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Growth kinetics of spherulitic apatite in some $MgO–CaO–SiO_2–P_2O_5$ glasses

JIIN-JYH SHYU
Department of Materials Engineering, Tatung Institute of Technology, Taipei, Taiwan 10451
JENN-MING WU
Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu, Taiwan 30043

Crystallization of glasses with compositions (wt%) of 11.2 MgO, 33.3 SiO_2, $(55.5-x)$ CaO, and xP_2O_5 ($x=18.3$, 16.65, 15.825 and 15.0) resulted in a spherulitic apatite phase with different crystal morphologies. An ellipsoidal morphology was observed for $x=18.3$, 16.65 and 15.825, and an anomalous morphology was observed for $x=15.0$. A metastable phase, which was similar in some characteristics to apatite, was also found for $x=15.0$. The growth kinetics of the spherulitic apatite crystals were investigated to explain the above observations. Both the dendrite arms along the $[0001]$ and $[11\bar{2}0]$ directions of the apatite crystals showed constant growth rates in each glass. Growth-rate anisotropy was found between these two directions. The ellipsoidal shape of the apatite crystals is explained by this growth-rate anisotropy. The growth rates, and the growth-rate anisotropy, varied with the P_2O_5 content in such a manner that the changes in phase formation behaviour can be explained on the basis of the kinetic results.

1. Introduction

Apatite-containing glass ceramics are potentially important for the development of materials suitable for surgical implantation [1–6]. In our previous papers [7, 8] on the crystallization of $MgO–CaO–SiO_2–P_2O_5$ glasses, several interesting phenomena were observed. The apatite particles which crystallized in a glass with a eutectic composition of 11.2 wt% MgO, 33.3 wt% SiO_2, 37.2 wt% CaO and 18.3 wt% P_2O_5 (denoted as G0) showed a single-crystal electron-diffraction pattern. The apatite crystals had a nearly ellipsoidal shape with dendrite arms growing from a nucleation centre. Fig 1a and b show, respectively, the longitudinal and transverse sections of the spherulitic apatite crystal in this glass. We regard this shape as the usual shape since it is also observed in other apatite-containing materials [2, 5, 9]. However, anomalously shaped apatite crystals were found in a glass (denoted as CP3) with a composition of 11.2 MgO, 33.3 SiO_2, 40.5 CaO and 15.0 P_2O_5 [8], this had a different CaO/P_2O_5 composition from that of glass G0. Fig. 2 shows the crystallization result in the glass CP3. Compare this morphology with that shown in Fig. 1a; a portion of the apatite dendrite arms no longer occurred (the grey regions in Fig. 2) and it was replaced by dendrite arms of another crystalline phase (denoted as H-phase). It can be seen that the apatite dendrite arms grow only along directions near the long axis, resulting in (Ap, H)-assemblage.

The H-phase is similar in some characteristics to the apatite [8]. It has an X-ray diffraction (XRD) pattern (both d and I/I_0) as well as a CaO/P_2O_5 composition very close to that of apatite. Both phases crystallized as dendritic forms except that the H-phase had no nucleation centre and it crystallized around the outer surface of the apatite. Moreover, there is a specific crystallographic orientation between the H-phase and the apatite crystal [8]. The major difference between them is that the H-phase is metastable compared to apatite phase. Previous investigations [10] on 16 glasses in the system $MgO–CaO–SiO_2–P_2O_5$ indicated that the H-phase only formed in glass CP3 and it no longer crystallized when CP3 samples were heated to a higher temperature. The apatite phase, however, formed in all the glasses including CP3, and it was stable under all heat-treatment conditions.

The crystallization of glass comprises processes of both nucleation and crystal growth, thus a metastable phase may form when the nucleation or crystal growth of the equilibrium phase is the limiting step. Previous work [8] indicated that the H-phase could nucleate and grow around the outer surface of the apatite, thus the apatite nucleation process was not the limiting step. Therefore, it is interesting to know if the formation of the metastable H-phase as well as the anomalous shape of the apatite crystal can be attributed to the variation in the crystal-growth kinetics of apatite as the glass composition changed from G0 to CP3.

