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

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A B S T R A C T

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-debonded 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.

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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
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.

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 \( \mu m \) 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, Wesel, 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.

![Sketch of screw used in previous work (A) and in this work (B).](image-url)
2.2. Sample manufacturing

All MIM experiments were conducted using an Arburg Allrounder 370U 700 100/100 2-component injection molding machine (Arburg GmbH, Loßburg, Germany). The feedstock was heated to 150 °C and injected at 90 MPa into a cylindrical mold 14 mm in diameter and 28 mm in length. Twenty samples of each composition were produced. After injection, samples were cut into 8 mm-long pieces and immersed in n-hexane for 24 h at 50 °C to remove paraffin wax and stearic acid. Afterwards, the pieces were desalinated in deionized water at 60 °C for 24 h to remove the space holder. The conical screw of the injection molding machine used by Cysne Barbosa et al. (2013) and Tuncer et al. (2014) to produce porous titanium was replaced with a cylindrical screw (Fig. 1) to avoid feedstock segregation during injection.

Plasma treatment was performed on at least 10 samples for each composition before debinding and sintering. A “nano” type microwave plasma device (Diener electronic, Ebhausen, Germany) was used. Plasma parameters were adapted from a previous study by Daudt et al. (2015), in which plasma treatment was applied to samples produced by the warm die compaction of MIM feedstock. First, a vacuum of 2 Pa was created, then the vacuum chamber was filled with argon under a pressure of 75 Pa, which was applied during the whole plasma treatment. The discharge power was set in the range of 150–294 W for 10–240 min. Debinding and sintering was performed in a 121212 WM vacuum furnace (Thermal Technology GmbH, Bayreuth, Germany). Prior to sintering, samples were heated to 500 °C in argon for 2 h to remove residual binder (mainly polyethylene). Samples were then sintered at 1200 °C for 3 h in vacuum (<10⁻³ Pa). A schematic of the processing route is shown in Fig. 2.

Optical emission spectroscopy (OES) was performed to investigate interaction of the plasma with partially-debinned MIM parts. OES measurements were collected during plasma processing with and without samples in the chamber using a high-resolution echelle spectrometer (LTN Laser Technik, Berlin, Germany). The National Institute of Standards and Technology (NIST, 2016) database was used for species identification.

2.3. Sample characterization

Highly-porous titanium samples were characterized by visual inspection and analysis of the open, closed and total porosity according to the work of Köhl et al. (2009). The closed porosity was determined by the Archimedes method using a XS204 balance (Mettler Toledo, Giessen, Germany) equipped with a floating device. Since distortion of MIM 80 samples were relatively small, the geometrical method could be used for determination of the total porosity with good accuracy. The obtained results were double-checked by numerical analysis of optical microscopy images. The open porosity was calculated as a difference between total and closed porosity. The direct determination of open porosity by measuring the water volume in an infiltrated sample was not possible since the water leaked too fast out of the macropores.

Sample surfaces were characterized using a Cyber Scan CT300 optical profilometer (Cyber Technologies, Eching-Dietersheim, Germany). The cross-sections of sintered samples were metallographically prepared and examined using an Axio Lab A1 light microscope (Carl Zeiss GmbH, Jena, Germany). The top surfaces and fractured surfaces of unsintered MIM parts were examined using a TM3030 scanning electron microscope (Hitachi High Technology America Inc., USA). The uptake of interstitial elements (oxygen and carbon) was evaluated by thermal conductivity and IR spectroscopy using a TCH/CS 600 equipment (LECO Corp., St Joseph, USA). Polyethylene pellets were plasma-treated and analyzed by Raman spectroscopy using a Bruker Verty 70 instrument (Bruker Optik GmbH, Ettlingen, Germany) connected to a RAMII module.
Table 2
Porosity and shrinkage (%) after sintering of MIM 80 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Open porosity</th>
<th>Closed porosity</th>
<th>Total porosity</th>
<th>Shrinkage (diameter)</th>
<th>Shrinkage (height)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated MIM 80</td>
<td>36.7 ± 1</td>
<td>8.3 ± 1</td>
<td>45.0 ± 4</td>
<td>22.8 ± 2.2</td>
<td>28.0 ± 3.3</td>
</tr>
<tr>
<td>Plasma-treated MIM 80</td>
<td>55.0 ± 4</td>
<td>8.0 ± 4</td>
<td>63.0 ± 8</td>
<td>16.0 ± 0.9</td>
<td>19.8 ± 3.0</td>
</tr>
</tbody>
</table>

with an excitation wavelength of 1064 nm to investigate the effect of the plasma.

3. Results

3.1. Feedstock optimization

The powder load in the feedstock was optimized based on the results of Tuncer et al. (2014) for samples produced by warm die compaction of MIM feedstock. The powder load was set to 72 vol.%, 75 vol.% and 80 vol.%. According to Li et al. (2007), high powder load improves mechanical properties and dimensional accuracy during sintering. However, there is an upper limit since the feedstock should also have good flowability. The challenge for feedstocks with high powder loads is avoiding powder/binder separation and clogging of the MIM nozzle during injection, as reported by German and Bose (1997). This can occur as the feedstock flows through the nozzle into the mold cavity. Tuncer et al. (2014) observed nozzle clogging with powder loads near 80 vol.%. Based on these results, MIM using a powder load of 80 vol.% was optimized and the conical screw used by Cysne Barbosa et al. (2013) and Tuncer et al. (2014) was replaced with a cylindrical screw (Fig. 1), which enabled the injection of feedstocks containing up to 80 vol.% powder load without blocking the screw during feeding. MIM parts with 72 vol.% powder load completely collapsed during thermal debinding and sintering (Fig. 3b). When the powder load was increased to 75 vol.%, shape distortion was reduced (Fig. 3c) and samples with 80 vol.% powder load retained their shape the best (Fig. 3d). Higher powder load increased the contact area between titanium particles, which improved shape stability and promoted particle sintering.

