Ceramics International 42 (2016) 15603–15609

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Calcium phosphate ceramics with continuously gradient macrochannels using three-dimensional extrusion of bilayered ceramic-camphene mixture/pure camphene feedrod

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ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form
24 June 2016
Accepted 2 July 2016
Available online 2 July 2016

Keywords:
Extrusion
Porous ceramics
Gradient pores
Biomedical applications

ABSTRACT

We herein demonstrate a novel, versatile approach to produce calcium phosphate (CaP) ceramics with continuously gradient macrochannels using three-dimensional extrusion of a bilayered ceramic-camphene mixture/pure camphene feedrod. In this technique, the pure camphene used as the upper part could be preferentially extruded because of the wall slip phenomenon. This enabled the formation of green filaments comprised of a camphene core surrounded by a ceramic/camphene shell, where the core/shell thickness ratio increased gradually as extrusion proceeded. CaP ceramics with continuously gradient macrochannels could be successfully produced by three-dimensionally depositing the extruded filaments layer-by-layer. With increasing the distance from the dense bottom layer, macrochannels created after the removal of the camphene cores via freeze-drying became larger, while the CaP walls became thinner. The local porosity could increase gradually and continuously from the dense bottom and reach up to ~72 vol%.

1. Introduction

Porous ceramics have been extensively used in diverse fields, for examples, as scaffolds for bone regeneration, components for thermal insulation and filters, and preforms for structural composites [1,2]. Fundamentally, the functions of porous ceramics are strongly affected not only by their porous structure (e.g., overall porosity, pore size, pore geometry, and pore interconnectivity), but also by the distribution of those pores. Thus, considerable effort has been made to locally tune the porous structure of porous materials for the creation of porosities and pore sizes which vary throughout a porous material. Materials featuring such gradient porous structures can have their functions tailored for specific applications [3]. For instance, gradient porous ceramics mimicking the architecture of natural bone comprised of a relatively dense outer layer and a highly porous core can provide excellent biomechanical functions with outstanding bone regeneration ability in vivo when used as bone scaffolds [4,5]. In particular, a porous core should have good interconnection between pores with sizes $> 100\ \mu m$ to provide a favorable environment for bone ingrowth into pores and controlled pore configuration to provide high mechanical strengths [1].

Thus far, a number of manufacturing techniques have been developed for the production of ceramics with a gradient porous structure, which include freeze casting [7–11], modified sponge replication method [12], multiple tape casting [6], and injection molding [5]. Meanwhile, solid freeform fabrication (SFF) techniques have the great ability to arbitrarily design the local porous structure of porous ceramics using computer aided design (CAD) data [13–19]. In addition, gradient porous ceramics can be produced by using porous templates that can be prepared by SFF techniques [20–22]. However, most research have been focused on the control over the distance between ceramic walls to achieve different porosities and pore sizes at local positions and little attention has been given to mimic the hierarchical gradient porous structures found in nature (e.g., bones, bamboos, and stems).

We herein propose a new strategy for the design and production of gradient porous ceramics with continuously gradient macrochannels using three-dimensional extrusion of a bilayered ceramic-camphene mixture/pure camphene feedrod, as shown in Fig. 1 (A–D). This innovative technique, whose basic concept was

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http://dx.doi.org/10.1016/j.ceramint.2016.07.013
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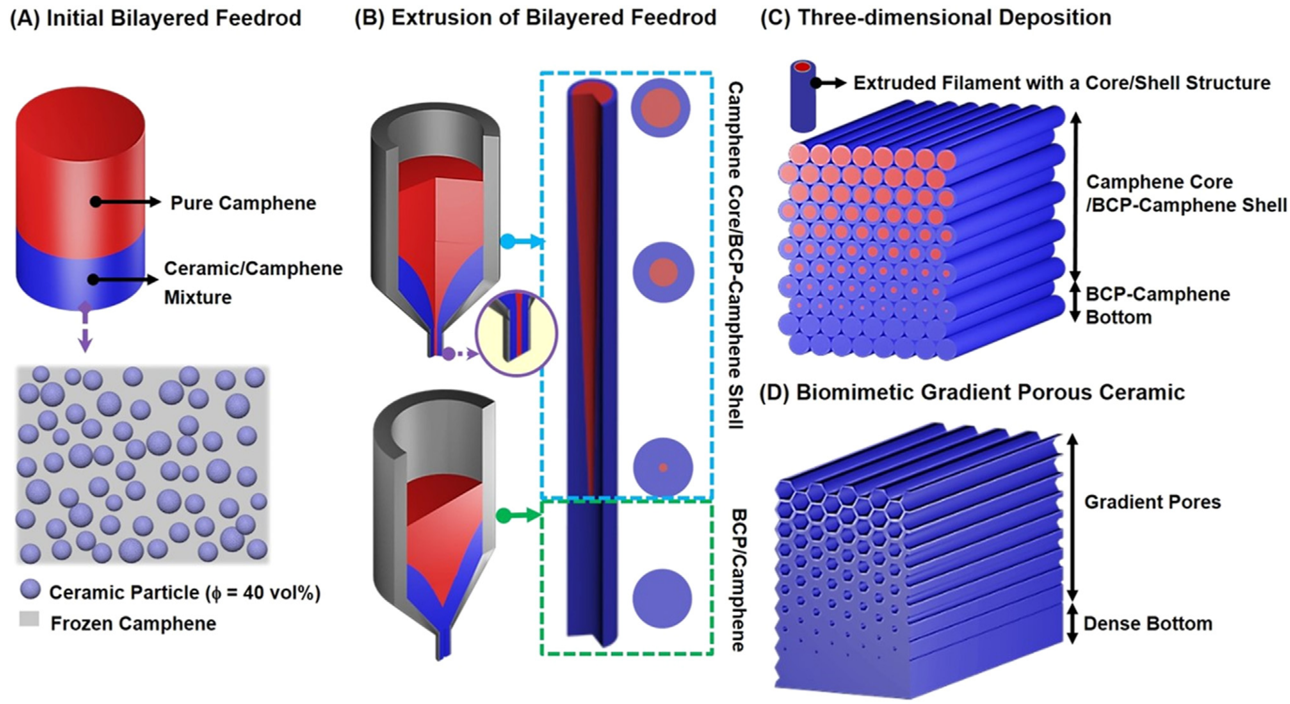