2. Experimental procedure

2.1. Composition selection and glass sample preparation

Table I lists the compositions of the glasses studied in

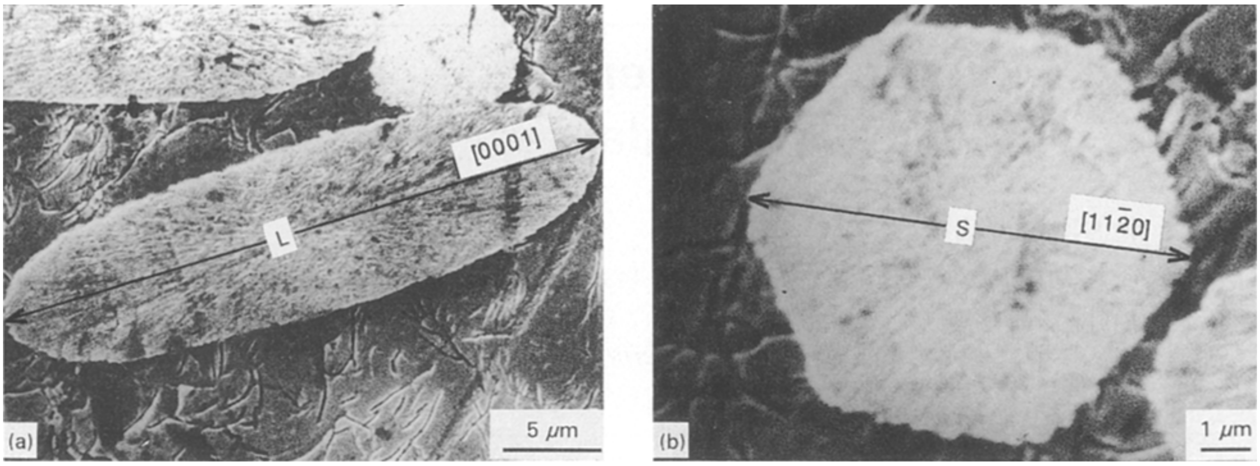

Figure 1 Scanning electron microscopy (SEM) photomicrographs for the glass G0 heated at 850 °C for 150 min showing (a) the longitudinal section and (b) the transverse section of the apatite crystal.

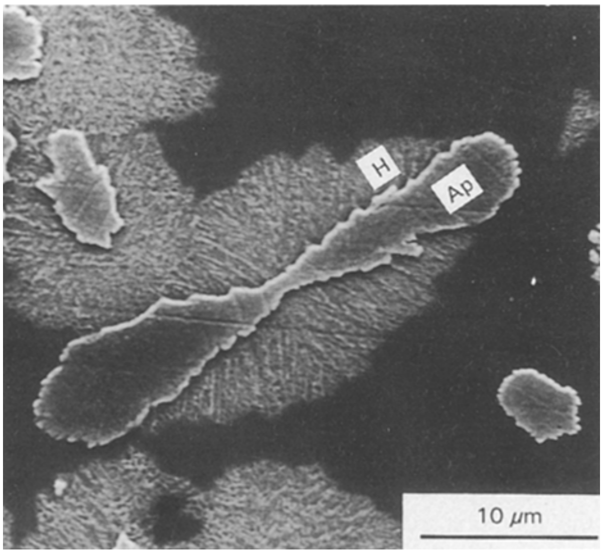

Figure 2 SEM photomicrograph for the glass CP3 heated at 850 °C for 2 h showing the (Ap, H)-assemblage [8].

