DEVITRIFICATION BEHAVIOR OF CALCIUM PHOSPHATE GLASSES CONTAINING Al$_2$O$_3$ AND SiO$_2$ ADDITIVES

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Abstract

The effects of Al$_2$O$_3$ and SiO$_2$ additives on the crystallization of calcium phosphate glasses were studied. When the Al$_2$O$_3$ content was higher than 7 mol%, surface devitrification occurred in the glasses. However, for glasses with Al$_2$O$_3$ contents higher than 10 mol%, bulk devitrification predominanted. For the glasses with SiO$_2$, a surface devitrification mechanism predominanted. Non-isothermal DTA techniques were applied in order to establish the devitrification mechanism, and the kinetic parameters of crystal growth were obtained. The parameter m depends on the mechanism and morphology of devitrification of calcium phosphate, glass containing SiO$_2$ as additive, the values of m being lower than 1.2. These results indicate that the devitrification is controlled by the reaction at the glass-crystal interface, or occurs from surface nuclei.

Keywords: Al$_2$O$_3$ and SiO$_2$ additives, CaO/P$_2$O$_5$ glasses, devitrification behavior

Introduction

From the aspect of bio-ceramics, calcium phosphate ceramics display good biological compatibility and safety in living tissues, but the bending strength is too low to allow their use as bio-materials for bone repair. Some work on microstructure improvement by introducting nucleating agents or precipitating agents has resulted in a changed nucleation mechanism [1]. It is believed that nucleating agents induce homogeneous crystallization and this can enhance the mechanical properties of calcium phosphate glass-ceramics.

The glasses in the system CaO–P$_2$O$_5$–TiO$_2$–SiO$_2$–Al$_2$O$_3$, containing about 40 mol% CaO and 40 mol% P$_2$O$_5$, developed by James and coworkers [2–4], were found to be machinery glass-ceramics. Around 7 mol% Al$_2$O$_3$ was particularly effective in promoting bulk nucleating. The crystallization behavior of CaO–P$_2$O$_5$ glasses containing TiO$_2$, SiO$_2$ and Al$_2$O$_3$ additives was also investigated by Nan and coworkers [5], whose results demonstrated that TiO$_2$ is an effective bulk nucleating agent additive at concentrations above 4 mol%.

The present study considers the crystallization and nucleation behavior in the $CaO-P_2O_5$ glass system and, in particular, the effects of various SiO_2 and Al_2O_3 contents. The crystallization results for fine (–325 mesh) and coarse (–30 to +50 mesh) powders were compared.

Experimental

The glass compositions listed in Table 1 were prepared by melting analytical grade reagents [$CaCO_3$, $Ca(H_2PO_4)_2 \cdot H_2O$, Al_2O_3 and SiO_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 the quenched glasses were then crushed very carefully, using a stainless steel with a pestle, and the crushed powder was re-melted at 1400°C for another 4 h. Glass rods were made by casting the melts into a graphite mold, and the sample powders were prepard by crushing the glass in a ball mill and then sieving in order to obtain a coarse powder between 30 and 50 mesh or very fine (–325 mesh) particles.

Table 1 Glass compositions

Oxide	Composition/ mole%									
	1	2	3	4	5	6	7	8	9	10
CaO	52.4	50.3	48.3	46.4	44.4	54	51.5	50.1	48.6	47.1
P_2O_5	47.6	45.7	43.8	42.1	40.3	49	46.9	45.5	44.1	42.5
SiO_2		4.0	7.9	11.6	15.2					
Al_2O_3							1.5	4.4	7.3	10.4

DTA curves of approximately 30 mg of fine and coarse glass powders were recorded at different heating rates (2 to 20°C min^{-1}) under static air atmosphere. A Rigaku-Denki thermoanalyzer (model 8121) was used, with powdered α-Al_2O_3 as reference material.

