KINETIC STUDIES ON CRYSTALLIZATION OF CaO · P₂O₅ GLASS BY DIFFERENTIAL THERMAL ANALYSIS

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ABSTRACT

The crystallization mechanism of $CaO \cdot P_2O_5$ glasses was studied using non-isothermal differential thermal analysis (DTA) by comparing the kinetic parameters of the fine and coarse glass powders. The effect of a small amount of TiO_2 on the nucleation and growth kinetics was also investigated. The kinetic parameters were evaluated from DTA curves by using the variation of heating rate method.

Experimental results suggest that the devitrification behaviour has a tendency to promote a change from surface nucleation to bulk nucleation when the particle size of the glass and/or the TiO_2 content is increased.

INTRODUCTION

The crystal growth of calcium phosphate glasses has received considerable attention recently because of their importance in biological calcification processes such as the formation of bone and tooth [1]. The devitrification of $CaO \cdot P_2O_5$ glass has been investigated by several authors [2,3]. It is of interest that this glass exhibits internal crystallization without the addition of any nucleating agent. Most experiments have revealed that crystallization starts at the surface and grows one-dimensionally towards the inside of the glass [4]. In general, surface crystallization is more dominant in fine powder than in coarse powder or bulk glasses [5].

In the present study, the addition of a small amount of TiO_2 to the glass matrix in order to change the surface crystallization behavior to bulk nucleation, especially in the case of fine powder, was studied. The kinetic parameters were also evaluated from DTA curves and related to the nucleation behavior.

THEORETICAL ANALYSIS

The process of nucleation and crystal growth in a glass can be formally described by the Johnson–Mehl–Avrami–Kolmogorov–Yerofeyev equation [6–8].

$$-\ln(1 - \alpha) = kt^m = At^m \exp(-E/RT) \tag{1}$$

where α is the degree of crystallization at time t, k is the rate constant, T is the Kelvin temperature and E is the activation energy to devitrification.

The parameter m is related to the mechanism of crystallization and morphology of devitrification, ranging from 1 for one-dimensional growth of surface crystallization, to 3 for three-dimensional growth of bulk crystallization controlled by interfacial effects and from 0.5 to 1.5 for bulk crystallization with diffusion controlled growth.

Equations have been derived from eqn. (1) in order to calculate the crystallization kinetics by many authors [7–9]. Therefore, the activation energy and m can be calculated from DTA curves with a variable heating method by these equations. The kinetic models that we used are given by the following equations and the assumptions for each equation are briefly described.

(i) $\ln \Delta T = -mE/RT_p + \text{constant}$ (2)

This is based on the assumptions that in the initial part of the DTA crystallization peak the change in temperature has a much larger effect on the change in ΔT compared with the change in α and that the ΔT deflection from the baseline is proportional to the instantaneous reaction rate at each temperature. Plotting $\ln \Delta T$ vs. $1/T_p$ gives a straight line; the value of mE can be calculated from the slope.

(ii) $\ln \beta = -E/RT_p + \text{constant}$ (3)

This is based on the assumption that the shift of the peak temperature T can be neglected, as can the number of nuclei formed during the DTA run (so that the crystals grow at each heating rate from the same number of nuclei), as the heating rate is changed. By plotting $\ln \beta$ vs. $1/T_p$ to give a straight line, the value of E can be calculated from the slope.

(iii) A modified form of the JMAKY kinetic model, which was extended for use in non isothermal method by Augis and Bennett [9] is given by the equation

$$\ln\left(T_p^2/\beta\right) = \ln(E/R) - \ln \nu + E/RT_p$$ (4)

By plotting $\ln(T_p^2/\beta)$ vs. $1/T_p$, the value of E can be calculated from the slope of the line.

