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Kinetic studies on devitrification of calcium phosphate glass with TiO_2, Al_2O_3, and SiO_2 additions

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Abstract

The devitrification phenomenon of CaO/P_2O_5 glass with TiO_2, Al_2O_3, and SiO_2 additions were investigated using thermal analysis techniques. To determine, whether, the devitrification begins at the surface or in the bulk of these glasses, we compared the peak temperatures of exothermic for coarse and fine particles. The devitrification mechanism of CaO/P_2O_5 glass will change by adding additives, such as TiO_2, Al_2O_3, and SiO_2. The addition of additives will induce the surface nucleation mechanism of these glasses, but the addition of additives, such as TiO_2 and Al_2O_3 are found to promote volume nucleation when the amount of addition exceeds 5 and 10 mol%, respectively.

Keywords: Devitrification; Coarse and fine particles; Calcium phosphate

1. Introduction

It has been reported that the direct bonding of bone to bioactive glass, such as D_p-bioglass, would tend to create an artificial interface between the living tissue and the biomaterial [1,2] and the strength of bonding of D_p-bioglass will overcome the problems of joint replacement and improve the long-term performance of prostheses if the bioactive glass is coated onto alloys or stainless steel [3].

Calcium phosphate ceramics have various applications in bio-related fields, and it has been reported that $Ca(PO_3)_2$ glass is nontoxic [4]. Glass-ceramics which contain long fibrous β-$Ca(PO_3)_2$ can be prepared by re-heating CaO/P_2O_5 glasses around the metaphosphate composition at a temperature close to the T_g. Glass-ceramics converted from the calcium ultraphosphate glasses ($Ca/P < 0.5$) consist of crystals such as β-$Ca(PO_3)_2$, $Ca_2P_6O_{17}$ and ultraphosphate glassy phase [5].

To achieve the fine and uniform-grained microstructure that imparts the required mechanical properties and bioactivity, careful control of heating programs and efficient nucleating agents are needed. The devitrification behavior and physical properties of calcium phosphate glass with additives, such as CaO_2 [6] and TiO_2 [7] were investigated in our early reports. Around the exact amount of additive being added into calcium phosphate glass, the additives would play an effect role on devitrification mechanism. This study considers the crystallization and nucleating behavior in the CaO/P_2O_5 glass system and in particular, the effect of varying TiO_2, SiO_2 and Al_2O_3 content.

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2. Experimental

The glass compositions listed in Table 1 were prepared by melting the analytical grade reagents [$CaCO_3$, $Ca(H_2PO_4)\cdot 2H_2O$, TiO_2, Al_2O_3 and SiO_2] at 1450°C in a platinum crucible in an electric furnace for 4 h. For homogeneity the melts were quenched in water and then the quenched glasses were crushed very carefully using a stainless steel mortar and pestle. The crushed powder was re-melted at 1400°C for another 4 h. Subsequently, the glass melts were cast into a preheated (about 280°C) graphite mold, then cooled to room temperature. The glass block was ground to produce a fine (−325 mesh, $\leqq 44\,\mu m$) and a coarse (–30 mesh, +50 mesh, 295–590 μm) in order to do the differential thermal analysis (DTA) experiments. DTA experiments were performed with a model 8121 Rigaku-Denki. α-Al_2O_3 powders were used as a reference material. 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.

3. Results and discussion

The non-isothermal devitrification is well described by the well-known equation [8,9]

$$-\ln(1-\alpha) = \frac{AN}{h^m}\exp\left(-\frac{mE}{RT}\right) \quad (1)$$

where α is the degree of crystallization, N is the nucleus number, A is a constant and h is the heating rate, E is the crystal growth activation energy. The parameter m depend on the mechanism and morphology of crystal growth; it ranges from $m = 1$ for one-dimensional growth (or the rod-like crystals) to $m = 1$ for three-dimensional growth [10]. The higher the value of m, the more sharper in the DTA crystallization peak when the same experimental condition. Assuming that at the peak temperature, T_p, the degree of crystallization α reaches the same specific value and is not dependent on the heating rate h, the activation energy E for the crystal growth can be evaluated from the DTA curves by the following equation

