



Surface modification and bio-activation of bio-inert glasses through thermal oxidation



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ABSTRACT

Bioactivity and bio-compatibility are inversely related to the mechanical and chemical stability of bio-glass. In this research, we suggest a new method of conferring bio-activity on bio-inert glass through the addition of a small amount of FeO and oxidizing annealing, that is, surface modification, without degrading mechanical and chemical durability. The surface of iron-bearing bio-inert glasses can be successfully modified to form a Na₂O-rich and SiO₂-depletion layer on the surface, which allows the bio-activation sites to form and grow hydroxycarbonate apatite (HCA) crystals. After immersion in a solution of simulated body fluid (SBF) the surfaces show the formation of HCA and silica gel layers. We suggest that glasses with $2.30 \leq \text{network connectivity (NC)} \leq 2.61$ and up to Na₂O/CaO = 1.25 can be modified into a bio-active surface by heat-treatment in an oxidizing atmosphere near the glass transition temperature. The reaction of the modified surface with SBF followed a process similar to typical bioactive glass. The thickness of the HCA surface layer after immersion in SBF for 7 days increased with a decrease in the Na₂O/CaO ratio of the mother glasses. Inducing a bio-activity to bio-inert glasses with a high SiO₂ content and good mechanical and chemical durability through thermal oxidation is a new method to produce a bio-active glass.

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1. Introduction

Bioactive glasses are known to form an integrated bond with mineralized tissue through the development of a surface layer of hydroxycarbonate apatite (HCA) [1,2]. It has been suggested that the hydroxycarbonate apatite (HCA) surface layer may be responsible for the forming of a chemical bond between the bioactive glasses and the surrounding tissues [3]. When bioactive glasses interact with the local environment in vivo, this modifies the surface into a dual layer composed of HCA and a silica gel degrading in the human body [4,5]. Elgayar et al. [6] confirmed that bioactive glasses are predominantly Q² in structure by using ²⁹Si MAS NMR. Thus, the compositions of bioactive glasses are limited to less than 50 mol% SiO₂, which is typical of invert glasses. Many bioactive glasses are based upon the formula “45S5” with the composition of 45% SiO₂, 24.5% Na₂O, 24.5% CaO, and 6% P₂O₅ [7]. However, these glasses have poor chemical durability and mechanical strength despite their excellent in vitro and in vivo bioactivity. To enhance the formation of an HCA layer, 45S5 Bioglass[®] includes 6 wt.% P₂O₅. Because the addition of P₂O₅ in soda-lime silicate glasses can cause phase-separations in the glasses [8,9], it is difficult to control the reactivity of the glass by altering its composition. One way to avoid these problems is to induce the formation of invert

glasses on the surface of the soda-lime silicate glasses without phosphate.

The glass surface can be modified by redox reactions. Barton and Billy [10] found that sodium deposits on the surface due to oxidation of Cu⁺ to Cu²⁺ when 0.4% copper-containing flint glasses are heated in air. Many studies on iron-bearing silicate glasses [11–16] showed that heat-treatment of the glasses in an oxidizing atmosphere at temperatures around the glass transition temperature results in diffusion of mobile network-modifying divalent cations from the interior towards the surface of the glass due to the oxidation of Fe²⁺. The studies propounded a mechanism of oxidation during which oxidation of the glass occurs not by the diffusive addition of oxygen to the glass, but rather by the diffusive removal of network-modifying cations that is charge-compensated by an inward flux of electron holes. The glasses studied by Cook Group [11–14] were mainly an alkaline earth aluminosilicate and basalt, and the FeO content was greater than 10 mol%. Kohlstedt et al. [17] also showed that oxidation occurs internally by the removal of cations rather than the addition of oxygen in iron-bearing crystalline oxides. In addition, when polyvalent-bearing silicate glasses are heat-treated in CO and H₂ gases at a temperature near the glass transition temperature, the inward diffusion of modifiers occurs during reduction of the ferric (Fe³⁺) ion to the ferrous (Fe²⁺) ion [16,18–20]. The glass used in studies for the inward diffusion of modifier ions was SiO₂–Na₂O–Fe₂O₃–RO (R = Mg, Ca, Sr, Ba) and the Fe₂O₃ content was in the range of 1–6 wt.% less than that studied by the Cook Group. Smedskjaer and Yue [18] studied the effect of the iron

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content on the diffusion process by analyzing secondary neutral mass spectroscopy (SNMS) depth profiles and showed that glass containing 1 wt.% Fe₂O₃ also displays inward cationic diffusion and the thickness of the modified layer decreases when the iron content of the glass is reduced for a given heat-treatment condition. Consequently, the surface composition of iron-bearing glass can be modified via oxidation or reduction.

It is well known that the composition of bio-active glass is almost fixed and behavior such as its mechanical strength and chemical durability, excluding bioactivity, are intrinsically very poor. Therefore, conferring bioactivity by surface modification of bio-inert glasses is the key to enhancing other physical properties such as mechanical strength and chemical durability, together with its excellent bio-activity. The objective of this study is to induce the formation of a bioactive surface layer by treatment with bio-inert glasses under the oxidizing atmosphere at a temperature near the glass transition temperature.