TABLE I Nominal compositions of the glasses studied

Glass	Component (wt %)			
	MgO	CaO	SiO_2	P_2O_5
G0	11.20	37.20	33.30	18.30
CP1	11.20	38.85	33.30	16.65
CP2	11.20	38.675	33.30	15.825
CP3	11.20	40.50	33.30	15.00

this paper. The CaO content increased and that of P_2O_5 decreased as the composition varied from G0 to CP3, while both the MgO and SiO_2 contents were fixed. Well-mixed powders containing appropriate amounts of reagent-graded $Mg(OH)_2$, $CaCO_3$, SiO_2, and H_3PO_4 were melted in a platinum crucible for 2 h at 1450 °C and quenched by pouring onto a copper plate. All the glasses were annealed at 685 °C for 2 h to remove the internal stresses developed during quenching. The as-annealed glasses were clear, transparent, and amorphous under XRD examination.

2.2. Characterization

Crystallization of the glasses was conducted by isothermal heating at 850 °C for 15, 30, 60, 90, 120 and 150 min. The crystallized samples were polished, etched with 0.03 *N* HCl at 25 °C for 15 s, and then coated with a thin film of gold for scanning electron microscopy (SEM) observations. (Model S/2300, Hitachi, Tokyo, Japan). The double lengths of the primary dendrite arms along the long and short axes of the apatite crystal, denoted respectively by *L* and *S* in Fig. 1a and b, were measured. The values of *L* were measured from those longitudinal sections with the longest length and a twofold symmetry and values of *S* were measured from transverse sections with a sixfold symmetry. The crystallographic orientations of these dendrite arms have been determined as [0 0 0 1] and [1 1 $\bar{2}$ 0], respectively [10]. The above kinetic analysis was conducted for all the glasses, except for CP3 since the growth of the apatite dendrite arms along the short axis did not occur in this glass (see Fig. 2).

Lattice-parameter measurements were performed on an X-ray diffractometer (Model D/max-2B, Rigaku Corp., Tokyo, Japan) by step scanning with a fixed time of 4 s for each interval of 0.006° (2θ). The operating power was 40 kV and the current was 30 mA. Cohen's analytical method for the analysis of lattice parameters in non-cubic substances [11] was used:

$$\sum\alpha\sin^2\theta = C\sum\alpha^2 + B\sum\alpha\gamma + A\sum\alpha\delta \tag{1a}$$

$$\sum\gamma\sin^2\theta = C\sum\alpha\gamma + B\sum\gamma^2 + A\sum\gamma\delta \tag{1b}$$

$$\sum\delta\sin^2\theta = C\sum\alpha\delta + B\sum\delta\gamma + A\sum\delta^2 \tag{1c}$$

where $C = \lambda^2/3a_0^2$, $\alpha = (h^2 + hk + k^2)$, $B = \lambda^2/4c_0^2$, $\gamma = l^2$, $A = D/10$, $\delta = 10\sin^2 2\theta$, λ is the wavelength of radiation (the weighted mean wavelength of the CuK_α doublet was used in the present calculation), and D is the specimen displacement from the diffractometer axis. The (2 0 0), (1 1 1), (0 0 2), (2 1 0), (3 0 0), (2 0 2), and

(3 1 0) lines of the apatite phase were used to calculate the quantities A, B and C. Once these quantities were found, the values of c_0 and a_0 could be calculated directly.

3. Results and discussion

3.1. Growth kinetics of apatite

The apatite crystals formed in the glasses G0, CP1 and CP2 exhibited almost the same morphology (that is, an ellipsoidal longitudinal and a hexagonal transverse section) as that seen in Fig. 1. No (Ap, H)-assemblages were observed.

