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Mechanical properties of silicate glass–ceramics containing tricalcium phosphate

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The flexural strength, elastic moduli, Vickers hardness and fracture toughness for silicate glass-ceramics (anorthite and diopside) containing tricalcium phosphate (TCP) were measured. The microstructures of the silicate glass–ceramics containing TCP were shown to consist of a complex structure of rod-like silicate and TCP crystals. The flexural strengths of glass–ceramics containing 32 wt% TCP for anorthite and 38 wt% TCP for diopside corresponding to a eutectic composition in the phase diagram were 236 and 226 MPa. The Young's modulus and fracture toughness of the eutectic compositions were 89.4 GPa and 2.5 $MPa \cdot m^{1/2}$ for anorthite and 126 GPa and 2.3 $MPa \cdot m^{1/2}$ for diopside, respectively. The anorthite glass–ceramic containing TCP has a lower Young's modulus in spite of a high strength as compared to other silicate glass–ceramics containing apatite or TCP.

1. Introduction

Glasses and glass–ceramics containing calcium phosphate have been used as artificial bone and tooth root materials [1]. Hench *et al.* discovered in 1971 that a Na_2O–SiO_2 glass containing CaO and P_2O_5 bonded to bone tissue [2]. Unfortunately, its strength was only 70 MPa. On the other hand, Kokubo *et al.* have reported that CaO–MgO–SiO_2–P_2O_5 glass–ceramics with precipites of wollastonite ($CaO \cdot SiO_2$) and apatite had a high strength of 213 MPa [3–5]. We have already reported that anorthite glass-ceramics ($CaO \cdot 2SiO_2 \cdot Al_2O_3$, An) have a low Young's modulus of 80 GPa whilst diopside glass–ceramics ($CaO \cdot MgO_2 \cdot 2SiO_2$, Diop) have a high strength of 300 MPa [6]. This paper reports on the mechanical properties of glass–ceramic composites of anorthite and also diopside with tricalcium phosphate (TCP). Both anorthite and diopside have a eutectic type phase diagram with TCP [7, 8], and it is expected that their grain sizes after sintering will become smaller than the particle sizes of the glass powder used as a raw material due to a eutectic-like reaction.

2. Experimental procedure

Commercially available $CaCO_3$, $CaHPO_4 \cdot 2H_2O$, $MgCO_3$, SiO_2 and Al_2O_3 powders (reagent grade 1, Kantoh kagaku) were used in the synthesis. After these powders were mixed into the stoichiometric compositions listed in Table I they were melted in a platinum crucible at about 1500 °C for 1 h and glass fragments were obtained by pouring the melt into a graphite mold. These glasses were pulverized into fine powders below 5 μm in particle size. After preforming in a metal mold, the glass powders were compacted into a green body by cold isostatic pressing. The compacted bodies were heated at 5 °C per min in air. After annealing for 2 h at a specific temperature at which sintering and crystallization proceeded simultaneously, they were cooled at 5 °C per min.

The sintered bodies were ground and polished into rectangular bars of $3 \times 4 \times 35$ mm for measuring the flexural strength and into cylindrical bars of 15 mm diameter and 15 mm length for measuring the elastic moduli. The surfaces of most of the specimens were polished with 6 μm diamond paste and the tensile side surface in specimens used to measure the strength was mirror-polished with 1 μm diamond paste. The bulk density of the sintered bodies was measured by the Archimedes method. The harness was measured by a micro-Vickers hardness instrument with a load of 0.1 kg. The elastic moduli namely the shear modulus, Young's modulus, bulk modulus and Poison's ratio were calculated from the sound velocities of longitudinal and shear waves measured by the sing-around method [9, 10]. The strength was measured in ten specimens using a 3-point bending fixture with a span of 30 mm at a crosshead speed of 0.5 mm per min. The fracture toughness was measured by an indentation fracture (IF) method using the Evans equation to calculate K_{IC} from the length of the crack and the semi-diagonal of the indentation [11]. The microstructures of the specimens were characterized by scanning electron microscopy (SEM) observations of both the mirror-polished surfaces and also the fractured surfaces that had been etched in 0.1 N acetic acid solution. Precipitated crystal phases were identified by powder X-ray diffraction.

