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Design, selection and characterization of novel glasses and glass-ceramics for use in prosthetic applications

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Abstract

The objective of this work is to design and characterize crystallizable silicate and borosilicate compositions for use in the production of smart, unconventional coatings on bioceramic implants. The concept behind this research is the development of a three-layer implantable system (joint prosthesis) comprising a ceramic substrate, a glass-derived trabecular coating and a glass-ceramic interlayer that joins the other two elements together. The outer porous coating should exhibit bone-like architecture, high mechanical strength and good bioactivity to bond to bone, whereas the interlayer should be chemically stable in biological fluids to avoid detachment between the joined parts. Glasses in the SiO_2–Na_2O–K_2O–CaO–P_2O_5–B_2O_3–Al_2O_3 system have been synthesized by a melting route and thermally treated to obtain glass-ceramic products. A selection of potentially suitable materials for the trabecular coating and interlayer was carried out on the basis of thermal properties and tendency to dissolve in simulated body fluids (SBF) so that the integrity of the final device might be maintained upon implantation. The glass selected for the trabecular coating was processed by sponge replica method to produce glass-ceramic scaffolds, in order to evaluate the material properties and performance in an embodiment plausibly close to the final application. The mechanical properties of the porous glass-ceramic, which mimicked the 3-D pore architecture of cancellous bone, were adequate for load-bearing applications such as joint prostheses. Formation of a surface apatite layer on scaffold struts upon soaking in SBF confirmed the excellent bioactivity of the material, which is a key precondition for in vivo osteointegration.

Keywords: D. Glass; D. Glass-ceramic; Bioactivity; Scaffold: Coating

1. Introduction

Bioactive glasses and glass-ceramics are a special set of bioceramics that are able to bond to bone and stimulate new bone growth, which make them ideal candidates for tissue engineering applications [1]. The first and best known bioactive glass is 45S5 Bioglass® (weight composition: 45% SiO_2, 24.5% CaO, 24.5% Na_2O, 6% P_2O_5), invented by Hench and co-workers at the end of the 1960s [2]. Since then, a great number of bioactive glass and glass-ceramic formulations have been developed and studied in order to tune their bioactivity and to adjust their properties for specific applications [3–8]. Nowadays, most bioactive glasses and glass-ceramics are based on mixtures of oxides in the SiO_2–CaO–MgO–Na_2O–K_2O–P_2O_5 system; these SiO_2-based compositions differ from classical silica-soda-lime ones used in everyday applications for the lower percentage of silica, the higher content of alkaline oxides, the typical absence (or very low content) of alumina and, often, for the presence of phosphorus oxide. In the last few years B_2O_3- and P_2O_5-based biomedical glasses, with high surface reactivity and resorption kinetics, have also been developed as novel degradable biomaterials for tissue engineering [4,5].

The strong bond between bioactive glasses/glass-ceramics and living bone is due to the formation of a biologically active

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layer of hydroxyapatite (HA), which grows on the implant surface upon immersion in biological environment [2]. Hench proposed a 12-stage model to describe the interfacial reactions between body fluids and material implanted; the first five steps occur in a few hours and include ionic reactions between the glass and the environment, while the subsequent stages also involve a role of cells and proteins [9]. Initially, alkaline and alkaline earth ions of the glass are exchanged with the environmental H^+ ions (from body fluids), the Si–O–Si bonds are hydrolyzed and, hence, new Si–OH bonds form at the surface. Subsequently, the Si–OH bonds condense resulting in the formation of a silica gel layer. Finally, Ca^{2+} and $(PO_4)^{3-}$ ions migrate to the glass surface through the silica-rich layer and from the surrounding fluid, thus forming a $CaO–P_2O_5$-rich film that progressively crystallizes in HA.

Recently, an additional advantage of silicate bioactive glasses has been disclosed: ion dissolution products released after implantation are thought to elicit specific responses, such as the growth and osteogenic differentiation of primary osteoblasts, the up-regulation and activation of some families of genes in osteoprogenitor cells, the induction of an anti-bacterial effect and the stimulation of angiogenesis [10].

