Journal of Thermal Analysis and Calorimetry, Vol. 83 (2006) 1, 151–156

THE EFFECTS ON THE DEVITRIFICATION MECHANISM FOR A CERTAIN COMPOSITION OF CaO/P$_2$O$_5$ GLASS WITH ADDITIVES OF HAp, TCP AND β-CaP$_2$O$_6$ WHISKER

K.-S. Jaw[*]

Department of Chemical Engineering, Northern Taiwan Institute of Science & Technology, Peito, Taipei, Taiwan, R.O.C.

In previous works, the effects on the devitrification mechanism of a certain composition calcium phosphate with additives of TiO_2, SiO_2, Al_2O_3, CeO_2 have been studied. It was found that some metal oxide additives played a key role as the nucleation agent in calcium phosphate glass-ceramics, and the devitrification mechanism of calcium phosphate glass system was changed drastically by addition such as metal oxide. Hydroxyapatite (HAp), tricalcium phosphate (TCP) and β-calcium phosphate (β-CaP_2O_6) whisker are the three most biologically compatible materials to human bone in bio-ceramics field. In this work, the effect on devitrification mechanism and the physical properties of certain composition calcium phosphate glass with three above additives were investigated, and the result shown that although no fine crystalline was induced in the certain composition of calcium phosphate glass when a large amount of additive was added, but such additives play a catalyst role by lowering the activation energies of devitrification. It would supplement the mechanical properties and the biocompatibility for the calcium phosphate glasses.

Keywords: *additives, hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker, devitrification mechanism*

Introduction

Calcium phosphate glass-ceramics are biologically compatible with living bone, and have been used in implants for teeth and some bone replacements. The physical properties of calcium phosphate glass with different Ca/P molar ratio were investigated and compared in previous studies [1, 2]. It was shown that calcium phosphate glass with Ca/P mole ratio equal to 0.55 possessed more suitable physical properties in artificial bone, calcium phosphate glasses containing some metal oxide have been used in implants but were found to have physical properties that were inappropriate for such a produce, however, optimum and enough high-strength sintered products of calcium phosphate glass-ceramics have not yet been developed. In general, the mechanical properties of ceramic or polymer materials are effectively improved by introducing some fibers into the bulk matrix and it has been reported that the unidirectional calcium phosphate glass-ceramics having fiber-reinforced composite crystallized structure was successfully produced by re-heat a calcium meta-phosphate glass rod under a temperature gradient around the glass transition temperature [3, 4]. Calcium phosphate glass-ceramic composed crystalline of β-calcium phosphate fibers shows high-bending strength of 400–600 MPa and low Young's modulus of 70–120 GPa, this implies that ß-calcium phosphate fibers are of high strength and flexibility, then β-calcium phosphate fiber is expected for the reinforcement materials of new composite bio-materials. β-CaP_2O_6 whiskers having aspect ratios of (16–400) with diameter of 3–30 μm was also found by Lee etc. [5] that exacted from a crystallized calcium phosphate glass with Ca/P molar ratio of 0.25 by leaching with distilled water or aqueous solution of 0.1–0.5N NaOH. The resultant whiskers show only 1% mass loss in TG curve and melt completely at 980°C with a sharp endothermic peak. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HAp)] and tricalcium phosphate [$Ca_3(PO_4)_2$, TCP] as two main composition of bio-ceramic that analogous to the constitute of human hard tissues are also interesting in bio-material fields recently [6], it is also knew, porous multiphase bio-ceramics are found to have better bone-bonding ability than pure hydroxyapatite in body sites.

