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Design, fabrication and characterization of titanium with graded porosity by using space-holder technique

Yadir Torres[a,]*, Juan Pavón[b,c], Paloma Trueba[a], Joaquin Cobos[d], Jose A. Rodriguez-Ortiz[d]

[a]*Grupo de Metalurgia e Ingeniería de Materiales, E.T.S. de Ingeniería, Universidad de Sevilla. Camino de los Descubrimientos s/n. 41092. Sevilla (España)*

[b]*Group of Advanced Biomaterials and Regenerative Medicine, Bioengineering Program, University of Antioquia, Medellín, Colombia*

[c]*School of Nuclear Engineering, Purdue University, West Lafayette, IN 47907*

[d]*Centro Nacional de Aceleradores, Universidad de Sevilla (España)*

Abstract

Bone resorption and further failure of titanium implants are often associated to stress-shielding phenomenon. This problem of mechanical incompatibility is even worst due to anisotropy of bone tissue to be replaced. In this work, different samples with gradient longitudinal porosity by using space-holder technique were fabricated and characterized. Main results of this work indicated that: 1) Experimental procedure for space-holder elimination was effective, feasible and reproducible, with better results for a compaction pressure of 800 MPa, and for highest salt contents; 2) 3-D images by micro-CT and images analysis of optical micrographs showed that initial designs were reasonably repeatable; this was observed in terms of both porosity and interfaces quality; and 3) Designs of 30/40/50 and 30/50/30, allowed to solve stress shielding without any important effect on mechanical strength, from the cortical bone point of view.

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1. Introduction

Biomaterials, dentistry and orthopedics communities widely recognize that commercially pure Titanium (cpTi)

* Corresponding author: Tel.: +34 954 482 276; fax: +34 954 460 475
E-mail address: ytorres@us.es

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and Ti6Al4V alloy are the better materials for bone replacement. This consensus is basically supported by their excellent *in vivo* response, as well as due to their suitable mechanical properties for load-bearing applications (Young's modulus of 100 – 110 GPa, yield strength 170 – 483 MPa and tensile strength of 240 – 550 MPa) (Collins (1984)). Despite their well-known clinical success, these biomaterials exhibit some drawbacks: 1) Interfacial issues associated to presence of fibrous tissue, which compromise implants osteointegration; 2) In order to reduce the risk of fatigue failure, it is required a design criteria from a damage prevention frame-work; and 3) Ti implants present higher stiffness than bone (100 GPa to 110 GPa against 20 GPa), which always implies a failure risk due to consequent bone resorption (Currey (1998)). Manufacturing of porous materials is one of the most plausible routes to address this issue (Banhar (2001)). In that sense, powder metallurgy (PM) techniques offer important advantages to reduce stress-shielding phenomenon. In order to control porosity parameters to get a desired balance between stiffness and mechanical strength, space-holder technique exhibits some unique advantages. This specific PM technique implies using some specific substances to retain porosity after they are removed. Some organic and inorganic compounds have been reported as examples of these species like carbamide, ammonium bicarbonate, sodium chloride (NaCl), sodium fluoride (NaF), sacarose, magnesium, polyvinyl alcohol, polymethyl methacrylate, etc.) (Andersen (2000)). In addition to open alternatives by space-holder to control Ti foams porosity, functionally graded/gradient materials (FGMs) are those which are purposely designed with a continuous change (gradient) or step-wise change (graded) in specific structural or chemical features. FGMs have been used as biomaterials for dental and orthopaedic applications (Miao and Sun (2010)). From this context, the aim of this work is to develop, process and characterize porous biomaterials with gradient structure and properties. It must be pointed out that human body itself has a highly graded structure; in that sense, architecture of bone is such that its porosity has a non-uniform nature. This is readily apparent in the longitudinal cross-section of long bones where they have sponge appearance at the ends (cancellous or trabecular bone); in contrast, the bone in the middle is rather dense or with a low porosity (cortical bone). In this work, longitudinal graded porosity of Ti samples obtained by space-holder technique is investigated. Space-holder substance was NaCl, due to its low cost, easy dissolution, and negligible residual toxicity. In that sense, the influence of both compaction pressure and space-holder content is also studied. Complete tasks about microstructural characterization, including micro computed tomography (microCT), compression testing, and dynamic Young's modulus estimations, were also performed.