Fig. 1. Schematic diagrams of three-dimensional extrusion of a bilayered ceramic-camphene/pure camphene feedrod for the production of porous BCP ceramics with continuously gradient macrochannels: (A) the bilayered feedrod, the lower part being a BCP/camphene mixture and the upper part being pure camphene, (B) filaments with a unique core/shell structure, where the camphene core can be created through the preferential extrusion of pure camphene as the extrusion proceeds, (C) three-dimensional deposition of the extruded filaments, (D) porous BCP ceramic with a gradient porous region faced with a dense bottom, in which the local porosity and pore size increases gradually from the dense bottom.

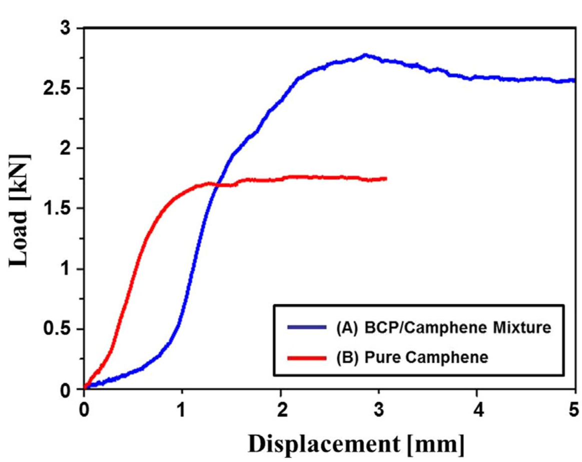

Fig. 2. Loads required to extrude (A) the BCP/camphene mixture and (B) the pure camphene through a reduction die with a diameter of 5 mm.

recently developed by our group [23], can make full use of the wall slip phenomenon generally observed in conventional extrusion processes - materials at the center of an extrusion die are extruded faster than their surroundings [24,25]. To accomplish this, we specially design a bilayered feedrod, the lower part being a ceramic/camphene mixture with 40 vol% ceramic content and the upper part being pure camphene (Fig. 1 (A)). This unique bilayered structure enables the pure camphene to be extruded faster than the ceramic/camphene mixture, thus resulting in the formation of green filaments comprised of a camphene core surrounded by a ceramic/camphene shell, while the core/shell thickness ratio can increase gradually as extrusion proceeds (Fig. 1 (B)). Subsequently, the extruded filaments can be deposited layer-by-layer in a 3-D pattern according to predetermined CAD data, creating a continuous gradient in the microstructure from the dense bottom to the porous top (Fig. 1 (C)). Macrochannels with various sizes can be readily produced by removing the camphene cores through freeze-drying, while dense ceramic walls can be created as a result of an extrusion of the ceramic/camphene mixture with a relatively high ceramic content of 40 vol% (Fig. 1 (D)). Calcium phosphate (CaP) with excellent biocompatibility and bioactivity in vitro and in vivo was employed as the ceramic because of its potential as a scaffold for bone regeneration [26,27]. To demonstrate the versatility of the present technique, several types of porous ceramics featuring porous structures were also produced.

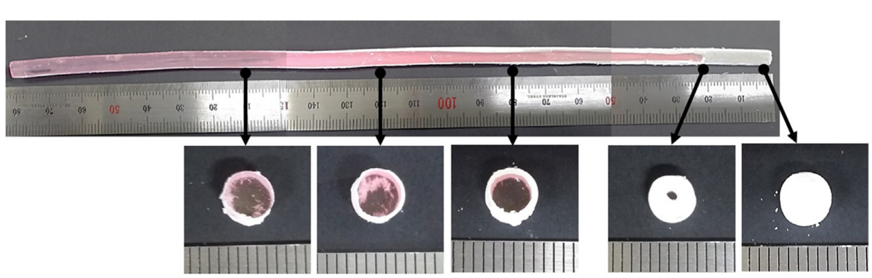

Fig. 3. Optical images of the BCP/camphene filament, where the camphene is dyed red for visualization. The bottom images show cross-sections of the filaments at different positions.