The devitrification behavior of calcium phosphate glass with TiO$_2$ addition[1]

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Abstract

The effects of TiO$_2$ addition on the devitrification behavior of the calcium phosphate glasses were investigated using thermal analysis techniques. Both the DTA traces of coarse powder and fine powder for calcium phosphate glasses indicated that the glass transition temperature (T_g), gradually increased. To determine whether the devitrification begins at the surface or in the bulk of these glasses, we recorded DTA curves of coarse powder and fine powder. By comparing the exothermic peak temperature of coarse powder and fine powder, we found that the two exothermic peak temperatures tend to be nearer when the amount of TiO$_2$ in calcium phosphate is increased. This indicates that bulk devitrification or, more appropriately, devitrification at the internal interface is easier, i.e., TiO$_2$ is an effective nucleating agent in these glass systems. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

CaO/P$_2$O$_5$ glass-ceramics is one of the most important materials in biological and industrial fields for making artificial bone and tooth [1]. From the point of view of bio-ceramics, calcium phosphate ceramics show good biological compatibility and safety in living tissues, but the bending strength is too low to use as bio-materials for bone repair. Some work on microstructure improvement by introducing nucleating agents or precipitating agents has resulted in changed nucleation mechanism. It is believed that the nucleating agents will induce the homogeneous crystallization and this can enhance the mechanical properties of calcium phosphate glass-ceramics. The glass in the CaO–P$_2$O$_5$-TiO$_2$–SiO$_2$–Al$_2$O$_3$ system containing about 40 mol% CaO and 40 mol% P$_2$O$_5$, which was developed by James and coworkers [2] was found to be mechanical glass-ceramics. Around 7 mol% Al$_2$O$_3$ was particularly effective in promoting bulk nucleation. The results of Nan and coworkers [3] also show that the TiO$_2$ is an effective bulk nucleating agent when added above 4 mol%.

The crystal growth of calcium phosphate glasses has received considerable attention recently, because it shows good bio-compatibility with human hard tissue. Although the devitrification phenomenon of calcium phosphate glass has been investigated by

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several researchers [4,5], it is of interest that this glass exhibits internal crystallization without the addition of a nucleating agent, but it always takes a long heat treatment procedure in order to obtain the crystallized glass-ceramics. At the same time, the defects such as cracking, shrinkage and void keep company with the glass-ceramic within sintering procedure.

It is found that metaphosphate glasses can crystallize below T_g. [4] but most glasses consist of a network structure which do not exhibit this abnormal crystallization. In general, the chains of glasses are randomly distributed below the glass transition temperature, upon crystallization, the irregular chains in glass can be transformed to regular chains, then crystal is formed. For glass, crystallization is always accompanied by reconstruction of the glass network, but this is not the case for some metaphosphate glasses. So the activation energy of the crystal growth for some metaphosphate glasses is only around 125 kJ/mol.

In this work, the effect of TiO_2 addition on the crystallization behavior and the related nucleation behavior of CaO/P_2O_5 glass system were investigated by comparing the exothermic peak temperature of DTA curves between coarse powder and fine powder, and the kinetic parameters were also evaluated using non-isothermal DTA techniques.

2. Theoretical analysis

Recently some amorphous materials are under extensive research and development, and the crystallization behaviors are investigated using DTA or DSC. For analyzing the kinetic parameters of crystallization of inorganic glasses and amorphous materials, mainly Kissinger plot [6] proposed for usual chemical reactions has been applied to the data. DTA has been widely used for the kinetic study of the non-isothermal crystallization of glass [7,8], but it is sometimes difficult to explain the kinetic results obtained by DTA from strictly physical and/or physicochemical point of view [9,10]. To compensate DTA, the modified form of the JMAKY kinetic model which was extended for use in non-isothermal method is given by the equation [11–15], and at heating rate $h=5$–$20°C \, min^{-1}$

$$\ln(T_P^2/h) = E/RT_P + \text{const.} \qquad (1)$$

The kinetic parameters and nucleation rate can be calculated from a set of DTA runs, but the assumptions for deriving each equation should be briefly described before being used, the equations that we used in this work are listed as the following:

$$\ln \Delta T = -mE/RT + \text{const.,} \qquad (2)$$

$$\ln I = mE(1/T_P - 1/T_P^o)/R + \text{const.} \qquad (3)$$

where h is the heating rate, T_P the exothermic peak temperature of DTA curve, E the activation energy of crystal growth, and R the gas constant. The parameter m is dependent on the morphology of the devitrification, the value ranging from 1 for one-dimensional crystal growth (surface nucleation) to 3 for three-dimensional crystal growth (bulk nucleation) and ΔT is the deflection from the baseline within exothermic peak. I is the kinetic rate constant of nucleation, T_P is the peak temperature of exothermic peak of DTA curve, and T_P^o are the peak temperature of exothermic peak of DTA curves, that the samples are held the same time t_n (2 h) at each temperature T_n of the heat treatment.