Thermal analysis has been successfully used to investigate the thermal behaviors and kinetics of chemical reactions and devitrification mechanisms of solid state amorphous material, many researchers describe methods for determining the activation energy for crystal growth and the mechanism of crystallization for bulk or surface nucleation from DTA/DSC or TG techniques [7–10]. It is not expected that any single kinetic expression would be applicable to a wide range of crystallization obeys elementary reaction order kinetic will be generalized. But, in some cases, the

---

[*] marble.lee@msa.hinet.net

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

non-isothermal thermal analysis technique is sufficient to explain the kinetic results from a strictly physical and/or physicochemical aspect. For analyzing the kinetic parameters of devitrification mechanism for inorganic glasses and amorphous materials, mainly Kissinger plot [10] proposed for usual chemicals reactions has been applied to the data. In this work, the effect on the devitrification behavior of a certain composition calcium phosphate glasses with hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker additives, and the related kinetic parameters of a certain composition calcium phosphate glasses were investigated using non-isothermal DTA technique, and the characteristic peak of devitrification phase that inducing of additives was examined by powder X-ray diffraction (XRD).

Experimental

Reagent grade of $Ca(H_2PO_4)_2{\cdot}H_2O$ (Osaka, Japan), and $CaCO_3$ (Riedel-Dehaen) with particle size less than 44 μm, were samples adopted for these works, batch of mixtures with Ca/P molar ratio (0.55) were prepared by mixing $Ca(H_2PO_4)_2{\cdot}H_2O$ and $CaCO_3$ with ethanol in ball miller for 30 min, after being dried, the powder of mixtures were melted in a platinum crucible and then put it in an electrical furnace holding the temperature at 1350°C for 2 h. Melted glasses were poured into a preheated graphite mold (about 280°C, for a few minutes), then cooled to room temperature in order to harden into a glass block. Powdered sample was prepared by crushing the glass block in a stainless steel mortar and pestle, then the crushed glass powder was sieved in order to obtain a very fine (–325 mesh) particles. Additives such as hydroxyapatite, tricalcium phosphate and β-calcium additives phosphate whisker (additives are added to fine particle size calcium phosphate glass powder, then making a well mixed by a shaker). Table 1 listed the relationship between the arranged under numbers of glass with the addition percentage of additives. DTA curves of each approximately 10 mg of glass powder at different heating rates (5–30°C min^{-1}), under a static air atmosphere were recorded. A Rigaku-Denki thermoanalyzer (model 8121) was used, and powder α-Al_2O_3 was used as reference material. The devitrification phases of the resultant products were also identified by Rigaku-Denki X-ray powder diffraction (XRD).

Results and discussion

In previous study [11], calcium phosphate glass and glass-ceramic with 0.55 Ca/P molar ratio have been recommended for matrix glass composition because it possesses higher Vicker's surface hardness and displays good compatibility and safety in living tissues. Some works on microstructure improvement by introducing nucleating agents induce homogeneous crystallization and this can enhance the mechanical properties of calcium phosphate glass-ceramics. Both of Nan [12] and Lee [1] suggest that the TiO_2 is an effective bulk nucleating agent of calcium phosphate glasses when added above 4–5 mol%. For analyzing the kinetic parameters of devitrification for inorganic glasses and amorphous materials, mainly Kissinger plot proposed for usual chemical reactions has been applied to the data, although the validity of applying the Arrhenius equation to heterogeneous reaction has been questioned, but the kinetic parameters have practical value even if their theoretical interpretation is difficult. DTA has been widely used for the kinetic investigation of the non-isothermal devitrification of glass, but sometimes difficult to explain the kinetic results obtained by DTA curves. The DTA curves of calcium phosphate glass with 0.55 Ca/P molar ratio were shown in Fig. 1, the exothermic peak temperatures of fine glass powder and coarse powder were all

Table 1 Arranged under numbers of glasses and the percentage of additives

Glass No.	HAp/%	Glass No.	TCP/%	Glass No.	$\beta Ca(PO_3)_2$whisker%
A	1	K	1	U	1
B	3	L	3	V	3
C	5	M	5	W	5
D	7	N	7	X	7
E	9	O	9	Y	9
F	11	P	11	Z	calcium phosphate glass with Ca/P molar ratio of 0.55
G	13	Q	13		
H	15	R	15		
I	17	S	17		
J	19	T	19		