Fig. 3a and b shows the variations of S and L, respectively, as a function of time at 850 °C. The straight lines were obtained by a least-squares fit. It can be seen that both S and L varied linearly with the time of heating, indicating constant rates of crystal growth. It has been indicated that when there is a sizeable difference in composition between the crystal and the glass matrix (as in the present study), the crystal growth should be diffusion-controlled, instead of interface-controlled [12]. It is generally accepted that a diffusion-controlled growth is characterized by a growth rate which decreases with the square root of time, while an interface-controlled growth is characterized by a constant growth rate. However, the relationship representing diffusion-controlled growth was not found in the present study, while constant growth rates were observed. Constant rates of crystal growth have also been found in several other systems undergoing large compositional changes on crystallization [12]. It has been suggested [12] that "constant diffusion-controlled growth rates" might be observed when the crystal length is large in comparison with the scale of the diffusion field and thus such growth might be expected for crystals with morphologies like those of fibrils in spherulites, elliptical paraboloids, ètc. In the present study, the spherulitic morphology of apatite crystal was consistent with the observed growth rates being independent of time, despite diffusion control.

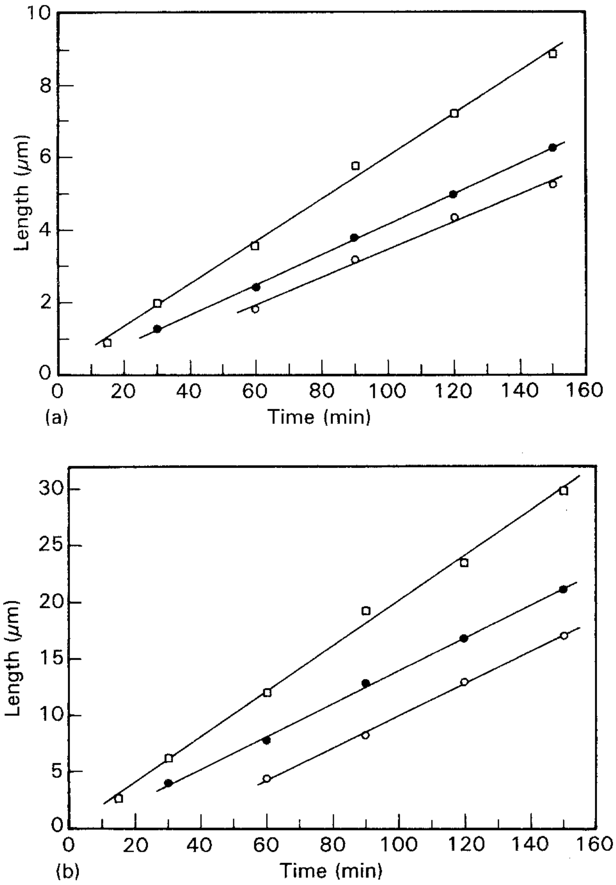

Figure 3 The dependence of the double lengths of the primary dendrite arms along (a) the [1 1 $\bar{2}$ 0] and (b) [0 0 0 1] directions as a function of the heating time at 850 °C, in: (□) G0, (●) CP1, and (○) CP2.

The regression results of fitting the data points in Fig. 3a and b can be listed as

$$S(\mathrm{G0}) = 5.870t + 17.04 \quad (2a)$$

$$S(\mathrm{CP1}) = 4.162t - 0.46 \quad (2b)$$

$$S(\mathrm{CP2}) = 3.806t - 35.17 \quad (2c)$$

$$L(\mathrm{G0}) = 19.87t + 23.18 \quad (3a)$$

$$L(\mathrm{CP1}) = 14.39t - 48.37 \quad (3b)$$

$$L(\mathrm{CP2}) = 14.14t - 42.21 \quad (3c)$$

where S and L are in units of 10^{-2} μm and t is in units of min. The zero-order coefficients essentially become more negative as the composition changed from G0 to CP2, indicating an increasing time of incubation for the crystallization of apatite. This result is consistent with the nucleation kinetics studied in [10], which showed that the nucleation rate of apatite decreased as the composition changed from G0 to CP2. The positive zero-order coefficients for the glass G0 might arise from the pre-existing nuclei which formed during the annealing treatment at 685 °C. The growth rates for the [1 1 $\bar{2}$ 0] and [0 0 0 1] directions can be obtained from the slopes. Fig. 4 shows the dependence of the growth rate on the glass composition. The standard errors are smaller than the area occupied by the markers. It can be seen that both the growth rates along [1 1 $\bar{2}$ 0] (denoted by R_s) and [0 0 0 1] (denoted by R_l) directions decrease as the composition changes from G0 to CP2. Note that R_l is always larger than R_s

