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Porous TiNbZr alloy scaffolds for biomedical applications

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Abstract

In the present study, porous Ti–10Nb–10Zr alloy scaffolds with different porosities were successfully fabricated by a "space-holder" sintering method. By the addition of biocompatible alloying elements the porous TiNbZr scaffolds achieved significantly higher strength than unalloyed Ti scaffolds of the same porosity. In particular, the porous TiNbZr alloy with 59% porosity exhibited an elastic modulus and plateau stress of 5.6 GPa and 137 MPa, respectively. The porous alloys exhibited excellent ductility during compression tests and the deformation mechanism is mainly governed by bending and buckling of the struts. Cell cultures revealed that SaOS2 osteoblast-like cells grew on the surface and inside the pores and showed good spreading. Cell viability for the porous scaffold was three times higher than the solid counterpart. The present study has demonstrated that the porous TiNbZr alloy scaffolds are promising scaffold biomaterials for bone tissue engineering by virtue of their appropriate mechanical properties, highly porous structure and excellent biocompatibility.

Keywords: Titanium alloy; Scaffold; Mechanical properties; Biocompatibility

1. Introduction

Porous materials are of significant importance for bone tissue engineering applications, as they provide good biological fixation to the surrounding tissue through bone tissue ingrowth into the porous network [1]. Although porous ceramics and polymers have been studied as scaffold materials, they cannot meet the mechanical requirements for load bearing conditions [2–5]. For this reason, porous Ti and Ti alloys have been developed. The major benefits of porous Ti and Ti alloys compared with other bone graft materials include their good mechanical strength, with an elastic modulus close to that of bone, porous structure, providing biological fixation, and good biocompatibility [6,7].

A number of approaches to the fabrication of porous Ti and Ti alloys have been reported, including sintering loose Ti powder or fibre [8,9], slurry sintering [10] and rapid prototyping [10,11]. Sintering a mixture of Ti powder and space-holder particles (e.g. urea or ammonium hydrogen carbonate) produced porous Ti with a porosity of 70% which exhibited a plateau stress of 53 MPa and an elastic modulus of 3.4 GPa [6]. However, the compressive strength of porous Ti is still lower than that of cortical bone (180–200 MPa) [12]. In order to achieve a porous scaffold combined with high strength and high porosity, some porous Ti alloy scaffolds were therefore developed [13]. A porous Ti–6Al–4V alloy scaffold was reported to achieve higher strength than unalloyed porous Ti at the same porosity [9,13]. However, research on the biological behaviour of metals has shown that the composition of implant biomaterials must be carefully selected to avoid or minimize adverse reactions [14]. The release of metal ions from some metal materials, e.g. aluminium (Al), nickel (Ni), iron (Fe), vanadium (V) and chromidium (Co), can generate adverse biological effects [14]. On the other hand, titanium (Ti), zirconium (Zr), niobium (Nb) and tantalum (Ta) are believed to be non-toxic metals with good biocompatibility [15] and they are widely used in low modulus β or α/β Ti implant materials [16]. Thus there is an increasing research interest in developing porous Ti-based alloys using non-toxic

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alloying elements. New generation porous Ti-based alloy scaffolds are expected to combine high mechanical strength and good biocompatibility.

In the present study Ti–10Nb–10Zr was designed with the addition of a β stabilizer of Nb and α stabilizer of Zr [16]. The TiNbZr alloy is expected to provide high yield strength due to the addition of Nb and Zr, which ensure a duplex microstructure of the α/β phase. The structure and mechanical properties of the porous TiNbZr were studied. Cell adhesion and proliferation of human osteoblast-like cells cultured on the porous alloy scaffolds were assessed.