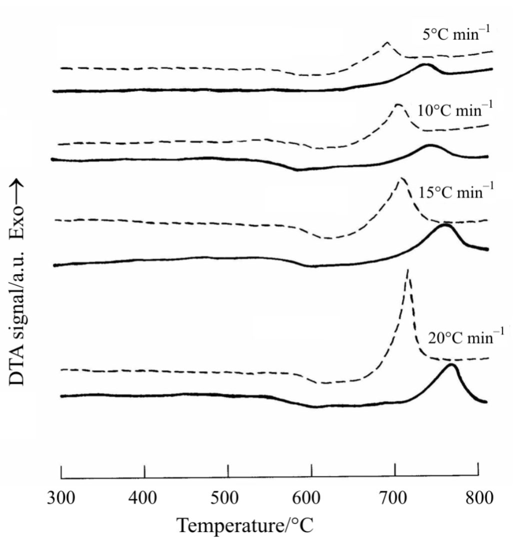

Fig. 1 DTA curves of fine glass powder (under 44 μm) and coarse glass powder (above 590 μm) for calcium phosphate glass with a Ca/P molar ratio of 0.55, under static air atmosphere and 5–20°C min^{-1} heating rate. — – Coarse glass powder. ---- – Fine glass powder

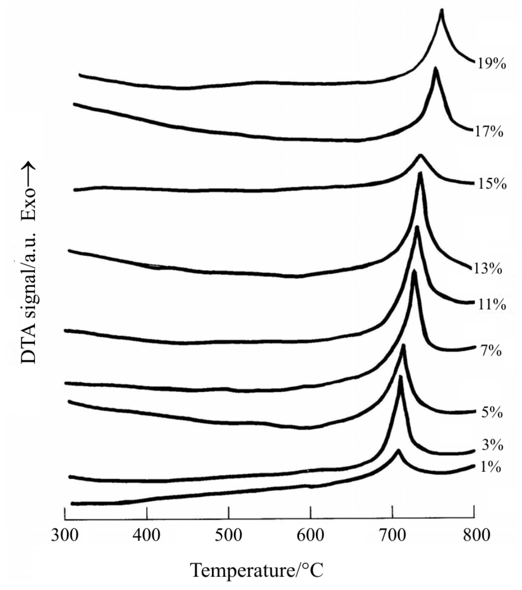

Fig. 2 DTA curves of different amount of hydroxyapatite addition for calcium phosphate glass with a Ca/P molar ratio of 0.55, under static air atmosphere and at a 10°C min^{-1} heating rate

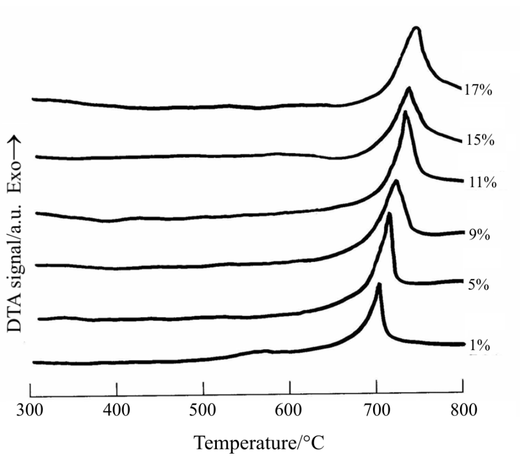

Fig. 3 DTA curves of different amount of tricalcium phosphate addition for calcium phosphate glass with a Ca/P molar ratio of 0.55, under static air atmosphere and at a 10°C min^{-1} heating rate

shift to higher temperature with increasing heating rate, and the difference of peak temperatures between coarse glass powder and fine glass powder are 53, 60, 61, 66°C for heating rate of 5, 10, 15 and 20°C min^{-1}, respectively. This result indicated that low m value in devitrification mechanism, where m is dependent on the morphology of the devitrification. Table 2 also shows the activation energies of devitrification and values m for calcium phosphate glass with 0.55 Ca/P molar ratio (glass No. Z). The activation energy and m values were 454.48 kJ mol^{-1}and 2.05, this result was agreed with above DTA description.