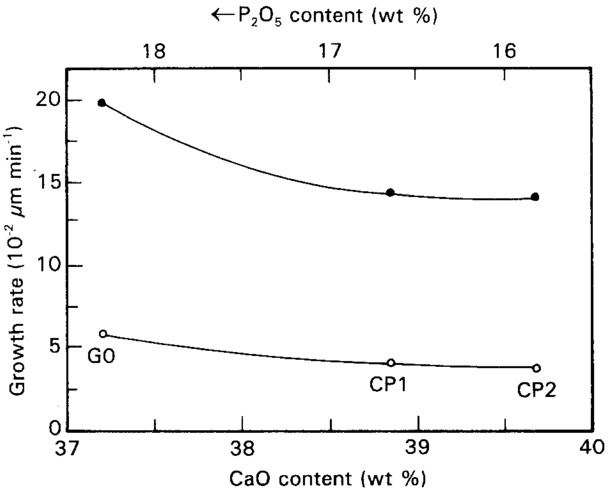

Figure 4 The dependence of the dendrite growth-rate as a function of the glass composition, for: (●) R_l, [0 0 0 1], and (○) R_s, [1 1 $\bar{2}$ 0].

for all compositions, indicating an obvious growth-rate anisotropy between the dendrite arms growing along these two directions. This result can suitably explain the observed ellipsoidal shape of apatite crystal (Fig. 1). The dendrite arm along the long axis (that is, in the [0001] direction) had the maximum growth rate, R_l. The greater is the divergence of the growing direction from [0001], the more is the reduction of the growth rate of the dendrite arm. The dendrite arm along the short axis (that is, the $[11\bar{2}0]$ direction) exhibited the minimum growth rate, R_s. Thus, the ellipsoidal shape of the apatite crystal developed.

The variation of the growth-rate anisotropy, defined here as the ratio of R_s to R_l, with the glass composition is shown in Fig. 5. As can be seen from Fig. 5, the growth-rate anisotropy changed with the glass composition. The value of R_s/R_l fell gradually as the glass composition varied from G0 to CP1, followed by a greater drop as the glass composition changed from CP1 to CP2. Extrapolating this trend, the value of R_s/R_l should have an abrupt drop from CP2 to CP3 (if CP3 has its arms along the $[11\bar{2}0]$ direction). That is, the growth rate along the short axis, R_s, decreased more and more rapidly than that along the long axis, R_l, as CaO increased and P_2O_5 decreased.

According to the above discussion on the glasses G0, CP1 and CP2, the formation of the H-phase and the anomalous shape of the apatite crystals in the glass CP3 can be explained as follows. For glasses G0, CP1, and CP2, the growth rate of the H-phase was considerably lower than both R_s and R_l. Thus the H-nuclei (if they were present) could not grow to stable crystals since the rapid crystallization of apatite arms exhausted almost all the CaO and P_2O_5 contents in the glass matrix. Therefore, due to the growth-rate anisotropy, the ellipsoidally shaped apatite could be fully developed. However, R_s decreased more and more rapidly than R_l as the glass composition changed from G0 to CP3. As a result, for the glass CP3, the growth rate of the H-phase was higher than R_s but it was still lower than R_l. Therefore, in the early stage of apatite growth, H-nuclei could grow to stable crystals in regions where the apatite, dendrite arms exhibited lower growth rates (that is, in the regions near the short axis), prohibiting the continual growth of these apatite arms. On the other hand, those H-nuclei which formed in regions where apatite dendrite arms exhibited greater growth rates (that is, in the regions near the long axis) could not grow to stable crystals. Consequently, no fully ellipsoidal crystal developed, instead, the anomalously shaped apatite crystal and the accompanying H-phase developed, as seen in the experiment. Other evidence [8] supporting this statement is the change in shape from anomalous to nearly ellipsoidal as the samples were heated to higher temperatures, where the crystallization of H-phase no longer occurred.