$$\ln(h) = -\frac{E}{RT_p} + \text{constant} \quad (2)$$

Multiple DTA runs were performed at different heating rates, h, and $\ln(h)$ versus $1/T_p$ was plotted. A straight line was obtained and the values of E were obtained from their slopes. If the deflection from the baseline ΔT, is proportional to the instantaneous reaction rate [11,12] and in the initial part of DTA crystallization peak, the change in the temperature has a much greater effect than α on the ΔT [13], Eq. (1) also gives

$$\ln(\Delta T) = -\frac{mE}{RT} + \text{constant} \quad (3)$$

The morphological index m relating to the crystal shape can be obtained by comparing the slope of Eq. (1) and the slope of Eq. (2). Table 2 lists the activation energies of crystal growth, the values of parameter m for CaO/P_2O_5 glasses and CaO/P_2O_5 glasses containing TiO_2, SiO_2 and Al_2O_3. The value of parameter m decreased sharply when the additives were added to CaO/P_2O_5 glass (especially SiO_2). This indicates that the additives induce the devitrification mechanism of these glasses by surface nucleation. To determine, whether, the devitrification begins at the surface or in the bulk of these glasses, we compared the exothermic peaks of coarse powder and fine powder (Fig. 1). For the glasses with higher amount of TiO_2 and Al_2O_3 addition, the temperatures of exothermic peak for both coarse powder and fine powder are very close, this indicated bulk nucleation occured in these glasses [14]. A survey of CaO/P_2O_5

Table 1
Glass compositions

Glass no.	Oxide (composition/mole%)				
	CaO	P_2O_5	TiO_2	Al_2O_3	SiO_2
1	52.4	47.6			
2	50.3	45.7			4.0
3	48.3	43.8			7.9
4	46.4	42.2			11.6
5	44.4	40.4			15.2
6	51.5	47.0		1.5	
7	50.1	45.5		4.4	
8	48.6	44.1		7.3	
9	47.1	42.5		10.4	
10	51.6	47.1	1.3		
11	50.4	45.9	3.7		
12	49.2	44.7	6.1		
13	46.2	41.7	8.7		

Table 2
Crystal growth activation energies and values m for CaO/P_2O_5 glasses containing TiO_2, Al_2O_3 and SiO_2 additives

Glass composition	Fine powder ($\leqq$ 44 μm)/Coarse powder (297–590 μm)		
	E_c (kJ mol^{-1})	$m\ E_c$ (kJ mol^{-1})	m
1	361/400	610/834	1.7/2.1
2	280/343	335/316	0.84/0.92
3	311/370	281/192	0.90/0.52
4	348/370	136/107	0.39/0.29
5	315/452	117/181	0.37/0.40
6	361/413	330/413	1.09/1.0
7	372/514	413/540	1.11/1.05
8	232/241	354/371	1.53/1.54
9	433/441	514/531	1.19/1.20
10	366/373	408/444	1.11/1.19
11	431/332	500/415	1.16/1.25
12	311/332	498/549	1.60/1.65
13	392/345	1181/845	3.01/2.50

