhere.[2]

Basalt glass and glass-ceramics find wide application in industry as abrasion and corrosion resistant tiles (and other shapes) and mineral wool for heat, noise and fire insulation. In mineral wool application, the crystallization of amorphous fibres impairs their mechanical properties. However, the literature cited the superior abrasion and chemical resistance of molten basalt. They can be used wherever the transport of material causes mechanical or chemical abrasion.[1,3]

The aim of the present work, which is part of the wider study on basalt glasses from volcanic rocks, is to study the crystallization behaviour of basalt glass by revealing the phases that are formed after heat treatments and to determine some parameter in the kinetic equations that described the process of crystallization.

2 EXPERIMENTAL PROCEDURE

The chemical composition of volcanic basalt rock sample from Thrace region of Türkiye is given in Table 1. In the table, Fe_2O_3 represents the total amount of FeO + Fe_2O_3 in the basalt rock. This chemical analysis result is the quantitative analysis result (Atomic Absorption spectroscopy, Perkin-Elmer 2300) of the well represented batch of the basalt source and this batch was used throughout the present work. The crystalline phase in the basalt rock was found to be augite which was determined by X-ray diffraction (XRD) analysis in a Philips PW 1050 diffractometer using Cu Kα radiation. Glass samples were prepared by melting the ground basalt in a platinum crucible, in a

*To whom correspondence should be addressed.

Table 1. Chemical composition of volcanic basalt rock (Fe_2O_3 represents the total amount of FeO + Fe_2O_3)

Compounds	Wt %
SiO_2	45.91
Al_2O_3	12.16
Fe_2O_3	10.74
CaO	9.12
MgO	12.16
TiO_2	2.93
MnO	—
K_2O+ Na_2O	4.25
Loss on ignition	2.72

laboratory electric furnace at 1450°C. The molten material was cast into graphite mould (approximately 5 mm high, 10 mm wide and 10 mm long) and annealed for 1 h at 600°C. The glass samples were heat treated from 800°C to 1100°C to promote internal crystallization. The crystallization kinetics were studied by differential thermal analysis (DTA) to determine the activation energies for the crystallization and the viscous flow. The crystalline phases were determined by XRD.

The crystalline phases which were formed during the crystallization of basalt glasses were identified again by XRD method. The kinetics of the crystallization of basalt glass were determined by DTA method which was performed in a Netzch STA 429 thermoanalyser using 200 mg powdered samples and employing heating rates of 10, 15 and 20°C min^{-1}. All DTA experiments were performed in air atmosphere with Al_2O_3 powder as reference material. Polished and chemically etched surfaces of the crystallized samples were examined using a JOEL-840 scanning electron microscope (SEM).

3 RESULTS AND DISCUSSION

3.1 Crystalline phases

The DTA curve of basalt glass (Fig. 1) shows a small endothermic dip around 700°C (the glass transition temperature, Tg) and two exothermic peaks at 788 and 845°C which indicate the crystallization.

Table 2. Values of parameter n for various crystallization mechanisms [3,6]

Mechanism	n
Bulk nucleation	
Three-dimensional growth	4
Two-dimensional growth	3
One-dimensional growth	2
Surface nucleation	1

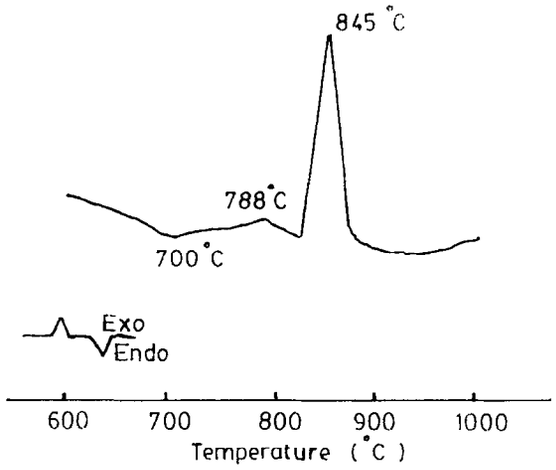

Fig. 1. DTA diagram of basalt glass.

