Thermochimica Acta 392–393 (2002) 169–172

thermochimica
acta

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A study on devitrification and nucleation of calcium phosphate glass with Si_3N_4 additive

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Received 18 November 2000; accepted 18 May 2001

Abstract

The devitrification phenomenon and nucleation of CaO/P_2O_5 glass with Si_3N_4 additive was investigated using thermal analysis techniques. To determine whether the devitrification begins at the surface or in the bulk of these glasses, we compared the exothermic peak temperature of DTA curves for coarse and fine particles, and it was found that the devitrification mechanism of CaO/P_2O_5 glass would change by adding Si_3N_4 powder. The addition of Si_3N_4 additive will induce the calcium phosphate glass to surface nucleation mechanism in this work, and the temperature of exothermic peak of DTA curves for calcium phosphate glass were also shift to higher temperature by increasing the weight percentage of Si_3N_4. On the other hand, the nucleation rate of calcium phosphate was decreased with increasing the weight percentage of Si_3N_4.

Keywords: Devitrification; Si_3N_4 additive; Nucleation

1. Introduction

Calcium phosphate ceramics and glass ceramics have receive much attention as potential bone implant materials because they can form a direct bond with bone tissue [1]. Recently, the effects of $A1_2O_3$, SiO_2 and TiO_2 additives on the crystallization of calcium phosphates glasses have been investigated [2,3]. The additives, such as TiO_2 and $A1_2O_3$ were played an effective bulk nucleating agent role at a certain concentration. But the additive SiO_2 was induced the surface nucleation mechanism of calcium phosphate glass. On the other hand, although, calcium phosphate ceramics are widely accepted since their elemental components are present in bone naturally. But calcium phosphate ceramics are extremely brittle and easy to degrade their mechanical properties at ambient environment. These are the major problems when they are utilized in weight-bearing areas of the human body and in processing, storage and so on. Recently, in order to improve the mechanical properties of biomaterial, a large number of studies are focusing on polymer-and ceramic-based composites [4,5]. To our knowledge, calcium phosphate glass ceramic with Si_3N_4 additive have not been reported. In this study, we attempted to characterized the devitrification mechanism of calcium phosphate glass ceramics with Si_3O_4 additive and the nucleation rate-temperature like curve of calcium phosphate ceramic with various amount of Si_3O_4, the surface Vicker's hardness were also investigated.

2. Experimental

A batch mixtures with $CaO/P_2O_5 = 1{:}1$ molar ratio was prepared using starting materials such as

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PII: S0040-6031(02)00098-9

Table 1
Composition of $CaO/P_2O_5/Si_3N_4$ glasses

Glass number	Si_3N_4 (wt.%)	$CaO/P_2O_5 =$ 1:1 molar ratio (wt.%)
A	0	100
B	1	99
C	3	97
D	5	95
E	6	94

$Ca(H_2PO_4)_2{\cdot}H_2O$, and $CaCO_3$. The mixture containing ethanol was in a ball miller for 1 h then the slurry mixture was dried in an oven at 50 °C for 2 h. The dry powder was melted in a platinum crucible at 1280 °C for 2 h before a heat procedure at 850 °C for 30 min. The melt was cast onto a graphite mold that heated at 280 °C. The glass rods that obtained from the graphite mold were then crushed and sieved to a powder of <200 mesh.

The glass compositions listed in Table 1 were prepared by re-melted the mixture of calcium phosphate glass and Si_3N_4 whisker at 1450 °C for another 2 h. Glass rode were made by casting the melts onto a graphite mold and the sample powders were prepared by crushing the glass in a ball miller and then sieving in order to obtain a coarse between 30 and 50 mesh or very fine (−325 mesh) particles. A Rigaku–Denki thermoanalyzer (model 1821) was used with powdered α-Al_2O_3 as reference material. DTA curves of approximately 20 mg of fine and coarse glass powders were recorded at different heating rate (5–20 °C min^{-1}) under static air atmosphere.