Non-isothermal devitrification is well described by the well known equation [13–15]

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

where α is the percentage of devitrification, N is the nucleus number, A is the constant and h is the heating rate, E is the devitrification activation energy. The parameter m dependent on the mechanism and morphology of devitrification, it ranges from m=1 for one-dimensional devitrification (or the rod-like devitrification) to m=3 or higher number for three-dimensional devitrification. (or the spherical devitrification) The higher the value of m, the sharper the DTA exothermic peak for devitrification under same experimental condition of DTA. If the temperature reaches the peak temperature of a DTA curve, Tp, the percentage of devitrification α also reaches the same specific value and is not depends on the heating rate h, then the activation energy E for the devitrification can be evaluated from a series of DTA curves by non-isothermal technique, (different heating rate created different exothermic or endothermic peak temperatures in DTA curves) then the equation shows as following

$$\ln(h/Tp^{2})=-E/RTp+\text{constant} \qquad (2)$$

A series of DTA runs were performed at different heating rates, h, and $\ln(h/Tp^2)$ *vs.* $1/Tp$ was plotted. A straight line was obtained and the values of E were obtained from the slopes of line. Assume the deflection from the baseline ΔT, is proportional to the instantaneous reaction rate and in the initial parts of DTA devitrification peak, the change in the temperature has a much greater effect than α on the ΔT, Eq. (1) also gives:

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

Table 2 Activation energies and values m for calcium phosphate glasses containing HAp,TCP and β-Ca(PO$_3$)$_2$ whisker additives

Glass No.	E/kJ mol^{-1}	R^2	mE/kJ mol^{-1}	R^2	m	Temperature range/°C	ΔT/°C
A	227.47	0.987	621.85	0.988	2.77	720–738	18
B	190.12	0.981	667.66	0.972	3.51	726–759	33
C	178.98	0.973	693.06	0.966	3.87	728–761	33
D	218.68	0.992	521.10	0.945	2.38	737–767	30
E	237.05	0.991	457.76	0.951	1.69	741–769	28
F	295.83	0.985	418.29	0.953	1.41	742–769	27
G	196.20	0.987	448.40	0.995	2.28	733–763	30
H	209.58	0.988	395.72	0.983	1.89	736–766	30
I	252.25	0.988	317.13	0.991	1.26	746–772	26
J	237.05	0.991	305.07	0.985	1.29	740–768	28
K	192.19	0.974	705.73	0.941	3.67	710–740	30
L	176.35	0.989	604.10	0.999	3.43	723–752	29
M	153.73	0.986	506.22	0.987	3.29	729–762	33
N	245.42	0.996	411.18	0.993	1.68	732–765	33
O	207.00	0.987	511.67	0.984	2.47	738–765	27
P	237.05	0.991	616.15	0.966	2.60	747–774	27
Q	127.50	0.991	365.32	0.983	2.86	748–775	27
R	176.35	0.989	529.39	0.949	3.00	741–774	33
S	216.19	0.942	436.90	0.993	2.02	750–775	25
T	237.05	0.991	469.50	0.968	1.99	750–774	24
U	449.43	0.999	765.78	0.993	1.70	654–675	21
V	422.89	0.998	634.42	0.990	1.50	651–675	24
W	436.03	0.996	626.93	0.995	1.44	652–675	23
X	426.54	0.998	598.19	0.994	1.40	652–675	23
Y	399.10	0.999	555.71	0.998	1.39	652–677	24
Z	454.48	0.992	993.15	0.994	2.05	705–724	19

