Devitrification Phenomenon and Physical Properties of Calcium Phosphate Glasses with Various $\text{CaO}/\text{P}_2\text{O}_5$ Mole Ratios

C.K. Hsu^{1,3}, J.S. Lee^{1,2}, and C.W. Huang¹

1. Department of Chemistry, Chung Yuan Christian University Chungli, 32023, Taiwan, R.O.C.

2. P.O.Box. No.90008-15-9, Chung Shan Institute of Science and Technology, Lungtan, Taiwan, R.O.C.

3. Department of Materials & Mineral Resources Engineering, National Taipei Institute of Technology, Taipei, Taiwan, R.O.C.

Abstract

The devitrification mechanisms of various $\text{CaO}/\text{P}_2\text{O}_5$ mole ratios calcium phosphate glasses were investigated by non-isothermal DTA technique and by observing the devitrification phenomenon of tested samples after heat treatment procedures. It was found that the devitrification mechanism changed from bulk nucleation to surface nucleation, owing to decreasing the $\text{CaO}/\text{P}_2\text{O}_5$ mole ratio of calcium phosphate glasses.

The major crystalline phase of the resultant products was $\beta\text{-Ca}(\text{PO}_3)_2$, the crystalline characteristic was examined by XRD and EDS. The rod-like type $\beta\text{-Ca}(\text{PO}_3)_2$ (5 μm in diameter and 60 μm in length) crystal was observed from the SEM micrograph.

INTRODUCTION

The devitrification of the glasses in the system $\text{CaO}/\text{P}_2\text{O}_5$ with high Ca/P mole ratio has been investigated by many researchers^[1,2]. In this study, the devitrification mechanism of calcium phosphate glasses with low $\text{CaO}/\text{P}_2\text{O}_5$ mole ratios was studied by non-isothermal differential thermal analysis technique. The devitrification phenomenon of calcium phosphate glasses with various $\text{CaO}/\text{P}_2\text{O}_5$ mole ratios were examined by the observation of the resultant products under different heat treatment conditions. In this work, $\beta\text{-Ca}(\text{PO}_3)_2$ crystal was found by traditional melting method. How to enhance the moisture resistance of lower $\text{CaO}/\text{P}_2\text{O}_5$ mole ratio calcium phosphate, and the separating technique of $\beta\text{-Ca}(\text{PO}_3)_2$ crystal from calcium phosphate glasses are the major goal in the future.

EXPERIMENTALS PROCEDURE

The compositions of different raw materials were listed in Table 1. Batch mixtures with $CaO/P_2O_5=0.72, 0.85, 1.0, 1.1$ in mole ratios were prepared by mixing $Ca(H_2PO_4)_2 \cdot H_2O$, $CaCO_3$ and H_3PO_4 . The mixtures were mixed with ethanol in a ball miller for 30 minutes. After being dried, the mixtures were melted in a platinum crucible at 850 °C for 30 minutes, then 1250 °C for 2 hours. The melts were poured onto a preheated graphite plate (280 °C) and cooled to room temperature. The sample powder was prepared by crushing the glass in an agate mortar, then sieved in order to obtain fine (-325 mesh) and coarse(-30+50 mesh) particle. The DTA curves for each 30 mg sample of glass powder were recorded in air atmosphere at different heating rates(2°C min⁻¹ to 20 °C min⁻¹). A Rigaku-Denki thermoanalyzer (model 8121) was used, and powdered $\alpha-Al_2O_3$ was used as a reference material.

The glass($CaO/P_2O_5=0.72$) obtained from graphite plate was reheated at nucleation temperature(575°C) for 2 hours then at crystallization temperature (664°C) for 8 hours. The crystalline phases in the resultant products were identified by a Rigaku-Denki X-ray diffraction analyzer(XRD). The crystalline morphologies were observed by a JEOL JSM-6300 Scanning Electron Microscopy(SEM). The physical properties such as Vicker's surface hardness, weight loss percentage after dipping in Ringer's solution for 14 days were examined.