3. Results and discussion

3.1. Microstructures

Figs 1 and 2 show the X-ray diffraction patterns for 68An–32TCP and 62Diop–38TCP corresponding to

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TABLE I Symbols for glass–ceramics and the compositions

Symbols	Composition
73An–27TCP	63 wt %$CaO \cdot 2SiO_2 \cdot Al_2O_3$ + 37 wt %$3CaO \cdot P_2O_5$
68An–32TCP	68 wt %$CaO \cdot 2SiO_2 \cdot Al_2O_3$ + 32 wt %$3CaO \cdot P_2O_5$
63An–37TCP	73 wt %$CaO \cdot 2SiO_2 \cdot Al_2O_3$ + 27 wt %$3CaO \cdot P_2O_5$
67Diop–33TCP	67 wt %$CaO \cdot MgO \cdot 2SiO_2$ + 33 wt %$3CaO \cdot P_2O_5$
62Diop–38TCP	62 wt %$CaO \cdot MgO \cdot 2SiO_2$ + 38 wt %$3CaO \cdot P_2O_5$
57Diop–43TCP	57 wt %$CaO \cdot MgO \cdot 2SiO_2$ + 43 wt %$3CaO \cdot P_2O_5$

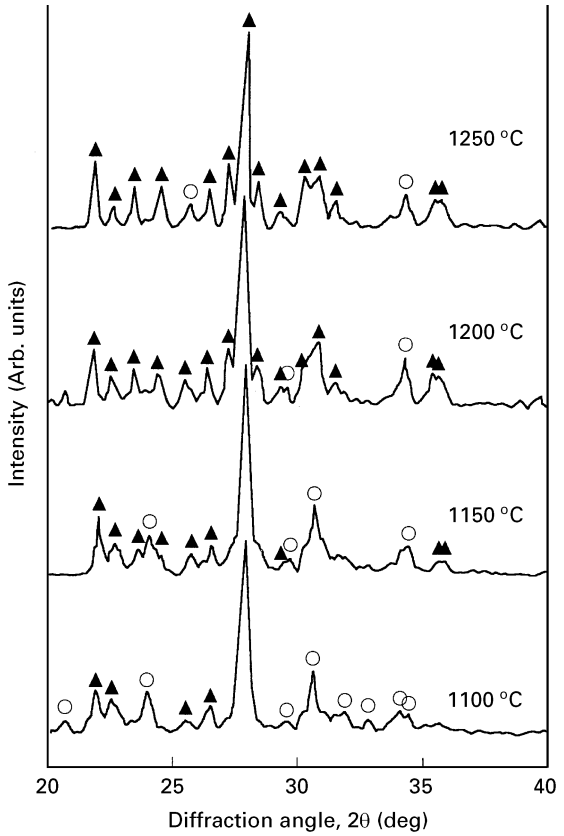

Figure 1 Powder X-ray diffraction patterns of anorthite glass–ceramics containing 32 wt % tricalcium phosphate (68An–32TCP), (○) αTCP (▲) anorthite.

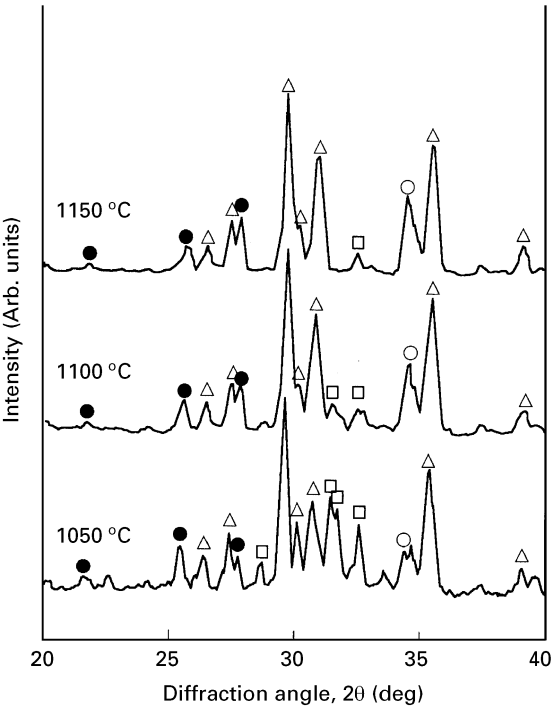

Figure 2 Powder X-ray diffraction patterns of diopside glass–ceramics containing 38 wt % tricalcium phosphate (62Diop–38TCP), (○) αTCP, (●) βTCP, (△) diopside and (□) apatite.

