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Feasibility of glass–ceramic coatings on alumina prosthetic implants by airbrush spraying method

Francesco Baino*, Chiara Vitale-Brovarone

Institute of Materials Physics and Engineering, Applied Science and Technology Department, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy

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Abstract

This work explores the feasibility of glass-derived coatings (SiO_2–CaO–Na_2O–Al_2O_3 system) on bioceramic devices of complex shape by a layer-wise slurry deposition using an airbrush spray gun. Specifically, glass–ceramic coatings with thickness in the 50–500 μm range were prepared on alumina curved substrates by airbrush spraying of glass-based aqueous suspensions followed by sintering. Investigations by scanning electron microscopy and micro-computed tomography revealed that, under appropriate optimization of slurry composition and spraying cycles, this technique is suitable to manufacture homogeneous and continuous coatings on model curved ceramic surfaces. It was observed that neither cracking nor delamination occurred at the interface between coating and substrate. Ad-hoc tensile tests were carried out by properly adapting the relevant ASTM standard to the specific case (curved geometry); the coating adhesion strength was found adequate (about 25 MPa) for biomedical applications. A simple model describing the relationship between coating thickness and number of spraying cycles was also developed and proposed as a useful tool to improve the design and manufacturing of bioceramic coatings.

Keywords: Coating; Bioceramic; Deposition; Joint prosthesis

1. Introduction

Biological fixation is defined as the process by which prosthetic components become firmly bonded to host bone by tissue on-grow or in-growth without the use of bone cement [1]. In this regard, the deposition of a bioactive coating on the surface of an implant has been shown to be a smart strategy to improve implant fixation to the surrounding tissue [2]. Over the last 25 years, a number of methods have been experimented to produce bioceramic coatings, including gravity-controlled deposition [3–5], sol–gel dipping [6], spin coating [7], plasma spraying [8], sputtering [9] and electrophoretic deposition [10]. Plasma sprayed hydroxyapatite (HA) coatings on metal implants were introduced in the mid 1980s, received FDA approval and were demonstrated to promote stronger bonding to bone in comparison with the loosely adherent layer of fibrous tissue at the implant interface in other cementless fixations; however, some controversies about their clinical use still linger on. The control of variables in plasma spraying is a complex issue and small changes of processing parameters can highly affect the properties of the final coating; furthermore, the high temperatures required by the process can induce HA decomposition into soluble calcium phosphate compounds undergoing undesired fast resorption in vivo [8,9,11]. Bioactive glasses have been proposed as a promising alternative to HA in the manufacturing of coatings on prosthetic implants due to their unique versatility in terms of processing and in vivo performance [4,6,7,12], which, in principle, can be finely adjusted by controlling their composition [13–15]. Although the literature has demonstrated that it is possible to deposit glass layers that retain bioactivity, a recurrent problem is the generation of large thermal stresses during processing that can cause cracking or delamination of the coating.

*Corresponding author. Tel.: +39 11 090 4668; fax: +39 11 090 4624.
E-mail address: francesco.baino@polito.it (F. Baino).

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The solution to the problem requires the development of coating procedures and bioactive glasses/glass–ceramics with adequate thermal expansion coefficients and softening points.

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 to explore the feasibility of an innovative single-piece acetabular cup for hip joint prosthesis [16]. As depicted in Fig. 1a, this bioceramic implant is constituted by three elements, i.e. a bioinert ceramic substrate that articulates directly with the (prosthetic) femur head, a bioactive trabecular coating (scaffold) that aims to promote implant osteointegration to the patient's pelvic bone, and a glass-derived interlayer with the aim of improving the adhesion between alumina substrate (cup) and trabecular coating (scaffold). The fabrication of such a device is a complex task that requires the development of suitable strategies to deposit the dense coating (interlayer) on the curved bioceramic substrate and, subsequently, to produce the trabecular layer in the form of a hemispherical shell. The present work addresses to the first of these two challenges, investigating the feasibility of a glass-derived coating by airbrush spraying of SiO_2–CaO–Na_2O–Al_2O_3 (SCNA) glass powder suspensions followed by thermal treatment. Airbrush spraying of ceramic slurries is a versatile method that allows the coating of substrates having complex shape with an adequate control of coating thickness [17–20]; however, there is a paucity of studies about its use in the field of bioceramics. Very recently, Pardun et al. reported the characterization of wet nanopowder-sprayed zirconia/HA composite coatings on dental implants (screws) [21]. To the best of the authors' knowledge, the use of airbrush spraying on orthopaedic implants has been never documented and, accordingly, the present article represents a pilot study. The challenge behind this work, schematically illustrated in Fig. 1b, was to develop a reproducible and relatively easy method to coat ceramic prosthetic components having curved shape with a glass layer [22].

