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Manufacturing of highly porous titanium by metal injection molding in combination with plasma treatment

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ABSTRACT

Highly-porous titanium was produced by metal injection molding (MIM) of feedstock containing potassium chloride particles as a space holder. Macroporosity was generated by dissolving the potassium chloride particles in water. Challenges for MIM of highly-porous parts include shape retention during debinding and sintering and achieving open surface porosity. This study demonstrates that plasma treatment can remedy both these effects for highly-porous titanium. Plasma treatment of unsintered MIM samples enables attaining porosities of up to 64% in combination with good dimensional accuracy. The effect of plasma treatment on the uptake of interstitial impurities, dimensional accuracy, sintered microstructure and porosity, as well as the interaction of the plasma with partially-debinded MIM samples, was investigated. Highly-porous titanium produced by MIM and plasma treatment is attractive for biomedical implants due to its low impurity content, good dimensional accuracy and shape stability in combination with enhanced open porosity, the latter contributing to bone ingrowth and implant fixation.

1. Introduction

Highly porous metals, also known as metal foams, have been attracting a growing interest due to their low density, high porosity, good liquid and gas permeability, high surface area, and other unique properties. Among porous metals, titanium (Ti) is favored for bone implants because of its combination of chemical resistance, mechanical properties and biocompatibility. Additionally, tailoring porosity enables matching the elastic modulus to that of human bone and attaining a pore size suitable for bone ingrowth. This reduces the risk of the stress-shielding effect and improves implant fixation. Although studies on highly-porous titanium have mainly focused on biomedical use, there is potential for other applications. For instance, Zhang et al. (2014) used porous titanium in electrochemical devices as a substrate for electrodes, Ito et al. (2012) used it in current collectors, and Jung et al. (2009) used it in separator plates for water electrolysis proton-exchange membranes and in fuel cells.

The space holder method (SHM) is an established technique for powder-metallurgy (PM) manufacturing of highly-porous titanium. It involves compacting a mixture of titanium and space holder powders into a desired shape. The space holder is removed by thermal decomposition or dissolution in a solvent (generating pores) and the compact is then vacuum sintered. The amount and size-fraction of porosity is determined by the quantity and particle-size of the space-holder powder.

Biomedical implants often have complex shapes, which are difficult to achieve by conventional PM forming techniques such as cold die pressing or cold isostatic pressing. Laptev et al. (2004) proposed shaping titanium implants by green-machining SHM compacts prior to space holder removal and sintering and demonstrated a porous acetabular cup hip prosthesis prototype. Imwinkelried (2007) applied this technique to produce spinal cage implants. Green machining requires a relatively high green strength, which can be achieved by using irregularly-shaped titanium powder. Such powders are usually produced by the hydrogenation-dehydrogenation (HDH) method and have high oxygen content. Further increases in oxygen and other interstitials

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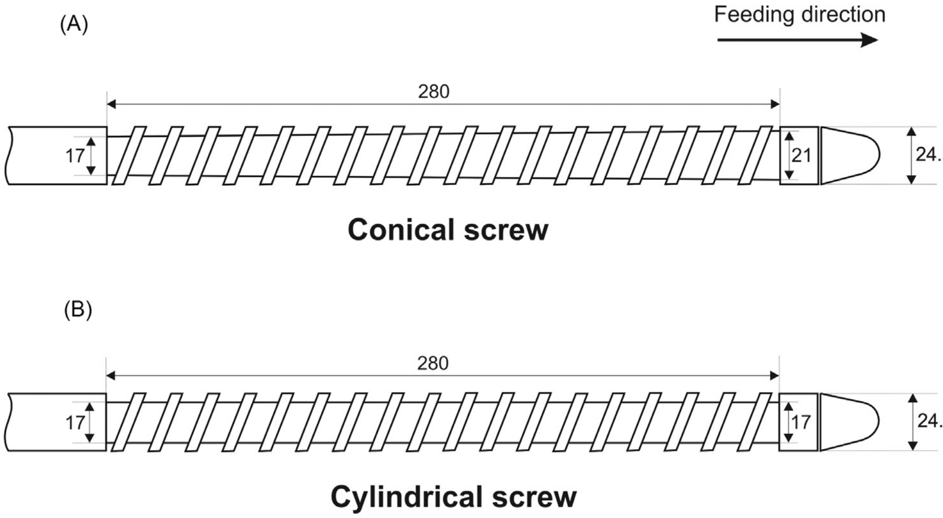

Fig. 1. Sketch of screw used in previous work (a) and in this work (b).

during sintering frequently leads to impurity contents above that prescribed for Grade 4 (ASTM F-67-06, 2006) titanium, resulting in unacceptable embrittlement.

