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Ceramics International 39 (2013) 6533–6542

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Micro-porous calcium phosphate coatings on load-bearing zirconia substrate: Processing, property and application

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Received 7 October 2012; received in revised form 25 January 2013; accepted 25 January 2013
Available online 8 February 2013

Abstract

This study presents the design, processing, properties and potential applications of a novel layered bio-ceramic composites consisting of three different micro-porous calcium phosphate coatings on strong zirconia cores manufactured using a recently developed slip coating-deposition and coating-substrate co-sintering technique. Detailed microstructures of the three graded micro-porous calcium phosphate coatings, and the coating/substrate interface have been investigated. Also, the flexural strength of the bio-ceramic composite and the bonding state between the coatings and zirconia substrate have been characterized. A preliminary and limited in vitro cell test indicates that the new scaffold composite has no cytotoxicity to the fibroblasts which can attach, proliferate and grow on the coating surfaces. Because of the combination of bio-function and strength, such layered load-bearing bio-ceramic composites are a potential candidate for large-scale head bone repairs.

Keywords: A. Sintering; B. Microstructure; C. Strength; E. Biomedical application; Apatite-zirconia composite

1. Introduction

The intended use of artificial bio-functional bone scaffolds is for implantation in critical size hard tissue defects which in some cases need to sustain mechanical loading [1]. The ceramic scaffolds have drawn significant interest in the past years and experimental data shows that hydroxyapatite/tri-calcium phosphate (HA/TCP) scaffolds structures with open pores larger than 100 μm are bio-resorbable and osteoconductive [2–5]. However, such scaffolds can be used as implants/spacers mostly for small bone defect and light-load-bearing bone defect repairs, because of their inadequate mechanical performance, with a compressive strength in the range of 2–36 MPa [6]. Even the fully dense hydroxyapatite ceramic only exhibits a bending strength of 100 MPa.

A load bearing device provides mechanical stability at the time of implantation and, by gradually transferring the load to the bone, stimulates bone healing [1]. Significant efforts have been made to build load bearing scaffolds. Cesarano et al. [7] used a robocasting technique to produce a load bearing HA lattice scaffold with hierarchical porosity and the compressive strength similar to the cortical bone. Using double slip-casting method, Zhang et al. manufactured a strong HA scaffold with a bending strength of 73.3 MPa [8].

Because the bending strength of compact bones ranges from 50 MPa to 300 MPa [9] the immediate or heavy load-bearing capacity of calcium phosphate based scaffolds for large scale bone defects such as cranioplasty or mandibular recosntructions is obviously limited.

In addition to carrying the motion generated by muscle contractions, some clinical applications of rigid scaffolds require for these to provide physical protection of the organs they cover, as is the case of titanium plates (Fig. 1a) and scaffold-like meshes [10,11] used for cranioplasty defect repair as it is essential to preserve the brain safety.

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http://dx.doi.org/10.1016/j.ceramint.2013.01.086

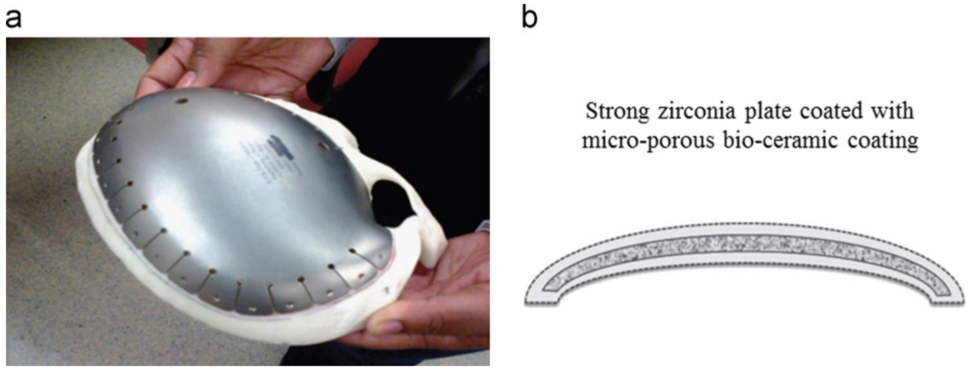

Fig. 1. (a) Commercial cranioplasty titanium plate used in Royal Perth Hospital [12]; (b) sketch of thick bio-ceramic coated zirconia based plate.

