Materials Science and Engineering C 29 (2009) 2226–2233

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Preparation and studies on surface modifications of calcium-silico-phosphate ferrimagnetic glass-ceramics in simulated body fluid

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ARTICLE INFO

Article history:
Received 18 February 2009
Received in revised form 24 April 2009
Accepted 14 May 2009
Available online 22 May 2009

Keywords:
Glass ceramic
XPS
Magnetite
Simulated body fluid (SBF)
Bioactivity

ABSTRACT

The structure and magnetic behaviour of $34SiO_2$–$(45-x)$ CaO–$16P_2O_5$–4.5 MgO–0.5 CaF_2 – x Fe_2O_3 (where $x=5$, 10, 15, 20 wt.%) glasses have been investigated. Ferrimagnetic glass-ceramics are prepared by melt quench followed by controlled crystallization. The surface modification and dissolution behaviour of these glass-ceramics in simulated body fluid (SBF) have also been studied. Phase formation and magnetic behaviour have been studied using XRD and SQUID magnetometer. The room temperature Mössbauer study has been done to monitor the local environment around Fe cations and valence state of Fe ions. X-ray photoelectron spectroscopy (XPS) was used to study the surface modification in glass-ceramics when immersed in simulated body fluid. Formation of bioactive layer in SBF has been ascertained using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The SBF solutions were analyzed using an absorption spectrophotometer. The magnetic measurements indicated that all these glasses possess paramagnetic character and the $[Fe^{2+}/Fe^{3+}]$ ions ratio depends on the composition of glass and varied with Fe_2O_3 concentration in glass matrix. In glass-ceramics saturation magnetization increases with increase in amount of Fe_2O_3. The nanostructure of hematite and magnetite is formed in the glass-ceramics with 15 and 20 wt.% Fe_2O_3, which is responsible for the magnetic property of these glass-ceramics. Introduction of Fe_2O_3 induces several modifications at the glass-ceramics surface when immersed in SBF solution and thereby affecting the surface dissolution and the formation of the bioactive layer.

1. Introduction

Calcium-silico-phosphate glasses have potential as implant materials for human body because of their bioactivity and biocompatibility. Hench [1] has reported the first bioactive glass having composition (wt.%) 45% SiO_2, 24.5% Na_2O, 24.5% CaO and 6% P_2O_5 commonly known as 45S5. The bioactivity of these materials is composition dependent. Addition of alumina tends to decrease the bioactivity of these glasses [2]. These glasses and glass-ceramics having Fe_2O_3 show an important application in cancer treatment by elimination of cancerous cells in bones; by means of hyperthermia [3]. The magnetic properties arise from magnetite [Fe_3O_4] that is produced from the Fe_2O_3. When this material is placed in the region of the tumor and is subjected to an alternating magnetic field, heat is generated by hysteretic losses [4]. The tumor is effectively heated and the temperature locally rises to 42–45 °C. As a result, the cancerous cells perish while the healthy ones survive [5–7]. Synthesis of glass-ceramics in SiO_2–CaO–Fe_2O_3, SiO_2–CaO–Fe_2O_3–B_2O_3–P_2O_5, SiO_2–Al_2O_3–Fe_2O_3–P_2O_5–Li_2O and CaO–SiO_2–P_2O_5–Na_2O–Fe_2O_3 bioglasses, have been reported [8,9]. However, the distribution and the bonding environment of Fe_2O_3 on these glasses and glass-ceramics have not been studied in great details. Since the magnetic properties of the material depend on the environment of Fe, therefore the knowledge of structure and oxidation states of iron ions is beneficial for synthesis of magnetic glass and glass-ceramic.

Since these materials are in contact with living tissues when implanted in the body, they should not elicit any harmful response from the host tissues. Therefore, the surface chemistry of materials needs to meet the requirements of host tissues. In fact, surface of the material has a critical influence on the biological response, therefore, most of the applications of these biomaterials are dictated by the way in which a given material interacts with body fluids. Therefore, a study of the surface interactions with body fluid is needed to improve the understanding of chemistry and physics taking place on surfaces/interfaces of glasses/glass-ceramics. In this regard, XPS spectroscopy is useful in understanding the surface interactions with body fluids as

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0928-4931/$ – see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.msec.2009.05.009

Table 1
Base glass compositions (nominal) in wt.%.

Sample	SiO_2	P_2O_5	CaO	MgO	Fe_2O_3	CaF_2
FB5	34	16	40	4.5	5	0.5
FB6	34	16	35	4.5	10	0.5
FB7	34	16	30	4.5	15	0.5
FB8	34	16	25	4.5	20	0.5

it provides information on the first 50–100 A° of the sample surface [10].

In the present work, we report preparation and a systematic study on magnetic behaviour and surface properties of $34SiO_2$–$(45-x)$ CaO–$16P_2O_5$–4.5 MgO–0.5 CaF_2 – x Fe_2O_3 (where $x = 5, 10, 15, 20$ wt.%) glass and glass-ceramics. This system is of particular interest due to its magnetic and bioactive properties. We have studied the effect of Fe_2O_3 on magnetic and bioactivity related properties in SBF. The surface modifications of these samples as a function of exposure time in SBF were investigated by XPS and SEM/EDX. The dissolution behaviour in the solution is explained on the basis of surface reactions.

