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Biocompatibility and the physical properties of bio-glass ceramics in the Na_2O-CaO-SiO_2-P_2O_5 system with CaF_2 and MgF_2 additives

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Biocompatibility of a new bio-glass composition was evaluated with the addition of fluorides, such as CaF_2 and MgF_2, for the substitution of Na_2O in the conventional bio-glass composition (SiO_2-CaO-Na_2O-P_2O_5). Also, the physical properties of Na_2O-CaO-SiO_2-P_2O_5 glass ceramics were investigated. When B_2O_3 (4 mol%) was added as a Na_2O substitution, the thermal expansion coefficient was decreased in sintered samples (650-950 °C). Compared to the low flexural strength (57 ± 3 MPa) and Vickers hardness (4.6 GPa) of sintered bio-glass ceramics without fluoride and B_2O_3 additions, new bio-glass ceramics substituted with 10 mol% MgF_2 for Na_2O showed more higher mechanical properties (flexural strength: 141 ± 5 MPa, Vickers hardness: 5.6 GPa). The thermal expansion coefficient of bio-glass ceramics due to the ion substitutions (Ca^{2+}, Mg^{2+} and B^{3+}) was decreased from 16 × 10^{-6}/ °C to 9.4-10 × 10^{-6}/ °C (~400 °C)

Key words: Bio-glass Ceramics, CaF_2, MgF_2, Physical Properties, Biocompatibility.

Introduction

Various types of bioactive materials, such as sintered hydroxyapatite (HAp) [1] and β-wollastonite ($CaO{\cdot}SiO_2$) in an MgO-CaO-SiO_2 glass-based matrix [2] have been developed for medical applications over the last three decades. The fluorapatite glass ceramic is known as a promising material for medical and dental applications due to the anti-bacterial effect of its F^- ions. Glass ceramics of the ternary CaO-MgO-SiO_2 system have been reported as good candidate materials for wear resistance, biomedical, and ceramic-coating applications due to their good mechanical and chemical properties [3, 4]. Biocompatibility known as bonding to bone was enhanced for a certain compositional range of bioactive glasses which contained SiO_2, Na_2O, CaO, and P_2O_5. Chemical compositions including three key factors, such as (1) < 60mol% SiO_2, (2) high Na_2O and CaO contents, and (3) a high CaO/P_2O_5 ratio, are expected to exhibit high bioactivity at surfaces when these were exposed to the aqueous media [5]. In particular, a bio-glass ceramic composition based on 45S5 (46.1SiO_2-26.9CaO- 24.4Na_2O-2.6P_2O_5, mol%) by Hench is known to have a good advantage in its high bioactivity, but it has limitations such as low chemical durability and mechanical strength due to the open structure of the CaO-SiO_2 glass system [6]. Therefore, we intend to increase the SiO_2 content up to 50 mol% to enhance the mechanical properties. In this study, we aimed to synthesize new bio-glass compositions with addition of B_2O_3 and fluoride additions, such as CaF_2 and MgF_2 instead of Na_2O to improve the densification and the biocompatibility.

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Experimental procedure

As starting powders, SiO_2 (purity > 99.9%), $CaCO_3$ (purity > 99.5%), H_3PO_4 (85%), Na_2CO_3 (purity > 99.5%), B_2O_3 (purity > 90.0%), CaF_2, and MgF_2 were used. CaF_2 and MgF_2 were synthesized by the mixing of calcium nitrate (purity > 99%) and magnesium nitrate (purity > 99%) with fluoric acid. After weighing the powder, ball-milling with Si_3N_4 balls was carried out for 24 h, and then dried in an oven for 24 h. The chemical compositions of glass powders with addition of fluoride and B_2O_3 are presented in table 1. A powder mixture was melted in a Pt crucible at 1,450 °C for 2 h in air, and the glass frits were quenched

Table 1. Chemical compositions of the glasses prepared with additions of fluoride and B_2O_3

Composition (mol%) / Notations	SiO_2	CaO	Na_2O	P_2O_5	B_2O_3	CaF_2	MgF_2
50S	50	26.9	20.5	2.6	-	-	-
4B			16.5		4	-	-
5CF			11.5			5	-
5MF						-	5
2.5CMF						2.5	2.5
10CF						10	-
10MF			6.5			-	10
5CMF						5	5

in cold water. Glass frits were dried, and then milled using a planetary mill with Si_3N_4 balls for 4 h. Green compacts were obtained cold isostatically pressed at 207 MPa after die compaction, and sintered at various temperatures (650 -950 °C) for 2 h. The SBF (simulated body fluid) solutions were kept at 36.5 °C in an incubator in a static condition for the following time intervals: 1, 2, and 5days. The density and thermal expansion coefficient of sintered bio-glass ceramics was evaluated with a pycnometer (Accupyc1330, Micromeritics, USA) and a dilatometer (DIL 402 C, Netzsch, Germany) up to 400 °C. Phase changes were identified with X-ray diffraction patterns, and microstructures were observed with a FE-SEM (S-4700, Hitachi, Japan). The mechanical properties of specimens were evaluated by testing the four-point flexural strength with a cross head speed of 0.5 mm minute^{-1} and Vickers hardness (HM-124, Akashi, Japan) results were obtained at a load 1.96 N for 10 s. Specimen dimensions of mechanical test samples was 3 × 4 × 40 mm and the inner span and outer span were 10 and 30 mm, respectively.

