Formation of a high-strength bioactive glass–ceramic in the system MgO–CaO–SiO$_2$–P$_2$O$_5$

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Formation of a high-strength bioactive glass–ceramic in the system MgO–CaO–SiO$_2$–P$_2$O$_5$ was investigated by observing the microstructure of the crystallized products. Crystallization of the parent glass in a bulk form led to the occurrence of large cracks in the crystallized product. This was attributed to the precipitation of fibrous β-wollastonite crystals growing perpendicular to the outer surfaces of the glass after uniform precipitation of fine oxyapatite/fluoroapatite crystals. On the other hand, crystallization of the same glass in a powder compact led to the formation of a crack-free dense crystallized product due to uniform precipitation of both apatite and wollastonite fine crystals throughout the glass article. The uniform precipitation of the wollastonite crystals was attributed to the simultaneous formation of fine crystals in the individual glass particles.

1. Introduction

It was recently revealed by the present authors [1–3] that a dense and homogeneous glass–ceramic containing apatite and wollastonite crystals is obtained when a glass powder compact in the system MgO–CaO–SiO$_2$–P$_2$O$_5$ is heat-treated on an appropriate heating schedule. The glass–ceramic showed an ability to form tight chemical bonds with living bone [2–4] as well as a high mechanical strength [2, 3, 5]. This glass–ceramic might be useful for prosthetic applications, especially in load-bearing conditions, such as segmental replacement of vertebra or long bone [6]. Animal and clinical experiments are now being conducted. The process of formation of the glass–ceramic is, however, not yet known in detail.

In the present study, formation of the glass–ceramic was investigated by observing the microstructure of the crystallized products. Crystallization of a bulk glass of the same composition was also examined for comparison.

2. Experimental procedure

A batch mixture of nominal composition MgO 4.6, CaO 44.9, SiO$_2$ 34.2, P$_2$O$_5$ 16.3, CaF$_2$ 0.5 in weight ratio was prepared from reagent grade chemicals of MgO, CaCO$_3$, SiO$_2$, Ca$_2$P$_2$O$_7$ and CaF$_2$. It was melted in a platinum crucible at 1450° C for 2 h. The melt was poured on to a stainless steel plate and pressed into a plate approximately 2 mm thick. The glass plate was pulverized into grains of − 325 mesh (44 μm opening) using a Spex 8000 alumina ball mill. The glass powder, mixed with water in 10 : 1 weight ratio, was pressed into a disc 40 mm in diameter and 5 mm thick at 40 Pa.

The glass powder compact and the parent glass plate were placed on a platinum sheet and heated up to various temperatures at a rate of 5° C min^{-1} in an SiC furnace. They were taken out of the furnace, usually immediately after reaching the appropriate temperature, and were allowed to cool in an ambient atmosphere.

Differential thermal analysis (DTA) of the glass powder compact and the parent glass plate, and measurement of thermal shrinkage of the glass powder compact, were made with a Shimazu DT–30 thermoanalyser at a rate of 5° C min^{-1}.

Crystalline phases precipitated in the heat-treated samples were identified by a powder X-ray diffraction analysis. The microstructure of the sample before and after heat treatment was observed under a polarizing microscope and a Hitachi S–450 scanning electron microscope (SEM). For SEM observation, the samples were broken and the fracture surfaces were ion-coated with platinum, usually after being etched with 0.5N HCl solution for 5 to 30 sec.

3. Results
3.1. Glass plate

Fig. 1 shows a DTA curve of the parent glass plate. Crystalline phases detected in the samples heated up to the respective exothermal peak termperatures are also shown in Fig. 1. It can be seen from Fig. 1 that in the glass plate oxyapatite and fluoroapatite (Ca$_{10}$(PO$_4$)$_6$(O, F$_2$)) mixed crystals are precipitated at 870° C and β-wollastonite (CaO·SiO$_2$) crystal at 1010° C.

