Bulletin of the *Transilvania* University of Braşov • Vol. 3 (52) - 2010
Series VI: Medical Sciences

BIOCOMPATIBILITY AND PHYSICAL PROPERTIES OF DOPED BIOACTIVE GLASS CERAMICS

Laura FLOROIAN [1]

Abstract: *Biocompatibility of a new bioactive glass composition for medical applications was evaluated with the addition of fluorides, such as CaF_2 and MgF_2, for the substitution of Na_2O in the conventional bioactive glass composition (SiO_2-CaO-Na_2O-P_2O_5). Also, the physical properties of these glass ceramics were investigated. When B_2O_3 was added as a Na_2O substitution, the thermal expansion coefficient was decreased in sintered samples. Compared to the low flexural strength and Vickers hardness of sintered bioactive glass ceramics without fluoride and B_2O_3 additions, new bioactive glass ceramics substituted with 10 mol% MgF_2 for Na_2O showed more higher mechanical properties.*

Key words: *Doped bioactive glass ceramics, Physical properties, Biocompatibility.*

1. Introduction

Various types of bioactive materials, such as sintered hydroxyapatite (HAp) [1, 2] and β-wollastonite (CaO-SiO_2) in an MgO-CaO-SiO_2 glass-based matrix [3,4] 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 [5, 7]. 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) < 60 mol% 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 [8]. In particular, a bioactive glass ceramic composition based on 45S5 (46.1 SiO_2-26.9 CaO-24.4 Na_2O-2.6 P_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 [5, 8]. Therefore, we intend to increase the SiO_2 content up to 50 mol% to enhance the mechanical properties.

In previous work, we reported the development of bioactive coatings using a new family of glasses in the SiO_2-Na_2O-K_2O-CaO-MgO-P_2O_5 system by pulsed laser ablation and deposition technique [9] and the analysis of the chemical and

[1]Physics Department, *Transilvania* University of Braşov.

microstructural evolution of the coatings under conditions that simulate their biological interaction with the body [10]. In this study, we aimed to synthesize new bioactive glass compositions in the SiO_2-CaO-Na_2O-P_2O_5 system 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.

2. Material and Methods

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 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 bioactivity of the films was assessed in vitro by soaking the composite material into simulated body fluid (SBF) that determines the extent of hydroxyapatite formation on the bioactive surface. The SBF was prepared by the mixing sodium chloride, sodium bicarbonate, potassium chloride, potassium phosphate, calcium chloride, dibasic potassium phosphate, hydrogen chloride, sodium sulphate and tris(hydroxymethyl)aminomethane into de-ionized water, according to Kokubo prescription [11]. The obtained solution had ionic concentration equal to human plasma. 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 5 days.

The density and thermal expansion coefficient of sintered bioactive glass ceramics was evaluated with a pycnometer (Pentapyc 5200e, Quantachrome Instruments, USA) and a dilatometer (L 75 PT 1600, Linseis, USA) up to 400 °C. Phase changes were identified with X-ray diffraction patterns, and microstructures were observed with a FE-SEM (JSM-7500F, JEOL, 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 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.

Chemical compositions of the glasses (in mol%) Table 1

Notation	SiO_2	CaO	Na_2O	P_2O_5	B_2O_3	CaF_2	MgF_2
BG1			20.5				
BG2			16.5				
BG3						5	
BG4			11.5				5
BG5	50	26.9		2.6	4	2.5	2.5
BG6						10	
BG7			6.5				10
BG8						5	5

Physical properties of bioactive glasses sintered for 2 h Table 2

Notation	Density (g/cm^3)	Porosity (%)	Flexural Strength (MPa)	Micro-hardness (GPa)	Thermal Exspansion Coeff.($x10^{-6}$ K^{-1}) 200 °C	Thermal Exspansion Coeff.($x10^{-6}$ K^{-1}) 400 °C
BG1	2.69	4.8	57	4.6	12.4	
BG2	2.74	3.6	57	4.8	10.8	11.4
BG3	2.76	12.7	110	4.6	10.7	11.3
BG4	2.73	1.3	128	5.4	10	10.5
BG5	2.75	11.7	116	4	9.1	9.4
BG6	2.78	2.3	127	5.5	9.4	9.7
BG7	2.74	0.8	141	5.6	8.9	9.5
BG8	2.76	4.5	121	5.6	9.5	9.9