For such mechanical demanding environments, titanium is the current material of choice. For example, there are 15 commercial titanium cranioplasty custom plates available for clinic applications at Royal Perth Hospital in Western Australia [12].

The mechanical properties of titanium based metal implants are excellent, well documented and adequate for load bearing large scale bone replacement. The major shortcoming however, is the bio-inert behavior of titanium that lacks osteoconduction. A common method to improve the biological integration of an otherwise bio-inert material is to cover it with a bio-active coating. Various coating techniques and materials have been described [13–16] and amongst which calcium phosphate coated stem surfaces have shown excellent bone on-growth [17]. A common shortcoming of coated metal implants is the thickness and porosity of the coat which is often limited [13,15,16] and as such offers a reduced volumetric anchorage for bone in-growth.

An alternative to coated metal could be to use a strong thin ceramic plate on which a graded scaffold-like porous bio-ceramic coating is build. A sketch of such a composite is shown in Fig. 1b.

The scope of the present work is to study the feasibility of manufacturing a strong layered bio-ceramic composite consisting of a graded porous bio-active calcium phosphate coating bonded on load bearing zirconia substrate using a newly-developed slip coating deposition and coating/substrate co-sintering technique [18]. The hierarchical porous structure of the coating and coating/substrate interface were characterized and preliminary analyses of the bending strength and in vitro biocompatibility were completed to identify the suitability of the proposed composite as an alternative to titanium.

2. Materials and methods

2.1. Raw materials

The main starting materials employed in this study were yttria stabilized zirconia (3Y-TZP) (TZ-3Y E, <200 nm, Tosoh Co., Japan), hydroxyapatite (HA) (<200 nm, Sigma-Aldrich Co., USA), and alumina (α-Al_2O_3) (AKP50, purity $>99.99\%$, <300 nm, Sumitomo, Japan). Besides, dolapix (Aschimmer and Schwarz Gmbh, Germany) was used as dispersant, PVA solution (9 wt%) as binder, and distilled water as solvent. Polymethylmethacrylate (PMMA, Sigma Aldrich, USA) micro-beads (20–50 μm) and cooking potato starch powders with size of 1–20 μm were chosen as pore generators.

2.2. Construction of scaffold-like coating

Zirconia based substrate containing 30 vol% HA was formed through die-pressing and then pre-sintered at 900 °C. One surface of the substrate was covered with three layers (transition, middle and top layer) of coating using slip-coating deposition technique. The processing details required to obtain the substrate and of the deposition technique are presented in detail in our previous study [18]. In brief, green coatings and pre-sintered substrates are dried in wet air for 24 h and in dry air for another 24 h, then finally co-sintered at 1300 °C for 2 h. During its final sintering step, the HA incorporated in the substrate will further decompose to tri-calcium phosphate and generate micro-pores. These micro-pores are required for the coating deposition and its bonding onto substrate. Because the substrate is pre-sintered, it has a good water-absorption ability which will facilitate thicker coating deposition compared with applying slip/slurry coating on the fully sintered ceramic substrate. After the coating process, thermal and intrinsic residual stresses are generated inevitably [19] due to the significant mismatch of thermal expansion coefficient and Young's modulus of the coating and the substrate. These residual stresses may cause cracks and delamination of the interfaces in the scaffold [20,21]. A number of processing procedures are therefore employed to reduce the residual stresses and to obtain a crack free composite material. Firstly, the coating is deposited in a multilayered fashion with graded composition and porosity and it has been shown previously that this technique assist with reduction of residual stresses and achieving a delamination-free substrate/coating interface [18]. Additionally, because HA is added in the substrate and ZrO_2 in