Results and discussion

In some cases, the non-isothermal DTA technique is insufficient to explain the kinetic results from a strictly physical and/or physicochemical aspect [6, 7]. Non-isothermal devitrification is well described by the well-known equation [8, 9].

$$-\ln(1 - \alpha) = (AN/h^m)\exp(-mE_c/RT) \tag{1}$$

where α is the degree of crystallization, N is the nucleus number, A is a constant and h is the heating rate. As in inorganic glasses the exothermic devitrification peak occurs in a temperature range higher than that of efficient nucleation. E_c is the crystal growth activation energy. The parameter m depends on the mechanism and morphology of crystal growth; it ranges from $m=1$ for one-dimensional growth (or growth

from surface nuclei) to $m=3$ for three-dimensional growth. To supplement DTA, the modified Kissinger equation [10, 11] has been widely used for the kinetic study of non-isothermal crystallization glasses:

$$\ln(h^n/T_p^2) = -mE_c/RT_p + \text{const.} \qquad (2)$$

T_p is the exothermic peak temperature of the DTA curve, R is the gas constant, while the numbers n and m are dependent on the morphology of the devitrification; in the Kissinger plots, $n=m=1$. If the value of α at the peak temperature is not dependent on the heating rate, Eq. (1) becomes

$$\ln h = -E_c/RT_p + \text{const.} \qquad (3)$$

If the deflection from the baseline, ΔT, is proportional to the instantaneous reaction rate, and in the initial part of the DTA crystallization peak the change in temperature has a much greater effect than α on ΔT. Eq. (1) also gives

$$\ln(\Delta T) = -mE_c/RT + \text{const.} \qquad (4)$$

Table 2 lists the crystal growth activation energies and the values of parameter m for CaO/P_2O_5 glasses and CaO/P_2O_5 glasses containing SiO_2 and Al_2O_3. The value of parameter m decreased sharply when the additives were added to CaO/P_2O_5 glass
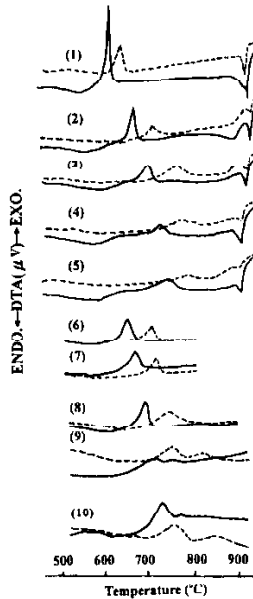

Fig. 1 DTA curves of calcium phosphate glasses with SiO_2 and Al_2O_3 additives, under static air atmosphere at a heating rate of $10^{\circ}C$ min^{-1} --- coarse powder, — fine powder

Table 2 Crystal growth activation energies and values of m for CaO/P_2O_5 glass and glasses containing SiO_2 and Al_2O_3

Glass composition	Fine powder (≤44 µm)/kcal mol^{-1}				
	E_{C1}	E_{C2}	E_{AV}	mE_C	m
1	85.75	86.73	86.24	145.75	1.69
2	67.19	66.60	66.90	80.16	1.20
3	74.15	74.63	74.39	67.28	0.77
4	83.32	83.18	83.25	32.47	0.39
5	75.78	74.67	75.23	27.84	0.37
6	100.20	95.14	97.68	141.97	1.45
7	88.90	83.71	86.30	78.85	0.91
8	91.54	86.24	88.90	98.71	1.11
9*	125.4/71.3	120.01/92.26	122.72/81.78	108.75/60.82	0.88/0.74
10*	111.5/58.7	137.78/56.95	122.68/59.82	103.60/55.32	0.83/0.96

Glass composition	Coarse powder (297–590 µm)/kcal mol^{-1}				
	E_{C1}	E_{C2}	E_{AV}	mE_C	m
1	95.52	95.79	95.52	99.34	1.04
2	81.94	81.86	81.90	15.56	0.19
3	88.45	88.44	88.45	22.11	0.25
4	88.39	88.44	88.42	24.78	0.28
5	107.95	107.95	107.95	19.43	0.18
6	80.49	75.19	77.85	115.22	1.48
7	101.58	96.01	98.79	121.54	1.23
8	125.82	120.05	122.94	129.09	1.05
9*	105.79/60.78	100.00/54.52	102.91/57.64	124.52/49.95	1.21/0.87
10*	108.35/74.39	102.63/68.01	105.49/71.23	177.22/67.67	1.68/0.95

E_{C1}: ln$h$ vs. $1/T_p \cdot 10^4$; E_{C2}: $\ln(h/T_p^2)$ vs. $1/T_p \cdot 10^4$; *A/B, A: exothermic peak 1, B: exothermic peak 2
mE_C: lnΔT vs. $1/T_p \cdot 10^4$; $E_{AV} = (E_{C1}+E_{C2})/2$; $m=mE_C/E_{AV}$.