Fig. 2 shows an optical micrograph of a cross-section of the glass plate heated up to 1050° C. The apatite crystals are uniformly precipitated in fine
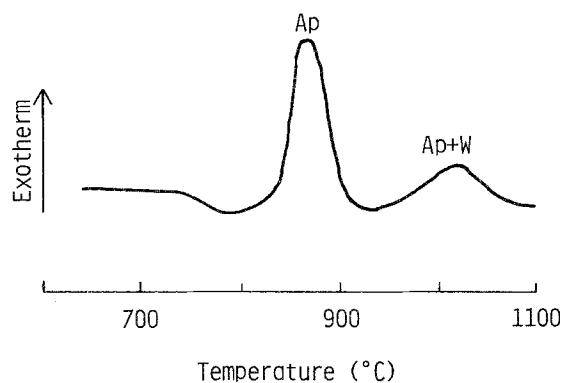
Figure 1 DTA curve of the glass plate. Ap, oxyapatite/fluoroapatite; W, β-wollastonite.

grains, whereas the wollastonite crystals are precipitated as long fibres, which are oriented perpendicular to the outer surfaces of the glass article. Large cracks are seen in the crystallized product. Such cracks were not observed in the glass plate heated up to 870° C, where only the apatite crystal is precipitated.

3.2. Glass powder compact

Fig. 3 shows a DTA curve and a thermal shrinkage curve of the glass powder compact. Crystalline phases detected in the samples heated up to the respective exothermal peak temperatures are given on the DTA curve. It can be seen from the DTA curve that in the glass powder compact oxyapatite/fluoroapatite crystals are precipitated at 870° C and β-wollastonite crystals at 900° C. The temperature of apatite precipitation for the glass powder compact is identical to that for the parent glass plate, whereas that for wollastonite precipitation is considerably lower. The thermal shrinkage curve indicates that the glass powder compact starts to densify at 750° C, where the DTA curve shows a deflection due to the glass transition, and ends at about 900° C, where the wollastonite crystal precipitates.

Figs. 4 to 6 show SEM pictures of fracture surfaces of the glass powder compact before and after heating up to different temperatures. These figures reveal the processes of densification and crystallization of the glass powder compact as follows.

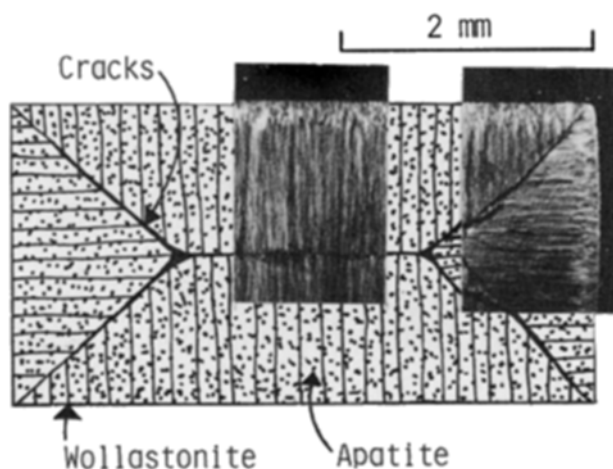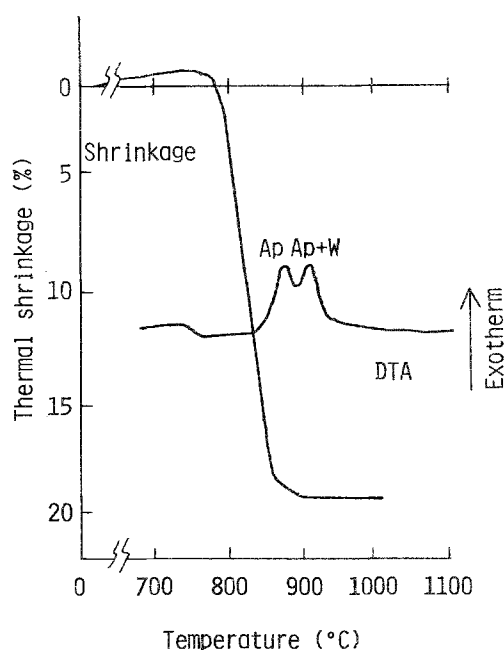Before heat treatment, the glass powder compact

Figure 3 DTA and thermal shrinkage curves of the glass powder compact.

consists of angular glass particles with sizes of a very wide distribution ranging from 1 to above 30 μm (Fig. 4). The glass particles become round near 750° C, starting to sinter (Figs. 5a and b). This temperature nearly coincides with the temperature where the DTA curve shows a deflection due to the glass transition, and thermal shrinkage starts (Fig. 3).