2. Experimental Approach

2.1. Obtaining compact graded porosity

Mixtures of cpTi powder (SE-JONG Materials Co. Ltd., Korea) and salt particles (Panreac Quimica SAU, Spain, purity>99.5), were processed within a NaCl concentration range between 30 and 70% (see Fig. 1). NaCl contents were selected to validate feasibility of the process for applications like spine discs replacements. The mixtures [cpTi + NaCl] were homogenized using a Turbula ® T2C Shaker-Mixer for a time ≥ 40 minutes, by using a previously optimized protocol (Torres et al. (2011)). Ti powder was obtained by a process of hydrogenation/dehydrogenation, and it shows an irregular morphology and sizes of 9,7 μm (< 10%), 23,3 μm (< 50%) y 48,4 μm (< 90%), respectively. The chemical composition of the powder used is equivalent to a grade IV Ti CP, ASTM F67-00 Standard (2002). Space-holder particles used have sizes of 183 μm (< 10%), 384 μm (< 50%) and 701 μm (< 90%), respectively. Then, combination of layers corresponding to specific designs (see Fig. 1), are placed into a compaction die of 12 mm diameter. Afterwards, layers are compacted (600 and 800 MPa), in order to prevent segregation. The mass of each mixture is calculated from corresponding compressibility curves; the aim was to obtain similar layers thicknesses, minimizing the effects of compaction pressure, and ensuring requirements for uniaxial compression tests (height/ diameter = 0.8). Elimination of space-holder from green compacts was done in distilled water (static, at temperature between 50-60 °C). Evaluation of mass lost (usually associated with NaCl) was performed every four hours, once they have been dried for 2 h in an oven at 110°C. Finally, the samples were sintered in a ceramic furnace tube (Carbolyte ® STF 15/75/450) at 1250 °C for 2 h under high vacuum ($\sim 5 \cdot 10^{-5}$ mbar).

2.2. Characterization of graded porosity

Density was measured by using the Archimedes method through immersion in distilled water (ASTM C373-88). The total and interconnected porosities were calculated from density values. Three samples were analyzed for each type of gradient, and three measurements were performed about each sample density (9 in total for each material). The image analysis (IA) allowed measuring of most important porosity parameters: form factor (Ff), average distance between pores (λ), equivalent pore diameter (Deq) and total porosity of each layer. The IA was performed in each zone of the gradient, as well as in the interfaces; the standard protocol was applied to 10 and 40 images (5X), respectively (Panorama Maker® y Adobe Photoshop®). Details of equipment, the protocol for sample preparation, and definition of microstructural parameters were described in previous works of the authors (Torres et al. (2011) and Torres et al. (2012)). The computerized microtomography study was conducted in an X-ray Tomograph, mark Bioscan, model Nano CT (installed by Philips Medical Systems).

The Nano CT system was operated at a voltage between 45 and 75 kVp, and images were captured with a spatial resolution up to 25 µm, with a vision field up to 270 mm, axial and transaxial, between 35 and 70 mm. A tube voltage of 65 kVp X-rays, and a current of 123 µA, with an exposure time of 1.5 s were used, and 360 projections were recorded. Images reconstruction was performed with a spatial resolution of 100 µm, in "Exact Cone Beam" mode, with Shepp Logan filter frequency of 98%. The data analysis was made with the program PMOD 3.306 and Biomedical Image Quantification using the 3D module.

2.3. Mechanical behavior of samples with graded porosity

Following ASTM E9-89a standard, uniaxial compression tests were performed in an electromechanical machine (Instron 5505). A deformation rate of 0.005 mm/mm min was applied for all tests, up to reaching deformation values of 50%. Young's modulus and yield strength were determined from stress-strain curves (considering the effect of stiffness of testing machine). Each graded design was tested through three cylinders, which were also used for measuring of density (total and interconnected porosities) and dynamic Young's modulus, Ed. The Ed values were obtained from ultrasound technique (Torres et al. (2011), Torres et al. (2012), Torres et al. (2012)), with a Krautkramer USM 35® flaw detector. This method allowed both the longitudinal and transverse propagation velocities of acoustic waves to be determined. To evaluate longitudinal waves, a Panametric S-NDT® 4MHz ultrasonic transducer was used with an ultrasonic couplant (Sonotrace grade 30®). For transverse waves a Panametric S-V153® 1.5MHz shear wave transducer was used with a shear wave couplant (Panametrics-NDT(TM)). As a reference, the Metals Handbook section on non-destructive evaluation and quality control (Metals Handbook (1989)) includes the results of measurements on nonporous CP Ti samples corresponding to velocities of longitudinal and transverse waves of 6.1 km/s and 3.12 km/s, respectively. Wave velocities through porous samples were measured by minimizing delay times of transducers, by following an iterative measurement protocol. Mathematical expression was employed to calculate the dynamic Young's modulus, once the acoustic wave velocities were measured. Müllner et al. (2008) used these equations, and their experimental results were consistent with poro-micromechanical model predictions based on the stiffness and strength properties of pure titanium, and on the specific porosity of the sample.

