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Kinetic parameters for crystallization in DICOR® glass

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Abstract

The reaction kinetics of crystallization of tetrasilicic flourmica in DICOR® glass was followed non-isothermally by differential thermal analysis (DTA), and analysed using Johnson-Mehl-Avrami equation for determining the activation energy, reaction order, and the pre-exponential parameters.

The DTA curves showed a single exothermic crystallization peak in the temperature range of 745–850°C, just above the glass transition temperature. The activation energy E_c, the reaction order n, and the pre-exponential factor ν, of crystallization were computed to be 203 kJ mol^{-1}, 3.4 ± 0.20, and 2.88×10^{11} s^{-1} respectively. These observations suggest that the crystallization of mica in DICOR® glass occurs by a cellular precipitation mechanism where the nucleation occurs only at the start of the transformation.

Keywords: Crystallization; DTA; DICOR® glass; Kinetic parameters

1. Introduction

DICOR® is a special kind of commercial product from a family of mica glass-ceramics. It is a castable and machinable glass-ceramic of K_2O-MgO-SiO_2-F system [1]. It is presently recommended for the construction of crown and veneer restorations in esthetic dentistry [1, 2]. Its composition in wt.% is 56–64 SiO_2, 15–20 MgO, 12–18 K_2O, 4–9 F and 0–5 ZrO_2 [3]. To obtain optimum strength and other desirable properties, it is heat treated (cerammed) by heating the material over a period of 2 h to

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1075°C, then holding at this temperature for 6 h, followed by cooling to 200°C over 2 h. The microstructure formed from such a combination of non-isothermal-isothermal heat treatment is composed of about 55% block-shaped tetrasilicic flourmica crystals of approximate composition $KMg_{2.5}Si_4O_{10}F_2$ [4], in about 45% silicate glass matrix [2, 4–7]. The details of nucleation and crystallization mechanism of this system are not well known [7].

The kinetic data of the crystallization of glass are of interest for elucidating the nature of crystal nucleation and growth. The kinetic expression for non-isothermal crystallization in amorphous materials has been derived and the method for determining the kinetic data from differential scanning calorimeter (DSC) curves has been proposed [8]. The differential thermal analysis (DTA) is also used extensively to understand the devitrification of glasses. Several mathematical relationships have been derived using Johnson-Mehl-Avrami (JMA) equation to obtain kinetic data from DTA curves [9–15]. The aim of this work is to utilize two of these relationships to determine the kinetic parameters, the activation energy E_c, the reaction order n, and the frequency factor v, for the devitrification process of DICOR® and suggest a possible crystallization mechanism.

2. Experimental

The samples of DICOR® glass were prepared from the company supplied ingot. A cylindrical mold (6.5 mm in diameter and 40 mm long) was prepared from phosphate bonded investment. The molten glass at 1350°C was forced centrifugally into the mold at 950°C with a casting machine. The as-cooled glass cylinders were broken to obtain several small 50 mg bulk samples. Differential thermal analysis thermograms of these specimens were obtained with a Netzsch model 404S apparatus at several different heating rates between 5 and 50°C $\min^{-1}$. Powdered α-Al_2O_3 (1 μ size) was added to sample port to improve heat transfer between the bulk sample and sample holder. The total weight of the specimen and powder was 100 mg. The reference material was powdered α-Al_2O_3 (100 mg). The DTA curves were corrected against the base line which was obtained by making a DTA run of α-Al_2O_3 vs α-Al_2O_3 for each heating rate.

3. Results and discussion

When crystallization of glass occurs during the DTA run, heat is evolved, and it is indicated by one or more exothermic peaks in the DTA curve. Fig. 1 shows a typical DTA curve for DICOR® glass. The presence of a fairly broad single exothermic peak just above the glass transition temperature of 658°C is observed. Fig. 2 shows the microstructure of the DICOR® glass at the end of the exothermic peak. A fine and uniform distribution of microcrystals is evident. Further, it was also noted that the number of these precipitated crystals per unit area remained fairly constant in samples subjected to different heating rates [6]. The morphology of these ~ 0.1 μm in diameter microcrystals, formed in non-isothermal heating, is significantly different from the