EXPERIMENTAL

The glass compositions listed in Table 1 were prepared by melting the analytical grade reagents ($CaCO_3$, $Ca(H_2PO_4)_2 \cdot H_2O$ and TiO_2) at $1450\,^\circ C$ in a platinum crucible in an electric furnace for 4 h. For homogenizing, the melt was quenched in ice-water and then the crushed powder was remelted at $1400\,^\circ C$ for another 4 h. Glass was made by casting the melt in a graphite

TABLE 1

Composition of $CaO \cdot P_2O_5$ glasses

Specimen	TiO_2		CaO	P_2O_5
	mol%	wt.%	wt.%	wt.%
A	0	0	30.3	69.7
B	1	1.3	29.9	68.8
C	3	3.7	29.2	67.1
D	5	6.1	28.5	65.4
E	7	8.7	27.8	63.9

mold. The sample powder was prepared by crushing the glass in a ball miller and then shifting to fine (passed 325 mesh) and coarse (passed 30 ~ 50 mesh) particle sizes by sieves.

DTA curves of each approximately 30 mg sample of fine or coarse glass powder were recorded in air at different heating rates ($2°C$ min^{-1} to $20°C$ min^{-1}). A Rikagu–Denki thermoanalyzer (model 8121) was used, and powdered α-Al_2O_3 was used as a reference material.

RESULTS AND DISCUSSION

Non-addition

The relationship between the kinetic parameters E and m and particle size and treatment of the glass, obtained by plotting $\ln \beta$ vs. $1/T_p$ (Fig. 1), $\ln(T_p^2/\beta)$ vs. $1/T_p$ (Fig. 2) and $\ln \Delta T$ vs. $1/T$ (Fig. 3) are given in Table 2.
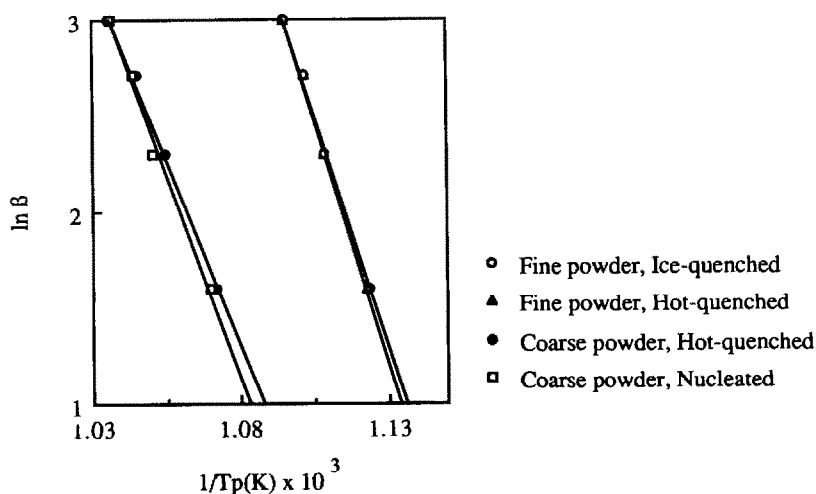

Fig. 1. Plot of $\ln \beta$ against $1/T_p$ used to determine the value of activation energy.
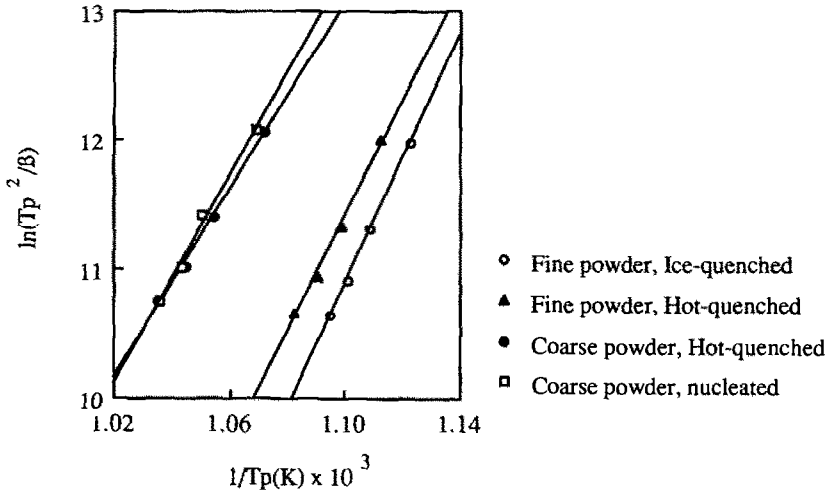
Fig. 2. Plot of $\ln(T_p^2/\beta)$ against $1/T_p$ used to determine the value of activation energy.