Near 830° C, the glass powder compact is almost fully densified, leaving only a small number of pores at the boundaries of the glass particles (Fig. 5c). The apatite starts to precipitate mainly from the surfaces of the original glass particles (Fig. 5c), exhibiting a rice-grain form (Fig. 5d). This temperature nearly corresponds to the temperature where the DTA curve starts to show an exotherm due to precipitation of the apatite and the abrupt change of the thermal shrinkage curve comes to an end (Fig. 3).

At 850° C, where the exotherm on the DTA curve becomes considerably higher (Fig. 3), the number of apatite grains is large in the interior as well as at the
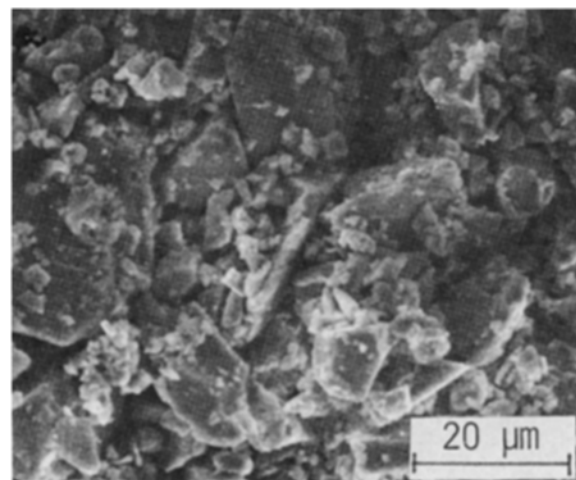

Figure 2 Optical micrograph of a cross-section of the glass plate heated up to 1050° C.