R^2: Correlation coefficient for linear regression; ΔT: The difference of peak temperature between high heating rate and low heating rate in DTA curves

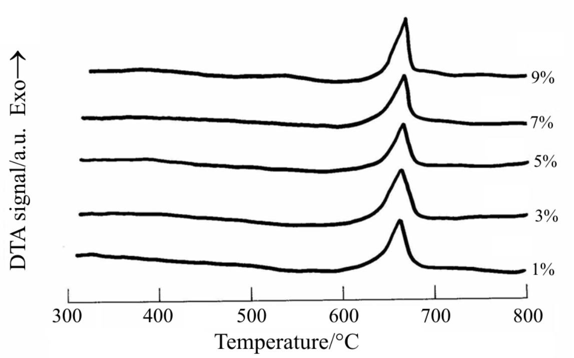

Fig. 4 DTA curves of different amount of β-calcium phosphate addition for calcium phosphate glass with a Ca/P molar ratio of 0.55, under static air atmosphere and at a 10°C min^{-1} heating rate

The morphological index m relating to the devitrification shape can be obtained by comparing the slope of Eq. (2) and the slope of Eq. (3). Table 2 listed the activation energies of devitrification, the values of parameter m for calcium phosphate glasses containing additives (hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker) and calcium phosphate glass with 0.55 molar ratio of Ca/P. The activation energies of devitrification of calcium phosphate glasses containing different amount of hydroxyapatite are ranging from 179 to 296, 154–237 kJ mol^{-1} for tricalcium phosphate and 399–449 kJ mol^{-1} for β-calcium phosphate whisker. Calcium phosphate glasses containing different amount of β-calcium phosphate whisker additives gave highest activation energy of devitrification than that of calcium phosphate glass with hydroxyapatite and tricalcium phosphate addition. But all of three additives lead lower devitrification activation energy than that of calcium phosphate glass with 0.55 molar ratio of Ca/P, this result may indicate that the additives created a more easily devitrification road. On the

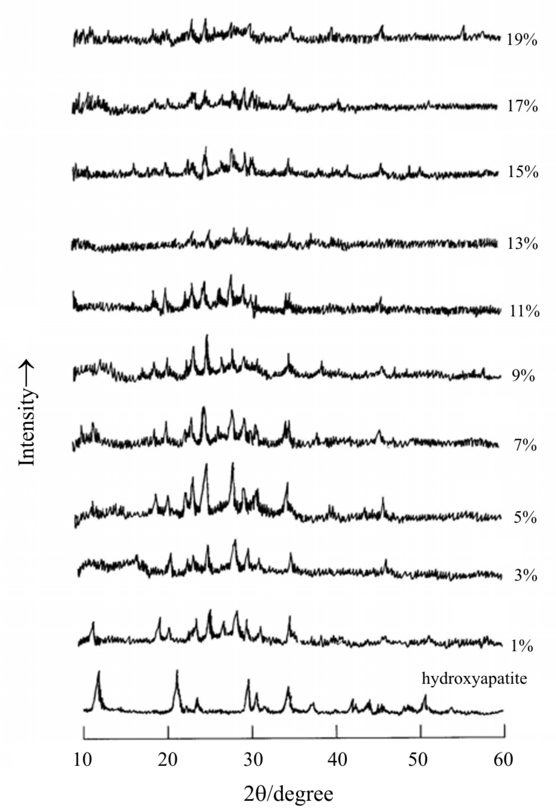

Fig. 5 XRD patterns of different amount of hydroxyapatite addition for calcium phosphate glass with a Ca/P molar ratio of 0.55 after a heat-treatment procedure

