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Bonding strength of glass-ceramic trabecular-like coatings to ceramic substrates for prosthetic applications

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ABSTRACT

A new approach based on the concepts of quantized fracture mechanics (QFM) is presented and discussed in this paper to estimate the bonding strength of trabecular-like coatings, i.e. glass-ceramic scaffolds mimicking the architecture of cancellous bone, to ceramic substrates. The innovative application of glass-derived scaffolds as trabecular-like coatings is proposed in order to enhance the osteointegration of prosthetic ceramic devices. The scaffolds, prepared by polymeric sponge replication, are joined to alumina substrates by a dense glass-ceramic coating (interlayer) and the so-obtained 3-layer constructs are investigated from micro-structural, morphological and mechanical viewpoints. In particular, the fracture strengths of three different crack propagation modes, i.e. glass-derived scaffold fracture, interface delamination or mixed fracture, are predicted in agreement with those of experimental mechanical tests. The approach proposed in this work could have interesting applications towards an ever more rational design of bone tissue engineering biomaterials and coatings, in view of the optimization of their mechanical properties for making them actually suitable for clinical applications.

1. Introduction

Biological materials are renowned for their unique combination of outstanding mechanical properties and smart microstructure. For instance, cancellous bone is a highly porous natural material with excellent stiffness and strength (typically 2–12 MPa in compression [1]), and these remarkable mechanical properties are attributed to its anisotropic structure possessing optimized strength-to-density and stiffness-to-density ratios [2,3]. Such features provide interesting cues on how to develop new scaffolds to mirror nature's efficient materials from architectural/mechanical viewpoints and to substitute natural tissue functions, which is one of the greatest challenges in modern regenerative medicine.

Architectural design of bone tissue engineering scaffolds is a complex issue because, from a structural viewpoint, two competing requirements have to be basically fulfilled: on the one hand, the scaffold should exhibit a sufficient mechanical competence, i.e. strength and stiffness comparable to those of natural bone, but, on the other hand, it should allow new bone in-growth after its implantation into the human body [4–6]. These requirements typically involve a porosity above 50 vol.% to allow blood vessels supply, cells migration and new tissue in-growth, as well as the presence of macropores in the 100–500 μm range [4]. These features compete with the mechanical requirements, which are further discriminated if the scaffold is resorbable, as its integrity progressively decreases over time during the contact with biological fluids [7]. Furthermore, another crucial issue concerns the scaffold ability to promote bone regeneration and angiogenesis; in this sense, bioactive glasses have a great potential and constitute a highly valuable class of biomaterials for tissue engineering [8,9].

The choice of a proper method of fabrication plays a key role in designing scaffolds structures on the basis of the final clinical use (e.g. load-bearing needs). At present, there is a great variety of methods for scaffolds processing that lead to porous body with different structures, architectures, pore sizes and interconnections, as well as different properties *in vitro* and *in vivo*, but, at present, a "gold standard" method for scaffolding has not been defined yet [6,10,11]. Sponge replication is a promising candidate for scaffolds fabrication due to its relative easiness of application, effectiveness, versatility and low cost; it was demonstrated that, by carefully setting the processing parameters [12,13] and/or by producing pore gradient structures [14], high-strength 3-D scaffolds closely mimicking human bone architecture can be successfully obtained. Some research groups investigated in detail the porosity–strength relationship in the attempt at optimizing the architectural properties of scaffolds, ideally at a pre-processing stage. Gerhardt and Boccaccini [15] showed that linear interpolation usually provides an acceptable approximation of the negative relationship

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between porosity and compressive strength of bioceramic scaffolds. Baino et al. [16] proposed simple quadratic models correlating the theoretical porosity, established at the design stage, with the real pore content and compressive strength of final glass-ceramic sintered scaffolds. Hellmich and co-workers [17–19] developed micromechanical models of porous ceramics and established non-linear strength–porosity relations that were in good accordance with experimental findings.

The keen attention of the scientific community towards the potential of bioactive glass-derived scaffolds for bone tissue engineering applications has been demonstrated by the dramatically increasing number of articles published since 2000 in the field, including four comprehensive reviews only in the last couple of years [6,10,20,21].

In a recently-deposited patent [22], the authors proposed the innovative use of glass and glass–ceramic scaffolds as bioactive trabecular-like coatings on prosthetic devices with the aim to enhance the implant osteointegration (Fig. 1). The feasibility of such an application was demonstrated and discussed in a preliminary work by Vitale-Brovarone et al. [23]; in the present work, the authors developed a mechanical model based on quantized fracture mechanics (QFM) [24–26] to describe the bonding strength at the trabecular coating (scaffold)/ceramic substrate interface.

The use of QFM for modeling the mechanical behavior of glass-derived porous coatings represents a new approach. Linear elastic fracture mechanics (LEFM) was often used in the past to describe the mechanical behavior of pore-free biomedical materials; for instance, Ritter et al. [27] employed LEFM to obtain lifetime predictions for bioglass-coated alumina implants. The mechanical behavior of porous ceramic scaffolds has been more recently described either by semi-empirical approaches based on data fitting [15,16] or through complex models based on continuum micro-mechanics [17–19]. However, all these works are based on the continuum, and therefore these methods are not suitable for the strength prediction of porous biomaterials without invoking often inaccurate homogenization techniques.

Differently from the above-mentioned methods and starting from the energy approach, Pugno and co-workers [24–26] developed QFM to treat fracture in discrete materials: comparison between the theory and the experimental results on several nanosystems, including carbon nanotubes and graphene, showed a very good agreement. Considering the case of porous scaffolds, characterized by an intrinsic structural discreteness, QFM has a unique advantage over LEFM and, in general, continuum theories.

