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Development of tantalum scaffold for orthopedic applications produced by space-holder method

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ABSTRACT

In the present study, production of tantalum porous scaffolds using the space holder technique was performed. The effect of size and content of sodium chloride particles, used as space holder, as well as compacting pressure on foam structure and mechanical properties have been investigated. The morphological characterization was carried out by means of scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and micro-CT technique. The relationship between the elastic modulus and yield strength of the tantalum porous scaffold and the pore structure was evaluated. Space holder technique allows obtaining tantalum open-cell structure (70% of porosity) and modulus of elasticity similar to cancellous bone, with reproducible processability into three-dimensional structures and reasonable manufacturing costs.

1. Introduction

General population still faces significant increase of bone and musculoskeletal problems, which consequently produces an increasing demand for long term clinical performance of a bone replacement implant [29]. Usually, for bone tissue engineering, grafting materials are designed with porous structures to facilitate space for bone in-growth and vascularisation [13,19,5]. The high porosity and its interconnected structure facilitate transport of body fluids, benefit the spread of cells into the implant, and promote proliferation of bone tissue by increasing the contact area [11,23]. In the literature, different materials such as ceramics [16], polymers [32,52] or metallic scaffolds [22,51,56] have been proposed as porous implants to be used in bone tissue engineering. Ceramics or polymer scaffolds have been studied showing promising bioactive features; however, the low strength of polymers as well as brittleness of ceramics are notable drawbacks for bone implant applications.

Currently, metallic scaffolds are the most suitable materials for load-bearing implants due to their mechanical properties: the elastic modulus similar to bone minimizes the stress-shielding effect [52] with high fracture toughness and load impact fractures. For that reason, numerous surface coatings and porous designs of commercially pure titanium, Ti6Al4V or NiTi foams have been developed to improve biological fixation in the orthopedic field [47,37,20,57]. Although good clinical results have been shown with these materials, they have several drawbacks (possible release of toxic ions, low osteoconductivity or low frictional characteristics). Further, a metallic scaffold will not form sufficiently strong chemical bonds with bone tissue and thus, 'loosening' of the implant over a long period may become a critical problem [26,44]. To overcome these limitations, tantalum has been proposed as a new material for designing porous metallic grafts [7,28]. Tests in vivo had demonstrated no dissolution of the tantalum metal after several weeks of implantation and inflammatory reactions in the tissues surrounding tantalum implants were not evident [36].

Tantalum, a metal of noteworthy interest for biomedical applications, especially in orthopedic and dentistry, has high strength, ductility and corrosion resistance with excellent biocompatibility [24,33]. Moreover, tantalum forms a self-passivating surface oxide layer that leads to the formation of a bone-like apatite coating in vivo. This surface allowed excellent bone and fibrous in-growth properties that led to a rapid and substantial bone and soft tissue attachment [30,15].

The historical and current use of tantalum in pacemaker electrodes, plates for cranioplasty, femoral stems or plates in nerve surgery, makes this material a good candidate for a wide variety

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of implants [13]. Furthermore, studies "in vitro", showed six times higher living cell density, excellent cellular adherence and growth with abundant extracellular matrix formation on Ta surfaces than on Ti surfaces [8]. Jafari et al. [21] demonstrated that tantalum cups presented better results than titanium cups in clinical cases presented with severe bone deficiency. Therefore, tantalum is gaining attention and has been proposed for designing new porous metallic grafts [41].

Nevertheless, the use of tantalum has been limited because of its high cost and difficult processing as it has a high melting point and high affinity for oxygen. Its high density is also a drawback which has prevented a larger development of Ta implants. Thus, several studies are now focusing either on tantalum thin film formation on other commonly used metallic implants or tantalum porous scaffolds development [31,34,54].

Metallic scaffolds can be produced in a variety of ways; the choice of the technique depends on the requirements of the final application [41]. The basic goal of the available manufacturing techniques is to produce a micro-architecture in a scaffold that is highly porous to allow for cell adhesion, vascularization, nutrient flow and appropriate mechanical properties [31].

Different methods for the fabrication of metallic scaffolds have been reported including conventional techniques such as sintered metal powders, space holder method, gas foaming; and advanced technologies like spark plasma sintering, laser-engineered net-shaping process (LENS) [24,9,6], selective laser sintering (SLS), electron beam melting (EBM), Direct Laser Processing [8], and spark-plasma-sintering (SPS) [2].

One technique successfully used for manufacturing open-cell porous tantalum structures is chemical vapor deposition (CVD)/injection (CVI) on an interconnected vitreous carbon skeleton. These structures are characterized by a volume porosity of roughly 75–85%, a pore size ranging from 400 to 600 μm and with sufficient strength to allow physiological load-carrying applications ([13,54,42]. Considering that its high cost is one of the main drawbacks of this technique, the "space holder method" has been selected in this work as an alternative method to produce non-homogenous porous tantalum samples with an open cell structure.