The appearance of two crystallization peaks on the DTA curve implies that at least two different crystal phases are formed during the heat treatment. This was also confirmed by XRD results. The diffraction pattern of the sample heat treated at 800°C for 1 h given in Fig. 2, shows the crystallization of diopside [(Ca Mg $(SiO_3)_2$] and augite [(Ca Fe Mg) SiO_3]. These two phases together are usually referred to as one phase named diopsidic augite in the literature.[1] Only augite phase was observed in samples which were heat treated at 900, 1000 and 1100°C for 1 h.

3.2 The kinetic of crystallization

Solid state reactions such as the crystallization glass can be described by the phenomenological Johnson–Mehl–Avrami (JMA) equation.[3,5]

$$X = 1 - \exp[-(kt)^n] \quad (1)$$

Taking natural logarithms and rearranging eqn (1)

$$\mathrm{Ln}[-\mathrm{Ln}(1 - X)] = n\mathrm{Ln}k + n\mathrm{Ln}t \quad (2)$$

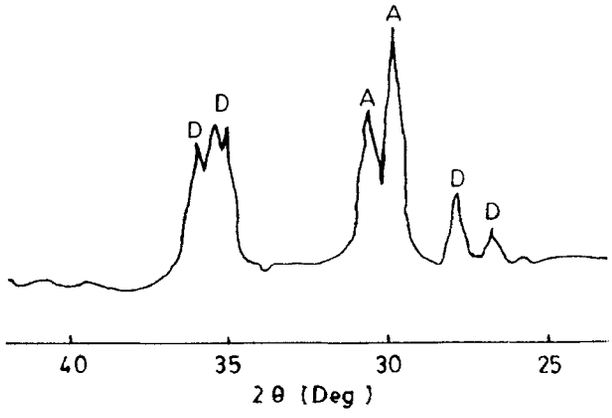

Fig. 2. X-ray diffraction pattern of a sample crystallized at 800°C for 1 h (D = Diopside, A = Augite).

Table 3. DTA measurements of basalt glass

Heating rate, β (K min^{-1})	Peak temperatures (K)		ΔT(K)
	Tg	Tp	
10	972	1118	24
15	979	1123	22
20	982	1139	20

can be obtained, where X is the volume fraction crystallized after time t, n a dimensionless parameter related to the reaction mechanism[6] shown in Table 2, and k the reaction rate constant (s^{-1}), whose temperature dependence is generally expressed by the Arrhenius equation

$$k = V\exp(-Ea/RT) \tag{3}$$

or taking natural logarithms

$$\mathrm{Ln}k = \mathrm{Ln}V - Ea/RT \tag{4}$$

where V is a frequency factor (s^{-1}), Ea the activation energy for crystallization (J mol^{-1}), R the gas constant (8.314 J mol^{-1}) and T the absolute temperature (K).

A new method has been developed recently to calculate the n values using the DTA results.[7] Figure 3 shows a crystallization exotherm in DTA measurement and the method employed to measure the ΔT value.

The following equation was used to calculate the n value[7]:

$$n = [2.5/\Delta T][T\mathrm{p}^2/Ea/R] \tag{5}$$

The activation energy for crystallization of basalt glasses was determined using a method based on JMA equation which was first introduced by Kissenger and modified by others.[3,8] This method is based on the dependence of the crystallization peak temperature (Tp) on the DTA heating rate (β) as follows:

$$\mathrm{Ln}T\mathrm{p}^2/\beta = \mathrm{Ln}Ea/R - \mathrm{Ln}Va + Ea/RT\mathrm{p} \tag{6}$$

Likewise, eqn (6) can also be used to predict the viscous energy, as described by Mahadevan *et al.*:[4]

$$\mathrm{Ln}T\mathrm{g}^2/\beta = \mathrm{Ln}Ec/R - \mathrm{Ln}Vc + Ec/RT\mathrm{g} \tag{7}$$

Here Ec is the corresponding activation energy for viscous flow, Va is the frequency factor for crystallization and Vc is the frequency factor for viscous flow.

