

Research Article

Study of the Bioactive Behavior of Hydroxyapatite/SiO₂-CaO-MgO Glass-Ceramics Synthesized by Transferred Arc Plasma (TAP)

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Abstract The Transferred Arc Plasma (TAP) melting method is a single step process which is reported to produce highly bioactive glass ceramics. Thus, the aim of the present work was the investigation of the bioactivity and evaluation of the developed apatite layer thickness of the hydroxyapatite/SiO₂-CaO-MgO systems under various compositions. Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy with associated Energy Dispersive Spectroscopy analysis (SEM-EDS) and X-ray Diffractometry (XRD) were used to characterize all specimens' surfaces before and after their immersion in c-SBF solution. It was concluded that the synthesized HA/glass-ceramic systems formed a well structured apatite layer even after the first 6 days of their immersion whilst pure glass pellets indicated a much slower apatite layer formation. SEM images and online cross sectional EDS analysis of the composite pellets after 18 days in c-SBF proved the development of an apatite layer 5–6 μm thick.

Keywords apatite; glass-ceramics; bioactivity; SBF; FTIR; SEM-EDS

1 Introduction

Bioactive glasses and glass-ceramics with bone-bonding ability have been extensively examined as key materials for bone regeneration, since their bioactivity and biore-sorbability can be easily controlled by modifying their composition [3]. To this day, a number of different methods and techniques are used to produce such materials including a few plasma-related procedures. Plasma technology is an enabling technology, which introduces new materials processing techniques and unique properties to already well studied materials [6,8]. This is due to a wide variety of physical, chemical and metallurgical transformations of glass-ceramics which can take place when they are exposed to plasmas. The TAP melting method is a single

step process of glass-ceramics preparation in which the raw materials are melted in the plasma and crystallization of the melt occurs while quenching [10]. Good mechanical and chemical properties of glassceramic materials in the SiO₂-CaO-MgO system indicated them as suitable candidate for use in wear resistant, thermomechanical, biomedical and ceramic coating applications [7], furthermore diopside (CaMgSi₂O₆), a Ca, Si and Mg-containing ceramic, has been reported by T Nonami and S Tsutsumi to possess apatite formation ability in SBF and can closely bond to bone tissue [4]. It is reported that in many cases the use of Mg in such systems enhances their bioactivity, yet its excess inhibits the formation of a thick apatite layer during their immersion in SBF [4]. In the present study, a natural bovine hydroxyapatite/SiO₂-CaO-MgO glass-ceramic system was produced using TAP melting method and the investigation of the bioactivity and study of thickness of the developed apatite layer of the synthesized system, for various compositions, was possible with the use of FTIR, SEM-EDS and XRD. The cross sectioned pellets, soaked in c-SBF solution for 18 days, were examined by SEM-EDS in order to study the thickness and structure of the formed apatite layer.

2 Materials and methods

Initially, SiO₂-CaO-MgO glass-ceramic (51.6% SiO₂, 35.6% CaO and 12.8% MgO) and homogeneous mixtures of 75% HA/25% SiO₂-CaO-MgO (75:25) and 50% HA/50% SiO₂-CaO-MgO (50:50) were obtained by TAP melting method, as described in details in literature [10]. In order to study the structure and thickness of the developed apatite layer, 50 mg from each material was compressed in a hydraulic press to form a 15 mm in diameter, pellet. The *in vitro* bioactivity assessment was performed by immersing each pellet in c-SBF solution for various immersion periods

