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Formation of a new bioactive glass–ceramic

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A new bioactive glass–ceramic with a nominal composition of CaO (54.5), MgO (6.0), SiO_2 (32.8), P_2O_5 (6.1) and CaF_2 (0.6), by weight ratio, has been developed. The crystalline phases termed hydroxyfluoroxyapatite, akermanite, and wollastonite were found to be present simultaneously at a temperature of 930 °C. Furthermore, no cracks appear after the bulk glass is crystallized. This newly developed glass–ceramic has an average flexural strength of 233 MPa and a fracture toughness of 2.95 MPa m$^{1/2}$, which are higher values than for dense hydroxyapatite and known glass–ceramic. An apatite layer containing Ca, P and Si is formed on the surface after the glass–ceramic is soaked in a simulated body fluid for a short period of time, which is indicative of a high bioactivity.

1. Introduction

Bioactive materials, such as Bioglass [1], Ceravital [2], A-W glass–ceramic [3, 4], and dense hydroxyapatite ceramic [5, 6], have been developed over the last two decades. Their accomplishments in the field of biomedical applications, especially in prosthetic applications, have attracted wide attention [7]. All the bioactive materials used in medical implants should meet the requirements of biocompatibility and bioactivity of physiological environments. When an application is subjected to a load-bearing condition, the mechanical properties such as strength, fracture toughness, modulus and hardness are the indispensable factors governing the osteoconduction, lifetime and performance between the implant and the living tissue. Among the bioactive materials already mentioned [1–6], A-W glass–ceramic [3] has been reported to have the highest mechanical properties and it also shows excellent bioactivity in prosthetic applications [8, 9]. However, it is difficult to obtain an A-W glass–ceramic via a glass preform, since the cracked body is usually found in the crystallization process to form both apatite and wollastonite phases [3].

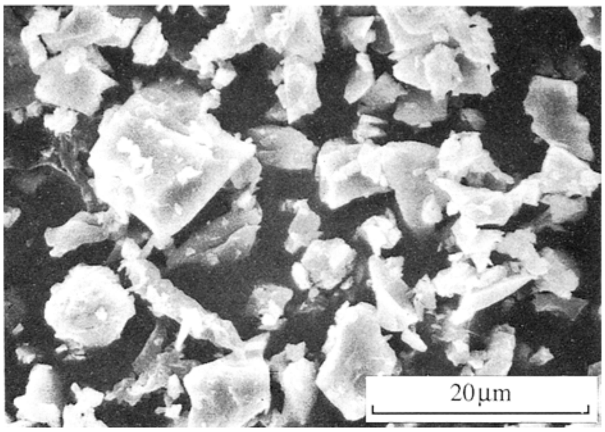

Figure 1 Particle sizes of the new glass–ceramic powder.

In the present study, a new composition in the system CaO–MgO–SiO_2–P_2O_5, with a composition different from that of the A-W glass–ceramic (CaO (44.2), MgO (4.6), SiO_2 (34.2), P_2O_5 (16.3) and CaF_2 (0.5)–by weight ratio), has been developed; it has a superior strength and fracture toughness compared to the A-W. The crystallization temperature of the newly developed material was determined using differential thermal analysis, and the crystalline phases were characterized by X-ray diffraction analysis. An *in-vitro* test has been performed in a simulated body fluid (SBF) in a constant-temperature water bath at 38 °C. The formation of apatite film on the glass–ceramic surface is analysed.

2. Experimental procedures

2.1. Preparation of the glass

Reagent-grade powders of $CaCO_3$, SiO_2, $NH_4H_2PO_4$, $MgCO_3$ and CaF_2 were mixed with a nominal composition of CaO (54.5%), MgO (6.0%), SiO_2 (32.8%), P_2O_5 (6.1%) and CaF_2 (0.6%). The powders were ball milled for 8 h with acetone as medium, then dried, and calcined in two steps at 300 °C(6 h)$^{-1}$ and 850 °C(6 h)$^{-1}$, respectively, to drive off the volatiles. The powder was reground after each heat treatment to ensure homogeneity. The as-calcined powder was melted in a platinum crucible at 1550 °C for 2 h, and then the melting glass was either poured into a water bath to obtain glass chips or it was cast a stainless-steel container to obtain a glass preform. The glass chips were further ball milled for 36 h to obtain powder with particle sizes range from 1 to 10 μm (Fig. 1). The cast glass preform was directly used as the parent glass to make glass–ceramic specimens.

2.2. Crystallization

The crystallization as well as the glass-transition temperatures of the glass powder obtained and of the bulk glass were determined using a differential thermal analysis (Netzsch, Model STA 409) from ambient temperature to 1120 °C at a heating rate of 10 °C min^{-1}.

The parent glass plate was placed into a furnace with the heat-treatment profile illustrated in Fig. 2. The crystalline phases of the crystallized glass were then determined by X-ray diffraction analysis.