3. Results and discussion

3.1. Kinetic parameters

The works of Šesták [6,7] and Lee et al. [2,3] described thermal studies of glass devitrification by non-isothermal DTA analysis. They agreed that non-isothermal DTA technique have been widely used for the kinetic parameters study of glasses, but it is sometimes difficult to explain the kinetic results that obtained by DTA from strictly physical and/or physicochemical point of view. For analyzing the kinetic parameters of devitrification of glasses and amorphous materials, mainly Kissinger plot [8] proposed for usual chemical reactions have been still applied to the date. As devitrification occurs in glass, the heat of devitrification gives rise to an exothermic peak in the DTA curve. The kinetic parameters can be evaluated from a set of DTA curves, the modified Kissinger plot which was extended for use in non-isothermal method is given by the equations [9,10].

$$\ln \Delta T = -\frac{mE}{RT} + \text{constant} \tag{1}$$

$$\ln h = -\frac{E'}{RT_\mathrm{p}} + \text{constant} \tag{2}$$

$$\ln \frac{h}{T_\mathrm{p}^2} = \frac{E''}{RT_\mathrm{p}} + \text{constant} \tag{3}$$

where E is the apparent activation energy, m the order of reaction, T_p the peak temperature of the DTA curve, and h the heating rate. From Eq. (1), the value of mE can be calculated from the slope of the straight line obtained by plotting ln ΔT against $1/T$. From Eq. (2), the activation energy (E') can be calculated from the slope of the straight line obtained by plotting ln h against $1/T_\mathrm{p}$. Thus, the kinetic parameter, m is obtained by comparing mE to E'. The activation energy (E'') also can be calculated from Eq. (3). All these results are compiled in Table 2.

$$\Delta T_\mathrm{p} = T_\mathrm{pc} - T_\mathrm{pf}$$

where T_pc is the maximum exothermic responses of DTA curve as a function of scan speed from 5 to 20 °C min^{-1} for coarse glass powder and T_pf the maximum exothermic responses of DTA curve as a function of scan speed from 5 to 20 °C min^{-1} for fine glass powder.

The values of m suggest that the surface devitrification takes place in the presence of Si_3N_4 with CaO/P_2O_5 glass. However the bulk devitrification occurs in the CaO/P_2O_5 glass without the presence of Si_3N_4. Fig. 1 shows the DTA traces of fine and coarse powder samples of calcium phosphate glasses. The DTA curves result shows that the exothermic peak shifted to higher temperature with increasing weight percentage of Si_3N_4, but only slightly increasing the glass transition temperature. It was also seen in Fig. 1, that only a sharp exothermic peak occurs in DTA curves (see Fig. 1 (1)) which indicated the bulk devitrification occurs in the CaO/P_2O_5 glass.

Table 2
Kinetic parameters of calcium phosphate powder with different contents of Si_3N_4

Glass number	Coarse powder				Fine powder				
	E	mE	m	T_g (°C)	E	mE	m	T_g (°C)	ΔT_p (°C)
A	383 (0.991)	872 (0.988)	2.3	558	395 (0.978)	595 (0.975)	1.5	555	28–38
B	423 (0.939)	237 (0.985)	0.6	595	396 (0.986)	118.4 (0.993)	0.3	590	60–75
C	557 (0.971)	267 (0.988)	0.5	600	405 (0.968)	206 (0.979)	0.5	595	73–76
D	590 (0.987)	259 (0.981)	0.4	603	316 (0.992)	196 (0.978)	0.6	600	75–83
E	595 (0.965)	663 (0.966)	1.1	611	351 (0.964)	449 (0.961)	1.3	608	48–55

$E = (E' + E'')/2$.

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. For the calcium phosphate glass, temperatures of exothermic peak are very close (see Fig. 1 (1) and Table 2). These results were indicated that bulk devitrification occur in the glass [11]. But for the glasses with Si_3N_4 addition, the exothermic peak occurs at a considerably higher temperature for coarse powder than that for fine powder (see Fig. 1 (2–5) and Table 2), these result indicates surface devitrification.

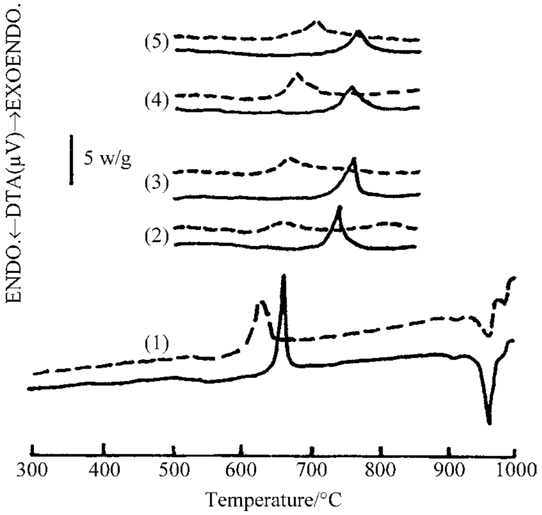

Fig. 1. DTA curves of fine and coarse powders of calcium phosphate glasses with Si_3N_4 additives, at 10 °C min^{-1} heating rate under static air atmosphere: (1) Ca/P_2O_5 molar ratio = 1:1; (2) 1% Si_3N_4 addition; (3) 3% Si_3N_4 addition; (4) 5% Si_3N_4 addition; (5) 6% Si_3N_4 addition; coarse powder (−30 + 50 mesh); fine powder(−325 mesh).