Figure 4 SEM picture of the fracture surface of the glass powder compact before heat treatment.
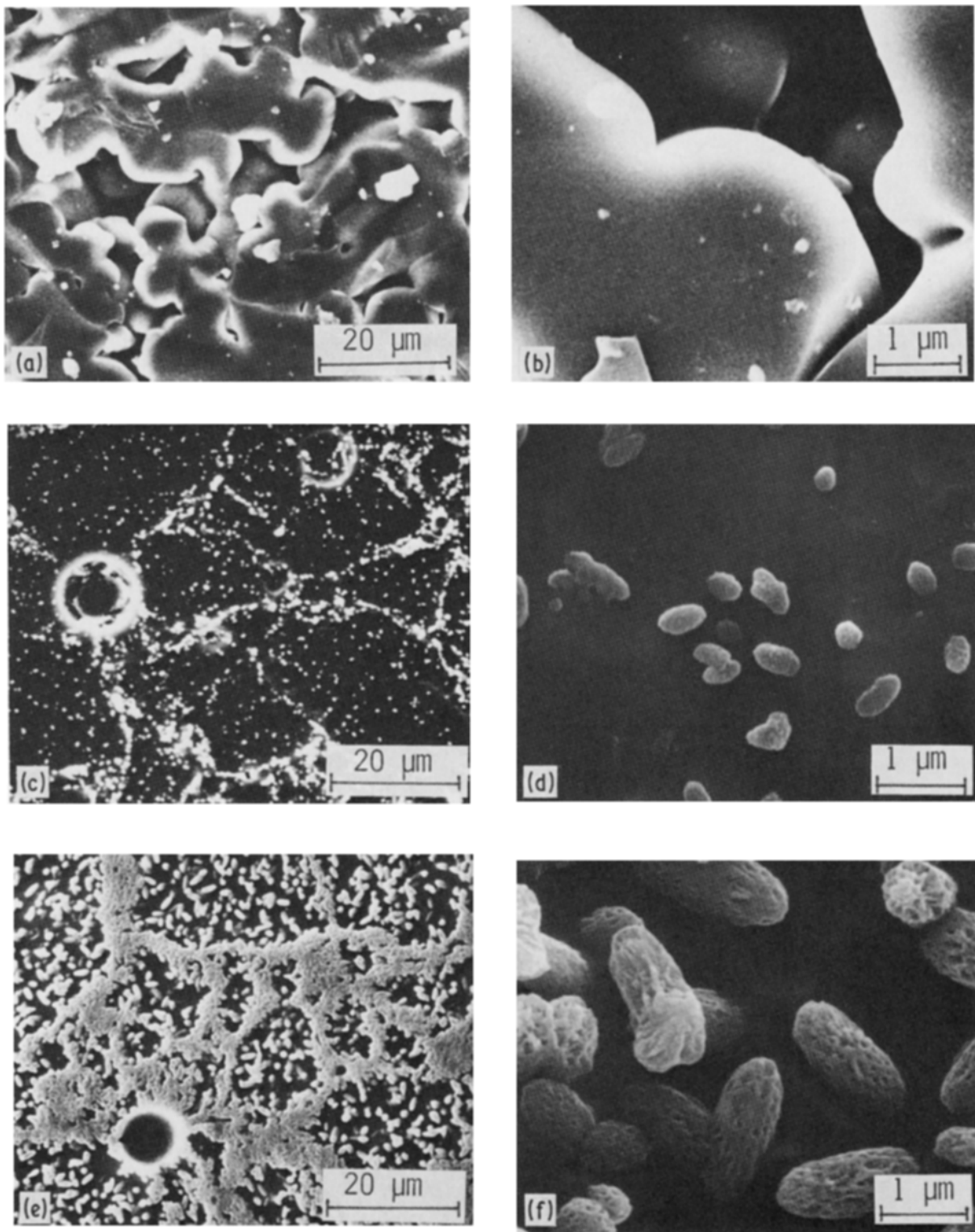
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Figure 5 SEM picture of HCl-etched fracture surfaces of the glass powder compacts heated up to different temperatures. (a, b) 750° C; (c, d) 830° C; (e, f) 850° C; (g, h) 870° C; (i, j) 900° C. Each right-hand picture is enlarged from the corresponding left-hand picture.

surfaces of the original glass particles (Fig. 5e). The size of the individual apatite grains also increases, which enables us to confirm that each apatite grain consists of many smaller crystallites (Fig. 5f).

At 870° C, which corresponds to the exothermal peak on the DTA curve (Fig. 3), the amount of apatite precipitated is almost saturated and the apatite grains are connected to each other without leaving free spaces between them (Fig. 5h). The apatite crystals have a dendritic form about 0.1 μm in diameter and 0.5 μm long, indicating that the crystallites in the rice-

like grains have grown radially from the centre of each grain.