The composition of glasses influences their interfacial reactions and hence their bioactivity; the possibility of achieving a bioactive fixation is closely connected to the formation of a HA layer, which, in turn, can develop only if the glass surface can create Si–OH bonds when immersed in biological fluids. Glasses with silica contents greater than 60 wt% were observed to induce the formation of a fibrous tissue, whereas a low bioactivity was observed for glasses with a percentage of silica between 55 and 60 wt% [11]. Finally, glasses with silica content below 55 wt% usually show high bioactivity. On the other hand, the glass ability to bond to bone can be completely inhibited by the addition of stabilizers, such as Al_2O_3, which reduce the glass solubility [12].

During the last 30 years, bioactive glasses and glass-ceramics have been clinically employed mainly as bulk materials in non-load-bearing situations, such as middle ear bone implants [13]. The applications of bioactive glasses – and bioceramics in general – as implantable biomaterials are limited by their poor mechanical properties and intrinsic brittleness. In order to overcome this drawback, bioceramics can be successfully used as coatings on tougher non-bioactive substrates to improve the bone-implant adhesion [14]. For example, good results have been reported for plasma-sprayed HA coatings in terms of both implant fixation and bone tissue ingrowth at the bone/implant interface, but concerns still remain about the long-term stability of such coatings in body environment [15].

In spite of their potentiality, bioactive glass and glass-ceramic coatings are still rarely applied. This presents the opportunity for further scientific research, especially on the method of coating application. There is interest in both improving the well-known techniques (e.g. classical enameling [16]) and developing new, more effective strategies (e.g. electrophoretic deposition [17] or airbrush spraying [18]) to produce reliable coatings on medical devices.

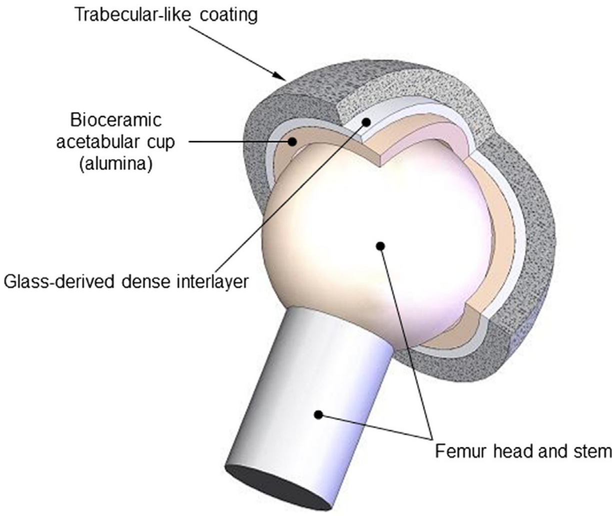

Fig. 1. Schematic drawing of the innovative full-ceramic acetabular cup for hip joint prosthesis proposed by the authors in the framework of the EU-funded project “MATCh”, during which the research work presented in this article was carried out.

Table 1
Full set of glass compositions designed in this work; the CTEs were estimated by making use of the Priven2000 program implemented on SciGlass software.

Glass name	Oxide composition (mol%)							CTE ($\times 10^{-6}$ °C^{-1})
	SiO_2	CaO	Na_2O	Al_2O_3	K_2O	P_2O_5	B_2O_3	
S57A7	57	30	6	7	–	–	–	8.28
S47B11	47	20	10	–	4	8	11	8.69
S50B2	50	35	7	–	–	6	2	8.68
S50B8	50	35	7	–	–	–	8	8.79
S48.5B4	48.5	30	11	0.5	–	6	4	8.90

The research work reported in this article was carried out in the framework of the European project “MATCh” (Monoblock acetabular cup with trabecular-like coating) that aims at exploring the feasibility of an innovative single-piece full-ceramic acetabular cup for hip joint prosthesis [19]. As shown in Fig. 1, the bioinert ceramic substrate (alumina cup) articulates directly with the (prosthetic) femur head, the bioactive trabecular coating aims at promoting implant osteointegration to the patient’s pelvic bone, and a glass-derived interlayer joins the adjacent elements together. The fabrication of such a device is a complex task that requires first of all the development of suitable glass/glass-ceramic compositions to be subsequently employed in the manufacturing of the coatings.

2. Materials and methods

2.1. Starting glasses

Different experimental glass formulations were designed and produced by a melting–quenching route. The names and formulations of the glasses are reported in Table 1. All of the