Plots of Ln $T\mathrm{p}^2/\beta$ vs $1/T\mathrm{p}$ and Ln $T\mathrm{g}^2/\beta$ vs $1/T\mathrm{g}$ obtained at various heating rates should be linear with slopes Ea/R and the intercept [Ln (Ea/R) − Ln Va] and [Ln $(Ec/R$ − Ln Vc]. Therefore, if Ea/R and Ec/R are estimated from the slope, the frequency factors can be calculated from the intercept. The peak temperatures (Tg and Tp) changing with heating rates and ΔT values for calculating n are listed Table 3. The same data are graphically plotted in Figs 4 and 5.

In accordance with published literature data, the temperature of the crystallization peak is higher at faster heating rates.[9] The values of Ea, Ec and Va,

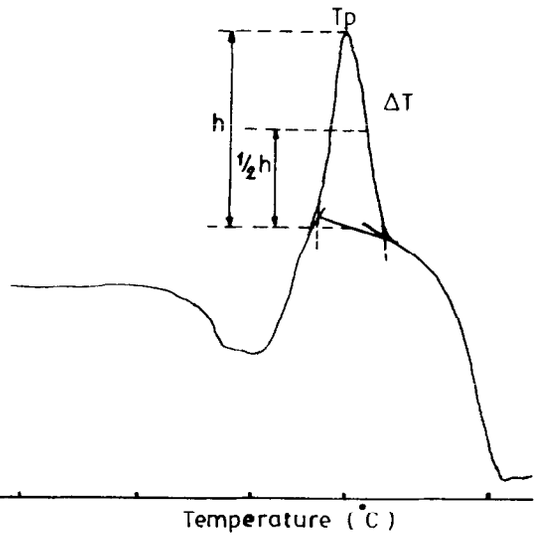

Fig. 3. Obtaining ΔT values from DTA crystallization peaks to calculate n.

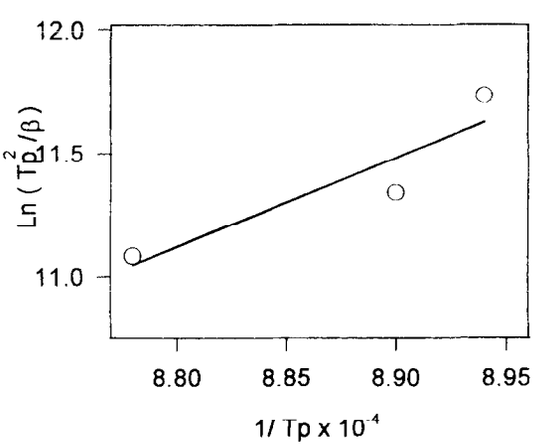

Fig. 4. Plot of Ln $T\mathrm{p}^2/\beta$ versus $1/T\mathrm{p}$ for the determination of the activation energy for the crystallization of basalt glass.

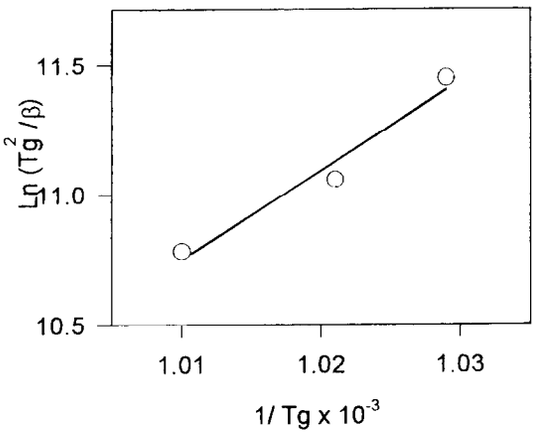

Fig. 5. Plot of Ln Tg^2/β versus $1/Tg$ for the determination of the activation energy for the viscous flow of basalt glass.