2. Experimental procedure

2.1. Preparation of glass and glass-ceramics

Base glasses of compositions as given in Table 1 were prepared by melt quench technique. About 100 g batches were prepared by mixing reagent grade SiO_2, $CaCO_3$, NH_4H_2PO4, $MgCO_3$, Fe_2O_3, and CaF_2. The charge was calcined at a maximum of 900 °C for 12 h, holding at intermediate temperature for 6–8 h, decided by the decomposition temperatures of various precursors. Melting was carried out in a covered Pt-10% Rh crucible at 1450–1500 °C in a lowering and raising hearth furnace. The melt was held for 2 h at this temperature for homogenization and then poured into a graphite mould followed by annealing at 500 °C. The base glass was powdered in a ball mill and pelletized using a hydraulic press. They were converted into glass-ceramics (hereafter called FBC) through controlled heat treatment. Glass-ceramics FBC5, FBC6, FBC7 and FBC8 with iron concentration 5, 10, 15, 20 wt.% respectively, were heat treated at 1000 °C for 6 h.

2.2. Structural and magnetic study of glass and glass-ceramics

X-ray diffraction (XRD) of the powder sample was carried out on Philips PW 1710 X-ray diffractometer. The magnetic response versus applied magnetic field H was measured at room temperature, with $|H| \leq 5$ kOe using a Superconducting Quantum Interference Device (SQUID) magnetometer. These data have been analyzed to obtain the saturation magnetization (M_s), remnant magnetization (M_r), and coercive field (H_c) for each material. Mössbauer spectra have been obtained using a spectrometer operated in constant acceleration mode. The source employed is ^{57}Co in Rh matrix of strength 50 mCi. The calibration of the velocity scale is done using iron metal foil. The Mössbauer spectra are fitted with appropriate paramagnetic doublets and magnetic sextets using least square fit program. The ratio of Fe^{2+} and Fe^{3+} ions has been determined from the relative areas obtained by computer fitting of experimental spectra.

2.3. In-vitro bioactivity analysis in SBF

The interactions of the samples with simulated body fluid were studied. The pellets were immersed in SBF solution for 1–4 weeks, incubated at 37.4 °C. Samples were removed periodically and their surfaces were analyzed using XPS technique. For XPS measurement, samples were mounted on the specimen holder using silver paste. The conducting path was provided from bottom to the top surface of the sample by silver paste, to avoid the surface charging effect. The sample chamber was then evacuated to a vacuum better than 1×10^{-9} Torr. The sample was excited by Mg-K_α radiations ($h\upsilon = 1254.6$ eV), photo-electron spectra were analyzed using a VG make CLAIM 2 analyzer system. The core level peaks for the constituent elements are identified and marked on the spectra.

Quantitative evaluation of chemical composition was made for the constituent elements of the immersed glass-ceramics by estimating the peak area and using the calculated cross sections (p) as sensitivity factors [11]. After the samples were removed, changes in concentration of Ca, P, Si and Fe in SBF solutions were measured using an absorption spectrophotometer (Atomic Absorption Spectrophotometer Chemito AA 203). The pH of the SBF solutions was monitored periodically during the experiment. The morphological analyses were carried out by means of SEM (Model: Tescan Vega MV 2300T/40) technique. Prior to mounting samples in analysis chamber of microscope, thin Au conducting coating was deposited on the sample surface to prevent charging effects.

3. Results and discussion

3.1. Structural and magnetic studies

The XRD patterns of heat treated samples are shown in Fig. 1. When glasses FB6, FB7 and FB8 were heat treated at 1000 °C for 6 h, calcium phosphate ($Ca_2P_2O_7$), wollastonite and magnetite were developed as major crystalline phases.

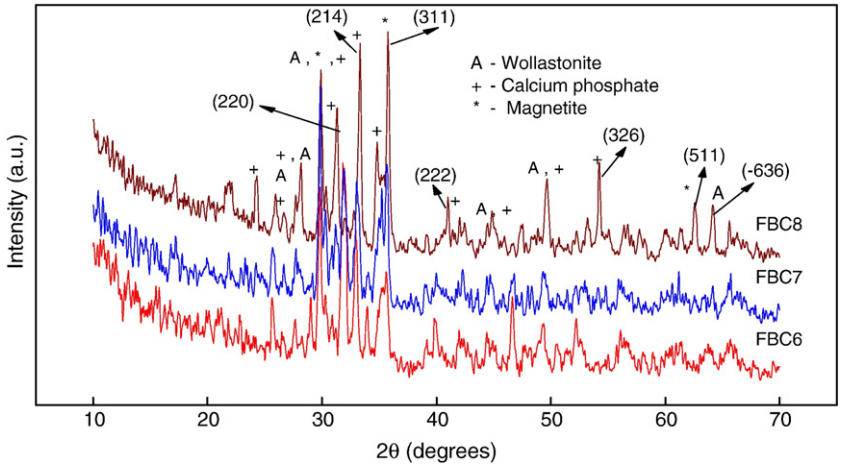

Fig. 1. XRD patterns of glass-ceramics having different Fe_2O_3 concentrations.