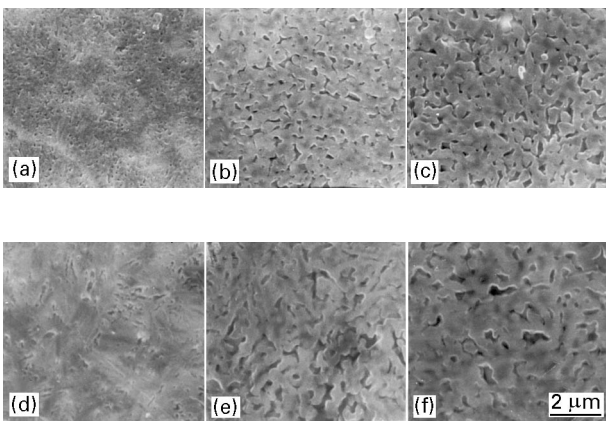

Figure 3 SEM photographs of mirror polished surfaces of (a–c), 68An–32TCP and (d–f) 62Diop–38TCP etched by 0.1 N acetic acid solution. (a) 1150 °C; (b) 1200 °C; (c) 1250 °C; (d) 1050 °C; (e) 1100 °C; (f) 1150 °C.

the eutectic compositions. Anorthite and TCP were detected in the X-ray diffraction patterns for 68An–32TCP. The precipitated TCP existed in both the α and β-forms, and the proportion of α-TCP decreased with increasing sintering temperature. The amount of anorthite crystals increased remarkably with increasing sintering temperature. On the other hand, the X-ray diffraction patterns for 62Diop–38TCP show the precipitation of diopside, α-TCP, β-TCP and hydroxy apatite. The precipitation of diopside is completed at 1050 °C. The amount of hydroxy apatite decreased with increasing sintering temperature.

Fig. 3(a–f) shows SEM pictures of mirror-polished surfaces etched by 0.1 N acetic acid solution at 20 °C for 30 mins. It is considered that the hollows left after the etching correspond to the locations where TCP existed, since TCP is soluble in acetic acid solution, whereas anorthite and diopside are insoluble. In other words Fig. 3(a–f) shows the morphology of precipitated TCP in the eutectic composition of silicate glass–ceramics containing TCP. The size of the precipitated TCP crystals increased with increasing sintering temperature. It was estimated from Fig. 3(a–f) that the average diameter of TCP crystals in 68An–32TCP sintered at 1200 °C was about 0.1–0.2 μm and their length was 0.4–0.6 μm, and the average diameter of the TCP crystals in

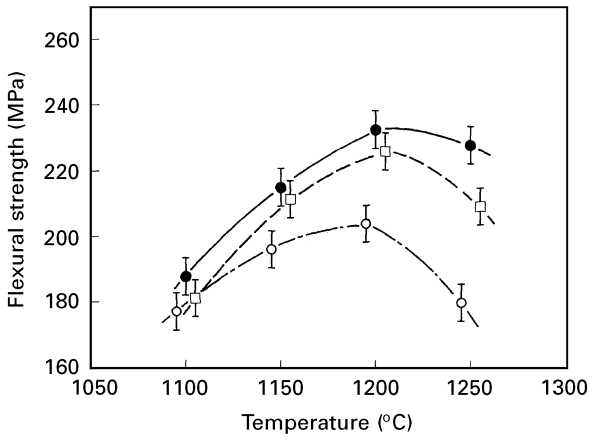

Figure 4 Flexural strengths of anorthite glass-ceramics containing TCP as a function of sintering temperature. The samples studied were (○) 63An–37TCP, (●) 68An–32TCP and (□) 73An–27TCP.

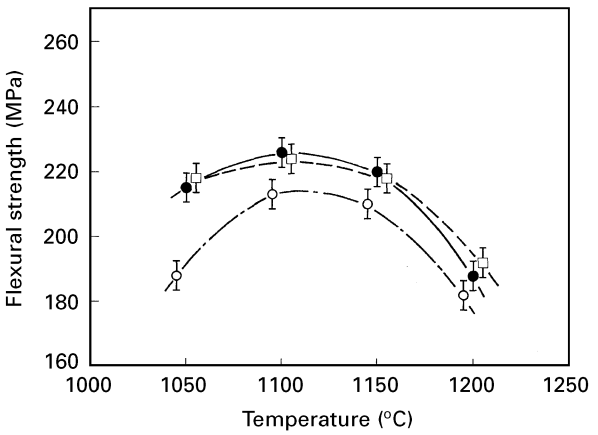

Figure 5 Flexural strengths of diopside glass-ceramics containing TCP as a function of sintering temperature. The samples studied were (○) 57Diop–43TCP, (●) 62Diop–38TCP and (□) 67Diop–33TCP.