RESULTS AND DISCUSSION

In some cases, non-isothermal differential thermal analysis(DTA) technique is not enough to explain the kinetic results from strictly physical and/or physicochemical point of view.^(3,4) To compensate DTA, the modified Kissinger equation^(5,6) has been widely used for the kinetic study of the non-isothermal crystallization glasses.

$$\ln h^n / T_p^2 = -mE_G / RT_p + const. \quad (1)$$

where h is the heating rate (°C min⁻¹), and T_p is the exothermic peak temperature of DTA thermograph. E_G is the activation energy of crystal growth, R is the gas constant, the parameter n and m are dependent on the morphology of the devitrification, while in the Kissinger plots $n=m=1$. Table 2 lists the apparent activation energies for these samples. The activation energy of devitrification decreased with decreasing CaO/P_2O_5 mole ratios of the calcium phosphate glasses, when the glass particle size was less than 44 μm, this is not true for the glasses at particle size ranging from 297 to 590 μm. According the isothermal crystallization data of $Ca(PO_3)_2$ glass powders 44 to 74 μm in size, for Y. Abe etc.,⁽⁷⁾ the E_G (=500 KJ/mole) was estimated by the relation between $t_{0.5}$ and temperature. When the values $n=3$ and $m=2$ for coarse A glasses, the activation energy E_{app} has a value closet to the E_G described above. This indicates that the devitrification mechanism of the large particle size fraction is bulk nucleation an three dimensional growth.

In general, the exothermic peak of DTA curves for a coarse sample give more sharply than a fine sample at same heating rate. And the DTA exothermic peak is observed at a lower temperature for the smaller particle sizes, when the crystallization is regulated by the surface crystallization mechanism. However, the temperature region for the invariant irrespective of particle size, as expected from the constant T_p for the volume crystallization⁽⁸⁾

Fig.1 shows the DTA crystallization peaks, two types of particle size for calcium phosphate glasses with various CaO/P_2O_5 mole ratios, at a heating rate of 10 °C min⁻¹. As shown in Figure 1, T_p increases with increasing the particle size. For the A glass, the T_p of glass powder which after nucleation procedure was very closed to the T_p of coarse glass, this also say that bulk nucleation devitrification mechanism was occurred in A glass.

The X-ray diffraction (XRD)analysis of the resultant product of glass D under different heat treatment conditions are shown in Fig.2. It is found that the intensity of characteristic peaks for $\beta - Ca(PO_3)_2$ crystalline were very clear. XRD analysis showed that a large amount of $\beta - Ca(PO_3)_2$ crystal exist in the crystallized product of lower CaO/P_2O_5 mole ratio calcium phosphate glasses. The surface microstructure of the resultant product of glass D is shown in Fig.3. The rod-like morphology is $\beta - Ca(PO_3)_2$ crystalline, which with 5 μm in diameter and 60 μm in length. And the aspect ratio was 12, the fiber-like $\beta - Ca(PO_3)_2$ crystals can be extract by using a leaching solution. The composition of $\beta - Ca(PO_3)_2$ crystalline analysis by EDX is shown in Fig.4. The weight percentage of oxides is approximately equal to the composition of

$\beta - \text{Ca}(\text{PO}_3)_2$ crystalline, this is an another evidence to indicate that the crystal of glass D is $\beta - \text{Ca}(\text{PO}_3)_2$ crystalline.

Glass-ceramic composed of crystalline $\beta - \text{Ca}(\text{PO}_3)_2$ fiber with Ca. 1 μm diameter exhibits extremely high bending strength of 400-600 Mpa and low Young's modulus of 70-120 Gpa, this result implies that $\beta - \text{Ca}(\text{PO}_3)_2$ fiber are high-strength and flexibility.⁽⁹⁾ Vicker's surface hardness gave some relationship with strength, i.e., the higher values of hardness, the higher strength of material. The Vicker's surface hardness of the resultant products under various heat treatment conditions were shown in Fig. 5. The resultant product of glass C appeared the highest Vicker's surface hardness, 670 kg / mm^2 . And the Vicker's surface hardness increased with increasing the time of crystal growth. The biodegradation weight loss percentage of calcium phosphate glasses with different $\text{CaO} / \text{P}_2\text{O}_5$ mole ratios were investigated by dipped the resultant products in Ringer's solution for 14 days. The weight loss percentage of glass D shows a highest weight loss percentage at a maximum value of 0.26%. The average weight loss percentage of glass A is lower than 0.1 %. In order to evaluate the biocompatibility of calcium phosphate glass-ceramics with lower $\text{CaO} / \text{P}_2\text{O}_5$ mole ratios, more detail biodegradation experiments should be done.

