Journal of the Mechanical Behavior of Biomedical Materials 77 (2018) 225–233

Contents lists available at ScienceDirect

Journal of the Mechanical Behavior of Biomedical Materials

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

# Bone-like apatite growth on controllable macroporous titanium scaffolds coated with microporous titania

Xi Rao[a,*], Jing Li[a], Xue Feng[b], Chenglin Chu[c]

[a] *Faculty of Materials and Energy, Southwest University, Chongqing 400715, China*
[b] *Department of Clinical Laboratory, University-Town Hospital of Chongqing Medical University, Chongqing 401331, China*
[c] *School of Materials Science and Engineering and Jiangsu Key Laboratory for Advanced Metallic Materials, Southeast University, Nanjing 211189, China*

## ARTICLE INFO

*Keywords:*
Cancellous bone
Macroporous Ti scaffold
Microporous titania coating
Apatite formation

## ABSTRACT

In this study, a simple, cost-effective approach of polymeric foam replication was used to produce three-dimensionally macroporous titanium scaffolds with controllable porosities and mechanical properties. Two kinds of porous titanium scaffolds with different porosities (74.7% and 87.6%) and pore sizes (360 μm and 750 μm) were fabricated. Both of the scaffolds exhibit good compressive strength (24.5 MPa and 13.5 MPa) with a low elastic modulus (0.23 GPa and 0.11 GPa), approximating the mechanical properties of nature human cancellous bone ($E = 10–50$ MPa, $\sigma = 0.01–3.0$ GPa). Thereafter, the scaffolds were surface modified using plasma electrolyte oxidation (PEO) process to gain a bioactive porous titania ceramic coating. The SBF immersion test indicates PEO treated scaffolds show excellent bioactivity as the apatite rapidly nucleates and grows on the scaffold surface during 3–28 days. The results suggest that the highly porous titanium scaffolds with titania bioactive coatings are promising in cancellous bone replacement.

## 1. Introduction

Human bone is a complex hierarchical material consisting of two major parts: the hard outer cortical bone, which predominates in the appendicular skeleton and can resist both tension and compression; the inner porous cancellous bone, which is concentrated in the axial skeleton and is structured to resist compression (Lubarda et al., 2012). Rod- and plate-like trabeculae form cancellous bone with open cell porous network structure that benefits in body fluids transport, vascularization, bone ingrowth and so on (Tancred et al., 1998). Due to the similar structure of nature bone, macroporous scaffolds are considered as a potential candidate in tissue engineering and have been presented in plenty of works (Wagoner Johnson and Herschler, 2011; Rezwan et al., 2006; Bansiddhi et al., 2008; Rubshtein et al., 2014).

Artificial bone scaffolds have been used in orthopedic implants for years, however, stress shielding often occurs as a result of mismatch in the stiffness of the implant with the surrounding bone. For instance, conventional scaffold materials e.g. ceramics and polymers could hardly achieve the mechanical requirements of elastic modulus and compressive stress for load bearing conditions (Yoshikawa and Myoui, 2005; Jr et al., 2007), while titanium and its alloys exhibit overall stiffness. It is noticed that Young's modulus and compressive stress could be reduced via changing pore characteristics (pore size, porosity, pore distribution) of scaffolds. Thus, porous titanium scaffold with superior biocompatibility and high corrosion resistance is recently considered as one of the most potential biomaterials (Ryan et al., 2006). Reported fabrication methods e.g. powder sintering (Zhu et al., 2004; Li et al., 2009), freeze casting method (Jenei et al., 2016; Deville, 2010; Li et al., 2012), space holder method (Li et al., 2015; Rao et al., 2014; Takata et al., 2017; Torres-Sanchez et al., 2017), electron beam melting (Liu et al., 2017; Hara et al., 2016), rapid prototyping (Lopez-Heredia et al., 2008; Li et al., 2006; Ryan et al., 2008) etc. indicate manufacturing titanium porous scaffold consisting of predictable large pore network in a simplified economic way still remains difficulty. Polymeric foam replication has been dedicated for controllable highly porous ceramics and glass of pre-designed characteristics for years (Nor et al., 2008; Fu et al., 2008). This method involves coating of open-cell polymeric foam templet with slurry followed by removal of templet through sintering process, producing a replica of porous sample from the original polymeric foam templet. Thus, the properties of the porous samples could be adjusted by varying the polymeric foam characteristics such as pore size, porosity, pore shape, pore distribution and so on. Besides, this approach can yield porous scaffold in a cost-effective way as it doesn't require complex, expensive equipment. Recently it is reported as a novel conception of fabricating titanium scaffold with high porosity and large interconnected pores for biomedical application

---

* Corresponding author.
*E-mail address:* raoxiemail@swu.edu.cn (X. Rao).

http://dx.doi.org/10.1016/j.jmbbm.2017.09.014
Received 13 June 2017; Received in revised form 10 August 2017; Accepted 6 September 2017