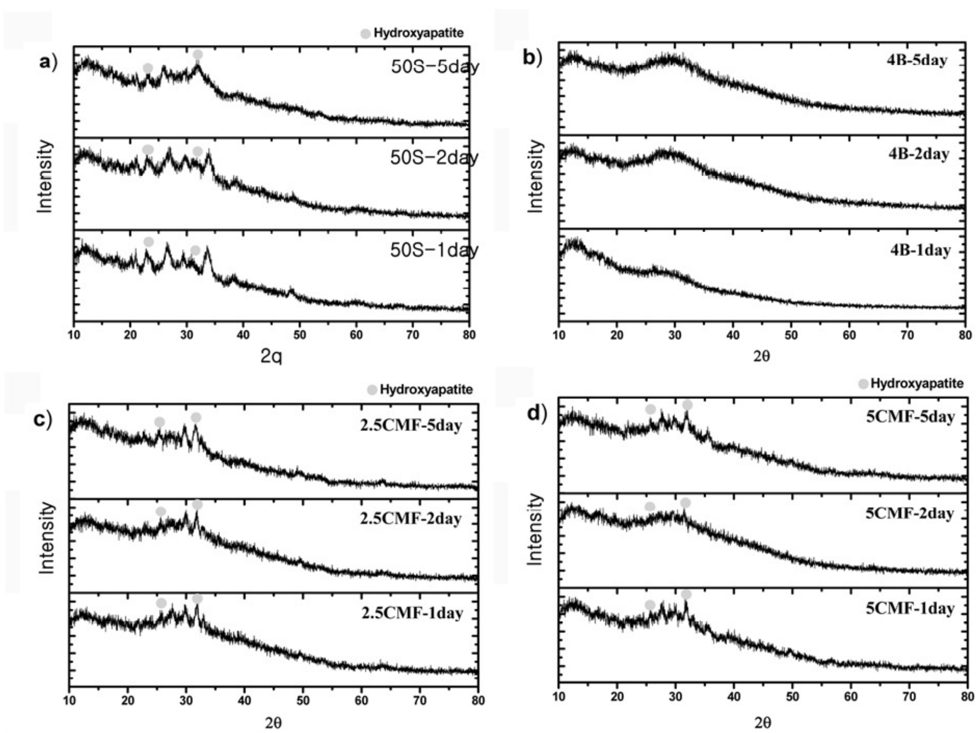

Fig. 1. *XRD analysis after reaction in SBF solution of bioactive glasses (a) BG1, (b) BG2, (c) BG5, and (d) BG8.*

3. Results and discussions

Table 2. shows the mechanical properties of sintered bioactive glass compositions. Compared to the BG1 and BG2 samples, in the case of CaF_2 and MgF_2 additions, a high degree of densification of the glass was observed. In particular, the BG7 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 [12-14]. Toya et al., [12] 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 bioactive ceramics after reaction with SBF. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) phases were observed in the X-ray patterns of BG1, BG5, and BG8 (Fig. 2(a), (c), and (d)). A phase change from amorphous to a crystalline phase was observed in the X-ray patterns of the BG2 sample. This result suggests that BG5, BG8 composition released the soluble Ca^{2+} ions into SBF solution, and the SiO_2-CaO-Na_2O-P_2O_5 glass forms Si-OH groups which act as nucleation sites of a hydroxyl-apatite (HAp) layer.

Fig. 2 shows a fully dense microstructure of bioactive glass ceramics after the reaction with the SBF solution. The microstructure of BG1 (Fig. 2(a)) shows the hydroxyapatite phase composed of small particle groups homogeneously distributed in the matrix. Large particles with a plate shape were observed only in the BG2 sample (Fig. 4 (b)).

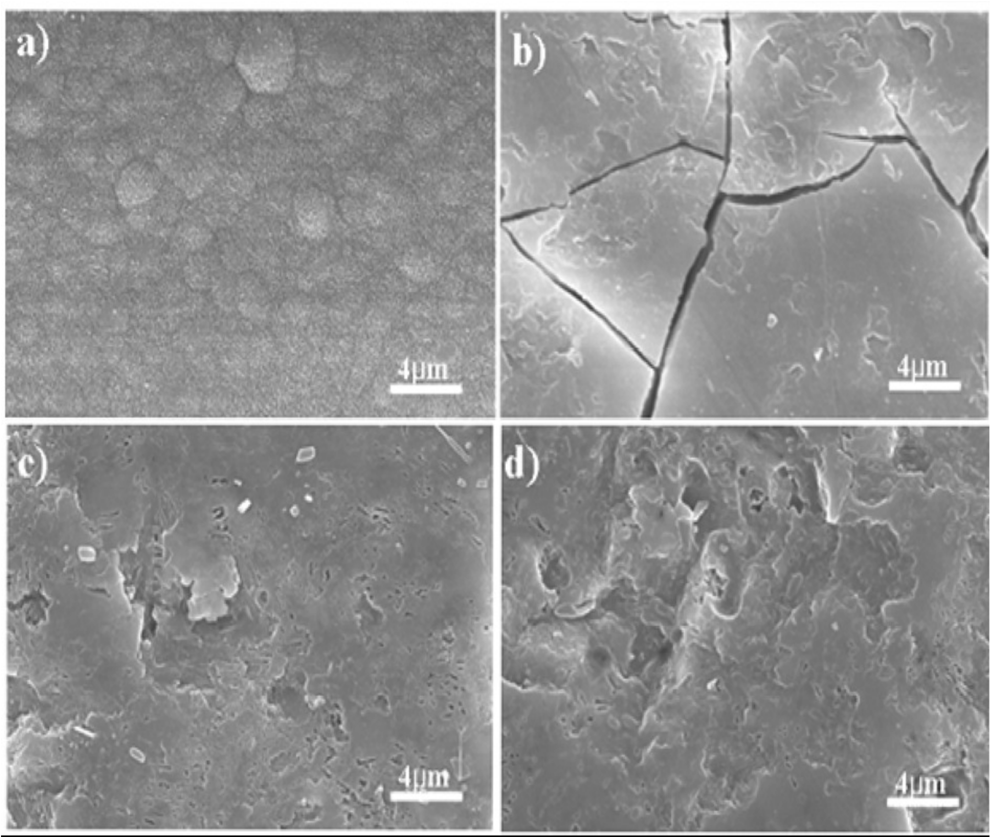

Fig. 2. *SEM microstructures after reacting glass surfaces with SBF solution; (a) BG1, (b) BG2, (c) BG5, and (d) BG8.*