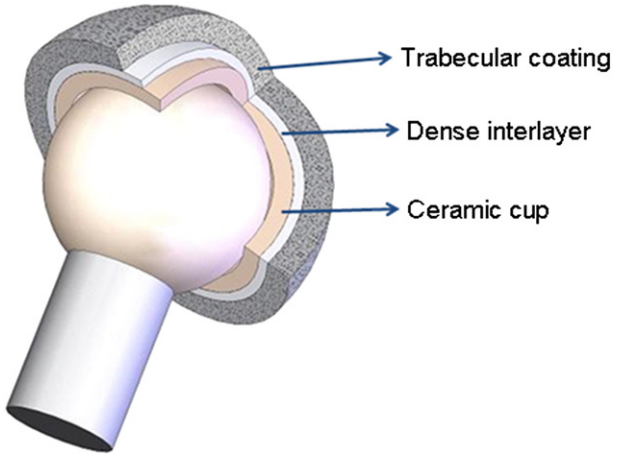

Fig. 1. Scheme of the innovative acetabular cup disclosed in the patent [22] deposited by the authors; this monoblock ceramic implant is constituted by three elements: (i) a bioinert ceramic substrate, that articulates directly with the (prosthetic) femur head; (ii) a bioactive trabecular coating, i.e. a glass-derived scaffold, that aims at promoting implant osteointegration to patient's pelvis bone; (iii) a glass-derived (pore-free or minimally porous) interlayer, able to improve the adhesion between alumina substrate (cup) and trabecular coating (scaffold). (Figure reproduced from Vitale-Brovarone et al. [23] with permission by Springer).

In this paper, in order to properly measure the bonding strength between trabecular coating and ceramic substrate from a quantitative viewpoint, three sets of experiments were performed and the results were compared with QFM predictions. By the fitting between experimental data and theoretical prediction, the strain energy release rate was obtained; then, it was employed to investigate the designable bonding strength influence by two dimensionless quantities.

It is worth mentioning that previous studies [28–30] on the bonding strength of biomaterials were mainly experimental, having a "descriptive" goal, and they concluded that, in general, the bonding strength was weak. On the contrary, the present model and method could quantitatively improve our ability not only in measuring but also in "designing" the bonding strength of biomaterials, making them more suitable for clinic applications in bone tissue engineering.

2. Experimental

2.1. Samples preparation

The innovative acetabular component shown in Fig. 1, wherein the trabecular coating (scaffold) plays a key role, was studied and modeled in a simplified flat geometry. These 3-layer plane samples, hereafter referred to as "complete plane samples", were fabricated according to a processing schedule described elsewhere by Vitale-Brovarone et al. [23]. The 6-stage preparation cycle is briefly summarized in Table 1; for better reader's understanding, the Stages 1–5 are also schematically depicted in Fig. 2.

Furthermore, other two kinds of samples, i.e. SCNA-derived dense coatings on alumina (Stages 1–3 and 6) and SCNA-derived scaffolds (Stages 2, 4 and 6), were prepared and mechanically tested to obtain key mechanical parameters used in the development of the QFM-based model (Section 3).

2.2. Samples characterization

Wide-angle (2θ within 10–70°) X-ray diffraction (XRD) by using a X'Pert diffractometer (working conditions: 40 kV and 30 mA; camera with Bragg-Brentano geometry, Cu Kα incident radiation, incident wavelength $\lambda = 1.5405$ Å, step size $\Delta(2\theta) = 0.02°$, fixed counting time of 1 s per step) was performed on SCNA before and after treatment at

Table 1
Cycle of fabrication of the samples investigated in this work.

Stage	Description
1	High-purity alumina (>99.5%) 1-mm thick sheets (Goodfellow, Cambridge, UK) were cut by means of a rotating diamond wheel (Accutom 5 Machine, Struers) to obtain squared 10 mm × 10 mm plates.
2	A silicate glass (SCNA; molar composition: $57SiO_2$–$34CaO$–$6Na_2O$–$3Al_2O_3$) was prepared by melting the raw products (SiO_2, purity 99.0%, Sigma-Aldrich; $CaCO_3$, purity 99.0%, Sigma-Aldrich; Na_2CO_3, purity 99.5%, Sigma-Aldrich; Al_2O_3, purity 99.9%, Alfa-Aesar) in a platinum crucible at 1500 °C for 1 h in air and then by quenching the melt in cold water to obtain a "frit", that was subsequently ground by a 6-ball zirconia milling and eventually sieved to obtain glass particles below 32 μm.
3	SCNA "green" coatings on the alumina plates were prepared by gravity-guided deposition after suspending a proper amount of glass particles (0.7 g) in ethanol (beaker diameter: 56 mm) to finally obtain a 100-μm thick layer.
4	Commercial open-cell polyurethane sponge (apparent density ~20 kg m^{-3}) was cut in 4-mm thick blocks to be impregnated with a water-based SCNA-containing slurry (the glass particles were prepared at the end of Stage 2), according to an optimized schedule proposed for sponge replication method [12].
5	SCNA-impregnated sponge (prepared in Stage 4) was stacked on the "green" SCNA coating (prepared in Stage 3).
6	The whole system was thermally treated in air at 1000 °C for 3 h (heating rate 5 °C min^{-1}; cooling rate 10 °C min^{-1}) to allow the burning-out of the polymer template and the glass powders sintering.