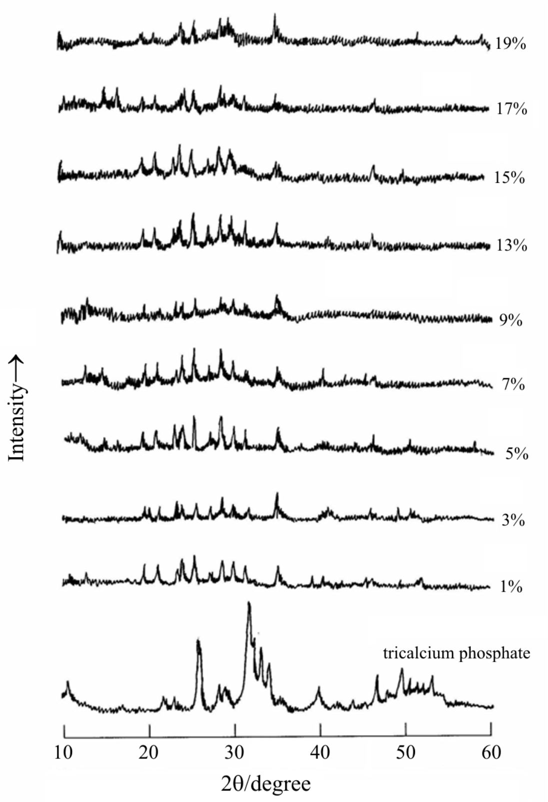

Fig. 6 XRD patterns of different amount of tricalcium phosphate addition for calcium phosphate glass with a Ca/P molar ratio of 0.55 after a heat-treatment procedure

other hand, the values of parameter *m* were decreased when more profusely additives were added to calcium phosphate glass with Ca/P molar ratio of 0.55, except the low addition amount of additives. This says calcium phosphate glass with mass additives put the devitrification of glass to lower dimensional crystal growth, this result is also same as comparing the difference of peak temperatures between coarse glass powder and fine glass powder of DTA curve.

Figures 2–4 show the DTA curves of calcium phosphate glasses with hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker additives. The glass transition temperature (T_g) become un-discernible for all calcium phosphate glasses with hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker additives, but an exothermic peak occurs at 700–800°C for both a certain composition calcium phosphate and calcium phosphate glasses with HAp and TCP additives, and the temperature of devitrification exothermic peak of calcium phosphate glasses with β-calcium phosphate whisker additives were lower to 600–700°C, the temperature of devitrification exothermic peak shift 52 to 54°C lower for β-calcium phosphate whisker additive does, and 5 to 48°C higher for hydroxyapatite and tricalcium phosphate by increasing the amount of ad-

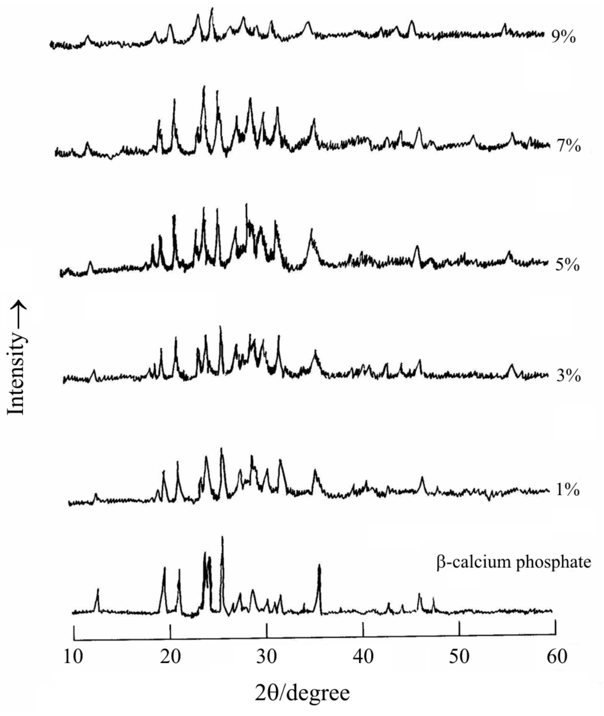

Fig. 7 XRD patterns of different amount of β-calcium phosphate addition for calcium phosphate glass with a Ca/P molar ratio of 0.55 after a heat-treatment procedure

ditives, respectively. In general, the sharply exothermic peak of DTA curves indicated high *m* value and represented fast devitrification, in the DTA curves of calcium phosphate glass with large amount of additives, the sharpness of exothermic peak decreased with increasing amount of additives, this result is same as the meaning of lowering *m* value of Table 2.