(especially SiO_2). This indicates that the additives induce the devitrification mechanism of these glasses to surface nucleation. The activation energies of crystal growth of CaO/P_2O_5 glasses with $CaO/P_2O_5=1.1$ (mole ratio) are close to the isothermal crystallization data on $Ca(PO_3)_2$ glass powders [10] (for particle sizes between 44 and 74 µm, presented by Abe et al., $E_c=120$ kcal mol^{-1}, estimated from the relation between $t_{0.5}$ and temperature) and the results of this work agree with those of Costantini et al. [11] ($E_c=128\pm14$ kcal mol^{-1} for the glass of composition $CaO\cdot0.1$ $P_2O_5\cdot0.9$ SiO_2).

In general the exothermic peaks in the DTA curves for coarse samples are sharper than those for fine samples under the same experimental conditions, i.e. in surface-nucleating glasses, the exothermic crystallization peak position is strongly dependent on the particle size used. Fine glass powders with high surface areas will crystallize at lower temperature, and the crystallization peak is therefore shifted to lower temperature. With efficient bulk nucleation, the effect of particle size upon the position of the exothermic peak is small.

Figure 1 shows the DTA crystallization peaks of calcium phosphate and those containing Al_2O_3 and SiO_2 with two ranges of particle size. The baseline shift at about 550°C is the glass transition temperature (T_g). A large exothermic peak occurs at about 625–825°C for all glasses, and a second exothermic peak is seen only for glasses 9 and 10, which have higher Al_2O_3 contents. The peak temperatures of crystallization increased on increase of the amount of additive, and the higher the amount of additive, the higher the peak temperature. As shown in Table 3, the peak temperatures were elevated by 117–145°C for Al_2O_3 and 136–170°C for SiO_2.

Table 3 Peak temperatures for calcium phosphate glasses and those containing Al_2O_3 and SiO_2 additives

Glass transition	Peak temperatures/°C		$\Delta T_p/$°C
	fine powder (≤44 μm)	coarse powder (297–590 μm)	
1	628	650	22
2	686	745	59
3	714	785	71
4	748	798	50
5	764	820	56
6	646	680	34
7	664	710	46
8	679	735	56
9	689/727	737/811	48/84
10	709/763	735/825	26/62

* Peak temperatures measured by DTA under static air atmosphere at a heating rate of 10°C min^{-1}

To determine whether the devitrification begins at the surface or in the bulk of these glasses [12], we compared the exotherm peak temperatures for coarse and fine particles. For the calcium phosphate glasses with SiO_2 and Al_2O_3 additives, the exotherm peak temperatures were considerably higher for coarse particles than for fine particles (Fig. 1, curves (2)–(5) and curves (7)–(10)): this result indicates that the surface nucleation mechanism predominated in these glasses. The values of parameter *m* listed in Table 2, which depends on the mechanism and morphology, are lower than or around 1, suggesting nucleation at the surface of these glasses. For the

calcium phosphate glass without additives, the exotherm peaks for the coarse and fine particles were very close (Fig. 1, curves (1) and (6)), and the parameter m is larger than 1. The results indicate bulk nucleation or, more appropriately, nucleation at the internal interface of the glass.

Conclusions

The non-isothermal method of comparing the exotherm peak temperatures of the DTA curves of coarse and fine glass powders, and the modified Kissinger equations are still valid and useful for studying the nucleation mechanism of calcium phosphate glasses. The nucleation mechanism of calcium phosphate glass changes on the addition of additives such as SiO_2, Al_2O_3, etc. These additives induce the surface nucleation mechanism of these glasses.

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