The values of m are all between 1 and 3, suggesting that both surface and bulk crystallization occurs in these four kinds of glass. However, comparison of fine and coarse powders indicates that surface crystallization is dominant in fine powder while bulk crystallization is dominant in coarse powder. The crystallization mechanism suggested by the value of m may indicate that nuclei are already present in the hot-quenched or nucleated coarse sample their growth being diffusion controlled. For this reason, the hot-quenched and nucleated samples have a tendency to bulk crystallization. Furthermore, the value of activation energy decreases with increasing particle size. The
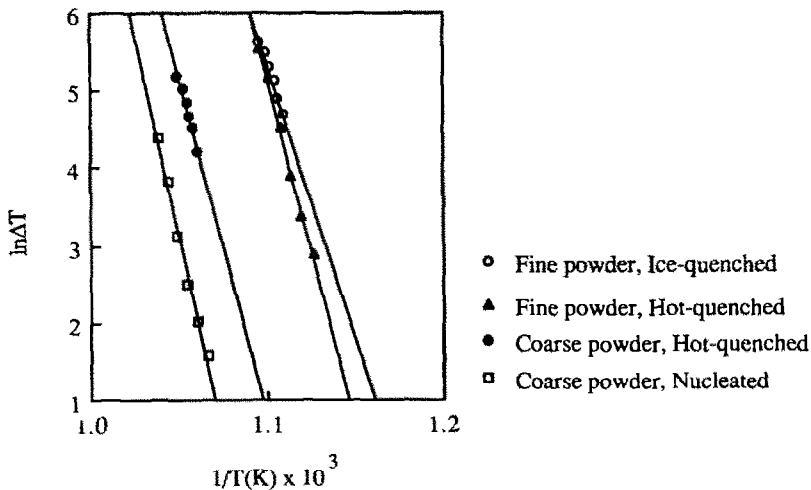

Fig. 3. Plot of $\ln \Delta T$ against $1/T$ used to determine the value of mE_a.

TABLE 2

Kinetic parameters varied with different particle size and treatment

Parameters [a]	Fine powder		Coarse powder	
	Ice-quenched [b]	Hot-quenched [c]	Hot-quenched [c]	Nucleated [d]
$E_a 1$ (kJ/mol)	402.8	419.8	319.4	349.8
$E_a 2$ (kJ/mol)	404.2	373.0	303.6	334.0
E_{av} [e]	403.5	396.4	311.5	341.9
mE_a	594.8	743.4	720.5	862.9
m	1.47	1.88	2.31	2.52

[a] $E_a 1$, activation energy calculated from the slope of ln β bs. $1/T_p$; $E_a 2$, activation energy calculated from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$.
[b] Ice-quenched: glasses quenched in ice-water.
[c] Hot-quenched: glasses quenched on a hot plate about 400°C.
[d] Nucleated: glasses nucleated at 550°C for 2 hours.
[e] E_{av}: the average of $E_a 1$ and $E_a 2$.

variation of the activation energy E and parameter m thus obtained was caused by the change of crystallization mechanism. In fact, samples of fine powder which have no nucleation agent are difficult to crystallize with bulk devitrification.