At 900° C, where the DTA curve shows the second exothermal peak, the β-wollastonite crystal is fully precipitated. However, the microstructure of the crystallized product is essentially unchanged (Figs. 5i and j) from that of the sample heated up to 870° C. This is because the wollastonite crystal is precipitated in the interstices of the apatite crystallites. At only a few spots, however, a relatively large fibrous texture is observed, as shown on the lower right part of Fig. 5j.
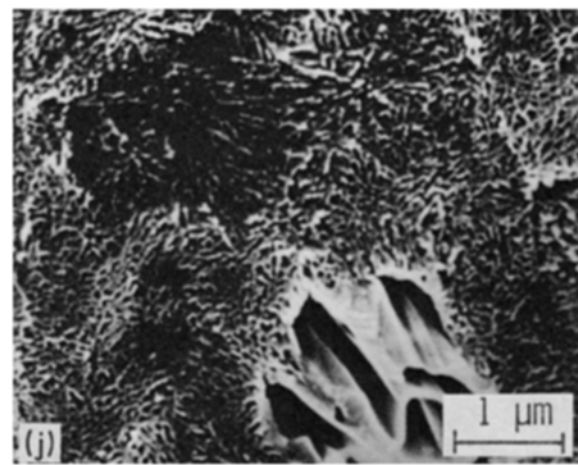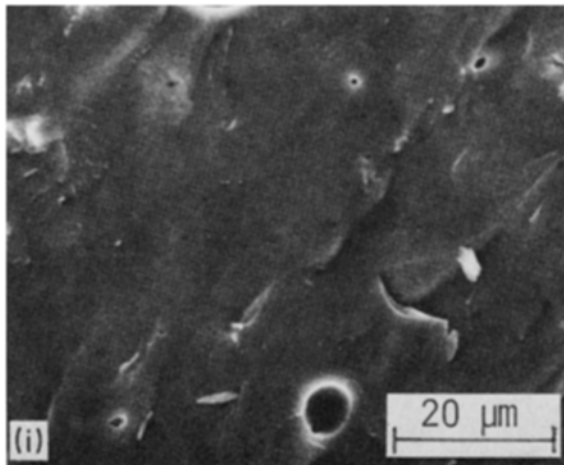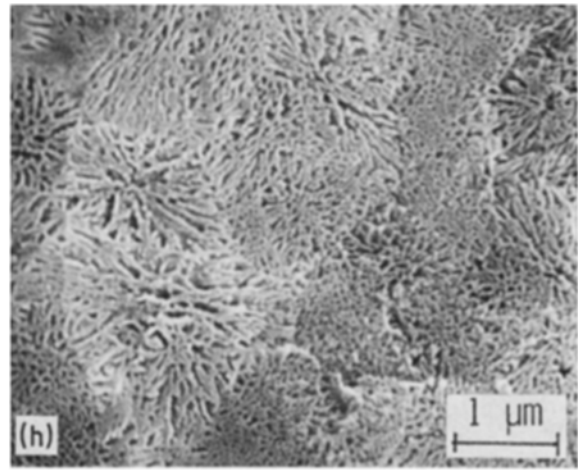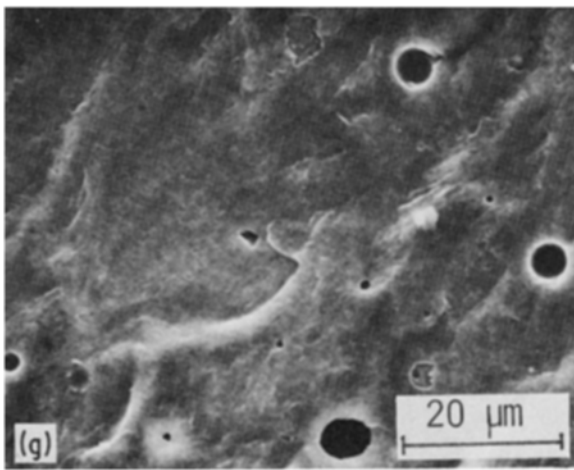
Figure 5 Continued.

This might be caused by an extraordinary growth of the wollastonite crystal.

Even after the glass powder compact was heat-treated at 1050°C for 2 h, the microstructure was essentially unchanged except that the size of the crystallites increased a little (Fig. 6b). X-ray diffraction from the surface showed the presence of only wollastonite crystal, indicating that the apatite crystal was probably dissolved away by the HCl treatment. It is then assumed that the positive image in Fig. 6b

corresponds to that of wollastonite, and the negative one to that of apatite.

