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Short communication

Effect of ZrO_2 on crystallization of $CaO–P_2O_5–SiO_2$ glasses

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Abstract

The influence of ZrO_2 content on the crystallization mechanisms of $CaO–P_2O_5–SiO_2$ biological glasses was investigated by DTA, XRD and SEM. Kinetic parameters such as the crystallization activation energy (E) and the crystal growth index (n) have also been evaluated according to the JMA equation. In the studied glass system, the larger the ZrO_2 content, the lower the crystallization peak temperature, T_p. Nevertheless the high value of T_p did not mean a large E value. The most effective addition of ZrO_2 in the $CaO–P_2O_5–SiO_2$ glasses was about 5.7 wt.%. The difference of E between the base glass (no ZrO_2 added) and the glass containing the most effective addition of ZrO_2 was about 100 kJ/mol, suggesting that ZrO_2 could promote the crystallization effectively.

Keywords: D. Glasses; Biomaterials; Crystallization

1. Introduction

Research and development activities on biological glass-ceramic materials have been underway for several years [1–6]. Natural bones and teeth are multiphase materials, so their combination of properties possibly can be simulated only by multiphase materials. Bioceramics appear to be well-suited for use in substitution of teeth and bone [7]. It has been reported [8–12] that some glass-ceramics in the $CaO–P_2O–SiO_2$ system, containing apatite and wollastonite phases, with good mechanical properties and the ability of forming tight chemical bonds with living bone can be produced through sintering and subsequent crystallization of glass powders. The effect of compositional changes on the bioactivity [13] and the crystallization behavior of some glass-ceramics located in certain compositional regions of the above system has also been investigated [14].

The main objective of the present investigation is to study the effect of ZrO_2 on the crystallization of glass ceramics of the $CaO–P_2O_5–SiO_2$ system. Sawai pointed out that ZrO_2 was not as effective as TiO_2 as nucleating agent for its solubility being limited within 3–4% in silicate glass-ceramics [15]. Tashiro suggested the solubility of ZrO_2 increases markedly in silicate glass-ceramics containing P_2O_5 [16]. Vomacka and Babushkin et al. [17,18] studied ZrO_2 as a nucleating-agent in the $Y_2O_3–Al_2O_3–SiO_2$ system glass and the Y–Si–Al–O–N system glass. They realized that the added ZrO_2 acted as a growth modifier rather than a nucleating agent. Deckwerth and Russel [19] found the added ZrO_2 in Mg–Ca–Si–Al–O–N oxynitride glasses to have a two-fold effect, i.e. not only as an efficient nucleating agent but also as an efficient toughening agent for the resulting glass-ceramics. In this paper, we investigated the influence of ZrO_2 on the crystallization of $CaO–P_2O_5–SiO_2$ glass-ceramics in order to find out the possible role of ZrO_2 as a nucleating agent in glass-ceramics of the $CaO–P_2O_5–SiO_2$ system.

2. Experimental

The glassy compositions studied are shown in Table 1. The starting materials were analytical grade SiO_2, Al_2O_3, MgO, $Ca(H_2PO_4)$, $CaCO_3$, ZrO_2. Glass batches were ball-milled for 24 h, and thereafter melted in a platinum crucible at 1400–1450 °C for 3 h. The melts were poured onto a steel plate, annealed for 1 h at 600 °C, and cooled to ambient temperature in the furnace. The resulting glass was crushed and sieved through a 200 mesh to produce a powder suitable for DTA. Measurements (differential thermal analyzer,

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Table 1
Compositions (wt.%) of various glass samples

Sample name	CaO	P_2O_5	SiO_2	MgO	Al_2O_3	ZrO_2
1	30	25	40	5	5	0
2	30	25	39	5	5	1
3	29	25	38	5	5	3
4	29	24	38	4	5	5
5	29	24	38	4	4	7

Dupont 2100) were performed with Al_2O_3 powders as reference material. The samples Nos. 1–5 were heated in air from ambient temperature to 1200 °C at heating rates of 5, 10, 15 and 20 °C/mm. After crystallization, the samples were polished and etched in 5.0% hydrofluoric acid for 4–5 mm, then washed, dried and coated with gold in an ion beam coater, and analyzed by SEM (Hitachi S-450). The precipitated crystalline phases were identified by XRD.