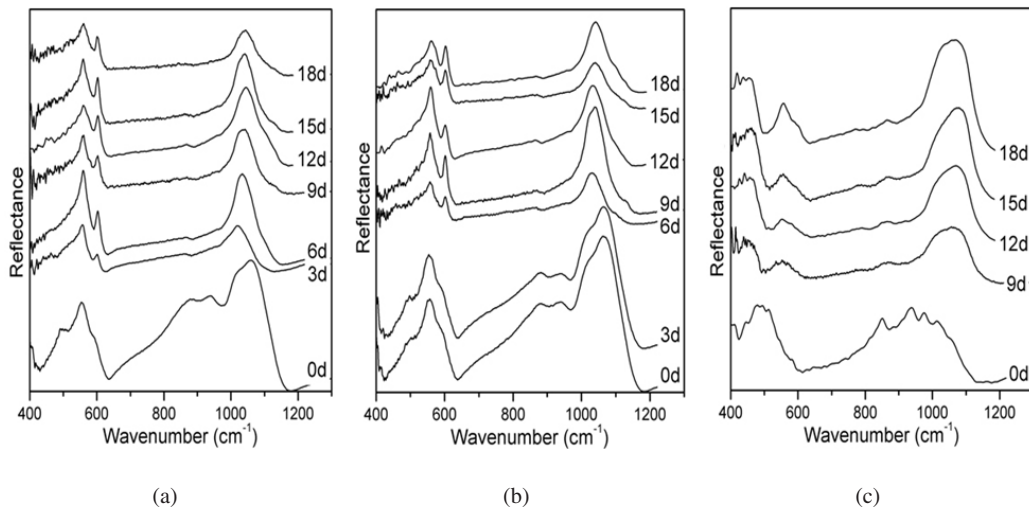


Figure 1: FTIR reflectance spectra of (a) 50:50, (b) 75:25 and (c) pure glass systems before and after immersion in c-SBF for various periods of time

of time. Before their immersion in c-SBF solution, which was prepared as described by Oyane et al. [5], all pellets had been sterilized. The FTIR measurements were carried out by a Bruker spectrometer IFS 113 v, in the Reflectance mode in MIR region, with 64 consecutive scans and resolution 2 cm^{-1} . Topographical evaluation and surface elemental compositional analysis were performed with a scanning electron microscope with associated EDS (JEOL J.S.M. 840A, Tokyo, Japan). XRD analysis was carried out using a Philips (PW1710) diffractometer with Ni-filtered CuK α radiation, while the counting statistics of the XRD study were: step size $0.05^\circ 2\theta$, start angle 5° , end angle 85° and scan speed $0.01^\circ 2\theta/\text{sec}$. Finally, the cross sections of the pellets soaked for 18 days in c-SBF solution, were obtained by a low-speed diamond disk under water cooling and they were examined by SEM-EDS analysis.

3 Results and discussion

The *in vitro* bioactivity of all composites—as pellets—was studied up to 18 days and the FTIR spectra are presented in Figure 1. In the FTIR reflectance spectrum of the 50:50 composite (Figure 1(a)) the characteristic peaks of crystalline apatite (HCAp) have evoked after only 3 days of soaking. In details, the 552 cm^{-1} peak and the shoulder at 580 cm^{-1} , which can be attributed to the contribution of HA to the composite, split into the double P-O bending peaks of crystalline HCAp at 604 and 556 cm^{-1} [1,2]. Additionally, the broad peak in the $1030\text{--}1060\text{ cm}^{-1}$ region that is ascribed to silica glass vibrations was shifted and sharpened after the first 3 days, also suggesting the onset of an HCAp phase formation. For longer reaction times the apatite layer covered a greater fraction of the pellet

surface, as revealed by SEM microphotographs (Table 1) and EDS analysis. As shown in Table 1 the apatite layer consists of spherulitic apatite aggregates even after 6 days in c-SBF solution. Particularly after 18 days, EDS analysis revealed a significant decrease of Mg and Si, which along with the cross sectional online analysis (Figure 2(a)) proved the formation of a $5\text{--}6\text{ }\mu\text{m}$ HCAp layer with a molar Ca/P ratio of about 1.62. In Figure 1(b) the spectrum of the 75:25 system revealed a crystalline HCAp layer after 6 days of soaking in c-SBF.

The FTIR findings were also confirmed by SEM microphotographs (Table 1), while EDS analysis revealed a considerable decrease of the Mg and Si on top of the pellet and the cross sectional online analysis (Figure 2(b)) proved the formation of a $5\text{--}6\text{ }\mu\text{m}$ HCAp layer with a molar Ca/P ratio of about 1.64.

Finally, in Figure 1(c) the reflectance spectra of the pure $\text{SiO}_2\text{--CaO--MgO}$ are presented. Although the studied glass ceramic does not show any alterations for the first 6 days in c-SBF, and therefore there is no reason to present the respective spectra, after 9 days we can see the shifted broad peak around 1060 cm^{-1} as well as a broad peak around 550 cm^{-1} , indicating the onset of a Ca-P phase formation. Finally, after 18 days of immersion, the peak at 558 cm^{-1} and the shoulder at 591 cm^{-1} are indicating the formation of a partially crystallized apatite phase.

SEM microphotographs showed traces of a Ca-P phase after 6 and 9 days of immersion in c-SBF solution and after 18 days a sporadically developed apatite phase. Additionally, EDS analysis showed a decrease of Si and Mg on the pellet's surface and the cross sectional online analysis indicated a thin apatite layer ($1\text{--}2\text{ }\mu\text{m}$).