Vc obtained from the slope and the intercept of lines (Figs 4 and 5) were,

$$Ea = 238 \text{ kJ mol}^{-1}$$
$$Ec = 413 \text{ kJ mol}^{-1}$$
$$Va = 2.62 \times 10^{10} \text{ s}^{-1}$$
$$Vc = 4.53 \times 10^{10} \text{ s}^{-1}$$

The value of Ea is in agreement with the value reported by Voldan ($Ea = 245$ kJ mol^{-1}) who studied the kinetics of crystallization of basalt glass using the isothermal method.[3]

The n values, which were calculated by using eqn (5), are given in Table 4. It can be seen that $n > 4$ which indicates that the crystallization mechanism for basalt glasses at all heating rates is caused by bulk nucleation with three-dimensional crystal growth.

The SEM micrograph of the polished and etched surface of the basalt glass-ceramic heat treated at 900°C for 1 h given in Fig. 6 shows a fine crystallized microstructure. This type of microstructure is a typical characteristic of the basalt glass-ceramic which is also observed and reported by others.[1,3]

In glass-ceramics, the fine and homogeneous distribution of crystalline phases is desirable for good mechanical and physical properties. To obtain this desired microstructure, it is common to use nucleating agents such as TiO_2, ZrO_2, P_2O_5. However, in basalt glass-ceramics such nucleating agents are not needed. The mechanisms of volume

Table 4. n values of basalt glasses

Heating rate, β (K min^{-1})	n	Mechanism
10	4.5 › 4	Bulk nucleation
15	5.1 › 4	Bulk nucleation
20	5.5 › 4	Bulk nucleation

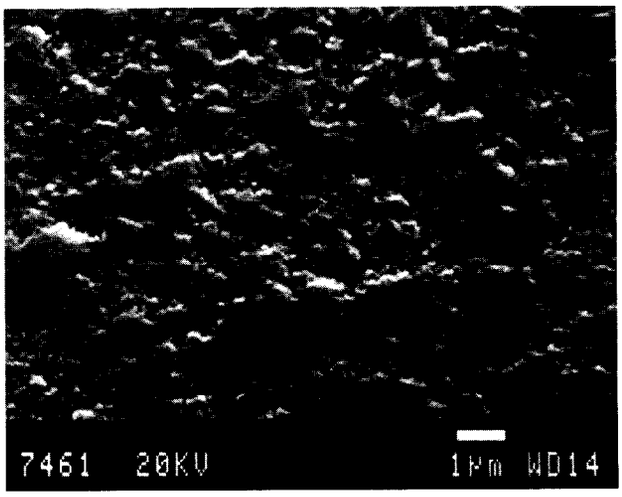

Fig. 6. SEM microstructure of a sample heated at 900°C for 1 h. Polished surface etched using 2.5% HF in ethanol for 45 s.

nucleation and crystallization in basalt glasses are attributed to the presence of FeO and Fe_2O_3. It was reported that during melting of basalt rocks, FeO (or Fe_2O_3) oxidizes to Fe_3O_4, which acts as nucleating agent and crystal growth site.[3] This behaviour of basalt glass-ceramics gives advantages over other glass-ceramics where nucleation agents are necessary to obtain similar microstructure.

4 CONCLUSION

In the crystallization of basalt glass, diopside crystallizes at 788°C, followed by the crystallization of augite at 845°C. Johnson–Mehl–Avrami, Kissenger and Mahadevan equations were used for the calculation of the activation energies for the crystallization and viscous flow. The dimensionless parameter (n) related to the reaction mechanism was determined by using ΔT values obtained from DTA measurements at different heating rates. Depending on the heating rate, the n values were found to vary between 4.5 and 5.5, which indicates the bulk nucleation in basalt glass by three-dimensional growth. The activation energies of the crystallization and viscous flow were calculated as 238 kJ mol^{-1} and 413 kJ mol^{-1}, respectively.

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