3. Results

The process of crystal growth in a glass is well described by a Johnson–Mehl–Avrami model [20–24], and the following two equations, (1) and (2), can be derived from them:

$$1n\alpha = -\frac{E}{R}\cdot\frac{1}{T_p} + \text{const} \quad (1)$$

$$1n\Delta Y = -\frac{nE}{R}\cdot\frac{1}{T} + \text{const} \quad (2)$$

where α is the heating rate of DTA, E is the crystallization activation energy, n is a parameter (also called the crystal growth index) related to the mechanism of the process ($0 < n < 3$, surface crystallization; $n \geqslant 3$, bulk crystallization), ΔY is the deviation from the baseline of the DTA curve to the line of the peak. The kinetic

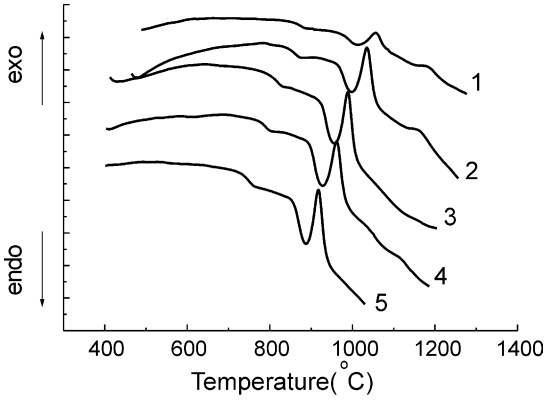

Fig. 1. DTA curves of glass samples subjected to the same heating rate, $\alpha = 10$ °C/min.

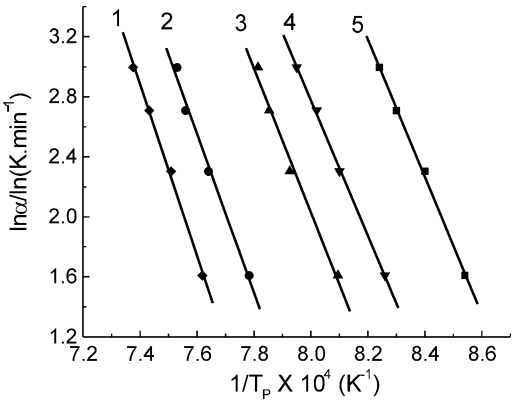

Fig. 2. Plots of ln $\alpha \sim 1/T_p$ for the glass samples, from which the crystallization activation energy values, E, for each sample can be derived.

parameters E and n can be obtained from the above two equations.

Typical DTA of the samples crystallized at the heating rate of 10 °C/min are shown in Fig. 1. Table 2 collects the values of the crystallization peak temperature, T_p, of DTA experiments of samples at different heating rates. Table 3 lists the E values calculated from the slopes of the ln α vs. $1/T_p$ curve shown in Fig. 2. The parameters, n, related to the mechanism of the process are listed in Table 3, which are derived from the plot of ln ΔY vs. 1/T (Fig. 4). Fig. 5 shows the SEM photographs of the sample 3. Fig. 6 shows the XRD pattern.

4. Discussion

With the increase of the ZrO_2 content in the CaO–P_2O_5–SiO_2 glasses, T_p gradually decreases (Table 2), whereas E gradually decreases up to 375 kJ/mol, corre-

Table 2
Values of T_p (°C) at different heating rates α of DTA

Sample name	$\alpha = 5$ °C/min	$\alpha = 10$ °C/min	$\alpha = 15$ °C/min	$\alpha = 20$ °C/min
1	1040	1059	1073	1083
2	1012	1036	1050	1055
3	962	989	1000	1007
4	938	962	974	985
5	898	918	932	941

Table 3
Values of activation energy E for crystal growth and parameter n related to the mechanism of the crystallization process

Sample name	E (kJ/mol)	n
1	477	2.9
2	440	3.9
3	399	4.5
4	375	4.9
5	380	4.8

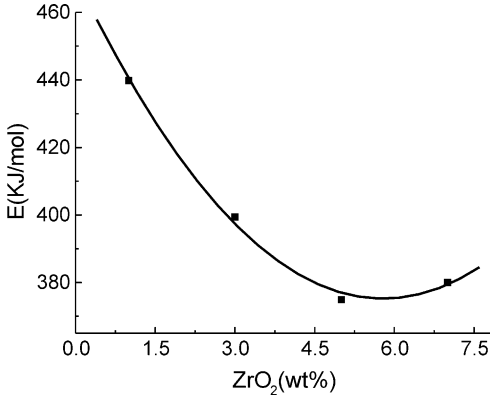

Fig. 3. Plot of the crystallization activation energy E versus ZrO_2 content for the $CaO–P_2O_5–SiO_2$ system glasses.