2.3. Sintering and characterization

The glass powder was compacted into a rectangular shape under a hydrostatic pressure of 200 MPa. The as-pressed glass compact was then fired at temperatures from 930 to 1150 °C for 4 h with the heat-treatment profile previously described for crystallization. The flexural strength and fracture toughness of the glass–ceramic obtained were determined using four-point-bending and a single-edge-notch-beam (SENB) methods, respectively.

In vitro tests had been performed in a water bath, constant at 28 °C. First, the parent glass and the glass–ceramic were cut by a low-speed diamond saw to dimensions of 1 × 4 × 0.4 cm, and they were then prepared by dry grinding with 600-grit silicon–carbide paper. The specimens were soaked in a polyester bottle containing 250 ml SBF at 38 °C, which simulates a human-body environment. The specimens were taken out of the SBF and dried, after a seven day soaking period; they were then characterized by scanning electron microscopy (SEM) and X-ray-energy-dispersive analysis (EDAX).

3. Results and discussion

Fig. 3a and b illustrates the differential thermal analysis (DTA) of the glass powder and the bulk glass, respectively, where endothermic-peak onset occurs at 760 °C in both glass forms, indicating the occurence of glass transition. As the temperature further increases, a strong exothermic peak demonstrates the onset of crystallization, at 980 °C for the parent glass and 930 °C for the glass powder. This difference is, in part, because the glass powder provides a larger surface area and a higher surface energy than the parent glass in bulk form and this results in a lower crystallization temperature, and also because contamination during powder processing may promote crystallization with a lower activation energy, which is subsequently undertaken at a lower processing temperature.

Fig. 4 demonstrates the X-ray diffraction analysis of the glass plates which crystallize at temperatures from 930 to 1200 °C. The crystallization temperature seems to be lower than that obtained from the DTA result, Fig. 3b, which is a result of difference in heating rates. As shown, three crystalline phases termed hydroxyfluoroxyapatite ($Ca_{10}(PO_4)_6(OH \cdot F_2)$), wollastonite ($CaO \cdot SiO_2$) and akermanite ($MgO \cdot 2CaO \cdot 2SiO_2$), appear simultaneously from 930 to 1150 °C. The apatite phase appears to present in small amounts compared to the other two crystalline phases judging from their diffraction intensities and this can also be substantiated by the composition of the components. A phase change, however, occurs as the temperature is above 1200 °C. The glass–ceramic processed above 1200 °C is associated with different mechanical properties and bioactivity, and the result will be reported elsewhere [10]. Nevertheless, the processing temperatures of interest in this study are below 1200 °C, at which the apatite phase is stable.

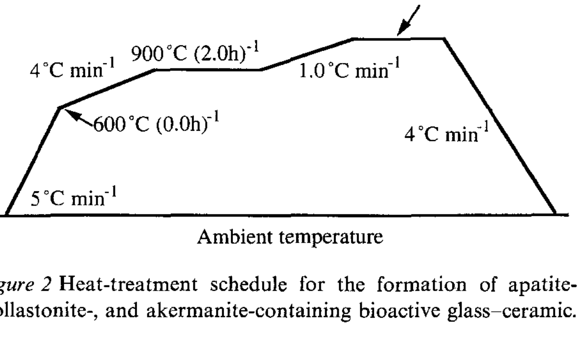

Figure 2 Heat-treatment schedule for the formation of apatite-, wollastonite-, and akermanite-containing bioactive glass–ceramic.

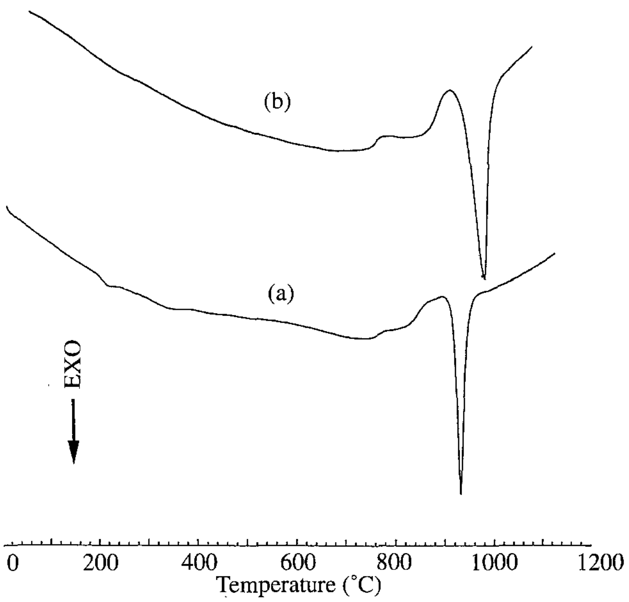

Figure 3 Curves of the DTA for (a) the glass powder, and (b) the bulk glass.