One possible solution is shaping titanium implants by metal injection molding (MIM), where it is possible to use spherical powders produced by gas atomization of titanium melts. These powders contain fewer impurities (especially oxygen) than HDH powders, thus decreasing the probability of embrittlement. MIM also enables the production of complex shapes with a high degree of automation and low large-scale production costs. However, MIM has been limited by a tendency of the titanium and space holder particles to separate during feedstock injection. This effect results in an outer shell consisting mainly of titanium particles on implant surfaces. After sintering, this shell forms a relatively dense layer that negatively affects bone ingrowth and implant fixation.

Imwinkelried (2007) showed that for porous titanium implants, a ratio of space holder to titanium powder higher than 65:35 (vol.%) is needed to achieve interconnected macroporosity, which is required for bone ingrowth and the formation of a blood vessel network within the implant. However, the shape retention of these implants during debinding and sintering is another challenge for MIM. Chen et al. (2009) reported successful production of titanium samples by MIM with up to 60 vol.% NaCl space holder in the powder load (the combined volume of titanium and space holder powders) of the MIM feedstock. When 70 vol.% space holder in the powder load was used, samples collapsed during debinding. Tuncer et al. (2014) reported successful injection molding of feedstocks containing gas-atomized titanium powder and up to 70 vol.% KCl space holder in the powder load. However, only samples with a space holder addition lower than 55 vol.% could be sintered without shape distortion. The higher space holder content resulted in excessive shrinkage and distortion and sometimes collapse of the porous parts.

The shape stability and porosity of porous titanium produced by MIM can be enhanced by replacing the water leaching space holder removal step with solid-state sublimation during vacuum sintering. Laptev et al. (2015) showed that vacuum sintering of injection-molded preforms with a KCl space holder content of 70 vol.% can render geometrically stable parts when the water leaching step is omitted. Nevertheless, the problem of reduced surface porosity remains. In a recent study by Daudt et al. (2015), it was found that plasma treatment enhances dimensional accuracy, open surface porosity and likely shape stability of highly-porous titanium produced by warm die compaction of similar MIM feedstocks.

Table 1
Feedstock compositions (vol.%).

Sample code	Powder load	Binder amount	Powder load composition	
			Ti	KCl
MIM 72	72	28	30	70
MIM 75	75	25	30	70
MIM 80	80	20	30	70

Based on these results, the main objective of this study was the fabrication of geometrically-stable titanium samples with open surface porosity and interconnected bulk porosity over 60 vol.% using MIM with the space holder technique and plasma treatment. A detailed investigation of processing parameters and mechanisms of surface modification during plasma treatment was undertaken and the properties of highly-porous titanium samples were examined.

2. Experimental

2.1. Starting materials and feedstock preparation

The MIM feedstock was composed of gas-atomized, spherical titanium powder ($d_{10} = 10.6\ \mu m$, $d_{50} = 19.1\ \mu m$, $d_{90} = 32.8\ \mu m$, TLS, Bitterfeld, Germany), KCl powder (Sigma-Aldrich, Steinheim, Germany) and binder. KCl particles were fractionized to 355–500 μm by sieving to achieve pore sizes suitable for bone and blood vessel ingrowth and implant fixation, as proposed by Wintermantel and Ha (1998). The binder system consisted of 60 vol.% paraffin wax (Sigma–Aldrich, Steinheim, Germany), 35 vol.% polyethylene (Hostalen GD 7260, Londell-Basell, Wesseling, Germany) and 5 vol.% stearic acid (Merck, Hohenbrunn, Germany), as recommended by Cysne Barbosa et al. (2013).

The feedstock was produced by mixing the powder load (titanium and space holder powders) and the binder in a Haake HKD-T 0.6D kneader (IKA Werke GmbH, Staufen, Germany). Three different feedstock compositions were used (Table 1). A constant ratio of space holder to titanium powder of 70:30 (vol.%) was used in all feedstocks to ensure percolation of the space holder and to produce samples with a high and interconnected porosity. The total powder load was increased from 72 vol.% to 75 and 80 vol.% to improve shape stability during thermal debinding and sintering.