62Diop–38TCP sintered at 1100 °C was about 0.2–0.3 μm and their length was 0.5–0.8 μm.

3.2. Flexural strength

Figs 4 and 5 show the relationship between flexural strength and sintering temperature for anorthite–TCP and diopside–TCP, respectively. The maximum strength for 68An–32TCP and 62Diop–38TCP were obtained at sintering temperatures around 1200 and 1100 °C, respectively. The flexural strength of the 68An–32TCP sample which corresponds to the eutectic composition [7] had at 236 MPa the highest value of the An–TCP specimens examined in this study. The maximum strength (226 MPa) of a 62Diop–38TCP sample corresponding to the eutectic composition was larger than that for 57Diop–43TCP and is similar to that for 67Diop–33TCP. The maximum strength (236 MPa) of 68An–32TCP prepared by a normal sintering method was slightly larger than the strength of pure anorthite (226 MPa) prepared by hot-pressing [6]. On the other hand, the maximum strength (226 MPa) of 62Diop–38TCP prepared by the normal sintering method was lower than the strength of pure diopside (300 MPa) prepared by hot-pressing [6].

TABLE II Mechanical properties of silicate glass–ceramics containing tricalcium phosphate

Specimens	68An–32TCP	62Diop–38TCP
Density ($g\,cm^{-3}$)	2.744	2.982
Longitudinal wave velocity ($km\,s^{-1}$)	6.541 ± 0.020	7.208 ± 0.018
Shear wave velocity ($km\,s^{-1}$)	3.553 ± 0.021	4.098 ± 0.013
Shear modulus (GPa)	34.6 ± 0.4	50.1 ± 0.3
Bulk modulus (GPa)	71.2 ± 1.3	88.2 ± 1.1
Young's modulus (GPa)	89.4 ± 0.9	126 ± 1
Poisson's ratio	0.291 ± 0.005	0.261 ± 0.004
Vickers Hardness (GPa)	5.32 ± 0.35	5.13 ± 0.30
Fracture toughness ($MPa{\cdot}m^{1/2}$)	2.5 ± 0.1	2.4 ± 0.1

3.3. Elastic moduli, hardness and fracture toughness

Table II lists values for the density, porosity, longitudinal wave velocity, shear wave velocity, various elastic moduli, Vickers hardness and fracture toughness obtained for 68An–32TCP sintered at 1200 °C and for 62Diop–38TCP sintered at 1100 °C.

The Young's moduli were 89.3 GPa for 73An–27TCP, 89.4 GPa for 68An–32TCP and 89.2 GPa for 63An–37TCP. That is, the Young's moduli of the anorthite glass–ceramics containing 27–37 wt % TCP were about 89 GPa and were independent of the TCP content. On the other hand, the Young's moduli of Diop–TCP glass–ceramics were 128 GPa for 33 wt % TCP, 126 GPa for 38 wt % TCP and 123 GPa for 43 wt % TCP, i.e., they slightly decrease with increasing TCP content. The Young's modulus for An–TCP is significantly lower than that of diopside glass-ceramics containing TCP and is also lower than the 124 GPa for glass–ceramics containing wollastonite and apatite reported by Kokubo *et al* [5]. A problem in the use of ceramics as artificial bones is that the Young's modulus of ceramics is much larger than that of bone [12]. It is a remarkable feature for An–TCP glass–ceramics that it has a lower Young's modulus in spite of the high strength comparable to diopside glass–ceramics containing TCP and also glass–ceramics containing wollastonite and apatite [5].

The Vickers hardness values were 5.32 GPa for the 68An–32TCP and 5.13 GPa for the 62Diop–38TCP, and decreased with increasing the TCP content which has a low hardness.

The values of the fracture toughness of 73An–27TCP, 68An–32TCP and 63An–37TCP were 2.6, 2.5 and 2.4 $MPa \cdot m^{1/2}$. On the other hand, the values for 67Diop–33TCP, 62Diop–38TCP and 57Diop–43TCP were 2.4, 2.4 and 2.2 $MPa \cdot m^{1/2}$, respectively. Their values are almost similar to or slightly larger than those of glass–ceramics containing wollastonite and apatite (2.1 $MPa \cdot m^{1/2}$) reported by Kokubo *et al.* [5].

