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Bioactive oxynitride glasses: Synthesis, structure and properties

Ahmed Bachar[a], Cyrille Mercier[a], Arnaud Tricoteaux[a], Anne Leriche[a], Claudine Follet[a], Stuart Hampshire[b,*]

[a] Laboratoire des Matériaux Céramiques et Procédés Associés, Université de Valenciennes et du Hainaut-Cambrésis, Valenciennes, France
[b] Materials and Surface Science Institute, University of Limerick, Limerick, Ireland

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ABSTRACT

The low mechanical strength of bioactive glasses restricts their use to non load-bearing applications. One way to increase strength of glasses is to introduce nitrogen into the silicate network. Oxynitride bioactive glasses in the SiO_2–CaO–Na_2O–Si_3N_4 system were successfully prepared. Structural characterization using ^{29}Si MAS-NMR shows that, as nitrogen is substituted for oxygen, formation of [SiO_3N] tetrahedra and Q^4 units occurs with extra bridging anions at the expense of Q^3 units. Glass transition temperature, hardness, Young's modulus and fracture resistance increase with nitrogen content because of the extra cross-linking of the glass network.

CaF_2 was substituted for CaO in these glasses which results in decreases in glass transition temperature. Thus, glasses can be melted at lower temperatures while addition of fluorine allows higher solubility of nitrogen and has no effect on the significant increases in mechanical properties induced by nitrogen substitution.

Initial assessment of bioactivity suggests that varying the N content may allow tailoring of the level of bioactivity of these glasses.

1. Introduction

Bioglass® was invented by Hench in 1969 following his efforts to find a material that would bond to living bone [1–4]. At that time, implant materials such as metals and polymers were "bioinert" and elicited a fibrous capsular response at the implant-tissue interface rather than forming a stable interface or bond. It was discovered that Bioglass® 45S5 of composition (in mol%): 46.1% SiO_2, 24.4% Na_2O, 26.9% CaO and 2.6% P_2O_5, bonded with bone rapidly, did not form any interfacial scar tissue isolating it from the host femoral bone and also stimulated bone growth away from the bone-implant interface. Instead the glass formed a bond so strong that it could not be removed from the implant site [5]. 45S5 signifies that the glass contains 45 wt.% SiO_2 and 5 is the ratio of Ca:P.

Bioglass® is known to bond to bone in the body through a sequence of surface reactions [4–7] with initial rapid release of soluble ionic species (Na^+, Ca^{2+}) from the glass into the interfacial solution. A high surface area hydrated silica and polycrystalline hydroxyl-carbonate apatite (HCA) bi-layer is formed on the glass surface within hours. The reaction layers enhance subsequent adsorption and desorption of growth factors and greatly decrease the length of time macrophages are required to prepare the implant site for tissue repair. The HCA layer is similar to the mineral content of bone and the final stage of the process is crystallisation of the HCA which interacts with collagen fibrils so integrating with the host bone. Application of Bioglass® 45S5 particles to bone defects resulted in new bone growth during the first few weeks after surgery [8].

Since the first investigations on Bioglass®, other bioactive glasses within a certain compositional range containing SiO_2, Na_2O, CaO and P_2O_5 were also found [9] that could be used as materials to repair, replace, or augment parts of the skeletal system promoting beneficial tissue response, encouraging new tissue formation and involving interactions of cells with the materials [3]. The rate of bone bonding depends upon the composition of the material [2–4]. There were three key compositional features to these bioactive glasses that distinguished them from traditional Na_2O–CaO–SiO_2 glasses; they had: (1) less than 60 mol% SiO_2, (2) high Na_2O and CaO contents and (3) high CaO:P_2O_5 ratio. This made the surface highly reactive when exposed to an aqueous medium. Glass compositions with the fastest rates of bone bonding also bonded to soft tissues [10].

Bone in-growth was also found to occur in a similar way for phosphate-free bioactive Na_2O–CaO–SiO_2 glass particles [11].

* Corresponding author: Fax: +353 61 338172.
E-mail address: stuart.hampshire@ul.ie (S. Hampshire).

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Other studies of the effects of composition of glasses in the P-free Na_2O–CaO–SiO_2 system on bioactivity have shown that potential bioactive glasses have compositions in the range (mol.%): 42–55% SiO_2:13.5–48% CaO:10–35% Na_2O [12–14]. At the lower content of silica, bioactivity is similar to that for Bioglass 45S5 with apatite forming after 24 h whereas as silica content increases up to 55 mol.%, apatite formation occurs after 48–60 h.

The low mechanical strength and inherent brittleness of these bioactive glasses restricted their use to non load-bearing applications [3] such as ossicles in the middle ear [15] and various maxillo-facial applications [16,17]. One way to increase strength of glasses is to introduce nitrogen into the silicate network [18,19]. It has been shown that when nitrogen replaces oxygen in silicate glasses, glass transition temperature, elastic modulus and hardness increase linearly with nitrogen content [20,21]. This is because N creates extra cross-linking of the glass network and so may be viewed as a network forming anion taking into account that the effects of nitrogen and modifiers on glass properties are independent [22]. Mechanical properties have been shown to increase when nitrogen is incorporated into a Na–Ca–Si bioactive glass composition [23]. Oxynitride glass-ceramics have also been shown to exhibit potential bioactivity [24].

When CaF_2 is substituted for CaO in bioactive glasses for use in dental applications, glass dissolution increases with F content [25] and if the P_2O_5 content is high, fluoroapatite is formed [26].