Addition of TiO₂

For the purpose of obtaining bulk nucleation, the effect of the addition of TiO_2 to the fine glass powder was studied. And also, taking the TiO_2 as a nucleating agent and the suitable contents were recognized by the kinetic study.
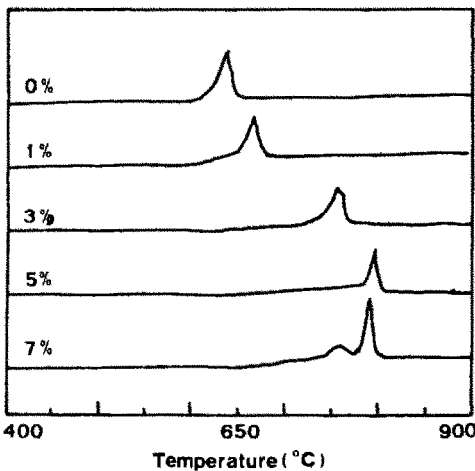

Fig. 4. DTA curves of fine $CaO \cdot P_2O_5$ glass powder with different proportions of TiO_2 recorded at 10°C min^{-1}.
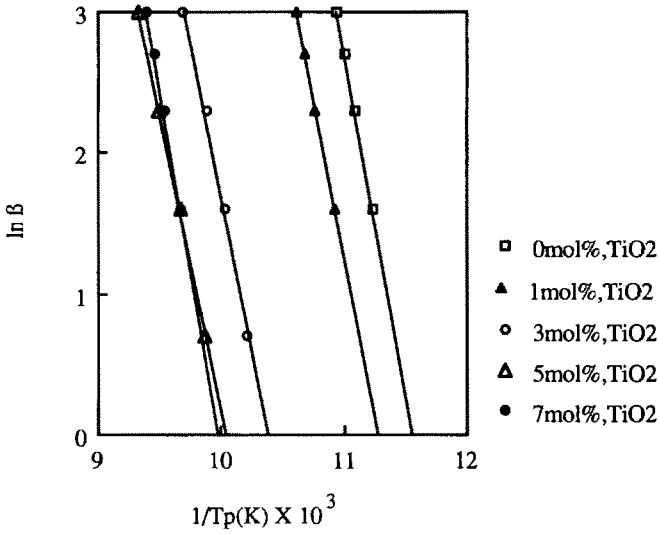
Fig. 5. Plot of $\ln \beta$ against $1/T_p$ used to determine the activation energy for crystallization of fine glass powder.

It was found that every DTA curve had one prominent exothermic peak in the temperature range between $580\,^\circ\text{C}$ and $830\,^\circ\text{C}$ due to the precipitation of crystalline calcium pyrophosphate ($\beta\text{-CaO} \cdot \text{P}_2\text{O}_5$), identified by X-ray diffraction methods. It was seen that the exothermic peak shifted to higher temperatures on increasing the proportion of TiO_2, as shown in Fig. 4. The phenomena is approximately true that the TiO_2 affect on the nucleation behavior of the glass.
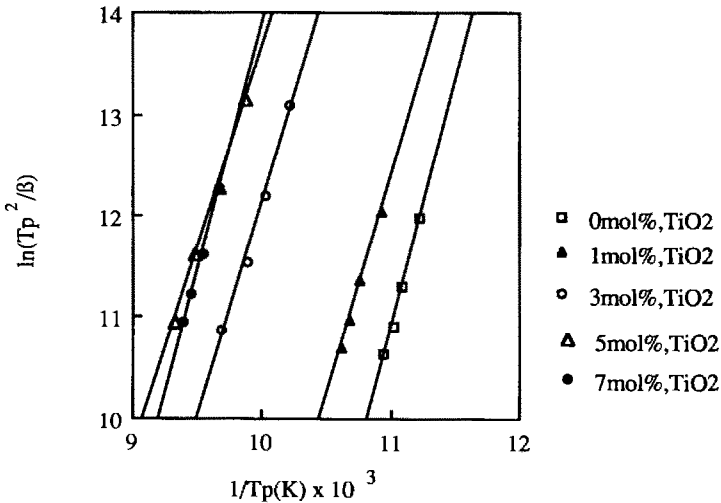