4. Discussion

As described above, large cracks were formed in the crystallized product, when the glass was heat-treated in a bulk form. Formation of these cracks is attributed to the oriented precipitation of fibrous wollastonite crystals, on the grounds that no cracks were found in the glass which precipitated only the apatite crystal.
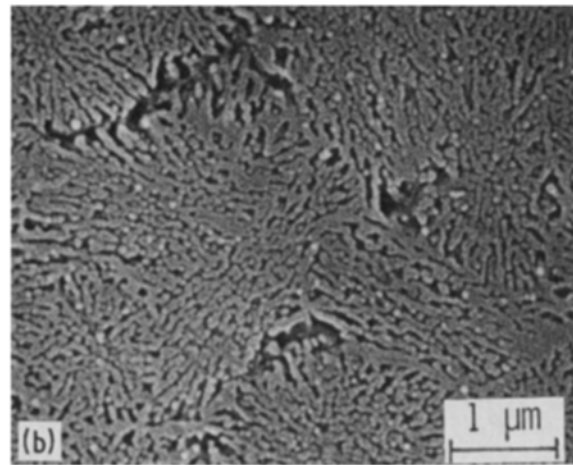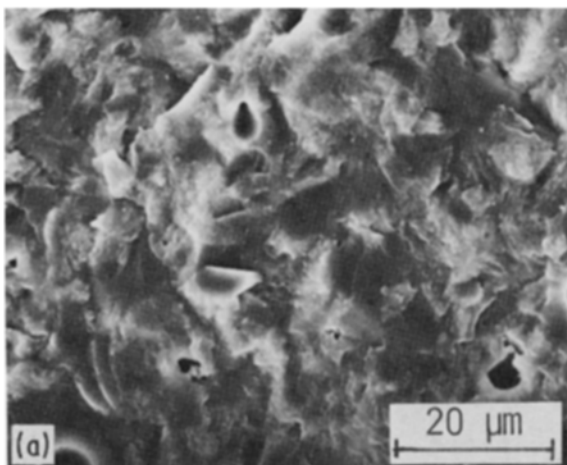

Figure 6 SEM pictures of an HCl-etched fracture surface of the glass powder compact heated up to 1050°C and held there for 2 h. (b) is enlarged from (a).

Oriented precipitation of crystal in a long fibrous form tends to induce a fairly large amount of directional volume change, causing large cracks in the interior of the crystallized product.

Precipitation of fibrous crystals which are oriented perpendicularly to the outer surface usually results from surface nucleation, in which nucleation is limited to the outer surfaces and only growth towards the interior is permitted. In such a case, it is expected that a crack-free dense glass–ceramic is obtained, when the glass is once pulverized and the glass powder compact is heat-treated. The fibrous crystals might grow perpendicular to the surfaces of the individual glass particles, resulting in a random arrangement relative to the whole articles produced from the glass powder compact.

In the present case, a dense crack-free glass–ceramic was actually obtained by heat-treating a glass powder compact. The microstructure of the glass–ceramic was, however, a little different from that expected from the above discussion. The wollastonite crystals did not grow perpendicular to the surfaces of the individual glass grains, but precipitated uniformly in the glass grains. This might be interpreted as follows.

Strictly speaking, nucleation of the wollastonite is limited not to the outermost surfaces of the glass, but to a surface layer with a certain thickness. It is assumed that this thickness is comparable to the size of the glass grains. This explains the fact that the wollastonite crystals precipitated in a long fibrous form growing perpendicular to the outer surface of the glass in the case of the bulk glass, whereas they precipitated uniformly in a fine dendritic form in the glass grains in the case of the glass powder compact. Nucleation limited to the surface layer might be attributed to a difference in composition and/or structure between the surface layer and the interior.

According to SEM observations of the glass powder compact, the apatite started to precipitate from the surfaces of the glass grains. This indicated that nucleation of the apatite crystals is also easier near the surface of the glass than in the interior. In this case, however, nucleation is not so difficult in the interior. Therefore, the apatite crystals precipitated not in an oriented fibrous form but in a random fine dendritic form, both in the bulk glass and the glass powder compact.

In the previous paper [5], the present authors showed that the mechanical strength of the present glass is only slightly increased by precipitation of the apatite crystal, but remarkably increased by precipitation of the wollastonite crystal. The remarkable increase in the mechanical strength was attributed to a marked increase in the fracture surface energy of the crystallized product, due to precipitation of the wollastonite crystal. It is interesting that the presence of wollastonite crystals can effectively increase the fracture surface energy of the crystallized product, even when they are present as fine dendrites rather than long fibres.

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