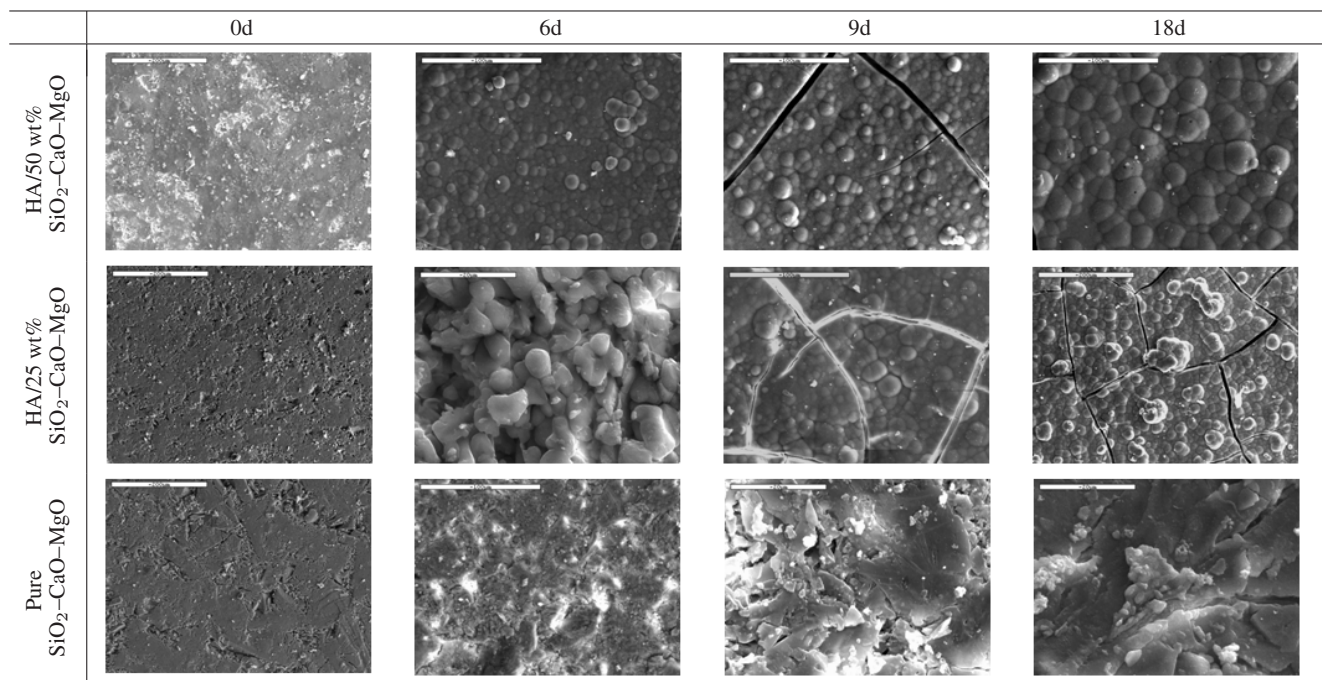


Table 1: SEM microphotographs of all composite materials before and after immersion in c-SBF for various periods of time.

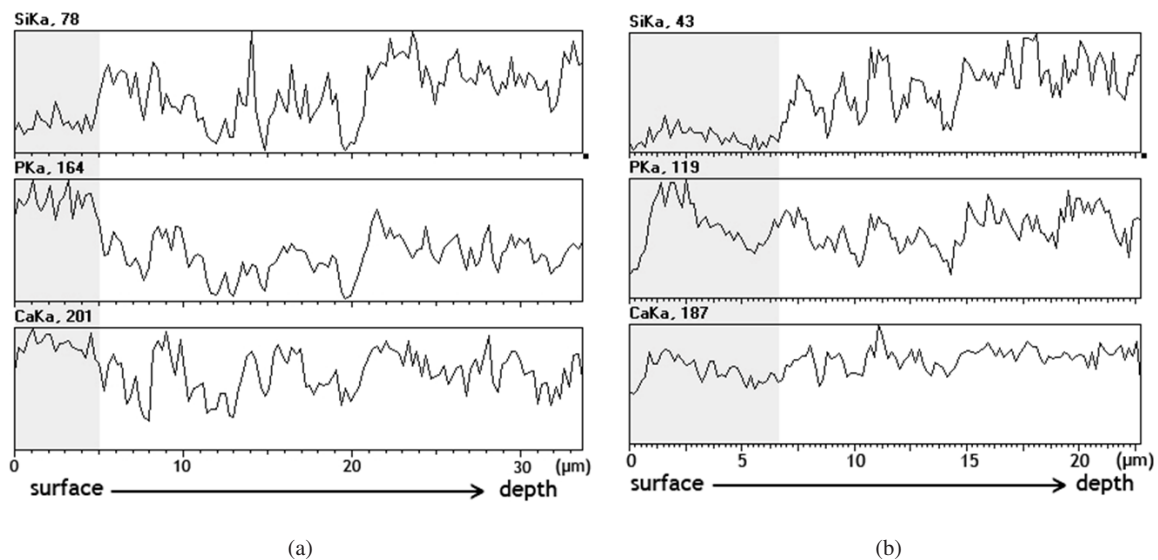


Figure 2: On line cross section analysis of (a) 50:50 and (b) 75:25 systems after immersion in c-SBF for 18d.