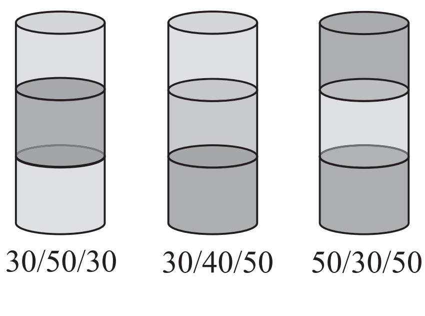

Figure 1: Outline of different designs of longitudinal porosity gradients (different NaCl percentages).

3. Results and Discussion

Figure 2 presents kinetics of NaCl elimination, as well as the influence of both compacting pressure and design; repeatability of the protocol implemented by the authors in previous works, was also tested (Torres et al. (2011) and Torres et al. (2012)). The results indicate a suitable reliability of the protocol, showing data consistency, no matter if the compaction pressure decreases or if space-holder increases. In addition, for the pressure range evaluated is not appreciated any change in the kinetics of the process, whilst is observed some change in the influence of spacer content: increased compaction pressure produces basically the same total dissolution time; however, greater NaCl contents implies an increase of connectivity between NaCl particles, which also means an easier remotion (fastest dissolution).

The figure 3 shows the images obtained on a cross section of the samples, as well as a 3D image using the micro-CT of the 50/30/50 design. These images indicate the following: 1) Homogeneity, proportion and distribution of graded porosity of each zone are reasonably acceptable, and they match with designs theoretically predicted; 2) General aspect of interfaces between gradient layers appears to be structurally suitable, indicating a smooth transition; 3) Proportion of pores with sizes larger than 100 µm ensures the growth of bone tissue into the implant (ingrowth) (Traini et al. (2008)); and 4) Micro-CT is an appropriate tool for evaluates the size, shape and spatial distribution of porosity. It must be noticed that micro-CT images can also illustrate plastically deformed areas (red areas) due to friction with the compaction die. Micro-CT studies conducted recently by the authors have shown that samples with homogeneous porosity can be also affected by plastic deformation during compaction step. In order to evaluate mechanical damage on the porous samples due to monotonic, static and cyclic loading, the authors are also using this damage prevention criterion. A summary of uniaxial mechanical properties of graded samples, and their relationships with porosity parameters appear in Table 1.

From these results, the following can be highlighted: 1) As it was expected, theoretical porosity is higher than experimental one; this is assumed to be associated with loss of space-holder during the sintering process; 2) No matter the type of design, porosity increases with the compaction pressure; this was previously observed and explained by the authors in a published work (Torres et al. (2011) and Torres et al. (2012)). This apparently unexpected effect is due to the higher coalescence between space-holder particles as compaction pressure is increased; 3) Porosity ratio (interconnected/total) increases with the space-holder content; 4) Dynamic Young's modulus were higher than those obtained conventionally from stress-strain curves, showing a good agreement with porosity (Torres et al. (2011) and Torres et al. (2012)); and 5) Values of Ed and yield strength were lower than those estimated for samples with homogeneous porosity, which is attributed to some interfaces effect between layers.

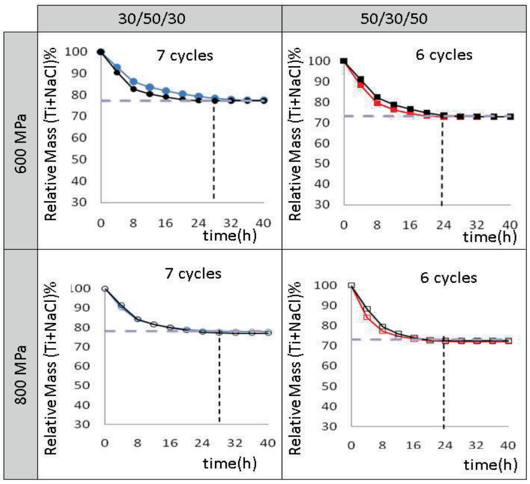

Figure 2:Kinetics of the spacer elimination; Influence of the compacting pressure and NaCl contents.