SUMMARY

The following conclusions can be drawn from this study.

- (1) The activation energy of devitrification for the calcium phosphate glasses with various $\text{CaO} / \text{P}_2\text{O}_5$ mole ratios decreased with decreasing $\text{CaO} / \text{P}_2\text{O}_5$ mole ratios at particle size less than 44 μm .
- (2) By decreasing the $\text{CaO} / \text{P}_2\text{O}_5$ mole ratios of the calcium phosphate glasses, the devitrification mechanism changed from bulk nucleation to surface nucleation
- (3) The major crystalline phase of glass D developed after heat treatment was $\beta - \text{Ca}(\text{PO}_3)_2$. The shape of $\beta - \text{Ca}(\text{PO}_3)_2$ crystalline is the rod-like type with 5 μm in diameter and 60 μm in length.
- (4) The maximum Vicker's surface hardness of resultant product was at 670 kg / mm^2 .

REFERENCES

1. A.Watanade, M. Mitsudou, S. Kihara and Y. Abe, *J. Am. Ceram. Soc.*, **72**, [8] (1989) 1499-1500.
2. A. Krajewski and A. Ravaglioli, *Biomaterial* vol.2 (1981) 105.
3. J. Sestak, *Thermochim. Acta*, 98(1986) 339.
4. J. Sestak, *ibid*, 203(1992) 361.
5. K. Matushita and S. Sakka, *J. Non-Cryst. Solids*, **38,39** (1980)741.
6. K. Matushita, T. Komatu and R.yokota, *J. Mater. Sci.*, **19** (1984)291.
7. Y. Abe, T. Arahori and A. Naruse, *J. Am ceram. Soc.*, vol 59, No 11-12(1976)487.
8. A. Marotta and A.Buri, *Thermochim. Acta*, **25**(1987) 155.
9. T. Kasuga, A.Ichino and Y. Abe, *J.Ceram.Soc.,Japan*, **100**[8] (1992)1088

Table 1 Composition of calcium phosphate glasses.

Glass	Composition		
	$\text{Ca}(\text{H}_2\text{PO}_4) \cdot \text{H}_2\text{O}$	CaCO_3	H_3PO_4
A	90.9	9.1	0
B	100	0	0
C	73.9	0	26.1
D	53.8	0	40.2

Table 2 Apparent activation energies E_{app} calculated using the Kissinger method for the non-isothermal crystallization of CaO/P_2O_5 glasses.

mm	Range of $T_p(^{\circ}C)$				$E_{app}(KJmole^{-1})$				$-\gamma^a$			
	A	B	C	D	A	B	C	D	A	B	C	D
< 0.044	591-624	620-664	666-656	625-684	442	347	299	266	0.9993	0.9983	0.9994	0.9961
0.297-0.59	640-690	661-707	654-699	685-742	325	356	348	301	0.9996	0.9985	0.9788	0.9875

A, B, C, D are glasses, the composition were listed in Table 1.

$-\gamma^a$: Correlation coefficient for the linear regression analysis of the Kissinger plot.

FIGURE 1. The thermograms of calcium phosphate glasses with various CaO/P_2O_5 mole ratio with different particle size fractions, heating rate= $10^{\circ}C/min$.

FIGURE 2. The X-ray diffraction analysis of the result product of glass D under different heat treatment conditions.

FIGURE 3. The surface micrograph of $\beta-Ca(PO_3)_2$ crystalline.

FIGURE 4. The EDS analysis of β -Ca(PO₃)₂ crystalline.

ELMT	APP.CONC	ERROR(WT%)				
CaK: 0	3.433	.040				
P K: 0	6.234	.091				
ZAF CALCULATIONS						
20.00 KV TITL = .00 ELEV =40.00 AZIM = .00 CONSIN =1.000						
Spectrum: *INITIAL START-UP*						
Last elmt by STOICH.,NORMALISED						
ELMT	ZAF ratio	%ELMT	Error	ATOM.%	% OXIDE	FORMULA
CaK :	0.956	20.597+-	.240	11.324	28.820	CaO
P K :	1.151	31.062+-	.454	22.101	71.180	P ₂ O ₅
O K :	0.000	48.341+-		66.575		
TOTAL		100.000		100.000	100.000

FIGURE 5. Vicker's surface hardness for resultant products.