3.2. Nucleation

If a glass heated at constant heating rate h, the crystallization degree y at temperature T is expressed as [12,13].

$$\ln(1-y) = \frac{AN}{h^m}\exp\left(-\frac{mE}{RT}\right) \tag{4}$$

The number of nuclei for unit volume N is the sum of surface nuclei N_s, bulk nuclei, formed during the DTA run N_b, bulk nuclei formed during a previous heat treatment of nucleation N_n [14]. For an as-quenched glasses, $N_n = 0$ in both the powdered and bulk samples, and in the bulk samples, owing to their low specific surface, the extent of surface crystallization is negligible. Assuming that at the temperature T_p of the crystallization peak, the crystallization degree y reaches the same specific value not depend on the DTA heating rate h, Eq. (4) becomes

$$m\ln h - \ln N = -\frac{mE}{R}\frac{1}{T_p} + \text{constant} \tag{5}$$

If the DTA runs are carried out on as-quenched sample of the same specific surface area at the same heating rate h, The sum N_o be obtained from Eq. (5).

$$\ln N_o = \frac{mE}{R}\frac{1}{T_p^\circ} + \text{constant} \tag{6}$$

For a previous nucleated sample

$$\ln(N_o + N_n) = \frac{mE}{R}\frac{1}{T_p} + \text{constant} \tag{7}$$

If low specific surface sample are used, the DTA curves are carried out at a high heating rate (20 °C min^{-1}) and the sample are nucleated for a long

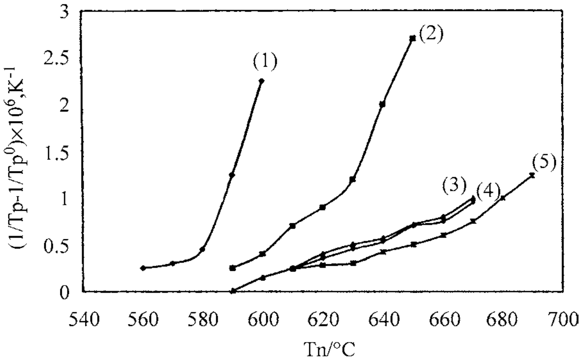

Fig. 2. Nucleation rate-temperature-like curves of calcium phosphate glasses with Si_3N_4 additives: (1) Ca/P_2O_5 molar ratio = 1:1; (2) 1% Si_3N_4 addition; (3) 3% Si_3N_4 addition; (4) 5% Si_3N_4 addition; (5) 6% Si_3N_4 addition.

time ($t_n = 2$ h), $N_n > N_o$. As 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 the parameter related to the nucleation mechanism, If the samples are held at the same time t_n at each temperature T_n of the heat treatment the following approximated equation can be derived from Eqs. (6)–(8) [15].

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

By plotting $(1/T_p - 1/T_p^\circ)$ against T_n, a nucleation rate-temperature like curve is obtained.

Fig. 2 for calcium phosphate glasses with Si_3N_4 additive shows that the nucleation rates are increased slowly when the heat treatment temperature is increasing, but not for calcium phosphate glass.

4. Conclusions

Adding Si_3N_4 to the CaO/P_2O_5 system glass leads to that the glass transition temperature, T_g and crystallization peak temperature, T_p, increases. The devitrification mechanism of calcium phosphate glass was changed from bulk nucleation to surface nucleation owing to the addition of Si_3N_4. When the Si_3N_4 are added to CaO/P_2O_5 system glasses, whether the Si_3N_4 content is high or not, the glasses begin crystallizing mainly from the surface and Si_3N_4 are not one kind of effective nucleating agent.

The nucleation rate of these glasses are increased slowly when the heat treatment temperature is above T_g of glass, but not for calcium phosphate glass. It is not good for further heat procedure.

Acknowledgements

Financial supports from the National Science Council under contract NSC 89-2213-E-027-058 are greatly acknowledged.

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