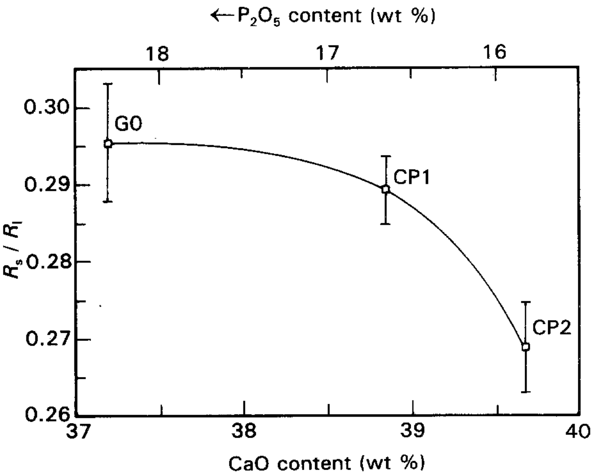

Figure 5 The dependence of the growth-rate anisotropy, R_s/R_l, as a function of the glass composition.

TABLE II Lattice constants of apatite for samples heated at 850 °C for 2 h

Glass	Lattice constant		
	a_0 (nm)	c_0 (nm)	c_0/a_0
G0	0.93229	0.68758	0.7375
CP1	0.95542	0.70434	0.7372
CP2	0.95243	0.70230	0.7374

3.2. Lattice-parameter measurements

The variation of the growth rates with the glass composition might result from changes in some parameters, for example, glass viscosity and the liquidus temperature [13]. However, when considering the growth-rate anisotropy in a crystal, these effects can be neglected since each dendrite arm always moved into the identical glass matrix. It is generally accepted [14] that the minimum growth rates are characteristic of planes with the closest packing in a crystal. Namely, the growth rate along a specific orientation is a function of a lattice parameter of the growing plane. Therefore, it seems that the growth-rate anisotropy R_s/R_l, might be a function of the ratio of a lattice parameter along $[11\bar{2}0]$ to a parameter along [0001], c_0/a_0. Table II lists the values of a_0, c_0, and c_0/a_0, obtained from XRD analysis. It can be seen that the G0 sample had values of a_0 and c_0 which were lower than those of the samples CP1 and CP2. The sample CP1 had values a little higher than the samples CP2. It is interesting that the c_0/a_0 ratios were almost the same for all the samples, although there was a sizeable difference in a_0 and c_0 between these samples. It is concluded that the variation of the growth-rate anisotropy was not controlled by this factor. More information (for example, the nature of the crystal-liquid interface) is needed for further study.

4. Conclusion

The growth kinetics of spherulitic apatite crystal were investigated for glasses with different CaO/P_2O_5 compositions in the system $MgO–SiO_2–CaO–P_2O_5$. Both dendrite arms along the [0001] and $[11\bar{2}0]$ directions exhibited constant growth rates in each glass. The former had a higher growth rate than the latter, indicating a rate anisotropy in the apatite crystal growth. The normally ellipsoidal shape of apatite crystals is thought to result from this growth-rate anisotropy. The growth rates and the growth-rate anisotropy were dependent on the CaO/P_2O_5 composition. An increase in CaO and a decrease in P_2O_5 reduced the growth rate in both the [000 1] and the $[1 1 \bar{2} 0]$ directions and enhanced the growth-rate anisotropy between these two directions. These results are relevant to the formation of the anomalously shaped apatite crystal as well as the formation of the metastable H-phase found as the P_2O_5 content dropped below a certain level. Moreover, X-ray analysis showed no obvious relationship between the growth-rate anisotropy and the c_0/a_0 ratio of the apatite crystal.

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