The X-ray powder diffraction pattern of heated calcium phosphate glasses with additive are shown in Figs 5–7, the XRD patterns show that the intensity of the characteristic diffraction peaks were decreased owing to dilute by additive, except the calcium phosphate glasses with low amount additives dose, this indicates that the heat-treatment procedure or the composition of glasses with higher amount additive is not good for inducing a large amount crystalline, so to identify the phase of crystalline for above calcium phosphate glass-ceramics becomes invalid. Additives, such as β-calcium phosphate whisker and tricalcium phosphate are surface reactive ceramics, and hydroxyapatite is absorptive ceramics. Some of those glasses with large amount additives were not found to promote volume nucleation of calcium phosphate glass in this work, but all of those glasses shift the exothermic devitrification peak to high temperature, except β-calcium phosphate whisker and lower the activation energies of devitrification, when the additives were added into the calcium phosphate glasses. Although large amount additives couldn't induce fine crystalline in a certain composition of calcium phosphate glass under this experimental condition, but such additives would supplement the mechanical properties and the biocompatibility for the calcium phosphate glass.

Conclusions

The chemical compositions of calcium phosphate glass-ceramics, β-calcium phosphate ceramics, tricalcium phosphate ceramics and hydroxyapatite ceramics are close to those of hard human tissues, and having high potential in using as bio-substitutive materials. Adding additives such as hydroxyapatite, tricalcium phosphate and β-calcium phosphate whisker to a certain composition of calcium phosphate glass with a Ca/P molar ratio of 0.55, leads to un-discernible glass transition temperature, shift the devitrification peak to higher temperature, except β-calcium phosphate whisker. And enhancement of the mechanical properties and biocompatibility for the calcium phosphate glass, but lower the activation energies for devitrification, this means above glasses easily to be a ceramic at certain temperature. All of three additives couldn't induce fine crystalline in calcium phosphate glass with higher amount additives under this investigation.

References

1 J.-S. Lee and C.-K. Hsu, Thermochim. Acta, 339 (1999) 115.
2 J.-S. Lee, C.-K. Hsu and C.-W. Huang, J. Therm. Anal. Cal., 56 (1999) 137.
3 C. P. A. T. Kelin, Y. Abe, H. Hosono and K. De Groot, Biomaterials, 5 (1984) 362.
4 C. P. A. T. Kelin, Y. Abe, H. Hosono and K. De Groot, Biomaterials, 5 (1987) 234.
5 J.-S. Lee and C.-K. Hsu, Thermochim. Acta 339 (1999) 103.
6 Y. Abe, Phosphorous Res. Bull., 1 (1991) 317.
7 T. Ozawa, Polymer, 12 (1971) 150.
8 J. Šeštak, Phys. Chem. Glasses, 15 (1974) 137.
9 A. Matrotta and A. Buri, Thermochim. Acta, 25 (1978) 155.
10 J. Augus and J. F. Bennett, J. Thermal Anal., 13 (1978) 283.
11 H. E. Kinnsinger, Anal. Chem., 29 (1957) 1702.
12 Y. Nan, W. E. Lee and P. F. James, J. Am. Ceram. Soc., 75 (1992) 1641.
13 C. K. Hsu, Thermochim. Acta., 392–393 (2002) 392.
14 K. Matusita and S. Sakka, Bull. Inst. Chem. Res. Kyto Univ., 59 (1981) 159.
15 D. R. MacFarlane, M. Matecki and M. Poulain, J. Non-Cryst. Solids, 64 (1984) 351.

DOI: 10.1007/s10973-005-7048-2