A crack-free glass–ceramic was successfully obtained after the parent glass was crystallized. The present result is significantly different from what was observed in the A-W glass–ceramic, where large cracks always result after crystallization from a cast glass body [4]. In fact, Kokubo *et al.* [4] reported that cracks occurred due to the formation of fibrous wollastonite crystals. A crack-free A-W glass–ceramic cannot be made by a direct casting preform, and can only be made via the crystallization of a glass-powder preform [4], which would increase the difficulty in the processing of a complicated-shape device. The reason that the newly developed glass–ceramic shows no crack via a parent preform after crystallization is probably due to annihilation of stresses among the randomly distributed and simultaneously precipitated crystals. Secondly, the formation of residual stresses by three phases may be more compatible than in the A-W system, and insufficient to generate cracks.

Mechanical properties such as flexural strength and fracture toughness are given in Table I. A-W glass–ceramics, hydroxyapatite ceramics and other

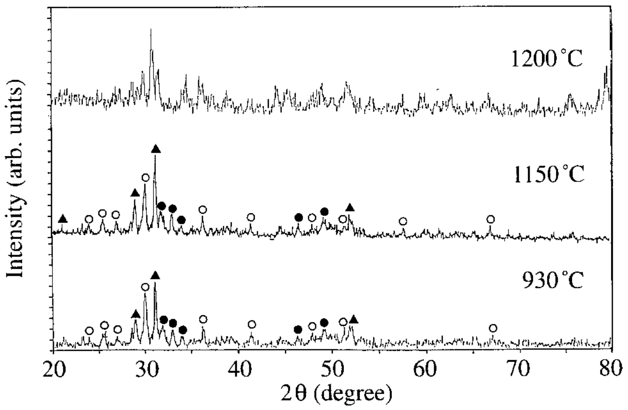

Figure 4 X-ray diffraction analysis of the glass–ceramic with heat-treatment from 930 to 1200 °C: (▲) akermanite, (○) wollastonite, and (●) apatite.

TABLE I Comparison of the flexural strength, S_f, and fracture toughness, K_{Ic} in systems of A-W glass–ceramics, hydroxyapatite, bioglass, ceravital and this present work

Material	S_f (MPa)	K_{Ic} (MPa m$^{1/2}$)
G [3]	72 ± 25	0.8 ± 0.1
A [3]	88 ± 12	1.2 ± 0.1
A-W [3]	178 ± 20	2.0 ± 0.1
A-W-CP [3]	213 ± 17	2.6 ± 0.1
Hydroxyapatite [5, 6]	117 ± 120	1.0 ± 1.2
Bioglass [12]	100	0.5
Ceravital [13]	150	–
Present work	233 ± 18	2.95 ± 0.13

bioactive glass–ceramics are listed for comparison. It can be seen (Table I) that the glass–ceramic, which was heat-treated at 950 °C for 4 h, exhibits a higher strength and fracture toughness than those prepared by Kokubo *et al.* [3, 4] under similar conditions of fabrication. The higher mechanical properties given in this composition are probably due in part to the precipitation of large amounts of fibrous or dendritic wollastonite crystal [4], and also in part to the formation of akermanite crystal. The exact reason is under investigation.

In vitro experiments have shown that a layer, shown in Fig. 5, formed after the parent bulk glass was soaked in the SBF for one week. This layer was composed of both dendritically formed (as the arrow indicates) and tiny ball-like materials of 0.1–0.2 μm diameter, Fig. 6. It is found that the layer is rich in Ca, P and Si, as revealed by EDAX in Figs 7 and 8, for the dendritically formed and the ball-like materials, respectively. However, the contents of Ca and P in Figs 7 and 8 are significantly different in their proportions, whereas the Si shows no or only a slight difference which is probably due to the reflection of the parent glass. However, an apatite film, with its surface morphology substantially different from that observed on the surface of the parent glass, was formed after the glass–ceramic was soaked in a SBF for seven days, in Fig. 9 (where the small area at the bottom left is the glass–ceramic substrate). The difference in film morphology between the parent glass and the glass–ceramic is not understood at present and will be reported on elsewhere.

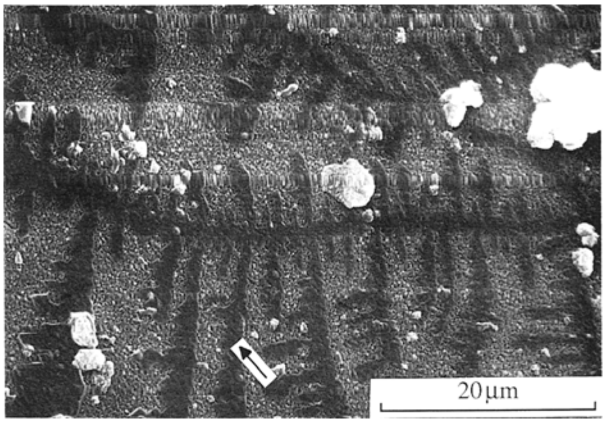

Figure 5 The layer formed on the surface of the parent glass after soaking in an SBF for seven days.