3.4. Observation of the fracture surface

Fig. 6(a–d) shows SEM pictures of fracture surface after measuring the strength. Fig. 6(a and c) show the

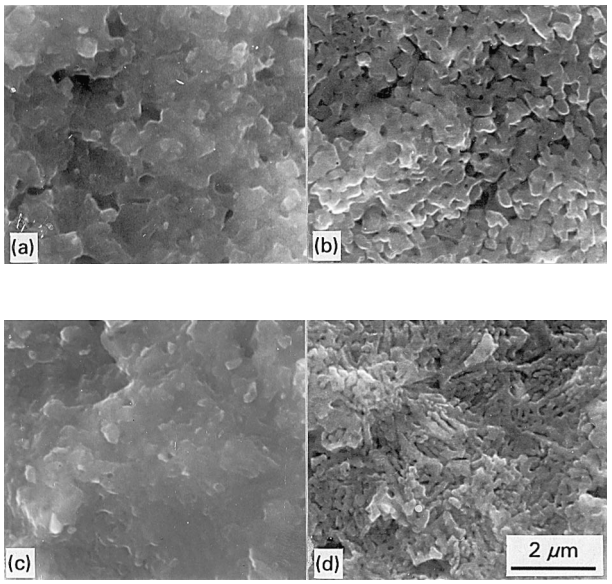

Figure 6 SEM photographs of fracture surfaces of glass-ceramics containing TCP sintered at 1200 °C for anorthite and at 1100 °C for diopside. The samples studied were (a, b) 68An–32TCP and (c, d) 62Diop–38TCP. (a, c) as fractured. (b, d) etched by 0.1 N acetic acid solution.

fracture surfaces and Fig. 6(b and d) correspond to the etched fracture surfaces. It was estimated from Fig. 6(a and c) that the fracture mode in the glass-ceramics containing TCP was transgranular fracture although the grain boundary could not be clearly observed. It is considered that the unevenness of the fracture surface etched by acetic acid solution shows the shape of anorthite or diopside crystals because the hollows in the etched fracture surface correspond to the location where TCP had existed and the matrices are anorthite or diopside. It was estimated from Fig. 6(b and d) that the grains in the matrices were rod-like shapes with a diameter of 0.2–0.4 μm and a length of 0.6–0.8 μm for 68An–32TCP, and a diameter of 0.2–0.4 μm and a length of 0.8–1.2 μm for 62Diop–38TCP.

In summary the microstructures of the anorthite or diopside glass-ceramics containing TCP changed to complex structures of rod-like silicate crystals (anorthite or diopside) under 0.2–0.4 μm in diameter and 0.6–1.2 μm in length, and rod-like TCP grains under 0.1–0.3 μm in diameter and 0.4–0.8 μm in length. This change was produced by a eutectic-like reaction that occurred simultaneously with sintering and crystallization it should be noted that the particle size of the glass powder used as a raw material was as large as 3–5 μm.

It was previously noted that the strength of An–TCP glass–ceramics produced by normal sintering became larger than the strength of pure anorthite produced by hot-pressing although the present glass–ceramics contained low strength TCP components. A probable reason for this behaviour is that the grain size of the glass–ceramics containing anorthite and TCP became smaller during the eutectic-like reaction. On the other hand, the microstructure of diopside glass–ceramics containing TCP after sintering also changed to a very fine one. However the strength was lower than that of pure diopside (300 MPa) because whilst the strength of diopside is high that of TCP is low.

4. Conclusion

The flexural strength, elastic moduli, Vickers hardness and fracture toughness for silicate glass–ceramics (anorthite and diopside) containing TCP were measured. These microstructures changed to very fine complex structures of rod-like silicate crystals (anorthite or diopside) under 0.2–0.4 μm in diameter and 0.6–1.2 μm in length, and rod-like TCP grains under 0.1–0.3 μm in diameter and 0.4–0.8 μm in length due to a eutectic-like reaction that occurred simultaneously with sintering and crystallization. These values should be compared to the particle size of the glass powder used as a raw material which was as large as 3–5 μm. The strengths of 68An–32TCP and 62Diop–38TCP which correspond to the eutectic composition were 236 and 226 MPa, the Young's moduli were 89.4 and 126 GPa and the Vickers hardness values were 5.32 and 5.13 GPa, respectively. The fracture toughness was 2.5 $MPa \cdot m^{1/2}$ for 68An–32TCP and 2.4 $MPa \cdot m^{1/2}$ for 62Diop–38TCP. The anorthite glass–ceramics containing TCP have the lowest Young's moduli despite a high strength which is comparable to the silicate glass–ceramics containing apatite or TCP.

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