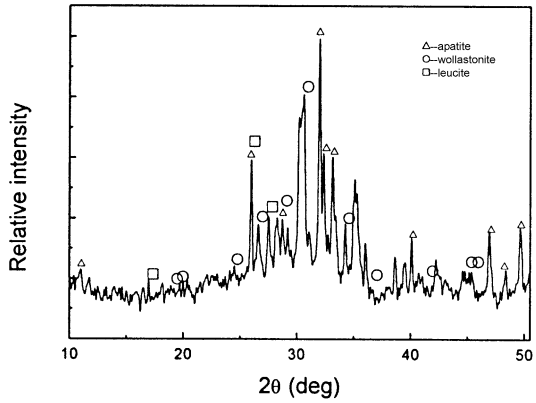

Fig. 6. XRD pattern of the crystallized $CaO–P_2O_5–SiO_2$ glasses.

sponding to a ZrO_2 amount of about 5 wt.% (Table 3). Futher increase of ZrO_2 content is uneffective on E values. ZrO_2 content affects both T_p and E. The above discussion indicates that there is a most suitable ZrO_2 addition amount in this glass-ceramic system. The plot of E vs. ZrO_2 content (Fig. 3) shows that the most effective ZrO_2 content corresponding to the minimum

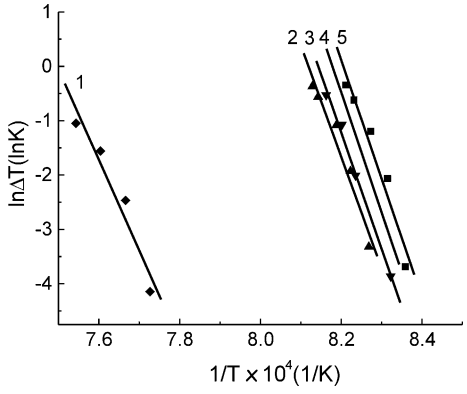

Fig. 4. Plots of ln $\Delta T \sim 1/T$ for the glass samples, from which the parameters n, related to the mechanism of the glass can be derived.

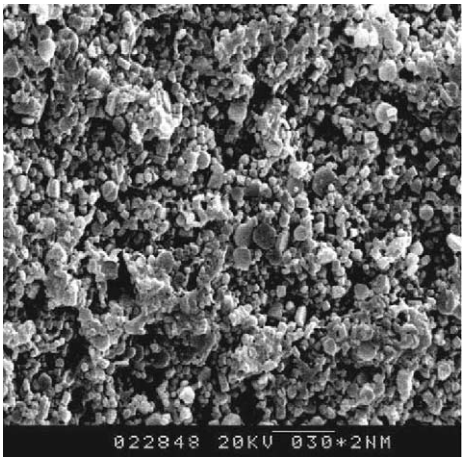

Fig. 5. Scanning electron micrographs of sample 3 containing 5 wt.% ZrO_2 heat treated firstly at 750 ° C for 2 h, then at 1050 ° C for 2 h.

value of E is about 5.7%. The variation of E and T_p, with ZrO_2 content differ each other. Indeed, with the increase of ZrO_2 content in the $CaO–P_2O_5–SiO_2$ system glass, the kinetics barrier to glass crystallization decreases gradually but the thermodynamics barrier, which is related to the constitution, property of nuclei and base glass, does not decrease as much. The activation energy, E, corresponding to the most effective ZrO_2 content is 374 kJ/mol, while E of the base $CaO–P_2O_5–SiO_2$ system glasses is 477 kJ/mol (Table 3), which means that ZrO_2 additions to this glass system can promote crystallization, i.e. ZrO_2 acts as an effective nucleating agent. At about 5.7 wt.% ZrO_2 additions, the nucleating role appears most effective.

Table 3 shows parameters, n, related to the mechanism of the crystallization process assure values higher than 3, with the exception of the base glass-ceramics, which means the ZrO_2 added to the $CaO–P_2O_5–SiO_2$ system glasses can help change the crystallization mode from surface to bulk crystallization [25,26].

Fig. 5 shows SEM micrographs of sample 3 firstly heated at 750 °C for 2 h, then at 1050 °C for 2 h. The average crystal size is ϕ 0.2∼0.3 μm, and the maximal crystal size is about ϕ 0.8 μm. The crystalline phases precipitated in the sintered glass-ceramics are identified from the XRD pattern of Fig. 6 as apatite, wollastonite and leucite, which are bioactive and possess good mechanical properties [8–12]. It can be seen from the flat baseline that the content of glass phase is low.

5. Conclusions

The influence of ZrO_2 on crystallization of the $CaO–P_2O_5–SiO_2$ glass-ceramics has been investigated. Addition of ZrO_2 to this glass system has been concluded to be able to promote crystallization acting as a valuable nucleating agent. The crystallization activation energy, E, gets the lowest value (375 kJ/mol), and the crystal growth index, n, gets the highest value (4.9) at a ZrO_2

content of about 5.7 wt.%. The crystalline phases precipitated in the sintered glass-ceramics have been identified as apatite, wollastonite and leucite.

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