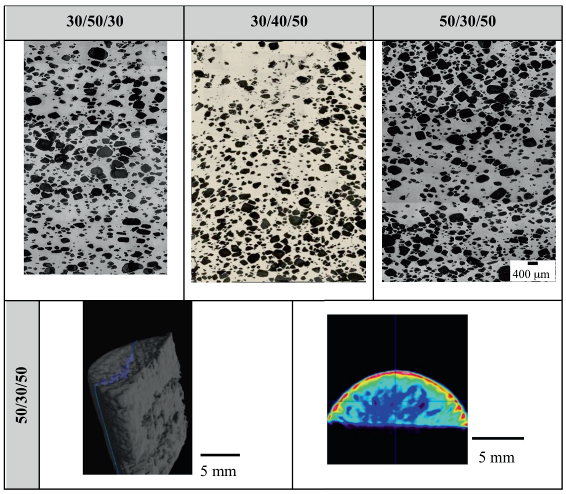

Figure 3: Optical microscopy images corresponding to the distribution of the graded porosity for the three designs and manufactured by micro-CT (spatial resolution of 100 µm) 50/30/50 design.

Table 1: Uniaxial mechanical properties associated with porosity parameters of the samples. Note that yield strength and Young's modulus of solid Titanium is 650 MPa and 110 GPa, respectively.

Type of graded testing	Compaction Pressure (MPa)	Porosity (%) Total (mixing rule)	Arquimedes Tot.	Arquimedes Interconn.	Young's modulus (GPa) Conventional (uniaxial compression)	Dynamic, E_d ultrasounds technique Estimated (E_d of monolithics)	Dynamic, E_d ultrasounds technique Exp.	Yield strength σ_y (MPa) Estimated (σ_y of monolithics)	Yield strength σ_y (MPa) Exp.
30/50/30	600	36.7	32.8	19.2	4.8	37.4	27.3	315	206
	800		34.1	21.6	5.6	33.8	26.7	323	171
30/50/30	600	40.0	37.5	24.0	7.9	32.3	25.1	233	160
	800		38.9	25.8	7.6	30.2	24.0	236	166
30/50/30	600	43.3	38.6	27.9	8.1	29.1	24.6	199	118
	800		39.5	29.5	5.3	26.8	23.3	202	136

4. Conclusions

The following remarkable findings can be drawn from results of design, fabrication and characterization of porous samples with graded porosity: 1) Experimental protocol used to remove the space-holder was successful, viable, economical, and repeatable; the better results corresponded to compaction pressure of 800 MPa, for the highest NaCl contents; 2) Reliability of proposed designs were validated through the estimation of percentages and homogeneity of graded porosity of each layer, as well as by the verifying the quality of the interfaces; 3) Ultrasound technique is recommended to evaluate the Young's modulus of porous samples; and 4) 30/50/30 and 30/40/50 designs exhibit a potential to solve the stress shielding issue without an important loss of mechanical strength; this can ensure their practical application as cortical bone substitutes.

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References

Andersen, O., et al., Advanced Engineering Materials, 2000. 2(4): p. 192-195.

Banhart, J., Progress in Materials Science, 2001. 46(6): p. 559-632.

Collins, E. W., The physical Metallurgy of Titanium Alloys, Ohio: ASM, Metals Park, 1984

Currey, J., Handbook of Biomaterials Properties, ed. J. H. Black, Garth, London: Springer – Verlag, 1998

Metals Handbook Ninth Edition, 1989. 17: "Non-destructive Evaluation and Quality Control". ASM International, Materials Park, OH, p. 235.

Müllner, H.W., Fritsch, A., Kohlhauser, C., Reihsner, R., Hellmich, C., Godlinski, D., Rota, A., Slesinski, R., Eberhardsteiner, J., 2008. Strain 44, 153–163.

Torres, Y., Pavón, J.J., Nieto, I., Rodríguez, J.A., Metallurgical and materials transaction B, 2011, 42B, p. 891-900.

Torres, Y., Pavón, J.J., Rodríguez, J.A., Journal of Materials Processing Technology, 2012, 212, p. 1061-1069.

Torres, Y., Rodríguez, J.A., Arias, S., Echeverry, M., Robledo, S., Amigo, V., Pavón, J.J., Journal of Materials Science, September 2012, Volume 47, Issue 18, p. 6565-6576.

Xigeng Miao, Dan Sun, Graded/Gradient Porous Biomaterials, Materials 2010, 3, p. 26-47