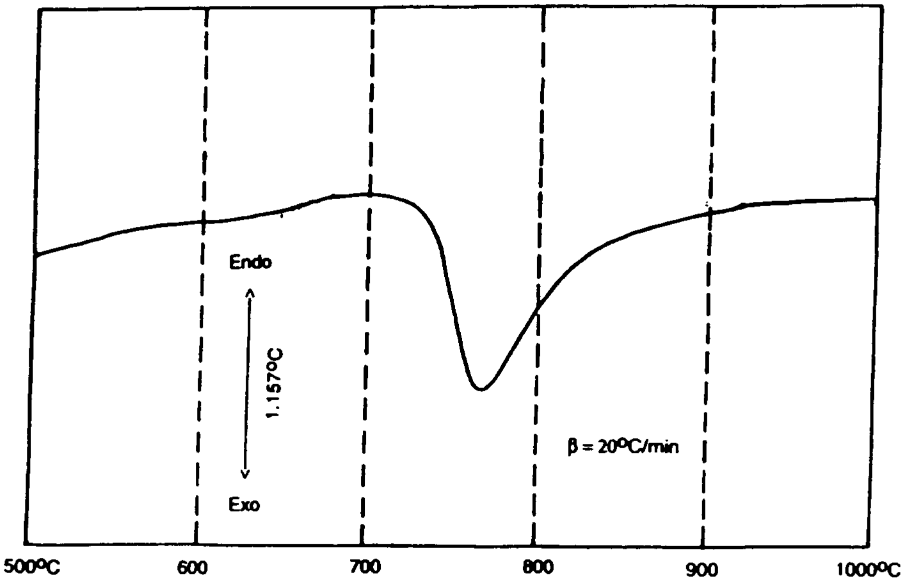

Fig. 1. A typical DTA curve obtained at 20°C min^{-1}.

Fig. 2. Scanning electron micrograph of DICOR® sample at the end of exothermic peak with a heating rate of 20°C min^{-1}, after 90 s swab-etch by 5% HF solution in 20% H_2SO_4.

block-shaped mica crystals obtained by the recommended non-isothermal-isothermal ceramming heat treatment of 8 h (Fig. 3). However, the energy dispersive X-ray analysis (EDAX) of the block-shaped crystals and the microcrystals produced EDAX patterns which were exactly identical [6]. It was concluded that the microcrystals and the

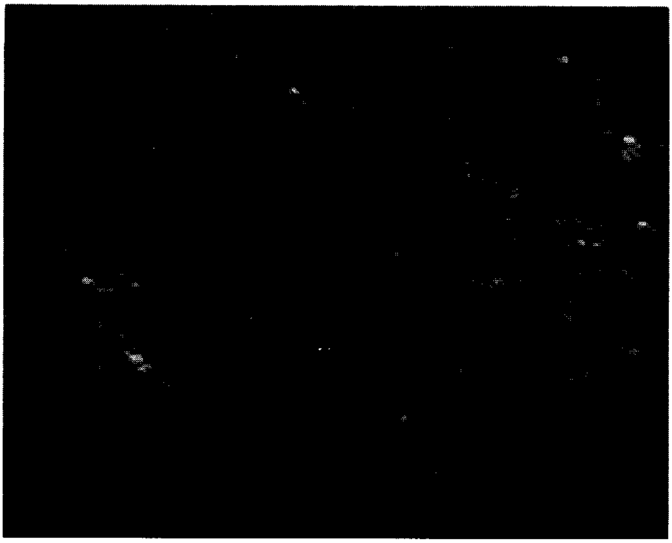

Fig. 3. Scanning electron micrograph of completely cerammed DICOR® sample after 90 s swab-etch by 5% HF solution in 20% H_2SO_4.

block-shaped crystals are compositionally similar [6]. It appears that these tiny crystals are of tetrasilicic flourmica which have changed to block-shape mica crystals by a dissolution and reprecipitation mechanism during the isothermal hold (6 h) at 1075°C.

The exothermic peak temperature varies between 745 and 850°C and is dependent upon the heating rate. The characteristics of crystal growth in glass have been extensively investigated using the Johnson-Mehl-Avrami equation [9–10]:

$$x = 1 - \exp[-(kt)^n] \tag{1}$$

where x is the volume fraction of crystallized phase at time t, and n is a dimensionless exponent related to the mechanism of crystallization. The constant k, is related to the absolute temperature T, by Arrhenius type equation:

$$k = \nu \exp(-E_c/RT) \tag{2}$$

where ν is a frequency factor, E_c is activation energy of crystal growth and R is a gas constant. Using Eqs. (1) and (2), and assuming the following: (1) in the earlier part of the peak in a DTA curve, the temperature differential at any given instant can be approximated as proportional to the instantaneous reaction rate, dx/dt, (2) during a DTA run, the time of heating t, is proportional to the reciprocal of the heating rate, and (3) that the number of nuclei formed is independent of heating rate, one can obtain these two relationships [11–15],

$$\ln \Delta T = -nE_c/RT + C_1 \tag{3}$$

and

$$\ln \beta = -E_c/RT_p + \ln \nu \tag{4}$$

where T_p is the peak temperature.

Fig. 4 shows the linear relationship between $\ln \beta$ vs $1/T_p$ with a correlation coefficient of 0.98. The activation energy, E_c, computed from this slope is 203 kJ mol^{-1} and the intercept of straight line on Y-axis gave the value of $\nu = 2.88 \times 10^{11}$ s^{-1}. A similar straight line relation (correlation coefficient 0.99) is observed when $\ln \Delta T$ is plotted against $1/T$(Fig. 5). The slope of the straight line gave the value of nE_c; and knowing the value of E_c from the other equation, the value of n was calculated to be 3.4 ± 0.20. This value of n, which is close to 3 indicates a three-dimensional growth of the fixed number of nuclei [8, 15].