In the microstructures of BG5, BG8 (Fig. 4(c), (d)) the hydroxyapatite phase was revealed with crystals homogeneously distributed in the matrix.

4. Conclusions

In this study, the biocompatibility of new bioactive glass compositions (46.1 SiO_2-26.9 CaO- 24.4 Na_2O-2.6 P_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 BG7 sample with a diopside phase showed higher mechanical properties values (flexural strength: 141 ± 5 MPa, Vickers hardness: 5.6 GPa) compared to the conventional bioactive glass composition (flexural strength (57 ± 3 MPa) and Vickers hardness (4.6 GPa)). Also, the thermal expansion coefficient of bioactive glass ceramics with ion substitutions (Ca^{2+}, Mg^{2+} and B^{3+}) was decreased from 16 × 10^{-6}/K to 9.4^{-10} × 10^{-6}/K (~ 400 °C). In terms of biocompatibility, the BG8 bioactive glass ceramics revealed a good biocompatibility in the SBF solution due to the formation of HAp at the reaction surface.

References

1. Nelea V., Ristoscu C., Chiritescu C., Ghica C., Mihailescu I.N., et al.: Pulsed laser deposition of hydroxyapatite thin films on Ti-5Al-2.5Fe substrates with and without buffer layers. In: *Applied Surface Science*, 2000, vol. 168, p. 127-131.
2. Pelletier H., Mille P., Nelea V., Mihailescu I.N., Muller D.: Mechanical properties improvement of PLD hydroxyapatite thin films by ion beam mixing. In: *Mater. Tech.*, 2006, vol. 94, p. 77-95.
3. Socol G., Torricelli P., et al: Biocompatible Nanocrystalline Octacalcium Phosphate Thin Films Obtained by Pulsed Laser Deposition. In: *Biomaterials* (2004) Vol. 25(13), p. 2539-2545.
4. Kokubo T., Ito S., Sakka S., Yamamuro T.: Formation of a high-strength bioactive glass-ceramic in the system MgO-CaO-SiO_2-P_2O_5. In: *Journal of Materials Science*, 1986, Vol. 21, (2), p. 536-540.
5. Hench L.L., Andersoon O.: *Bioactive glass coatings*. In: *An introduction to bioceramics*. Hench LL, Wilson J, (ed.). New Jersey, 1993, p. 239-260.
6. Sousa S.R., Barbosa M.A.: Effect of hydroxyapatite thickness on metal ion release from Ti6Al4V substrates. In: *Biomaterials*, 1996, vol. 17, p. 397–404.
7. Santos J.D., Silva L.P., Knowles J.C., Talal S., Monteiro F.J.: *Reinforcement of hydroxyapatite by adding P_2O_5-CaO glasses with Na_2O, K_2O and MgO*. In: J Mater Sci, Mater Med, 1996, vol. 7, p. 187-189.
8. Hench L.L.: Bioceramics: from concept to clinic. In: *J Am Ceram Soc.*, 1991, vol. 74, p. 1487-1510.
9. Floroian L., Savu B., Sima F., Mihailescu I. N., Tanaskovic D., Janackovic D.: Synthesis and characterisation of bioglass thin films. In: *Digest Journal of Nanomat And Biostructures* (2007) Vol. 2, p. 285-291.
10. Floroian L., et al. Nanostructured bioglass thin films syntherized by pulsed laser deposition: CLSM, FTIR investigations and in vitro biotests. In: *Applied Surface Science* (2008) Vol. 255, p. 3056-3062.
11. Kokubo T., Kushitani H., Sakka S., Kitsugi T., Yamamuro T.: Solutions able to reproduce in vivo surface-structure changes in bioactive glass-ceramic A-W3. In J Biomed Mater Res, 1990, vol. 24, p. 721-734.

12. Toya T., Kameshima Y., Yasumori A., Okada K: Preparation and properties of glass-ceramics from wastes (Kira) of silica sand and kaolin clay refining. In: *Journal of European Ceramic Society*, 2004, vol. 24, p. 2367-72.
13. Tulyaganov D., Ribeiro M. J., Labrincha J.A.: Development of glass-ceramics by sintering and crystallization of fine powders of calcium-magnesium-aluminosilicate glass. In*: Ceramic International*, 2002, vol. 28, p. 515-520.
14. Strnad J., Strnad Z., Šesták J.: Physico-chemical properties and healing capacity of potentially bioactive surfaces. In: *J. Thermal Anal. Calor.*, 2007, vol. 88, p. 775-783.