Several review articles on scaffold materials and fabrication technologies highlight the space holder method as one of the effective methods for the fabrication of metallic biomedical scaffolds, owing to its ability to produce a wide range of porosity levels and controllable pore geometry in scaffolds [43,10]. Type, size and morphology of the space-holding particles determine the porous structure and mechanical properties of the manufactured structure [3]. A number of space holder materials have been used such as carbamide ($CO(NH_2)_2$) [50], ammonium hydrogen carbonate (NH_4HCO_3) and sodium chloride (NaCl) [53,12,49].

Even though there is prolific literature on the use of this method to produce porous structures of titanium and titanium alloys [45,39], there have been only limited attempts to apply it to produce tantalum structures [55]. The purpose of this work is to analyze the effects of porosity, size of NaCl holding-space particles, and compaction pressure on the morphological and mechanical properties of open cell tantalum structures produced using the space holder technique.

2. Materials and methods

2.1. Sample preparation

Scaffold fabrication with the space holder method relies on temporary particles added to metallic matrix powder (space holding particles) that act as a pore former. Fig. 1 schematically shows that four processing steps are involved: mixing of metal matrix powder and space-holding particles, compaction of powders materials, removal of space-holding particles and sintering of porous green compact. The process has been described on a recent patent developed by our research group [40].

As a space holder, sodium chloride particles have been selected in order to minimize undesirable reactions between matrix powder (Ta) and space-holding particles as well as for their biocompatibility and non-cytotoxicity properties.

Elemental metal powders of Ta (Alfa Aesar, Puratronic 99.97%) and particles of NaCl (Panreac Química S.A.U., Spain, purity > 99.5) were weighed to get a porosity of 60–80% vol. For a given porosity and from tantalum and sodium chloride density (ρ_{Ta} and ρ_{NaCl} respectively), the mass of each component (m_{Ta}, m_{NaCl}) required to make the blends was calculated according to Eq. (1):

$$\%\text{vol.Porosity} = \frac{m_{Nacl}/\rho_{Nacl}}{m_{Nacl}/\rho_{Nacl} + m_{Ta}/\rho_{Ta}} \times 100 \qquad (1)$$

In this paper we have evaluated morphological and mechanical properties of tantalum porous structures with 60%, 70% and 80% of porosity and compacted at 350 and 450 MPa. Given that size of space-holder particles will define the final pore size, the degree of pore interconnectivity and thus the final mechanical properties of the Ta scaffold, two NaCl particles size ranges were studied (S, small:100–397 μm and L, large: 397–940 μm). Three space holder blends were tested: 100% of large particles (0:100), 50% of small and big size particles respectively (50:50) and samples with higher percentages of smaller size particles (70:30). Table 1 shows the different test conditions that were performed.

The mixing of Ta powder and NaCl particles was carried out with a mixer (SPEX SamplePrep 8000-series) using ethanol as a binder. Subsequently, uniaxial die compaction was performed with the aid of a pair of punches that moved uniaxially through a die filled with granular materials using a servo-hydraulic testing machine (MTS-Bionix, USA). Cylindrical specimens were compacted to 7 mm in diameter and 9 mm in length at two compaction pressures of 350 MPa and 450 MPa.

In order to ensure a complete removal of space-holding particles and a quick dissolution process, water at 60 °C was chosen as the leaching medium. As any reaction between decomposed space-holding particles and the scaffold framework material may negatively impact on the mechanical properties of the scaffold, the total NaCl dissolution was assessed by means of electric conductivity measurements of the waste water.

The sintering process was performed at 1500 °C under vacuum conditions in a tubular furnace (Carbolite, Horizontal vacuum tube furnace) for two hours.

2.2. Structural characterization of the sintered scaffolds

The morphological characterization of tantalum powders and NaCl particles were carried out by means of scanning electron microscopy (SEM; JEOL 6400 JSM). The size distribution, mean size and percentages ratios of NaCl and tantalum particles were characterized by laser diffraction technique (Beckman Coulter LS Particle Size Analyzer).

Porosity of sintered tantalum structures (open cells), the pore size distribution and its isotropy were characterized by means of mercury intrusion porosimetry (MIP, Micromeritics' AutoPore IV 9500), metallographic examination with a scanning electron microscope (JEOL 6400 JSM) and micro-CT.

The three dimensional structure of the sintered Tantalum specimens was determined using a Microcomputed tomographer (μ-CT, HMX-XT 225, X-tek system, United Kingdom) at 190 kV and 330 μA. A total of 720 projections and 4 frames per projection were acquired. The volumetric reconstruction with the