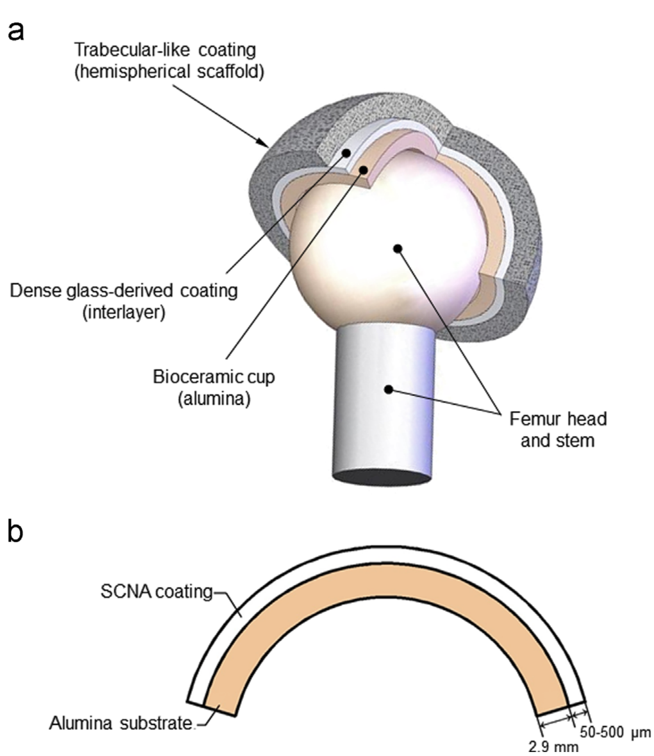

Fig. 1. The concepts behind the research work presented in this article: (a) drawing of the innovative acetabular cup for hip joint prosthesis proposed by the authors in the framework of the EU-funded project "MATCh"; (b) schematic picture of the SCNA-coated curved bioceramic substrate investigated in this article.

2. Materials and methods

2.1. Samples preparation

The model curved substrates to be coated were obtained by cutting high-purity (> 99 wt%) alumina crucibles in sectors (length of the external arc: 40 mm; external radius: 19 mm; wall thickness: 2.9 mm; width: 10 mm) using a diamond blade (Accutom 5, Struers). Before treatment the curved alumina substrates were washed with deionized water and acetone; the surface of the specimens was not abraded.

The material used for coating preparation was a silicate quaternary glass with the following molar composition: $57SiO_2$–34CaO–$6Na_2O$–$3Al_2O_3$ (SCNA) [22,23]. The glass reagents (high-purity powders of SiO_2, $CaCO_3$, Na_2CO_3 and Al_2O_3 purchased from Sigma-Aldrich) were molten in a platinum crucible at 1550 °C for 1 h in air; the melt was quenched in cold water to obtain a frit, that was subsequently ground by a 6-balls zirconia milling machine and sieved (stainless steel sieves, Giuliani Technologies Srl) to a final particle size below 32 μm. Preliminary experiments showed that the use of glass powder with higher particle size for slurry preparation resulted in an enhanced risk of blocking the nozzle of the airbrush system.

Different SCNA-based slurries were produced from SCNA powder, water and, optionally, additives as reported in Table 1. Poly(vinyl alcohol) (PVA) was used as a binder; glycerine was introduced as an additive in the attempt to ensure a more uniform drying. All slurries were prepared under continuous magnetic stirring at 300 rpm. As to slurries D and E, glass powder was added after PVA hydrolysis. Glycerine was introduced into the slurries C and E together with glass powder. After the addition of glass powder, the slurries were always stirred at 300 rpm for 15 min to ensure homogeneity and then the layer-wise slurry deposition on the alumina

Table 1
Compositions and labelling of the slurries.

Slurry	Composition (wt%)			
	SCNA powder	Water	PVA	Glycerine
A	50	50	–	–
B	30	70	–	–
C	30	64	–	6
D	30	64	6	–
E	50	40	3	7