3. Experimental

The glass composition 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 $1450°C$ in a platinum crucible in an electric furnace for 4 h. For homogeneity, the melt was quenched in ice-water and then the quenched glasses were crushed very carefully using a stainless steel mortar and a pestle, the crushed powder was re-melted at $1400°C$ for another 4 h. Glass rod was made by casting the melts into a graphite mold, the sample powder was prepared by crushing

Table 1
Composition of CaO/P_2O_5 glasses

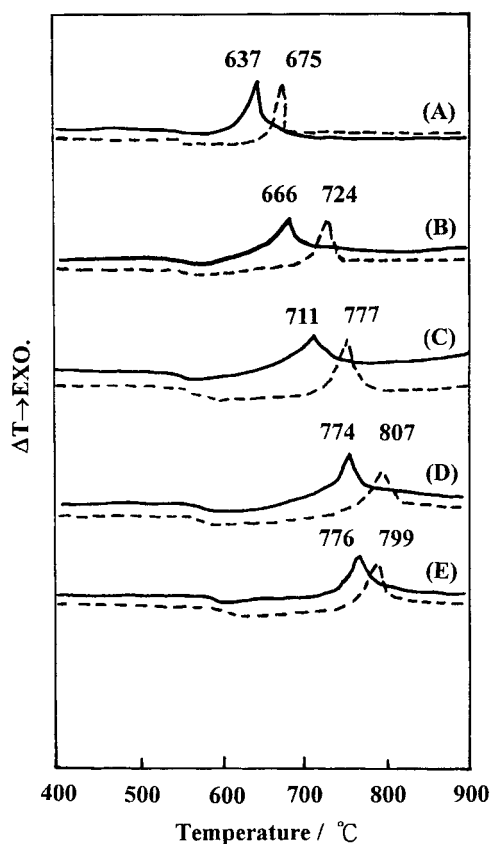| Glass no.	TiO₂		CaO wt%	P₂O₅ wt%
	mol%	wt%		
A	0	0	30.3	69.7
B	1	1.3	29.9	68.8
C	3	3.7	29.2	67.1
D	5	6.1	28.5	65.4
E	7	8.7	27.8	63.9

Fig. 1. DTA curves of calcium phosphate glasses with TiO₂ additives, under static air atmosphere with a 10°C min⁻¹ heating rate. (A) 0, (B) 1, (C) 3, (D) 5, (E) 7 mol%, (- - -) coarse powder, (———) fine powder.

the glass in a ball miller and then sieved in order to obtain a coarse powder between 30 and 50 mesh and very fine (−325 mesh) particles.

DTA curves of each 30 mg of fine and coarse glasses powder at different heating rates (2–20°C min⁻¹) under static air atmosphere were recorded. A Rikagu-Denki thermoanalyzer model 8121 was used, and powered α-Al₂O₃ was used as a reference material.

4. Result and discussions

Fig. 1 shows the DTA traces of fine- and coarse powder samples of calcium phosphate glasses, one is under 44 μm (fine powder), the other one is between

297 and 590 μm (coarse). DTA traces indicated that with the increase of the TiO₂ content in the CaO–P₂O₅ system glasses, the glass transition temperature, T_g, gradually increases, that is T_g shifts to slightly higher temperature with increasing TiO₂ substitution. And the higher the amount of addition, the higher the T_g shift, this result was in agreement with Nan's report [16]. Increasing T_g with higher TiO₂ content suggests that it raises the glass viscosity and may be strengthens the glass network.

It was also seen in Fig. 1, that the exothermic peak shifted to higher temperature with the increasing mol% of TiO₂, the phenomena is approximately true that the TiO₂ affect the nucleation behavior of the calcium phosphate glasses. To determine whether the devitrification begins at the surface or in the bulk of these glasses, we compared the exothermic peak temperatures of coarse and fine particles (as shown in Fig. 1). For the glasses with higher amount of TiO₂ addition, the temperatures of exothermic peak are very close (Fig. 1(D) and (E)). This indicated bulk devitrification occurs in the glass [17]. But for the glasses with lower amount of TiO₂ addition, the exothermic peak occurs at a considerably higher temperature for coarse powders than that for fine powders, see Fig. 1(B) and (C): this result indicates surface devitrification.