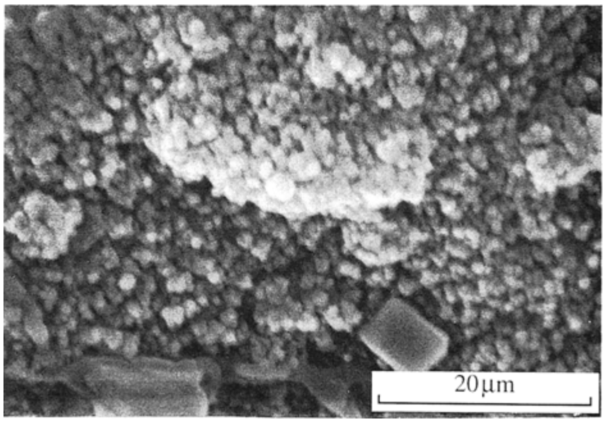

Figure 6 Tiny ball-like materials of 0.1–0.2 μm diameter.

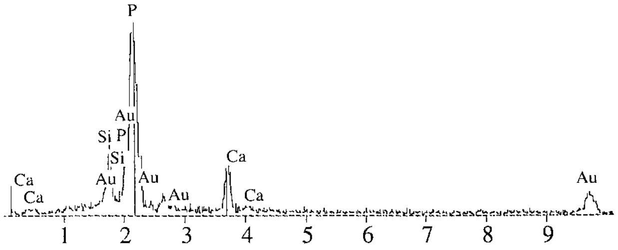

Figure 7 EDAX results for the dendritically formed material.

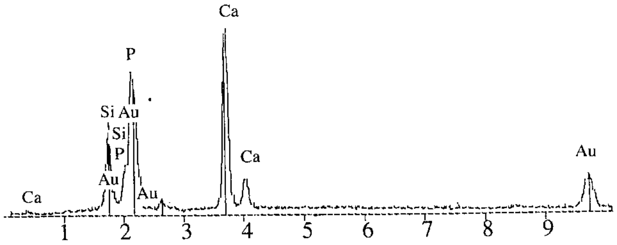

Figure 8 EDAX results for the ball-like material.

Ohura *et al.* [14] have reported that a Ca,P-rich layer in combination with a Si-layer formed on the surface of the glass systems they developed, and glass systems illustrated a bioactive character. Hench and Wilson [15] observed that a Si-rich layer formed on the bioactive Bioglass and a Ca,P-rich layer formed

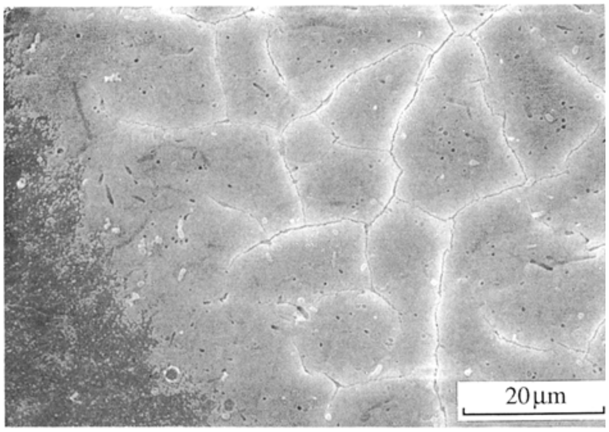

Figure 9 The apatite film formed on the surface of the glass–ceramic after soaking in an SBF for seven days.

between Bioglass and bone. Hence it is postulated that the formation of the Ca,P,Si-rich layer also possesses the capability of bonding to living tissues, and *in vivo* experiments are in progress. Further, the ball-like materials are very similar in morphology to those observed by Chou and Li [11] in their experiment on the formation of apatite-films on the surface of A-W glass.

4. Conclusion

A new glass–ceramic with the nominal composition of CaO (54.5%), MgO (6.0%), SiO_2 (32.8%), and P_2O_5 (6.1%) and CaF_2 (0.6%) has been synthesized. This glass–ceramic exhibits stable crystalline phases – termed hydroxyfluoroxyapatite, akermanite, and wollastonite phases–at temperatures of 930 to 1150 °C. The phases decompose at temperature above 1200 °C. The new glass–ceramic has an excellent flexural strength and fracture toughness, and *in vitro* results indicate sufficient bioactivity. The utilization of the new glass–ceramic in prosthetic applications especially those requiring load-bearing is hopeful.

Acknowledgement

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