The bioactive behavior of both composites is attributed to the crystallization of a calcium phosphate silicate (CPS) phase, as revealed by XRD patterns shown in Figure 3 that is proved to be bioactive. A semi-quantitative XRD analysis was also performed revealing that CPS concentration in the 50:50 composite was approximately 71%, while in the 75:25 one, was set around 59%. Therefore, the slower onset of apatite formation for the 75:25 pellet, compared to the 50:50

one, can be attributed to the lower CPS concentration in this composite material. Finally, the delay of apatite formation in the case of pure SiO₂-CaO-MgO glass can be probably attributed to the slow rate of apatite formation of akermanite (Ca₂MgSi₂O₇) that is the dominant crystalline phase of the glass, as shown in Figure 3. Akermanite is reported to possess bone-like apatite-formation ability after 20 days of soaking in SBF [9].

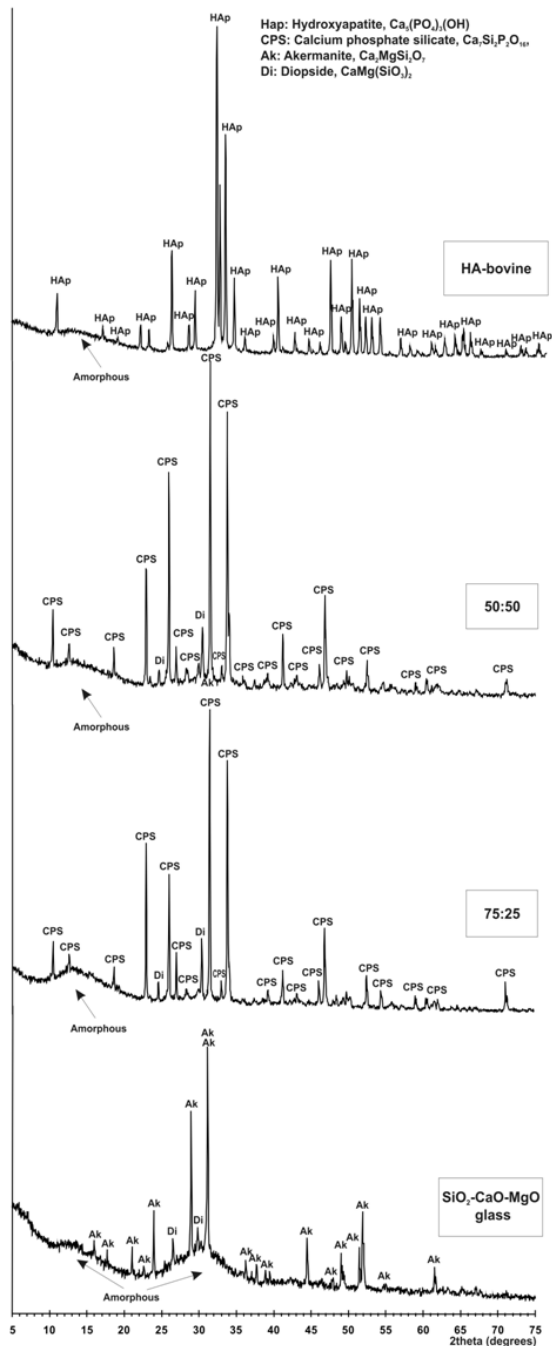


Figure 3: XRD patterns of all composite materials before immersion in c-SBF.

4 Conclusions

The results of this study for all synthesized materials showed the formation of an HCap layer on top of every pellet. While on both 50:50 and 75:25 composite systems the HCap layer was rather thick (5–6 μm), the one formed on top of the pure glass pellet was much thinner (1–2 μm). Thus, the crystallization of a thick and well structured HCap layer on TAP

synthesized glass-ceramics was proved, suggesting that the use of TAP processing method is an acceptable alternate method for fabrication of bioactive glass-ceramic materials, which can also be used as bulk materials.

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