The kinetic parameters E and m of these glasses were obtained by plotting $\ln(T_P^2/h)$ vs. $1/T_P$, and $\ln(\Delta T)$ vs. I/T to give straight lines. The values of E and m that are listed in Table 2 are calculated from the slope of the lines.

The values of activation energy of this glass range from 265 to 435 kJ/mol, which is slightly lower than the P–O–P bonding energy (460 kJ/mol). And the values of m for glasses B and C are close to 1, this suggests that surface devitrification takes place in the glasses in which the content of TiO₂ is lower than 4% by weight. But bulk devitrification occurs in glasses D and E, these results are consistent with the above analysis of comparing the exothermic peak temperatures between coarse and fine powders. i.e., that additions of TiO₂ above 4 wt% were found to promote volume nucleation of calcium phosphate glass in this work.

It is assumed that there is no heterogeneous bulk nuclei, N_c in the samples, the samples have same specific surface, S, and the DTA is carried out at

Table 2
Kinetic parameters of calcium phosphate glass powder with different contents of TiO_2

Glass no.	Coarse powder			Fine powder		
	E[a]	mE[a]	m	E[a]	mE[a]	m
A	383 (0.9910)	872 (0.9879)	2.3	395 (0.9778)	595 (0.9745)	1.5
B	435 (0.9877)	563 (0.9853)	1.3	265 (0.9921)	422 (0.9864)	1.2
C	378 (0.9943)	500 (0.9927)	1.3	358 (0.9847)	513 (0.9732)	1.4
D	391 (0.9789)	1181 (0.9850)	3.0	338 (0.9935)	894 (0.9682)	2.9
E	392 (0.9865)	1318 (0.9818)	3.4	412 (0.9863)	1315 (0.9769)	3.2

[a] Unit is kJ/mol.
(C): C is the correlation coefficient for the linear regression analysis.

the same heating rate, so the total nuclei, N_n, is constant. The number of nuclei N_n is related to the time t_n of nucleation heat-treatment by $N_n = It_n^b$, where b is a parameter related to the nucleation mechanism, then Eq. (3) can be derived. By plotting $(1/T_P - 1/T_P^o)$ versus the temperature T_n of the nucleation heat treatment, a nucleation-temperature-

like curve was obtained (Fig. 2), the nucleation rates are rapidly increased when the heat-treatment temperature is higher than that of glass transition temperature for this glass.

5. Conclusions

In the $CaO–P_2O_5–TiO_2$ glass system:

1. TiO_2 above 4 wt% is an effective bulk nucleating agent for calcium phosphate glass, and increased T_g with higher TiO_2 content suggests that it is raises the glass viscosity and may be Ti^{4+} ions play a role of network modifiers.
2. The activation energy of this glass ranges from 265 to 435 kJ/mol, which is slightly lower than the P–O–P bonding energy (460 kJ/mol), but it is higher than that of some metaphosphate glasses (the activation energy for the crystal growth is around 125 kJ/mol).
3. The nucleation rate of this glass is rapidly increased when the heat-treatment temperature is above T_g of glass.
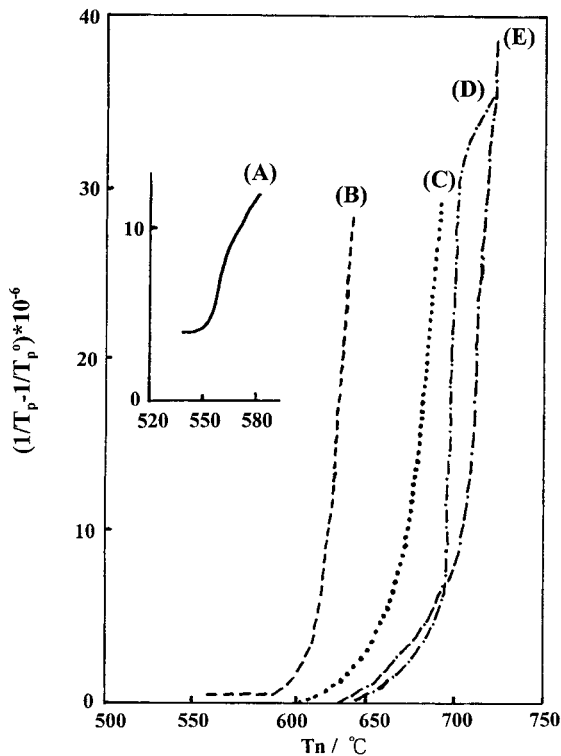

Fig. 2. Nucleation-temperature (Tn) like curves of calcium phosphate glasses with TiO_2 additives.

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