2. Experiment

Non-bioactive soda-lime silicate glasses were melted in a platinum crucible at 1450 °C for approximately 3 h using a mixture of reagent grade Na₂CO₃, CaCO₃, Fe(C₂O₄)₂H₂O and SiO₂. Each melt was quenched by pouring it into a cylindrical graphite mold, which was annealed in air for approximately 2 h at 400 °C. Glass samples in the shape of a disc (diameter 14 mm, thickness 2 mm) were prepared by cutting the glass cylinder using a diamond saw. The samples were ground and polished using 1 μm ceria at the final step for XPS analysis. The surfaces of the samples, used to evaluate bioactivity, were ground with #400 SiC-paper, to increase the area exposed to SBF. The glass composition in Table 1 and elsewhere in the present paper is the batch composition in mol%. A sample with the same composition as 45S5 Bioglass, the reference glass, was also produced in the same manner.

The glass transition temperature (T_g) was measured from the onset temperature of the endotherm using differential thermal analysis (DTA). Two analyses were performed for each glass and the random uncertainty at 95% confidence level was estimated from the result.

The oxidation treatment was conducted in an electric furnace under a flow of O₂/N₂ gas with a fixed oxygen partial pressure of 0.05 atm in order to prevent all Fe²⁺ ions from being oxidized before the modifier ions start to diffuse. We have previously found that the formation of HCA is weak when iron-containing glass is heat-treated in the high oxygen partial pressure [21]. This trend is also shown for the thermal reduction as a mirror-image of thermal oxidation, that is, inward diffusion of the modifying cations in iron-containing silicate glass treated in a reducing atmosphere near the glass transition temperature decreases with increasing hydrogen pressure [18]. The glass samples were inserted into the cold furnace and the gas-flow was turned on. Heating and cooling were conducted at 10 K/min. The oxygen partial pressure in the furnace was monitored via a flow-through stabilized zirconia solid-electrolyte sensor that operates at 750 °C in a separate furnace downstream of the reaction furnace. The glasses were heated at a temperature near their T_g for 10 h.

Simulated body fluid (SBF) was prepared according to Kokubo and Takadama [22]. The apatite-forming ability test was also performed following the procedure recommended by Kokubo and Takadama. The samples heated under an oxygen atmosphere were immersed in a conical centrifuge plastic tube filled with the SBF pre-heated to 36.5 °C. The ratio of the apparent surface area to the volume of SBF has to be maintained at 0.1 ml/mm². After soaking at 36.5 °C for different periods of time, the samples were removed from the SBF and rinsed with distilled water and acetone to remove any residual salts and halt reactions. The samples were then dried at 60 °C overnight and stored in a vacuum desiccator until required.

For the Fourier transform infrared (FTIR) analysis, surface films were removed by polishing and the powder was pressed with KBr in a hydraulic press to prepare thin transparent discs. The infrared spectra of the samples were recorded at room temperature in the range 400–1500 cm⁻¹ using a Vertex 80v FTIR spectrometer. The Raman scattering analyses were performed on a Labram HR800 micro-Raman spectrometer in the backscattering geometry. The excitation line was provided by a 17 mW Ar ion laser at 514 nm focused onto a 2 μm-sized spot on the sample surface. All spectra were collected with a microscope equipped with 100× lenses and two accumulations at an integration time of 60 s and a resolution of 2 cm⁻¹.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo K-alpha XPS spectrometer with a hemispherical analyzer. Spectra were obtained by using monochromatic Al Kα radiation source operating at 72 W. Neutralization of the surface charge was performed by using a low-energy flood gun (electrons in the range of 0–14 eV). The shift of the binding energy due to the surface charging effect was calibrated by assuming a C 1s binding energy to be always 284.6 eV. Depth profiles were recorded using an argon ion beam with an energy of 1 keV and a current density of 2 μA/cm². The milling rate of the surface was approximately 216 nm/min. This rate was approximated using a stylus profilometer on the assumption that the milling rate stayed constant throughout the milling process.

Microstructure observations were performed by field emission scanning electron microscopy (FE-SEM Jeol JSM 6701 F) under the secondary electron mode. Energy dispersive spectroscopy (EDS, INCA X-Stream) was employed for chemical analysis. The element mapping technique was performed to obtain a qualitative image of the distribution of elements throughout the cross-section.

3. Results

The glasses studied in series R, in which calcium oxide is systematically substituted for sodium oxide on a molar basis, were made in order to examine the influence of sodium oxide content on the surface modification after heat treatment while keeping the network connectivity constant (NC) at 2.3, where NC is an abbreviation of the network connectivity or crosslink density of glass introduced by Hill [23] to predict its surface reactivity. The Na₂O/CaO ratio was 2.0 for R1, 1.25 for R2, 0.8 for R3, and 0.5 for R4. On the other hand, the glasses in series G have different network connectivities, keeping the Na₂O/CaO ratio fixed at 0.5 (Table 1).

Table 1
Composition (mol%), T_g , heat-treatment temperature (T_h), onset temperature of exothermic peak (T_c) and NC of the investigated glasses.

Label	SiO ₂	CaO	Na ₂ O	FeO	T_g (°C)	T_h (°C)	T_c (°C)	Na ₂ O/CaO	NC
R1	54	15	30	1	500 ± 2	530	570 ± 1	2.0	2.30
R2	54	20	25	1	528 ± 2	550	655 ± 1	1.25	2.30
R3	54	25	20	1	567 ± 3	580	690 ± 1	0.8	2.30
R4	54	30	15	1	586 ± 2	620	697 ± 1	0.5	2.30
R5	54.0	30.5	15.5	0	584 ± 2	620	692 ± 1	0.5	2.30
G1	57	28	14	1	588 ± 3	620	615 ± 1	0.5	2.49
G2	58.0	27.3	13.7	1	591 ± 2	620	627 ± 1	0.5	2.55
G3	59.0	26.7	13.3	1	598 ± 2	630	715 ± 1	0.5	2.61

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