Fig. 6. Plot of $\ln(T_p^2/\beta)$ against $1/T_p$ used to determine the activation energy for crystallization of fine glass powder.
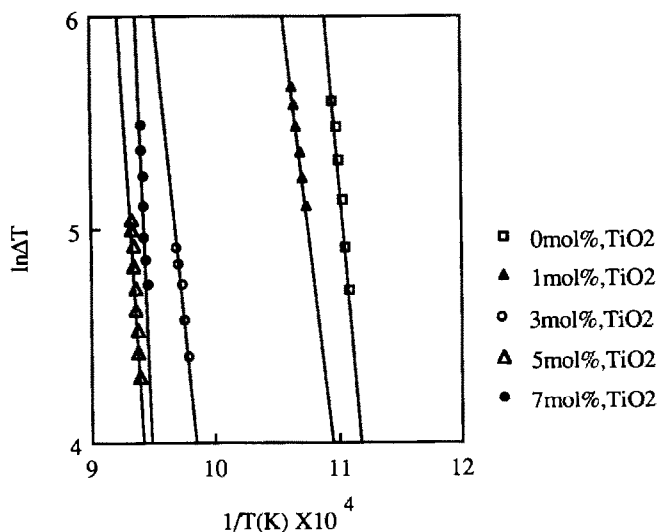
Fig. 7. Plot of ln ΔT against $1/T$ used to determine the value of mE_a for fine glass powder.

Figures 5 and 6 show the relationship between the maximum exothermic peak temperature T_p and heating rate β plotted as log β vs. $1/T_p$ and $\log(T_p^2/\beta)$ vs. $1/T_p$ for the fine powder glass that contained different proportions of TiO_2. The activation energies E_a1 and E_a2 can be calculated from the slope of these straight lines according to eqns. 3 and 4.

The values of m were calculated from the slopes of the straight lines obtained by plotting ln ΔT vs. $1/T_p$ as shown in Fig. 7. (The average of E_a1 and E_a2 was taken.)

The values of the kinetic parameters E and m calculated from the slopes are reported in Table 3. It is seen that the value of m increases from 1.5 to 3.3 when the TiO_2 content increases from 0 to 7 mol%. It is suggested that surface crystallization associated with diffusion controlled crystal growth

TABLE 3

Kinetic parameters of fine $CaO \cdot P_2O_5$ glass powder varied with different content of TiO_2

Specimen	Fine powder (kJ mol^{-1})				m
	E_a1 [a]	E_a2 [b]	E_{av} [c]	mE_a	
A	387.7	402.8	395.2	594.9	1.50
B	356.7	372.2	264.7	422.4	1.16
C	350.0	366.8	358.4	512.9	1.43
D	328.7	345.8	337.5	893.9	2.65
E	403.2	420.4	412.0	1315.1	3.19

[a] E_a1: activation energy calculated from the slope of ln β vs. $1/T_p$.
[b] E_a2: activation energy calculated from the slope of $\ln(\beta/T_p)$ vs. $1/T_p$.
[c] E_{av}: the average of E_a1 and E_a2.

occurs in this glass when the TiO_2 content is lower than 5 mol%. When the TiO_2 content is greater than 5 mol%, bulk nucleation is dominant and each crystal grows three-dimensionally in the glass. This means that TiO_2 promotes the bulk nucleation of $CaO \cdot P_2O_5$ glass when its content is larger than 5 wt.%. In addition, the XRD pattern shows the appearance of the $P_2O_5 \cdot TiO_2$ phase when the TiO_2 content is greater than 5 mol%. Thus TiO_2 is a nucleation agent.

CONCLUSIONS

From these kinetic parameters, which were calculated by a non-isothermal method, the crystallization mechanism of $CaO \cdot P_2O_5$ glass can be derived. The results suggest that the mechanism changes from surface to bulk nucleation when the TiO_2 content is increased to more than 5 mol%. TiO_2 can therefore serve as a good nucleation agent in the $CaO \cdot P_2O_5$ glass system.

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