When CaF_2 is added to various oxynitride glasses, glass melting temperature decreases making it easier for preparation and the amount of nitrogen that can be dissolved into the glass increases[27,28]. Elastic modulus and microhardness increase as oxygen is substituted by nitrogen but these properties are not affected by the presence of fluorine [29,30].

In the present work, a bioactive glass in the Na_2O–CaO–SiO_2 system has been used as a base glass and the effects of substituting nitrogen for oxygen and further substitution of CaF_2 for CaO on glass structure, thermal and mechanical properties and bioactivity have been investigated.

2. Materials and methods

2.1. Glass Synthesis

Based on previous investigations of glass melting and bioactivity by some of the present authors [13,14], a base oxide glass was chosen with composition (mole%): 55SiO_2-13.5CaO-31.5Na_2O. Synthesis was carried out by mixing and melting appropriate amounts of carbonate precursors, Na_2CO_3 (Merck, purity 99.9%) and $CaCO_3$ (Chimie-Plus-Laboratoire, 99%) with SiO_2 (Merck, pure quartz) in a platinum crucible at 1450 °C in air for 4 h.

Oxynitride glasses were then prepared by adding silicon nitride to give glasses with the following compositions (mole%): (55-3x)SiO_2-13.5CaO-31.5Na_2O-xSi_3N_4 where $x = 0$ (base oxide), 1–4. Glass compositions are designed so that cation ratios are kept constant and therefore N:O ratio is the only compositional variable which could affect structure and properties of the glasses.

The oxide base glass was milled and mixed with varying amounts of silicon nitride powder (UBE, Industries, min. purity 99.9%) to prepare 10 g samples. Mixing was carried out in a glass dish using a magnetic stirrer in 50 ml isopropanol and then the alcohol evaporated using a hot plate. The silica present on the surface of the silicon nitride particles was taken into account in calculating the amount of Si_3N_4 required for the composition.

The powder was pressed under a pressure of 300 MPa to form a compact of 10 mm height and 26 mm diameter which was melted in a boron nitride lined graphite crucible in a vertical tube furnace under flowing high purity N_2 at 1400 °C for 15 min, after which the crucible was withdrawn rapidly from the hot zone. The glass obtained was then annealed to eliminate stresses just below its glass transition temperature for 6 h prior to slow cooling to ambient.

The effects of substituting CaF_2 for CaO on the structure and properties of these glasses was investigated by peparing a further series of compositions (mole%) as follows: (55-3x)SiO_2-8.5CaO-5CaF_2-31.5Na_2O-xSi_3N_4 with x varying from 0 to 4. In this series of oxyfluoronitride glasses, the Na:Ca ratio is constant. With addition of CaF_2 (Carlo Erba, 98%), the base oxyfluoride glass was melted in a platinum crucible at 1350 °C for 30 mins, the shorter time avoiding any loss of fluorine which also lowers the melting temperature of the oxide glass. Oxyfluoronitride glasses were then prepared as outlined above for the oxynitride glasses. Glass compositions in atomic % of Si, Ca, Na, O, F and N are given in Table 1 for the oxynitride (marked GNx) series and in Table 3 for the oxyfluoronitride (GFNx) series.

2.2. Characterisation of glasses

In order to determine if the glasses were completely amorphous, samples were analyzed using X-ray diffraction (XRD) (PanAlytical X-ray diffractometer, The Netherlands) with monochromated CuKα (λ = 1.54056 Å) radiation over a range of 2θ of 20–80° with a speed of 2.4°/min. Data was analyzed using X'pert Quantify software.

The glass samples were embedded in epoxy resin and polished using SiC papers down to 0.25 μm to provide a completely flat surface. Nitrogen analysis was carried out using wavelength dispersive spectroscopy (WDS) and a Cameca SX100 electron probe microanalyser (EPMA) at 15 kV and 200 nA. A PC2 (Ni/C) crystal was used to detect the Kα X-rays. BN was used as a standard. 10 measurements were performed on each glass to assess nitrogen homogeneity and to determine the average nitrogen content. The background noise used for the calculation of the N Kα peak height was measured on a glass without N. The relative Si, Ca, Na, O and F contents were measured on polished samples using scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDS) (Noran System Six-type), the analyzed area being about 1 μm^3.

The embedded glass samples were examined by Scanning Electron Microscopy (SEM) to analyze homogeneity and the presence of bubbles. Glasses without N, containing F, were free of bubbles but those without F contained some fine residual bubbles from loss of CO_2 during melting. F reduces melting temperatures and viscosities thus allowing easier gas evolution during melting. Glasses containing N always contained evidence of bubbles, both from CO_2 loss and from some loss of N, leaving macroporosity in the glasses. This has implications for further characterization of mechanical properties.

The density was measured using a Helium pycnometer. Glasses were crushed before density measurements so that any internal porosity (i.e. bubbles) did not affect the results.

Differential thermal analysis (DTA) was carried out (Setaram Setsys 16/18 simultaneous TG/DTA analyzer) in order to determine the glass transition temperature, Tg. Samples of 50 mg were heated at 10 °C/min up to 1200 °C in alumina crucibles in a flowing nitrogen atmosphere. Al_2O_3 was used as the reference material. Tg is taken as the inflexion point of the endothermic drift on the DTA curve.

2.3. Structural analysis of glasses by MAS-NMR

A Bruker Avance 400 MHz (9.4 T) spectrometer at a Larmor frequency of 79.5 MHz was used to obtain ^{29}Si MAS-NMR spectra with 320 to 1408 scans and a pulse length of 5 μs (π/2) and a relaxation delay of 180 s. The samples were spun at the magic angle