The value of the exponential factor, n, has also been related to the crystallization mechanism [16–18]. The computed value of 3.4 ± 0.20 seems to suggest that the crystallization mechanism is composed of cellular transformation on the nuclei formed

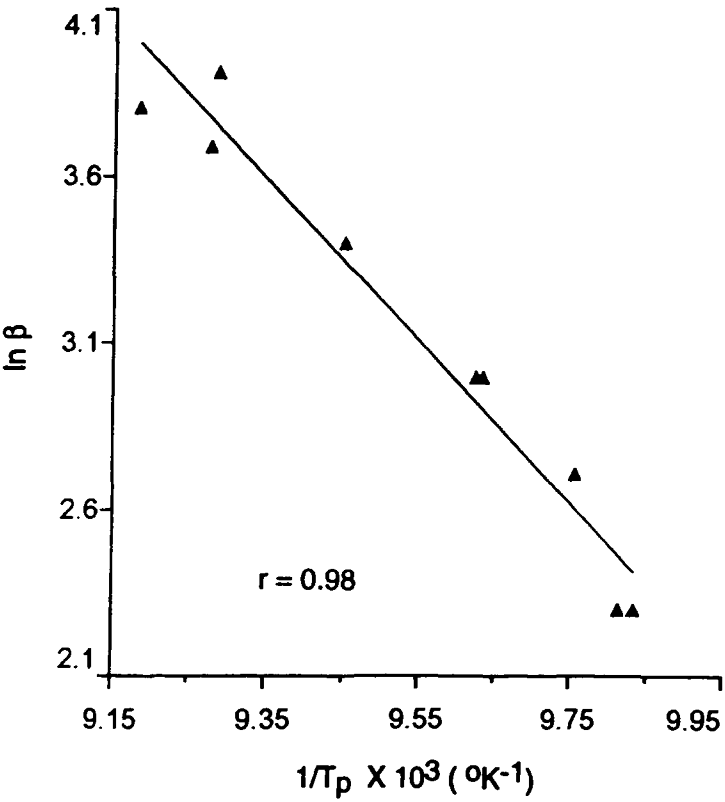

Fig. 4. Plot of $\ln \beta$ vs $1/T_p$ (the peak temperatures, T_p, were obtained from DTA curves recorded at different heating rates, β; and r in figure is correlation coefficient).

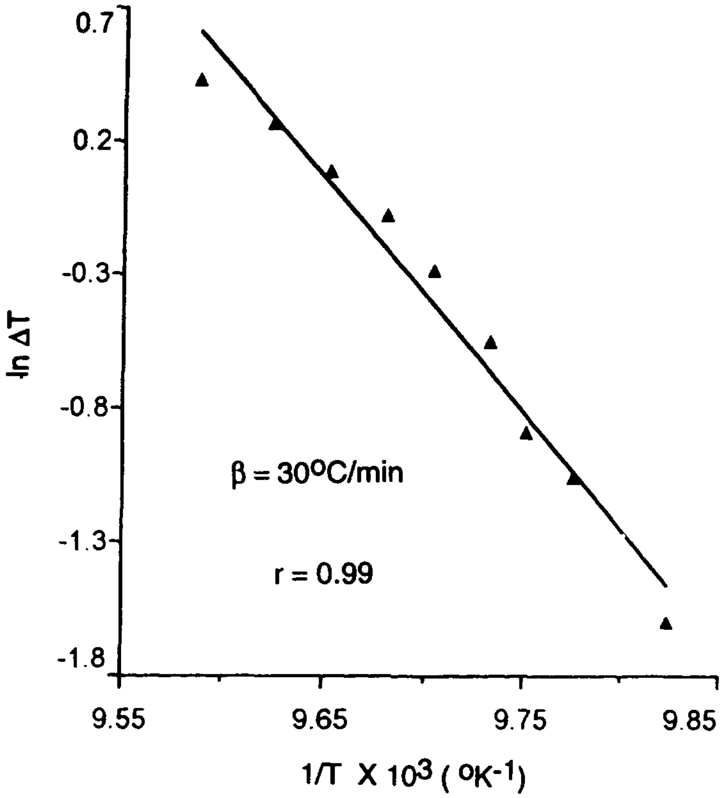

Fig. 5. Plot of $\ln \Delta T$ vs $1/T$ (the values of ΔT and T were obtained from DTA curve recorded at 30°C min^{-1}).

only at the start of transformation (that is on the fixed number of nuclei) [17, 18]. In cellular transformation, regions of precipitate grow into undepleted matrix [18].

4. Conclusion

The devitrification of DICOR® glass as determined by DTA is a one-step process. The presence of any intermediate metastable phases is not indicated by the DTA study. The process appears to be consistent with cellular growth of the precipitate with an activation energy of 203 kJ mol^{-1} on a fixed number of nuclei formed at the beginning of the transformation.

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