Results and discussion

Table 2. shows the mechanical properties of sintered bio-glass compositions. Compared to the 50 S and 4B samples, in the case of CaF_2 and MgF_2 additions, a high degree of densification of the glass was observed. In particular, the 10 MF sample (10 mol% MgF_2) was revealed as having the best mechanical properties (flexural strength: 141 ± 5 MPa, microhardness: 5.6 GPa). These values are relatively higher than the conventional glass ceramics values reported for similar glass ceramic compositions with values lower than 100 MPa and 4.5 GPa [7-9]. Toya et al., [7] have proposed that diopside is a preferable crystalline phase since it provids strong materials compared to glass-ceramics based on wollastonite or anorthite.

Fig. 1 shows X-ray diffraction patterns of bio-glass ceramics after reaction with SBF. Hydroxyapitite ($Ca_{10}(PO_4)_6(OH)_2$) phases were observed in the X-ray patterns of 50S, 2.5CMF, and 5CMF (Fig. 2(a), (c), and (d)). A phase change from amorphous to a crystalline phase was observed in the X-ray patterns of the 4B sample. This result suggests that 2.5 CMF, 5 CMF compo

Table 2. Physical properties of bio-glasses sintered for 2 h

Group	Density (g/cm^3)	Porosity (%)	Flexural Strength (MPa)	Micro-hardness (GPa)	Thermal Exspansion Coeff.(x10^{-6}K^{-1}) ~200 °C	~400 °C
50S	2.69	4.8	57 ± 3	4.6	12.4	
4B	2.74	3.6	57 ± 5	4.8	10.8	11.4
5CF	2.76	12.7	110 ± 5	4.6	10.7	11.3
5MF	2.73	1.3	128 ± 7	5.4	10.0	10.5
2.5CMF	2.75	11.7	116 ± 8	4.0	9.1	9.4
10CF	2.78	2.3	127 ± 6	5.5	9.6	9.7
10MF	2.74	0.8	141 ± 5	5.6	8.9	9.5
5CMF	2.76	4.5	121 ± 13	5.6	9.5	9.9

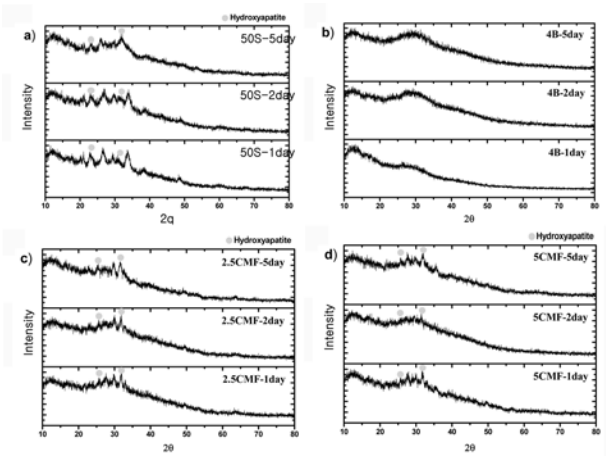

Fig. 1. XRD analysis after reaction in SBF solution of bio-glasses; (a) 50S, (b) 4B, (c) 2.5CMF, and (d) 5CMF.

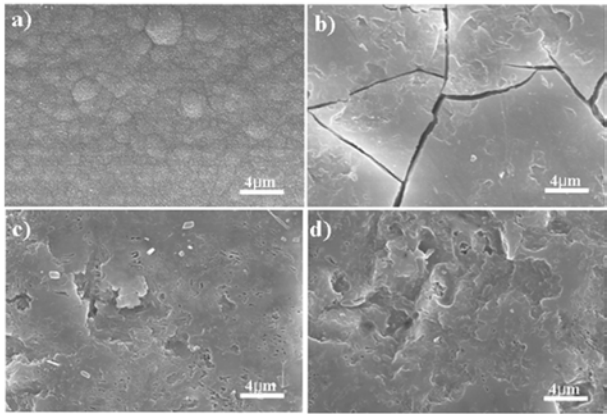

Fig. 2. SEM microstructures after reacting glass surfaces with SBF solution; (a) 50S, (b) 4B, (c) 2.5CMF, and (d) 5CMF.

-sition released the soluble Ca^{2+} ions into SBF solution, and the Na_2O-CaO-SiO_2-P_2O_5 glass forms Si-OH groups which act as nucleation sites of an hydroxyapitite (HAp) layer.

Fig. 2 shows a fully dense microstructure of bio-glass ceramics after the reaction with the SBF solution. The microstructure of 50S (Fig. 2(a)) shows the hydroxyapitite ($Ca_{10}(PO_4)_6(OH)_2$) phase composed of small particle groups homogeneously distributed in the matrix. Large particles with a plate shape were observed only in the 4B sample (Fig. 4(b)). In the microstructures of 2.5 CMF, 5 CMF (Fig. 4(c), (d)) the hydroxyapitite ($Ca_{10}(PO_4)_6(OH)_2$) phase was revealed with crystals homogeneously distributed in the matrix.

Summary

In this study, the biocompatibility of new bio-glass compositions (46.1SiO_2-26.9CaO- 24.4Na_2O-2.6P_2O_5, mol %) we evaluated with fluoride additions, such as CaF_2 and MgF_2, for the substitution of Na_2O. The physical properties of the 10 MF sample with a diopside phase

showed higher mechanical properties values (flexural strength: 141 ± 5 MPa, Vickers hardness: 5.6 GPa) compared to the conventional bio-glass composition (flexural strength (57 ± 3 MPa) and Vickers hardness (4.6 GPa)). Also, the thermal expansion coefficient of bio-glass ceramics with ion substitutions (Ca^{2+}, Mg^{2+} and B^{3+}) was decreased from 16×10^{-6}/K to $9.4\text{-}10 \times 10^{-6}$/K (~400 °C). In terms of biocompatibility, the 5 CMF bio-glass ceramics revealed a good biocompatibility in the SBF solution due to the formation of HAp at the reaction surface.

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