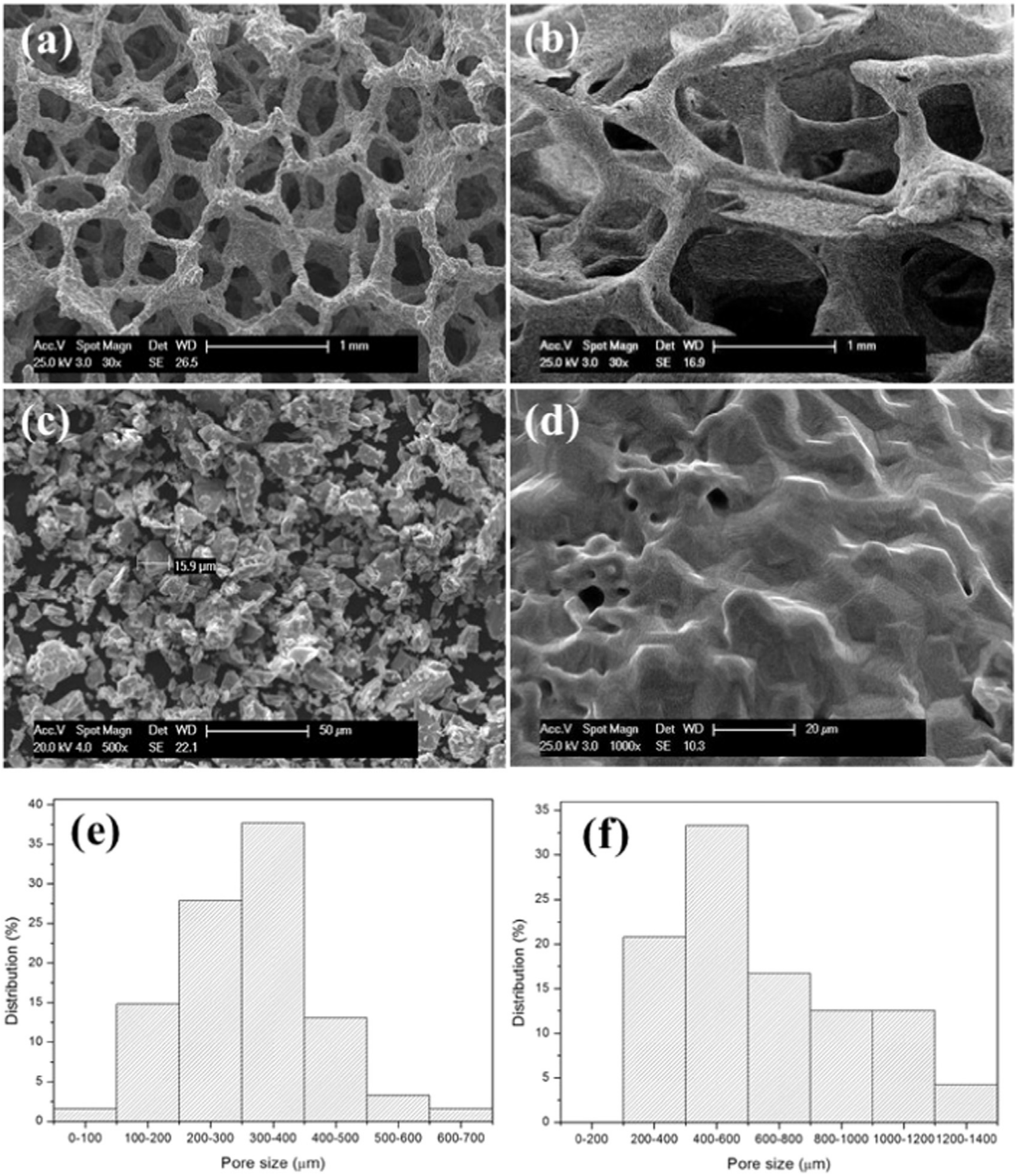

**Fig. 1.** (a) SEM image of as-sintered $T_1$ scaffold; (b) SEM image of as-sintered $T_2$ scaffold; (c) SEM image of raw Ti power; (d) high magnification of sintered scaffold surface; (e) pore distribution of as-sintered $T_1$ scaffold; (f) pore distribution of as-sintered $T_2$ scaffold.

(Ryan et al., 2008; Cachinho and Rui, 2007; Lee et al., 2010, 2009).

In terms of designing optimal porous implants, surface modification has to be taken into account (Sul et al., 2005). Plasma electrolyte oxidation (PEO), which is also named as micro-arc oxidation, is a relatively convenient technique for formation of bioactive films on Ti surface (Wei et al., 2008; Yang et al., 2008). On one hand, the PEO treated surface shows good biocompatible, high corrosion resistance and so on; On one hand, the PEO treated surface shows good biocompatible, high corrosion resistance and so on; on the other hand, PEO could easily work on different samples with complex geometric shapes, e.g. porous scaffolds. Furthermore, the multi-nano/microporous structure layer formed on surface has also presented positive influences on bioactivity, cell adhesion, proliferation response and differentiation (Guglielmo and Gulotta, 2008; Yun et al., 2011; Chen et al., 2009; Tao et al., 2009).

Concerning the requirements mentioned above, the aims of the present study are two-fold: (i) Fabrication of controllable high porous network titanium scaffolds at different pore sizes using the polymeric foam replication method; (ii) Formation of multi-macroporous bioactive titania layers on complicated surfaces using plasma electrolyte oxidation. Afterward the in vivo behaviors of scaffolds are investigated by soaking in simulated body fluid (SBF).

## 2. Materials and methods

### *2.1. fabrication of porous scaffolds with two different pore size*

Pure titanium powder (Nanjing Guo Ding Co., China) with an average particle size of 30 µm was used as raw materials in this study. Gelatin (Chemreagent, China) was used as binder. Polyurethane foams (Nanjing Chemical Factory, China) with two different pore sizes at 0.2–1 mm and 1–1.5 mm were chosen for carrier of soaking slurry, respectively. The samples fabricated from 0.2 to 1 mm type foam was named $T_1$, while samples fabricated from 1 to 1.5 mm type foam was named $T_2$.