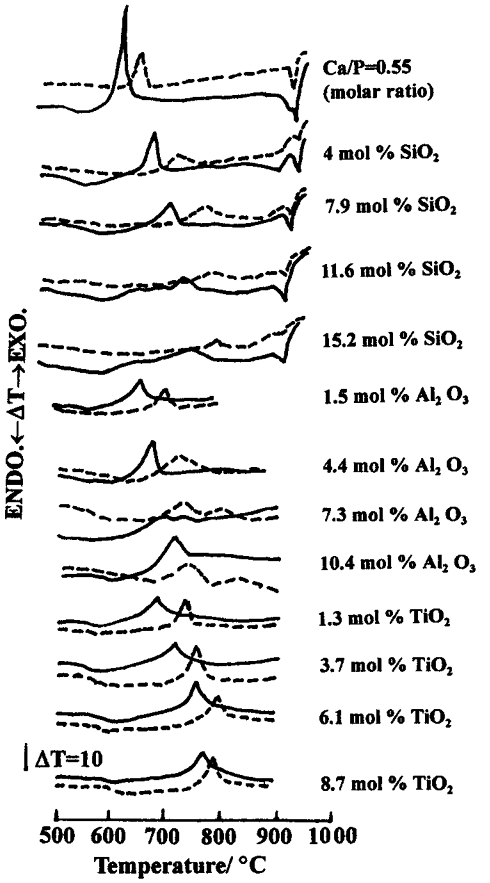

Fig. 1. DTA curves of calcium phosphate glasses with SiO_2, Al_2O_3 and TiO_2 additives, under static air atmosphere with a 10°C min^{-1} heating rate (- - - coarse powder, — fine powder).

glasses studied and their crystal growth activation energies E is listed in Table 3.

The number of nuclei for unit volume N is the sum of surface nuclei N_s, bulk nuclei formed during a previous heat treatment of nucleation N_h, heterogeneous bulk nuclei N_c.

$$N = N_s + N_h + N_n + N_c \tag{4}$$

The values of N_s, N_h, N_n and N_c are proportional to the sample specific surface, S, the reciprocal of DTA heating rate, h, the time, t_n, of the nucleation heat treatment and the amount of nucleating agent, respectively. As the DTA runs are carried out on as-quenched glasses, $N_n = 0$, in the samples and assuming that at the temperature T_p of the crystallization peak, the crystallization degree y reaches the same specific value not depending on the DTA heating rate h. It is also assumed that there are no heterogeneous bulk nuclei, N_c, in the samples. The samples have same specific surface, S and the DTA is carried out at the same heating rate, h, so the sum, N_o, of surface nuclei, N_s and bulk nuclei, N_h, formed during the DTA run is constant, and the following equation can be derived

$$\ln(N_o + N_n) = \frac{E}{RT_p} + \text{constant} \tag{5}$$

For an as-quenched sample ($N_n = 0$)

$$\ln(N_o) = \frac{E}{RT_p^o} + \text{constant} \tag{6}$$

Table 3
Survey of the activation energies of the studied CaO/P_2O_5 glasses

Glass no.	Composition (mol%)	Activation energies ($kJ\ mol^{-1}$)	Reference
A	$52.5CaO$-$47.5P_2O_5$	502	[15]
B	Some meta phosphate glasses	125	[16]
C	P–O–P bonding energy in glasses	460	[16]
D	$34CaO$-$11.3\ P_2O_5$-$28.7MgO$-$26SiO_2$	763	[17]
E	Viscous relation	1000	[17]
F	$50CaO$-$5\ P_2O_5$-$45SiO_2$	536	[18]

From Eqs. (5) and (6), the following equation can be drawn

$$\ln\left(\frac{N_o + N_n}{N_o}\right) = \frac{E}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^o}\right) \tag{7}$$