2. Materials and methods

2.1. Specimen preparation and characterization

The fabrication method of the porous TiNbZr alloy was similar to that used in previous studies [6,17,18]. Elemental metal powders of Ti (purity >99.7%, particle size <45 μm), Nb (purity >99.8%, particle size <45 μm) and Zr (purity >99.9%, particle size <45 μm) were weighed to give a nominal composition of Ti–10Nb–10Zr (hereafter wt.%). The powders were blended in a planetary ball milling system with stainless steel containers and balls (PM400, Retsch) for 4 h with a weight ratio of ball to powder of 1:2 and rotation rate of 100 rpm. The blended TiNbZr powder was mixed with ammonium hydrogen carbonate (NH_4HCO_3), which was used as the space-holder material. The size of space-holder particles was selected to be 500–800 μm. The mixture of Ti, Nb, Zr powder and NH_4HCO_3 was cold pressed into green compacts in a 50 ton hydraulic press and the green compacts were sintered in a vacuum of 10^{-4}–10^{-5} Torr in two steps. The first step was carried out at 175 °C for 2 h to burn out the space-holder particles. In the second step the compacts were heated up to 1200 °C and held for 10 h. Porous TiNbZr alloys with porosities of 42%, 50%, 59%, 69% and 74% were fabricated by adding 20, 30, 40, 50 and 60 wt.% ammonium hydrogen carbonate to the powder mixture.

The general porosity of the porous alloys was calculated by the formula

$$\varepsilon = \left(1 - \frac{\rho}{\rho_s}\right) \times 100 \quad (1)$$

where ρ and ρ_s are the density of the porous alloy and its corresponding theoretical density, respectively. The density of the porous alloy was determined from its weight and dimensional measurements. The theoretical density is 5.1 g cm^{-3} (based on the alloy composition of Ti–10Nb–10Zr). The general pores inside the porous alloys consist of two parts, interconnected pores (open pores) and closed pores. The interconnectivity of the porous TiNbZr was evaluated by measuring the weight of paraffin penetrating into the porous structure when they were boiled in paraffin in a vacuum chamber. The interconnectivity was calculated by comparing the volume of paraffin penetrating into the porous structure and overall pore volume. Scanning electron microscopy (SEM) combined with quantitative image analyse using Image-Pro Plus (Media Cybernetics, Inc., Silver Spring, MD) software were used to characterize the pore structure and pore size distribution. X-ray diffraction (XRD) was used to characterize the phase constituents of the porous alloys. Surface roughness was measured using Surtronic 3+ Roughness checker.

2.2. Mechanical test and simulation

Cylindrical samples with a diameter of 10 mm and length of 15 mm were used to examine the mechanical properties. Five samples were tested for each condition. The samples were cut by electrical discharge machining (EDM), which ensures plane and parallel end faces of the samples. Compression tests were carried out in a 30 kN Instron, equipped with a non-contact extensometer (resolution 0.5 μm) and the initial strain rate was set at 10^{-3} s^{-1}. Compression tests were also conducted on solid Ti–10Nb–10Zr cylinder samples prepared by powder metallurgy.

The elastic modulus and yield strength of porous TiNbZr from this study were compared with the predictions of the Gibson–Ashby (G&A) model [19] and Finite Element Method (FEM) model proposed by Roberts and Garboczi [20–22]. In the Gibson–Ashby model the structure of the porous material was simplified and it was assumed that the open-cell foam consists of periodic arranged beams. Bending of the beams dominated the deformation mechanism. The relationships between plateau stress, elastic modulus and relative density are given by:

$$E/E_s = C_1(\rho/\rho_s)^{n_1} \quad (2)$$

$$\sigma_{pl}/\sigma_{ys} = C_2(\rho/\rho_s)^{n_2} \quad (3)$$

where E is the elastic modulus of the foam, E_s is the elastic modulus of the cell surface solid material, σ_{pl} is the plateau stress of the porous material, σ_{ys} is the yield strength of the cell surface solid material and C_1, C_2, n_1 and n_2 are constants, depending on the cell structure. To date, the complex dependence of C_1, C_2, n_1 and n_2 on structure is not well understood. Experimental evidence suggests that $n_1 = 2$, $n_2 = 1.5$ for open-cell foams, C_1 is a constant of 1 for rigid polymers, elastomers, metals and glasses and C_2 is a constant of 0.3 for cellular metals and polymers.

Elastic moduli of both open-cell and closed-cell foams based on the FEM have been proposed by Roberts and Garboczi [20–22]. The "Gaussian Random Filed" model was used in the present study, as this model deals with structures similar to the cellular structures of porous TiNbZr scaffolds. The FEM model is assumed to be a highly irregular structure with curved struts of variable thickness. Equations to fit the results of their simulations are:

$$E/E_s = 4.2(\rho/\rho_s)^{3.15} \text{ for } 0.05 < \frac{\rho}{\rho_s} < 0.20 \quad (4)$$