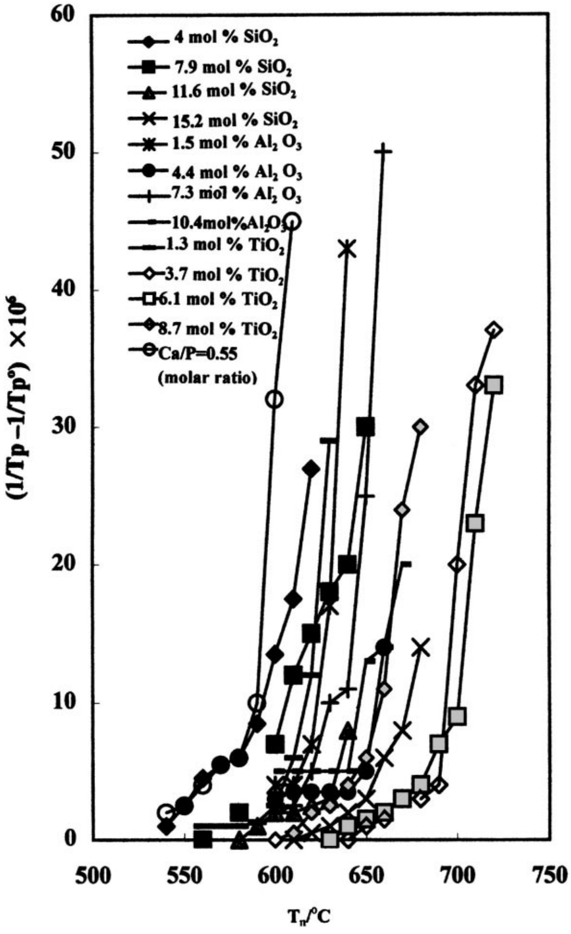

Fig. 2. The nucleation rate — temperature like curves of calcium phosphate glasses containing SiO_2, Al_2O_3 and TiO_2 additives.

The number of nuclei N_n is related to the time t_n of nucleation heat treatment by

$$N_n = It_n^b \tag{8}$$

where I is the kinetic rate constant of nucleation and b is a parameter related to the nucleation mechanism. If the samples are held at the same time t_n (a long time) at each temperature T_n of the heat treatment and the DTA runs are carried out at high heating rate [15,16], the following approximate equation can be derived from Eq. (8)

$$\ln(I) = \frac{E}{R}\left(\frac{1}{T_p} - \frac{1}{T_p^o}\right) + \text{constant} \tag{9}$$

By plotting $(1/T_p - 1/T_p^o)$ against T_n, a nucleation rate-like curve is obtained. Fig. 2 shows the nucleation rate like curves of CaO/P_2O_5 glass containing TiO_2, Al_2O_3 and SiO_2 additives. It was found that the temperature T_n of the heat treatment corresponded to the maximum nucleation rate of the samples, and increased with the TiO_2, Al_2O_3 and SiO_2 amounts added to the CaO/P_2O_5 glass. The higher the additives content, the higher is the temperature T_n of the heat treatment.

4. Conclusion

Adding additives, such as TiO_2, Al_2O_3 and SiO_2, to the CaO/P_2O_5 glass leads to an increase in both of the glass transition temperatures, T_g, and crystallization peak temperature, T_p. That the glass crystallization peak temperature, T_p, is high or low does not mean that the glass crystallization is difficult or easy.

Around 5 mol% TiO_2 is particularly effective in promoting volume nucleation. The reduced peak shift of crystallization temperature between coarse and fine glass powders at higher TiO_2 contents, suggests that volume nucleation is easier. But the nucleation mechanism of CaO/P_2O_5 glass changes on the addition of the additives, TiO_2, Al_2O_3 and SiO_2, etc. These additives induce the surface nucleation mechanism of these glasses, except for the CaO/P_2O_5 glass containing higher amounts of Al_2O_3 and TiO_2.

The activation energies of these glasses range from 265 to 513 kJ mol^{-1} for fine powder samples, and 342 to 514 kJ mol^{-1} for coarse powder samples, respectively. These values close to the value of P–O–P bonding energy (460 kJ mol^{-1}), but they are moderately higher than that of some metaphosphate glasses (the activation energy for the crystal growth is around 125 kJ mol^{-1}). However, the activation energy of crystal growth of CaO/P_2O_5 glass with higher amounts of additives, in this work, are close to the isothermal crystallization data on $Ca(PO_3)_2$ glass powders [17–19] (for particle size between 44 and 74 μm, presented by Abe et al., $E_c = 502$ kJ mol^{-1}, estimated by the relation between $t_{0.5}$ and temperature). The activation energy reported here is also in agreement with those of Costantini et al. [20] ($E_c = 534 \pm 59$ kJ mol^{-1}, for the glass of composition $50CaO–5P_2O_5–45SiO_2$).

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