3.2. Plasma treatment

Samples were plasma-treated to improve shape retention during debinding and sintering and to increase open surface porosity. Plasma treatment of MIM 72 samples prevented collapse of the porous structure and permitted good dimensional accuracy (Fig. 4). Optimal plasma parameters were a discharge power of 294 W (maximum power of plasma device) and 15 min dwell time. Lower discharge powers did not ensure sample shape stability. Longer dwell times resulted in sample distortion during plasma treatment and shorter dwell times were insufficient to ensure significant changes in the sample surface and to avoid shape distortion during subsequent thermal debinding and sintering.

Plasma treatment with the optimized parameters was also applied to MIM 80 samples. These samples were more stable during thermal debinding and sintering due to the higher powder load, but additional plasma treatment further improved their dimensional accuracy (Fig. 5). Untreated samples displayed pronounced bending and had a densified surface layer (Figs. 5 and 6a). Whereas, plasma-treated samples had a more homogeneous pore distribution and higher dimensional accuracy (Figs. 5 and 6b). Topography analysis (Fig. 5) confirmed the reduction of bending at the lateral surfaces in plasma-treated samples compared to untreated samples. Additionally, higher porosity was indicated on the surface of plasma-treated samples (Fig. 6b). Furthermore, plasma treatment significantly reduced shrinkage and increased open and total porosity (Table 2). Higher porosity in plasma-treated samples was related with reduced shrinkage, so that larger voids were formed.

Table 3
Interstitial analysis of porous titanium samples after sintering (1200 °C, 3 h).

<table>
<thead>
<tr>
<th>Sample</th>
<th>O (wt.%)</th>
<th>C (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated MIM 80</td>
<td>0.342</td>
<td>0.0435</td>
</tr>
<tr>
<td>Plasma-treated MIM 80</td>
<td>0.348</td>
<td>0.0465</td>
</tr>
<tr>
<td>Porous MIM implant</td>
<td>0.340</td>
<td>0.0600</td>
</tr>
<tr>
<td>Starting Ti powder</td>
<td>0.216</td>
<td>0.002</td>
</tr>
<tr>
<td>ASTM F-67-06 (2006), Grade 4</td>
<td>0.400</td>
<td>0.080</td>
</tr>
</tbody>
</table>

Sample oxygen and carbon uptake was determined by chemical analysis of untreated and plasma-treated sintered MIM 80 samples (Table 3). Contamination was found to be within the tolerances for Grade 4 (ASTM F-67-06, 2006) titanium implants. Cysne Barbosa et al. (2013) reported similar interstitial contents for porous titanium parts produced by MIM with a NaCl space holder, but without plasma treatment. These results indicate plasma treatment has no significant influence on the uptake of interstitial oxygen and carbon in porous titanium.

3.3. Investigation of plasma interactions with MIM parts

Optical emission spectroscopy was performed to identify plasma species and to determine their effect on partially-debonded MIM samples. Fig. 7 shows the spectra of plasma with and without samples inside the chamber. Both spectra contain argon peaks originating from the gas supply, and also oxygen, nitrogen and hydrogen peaks. Since the gas tightness of the plasma device is weak, residual oxygen, nitrogen and hydrogen were not unexpected. Iron peaks were also observed. Sputtering of the steel walls of the vacuum chamber is one of two sources of these peaks. Titanium, carbon as well as iron peaks are products of plasma interactions with partially-debonded MIM samples.

Certain ranges of the plasma spectra were analyzed in more detail (Fig. 7, bottom). An increase in the intensity of the 704.6 nm peak was detected when MIM samples were placed in the plasma device. This peak is related to the light emission of C species formed during degradation of polymeric binder chains. The presence of a slight emission of C species in the plasma spectra without samples may be due to contamination of the vacuum chamber during previous treatments. An increase in the intensity of the peaks at 736.1 nm and 747.4 nm during plasma treatment of MIM samples was also observed. These peaks are related to excited titanium atoms, indicating titanium atoms were sputtered from the sample surface.

In order to estimate the temperature during plasma treatment, hardened samples of 111 Cr V3 steel were treated in conditions similar to those for MIM samples. The hardness of plasma-treated steel samples was equivalent to the hardness of the same steel tempered at 150 °C ($829.1 \pm 15$ HV), indicating the average sample temperature during plasma treatment was below 200 °C, suggesting low enough temperatures to avoid contamination by the uptake of interstitial elements.

Raman spectroscopy was performed on polyethylene (the backbone component of the binder system) before and after plasma treatment (Fig. 8). The Raman spectrum of plasma-treated polyethylene shows a reduction of the shoulders at 1320 cm$^{-1}$ and 1080 cm$^{-1}$ (arrows) compared to untreated polyethylene. This indicates a reduction of amorphous polyethylene fractions and a slight increase in crystallinity. The breakdown and chemical degra-
Fig. 5. Topography of MIM 80 samples sintered at 1200 °C for 3 h: untreated (a) and plasma-treated sample, 294 W, 15 min (b).

Fig. 6. Cross-sections of MIM 80 parts sintered at 1200 °C for 3 h and their microstructure: untreated (a), plasma-treated, 294 W for 15 min (b).
dation of polymeric chains during plasma treatment, which was also indicated by IR spectroscopy by Daudt et al. (2015), may cause this increased crystallinity. The breakdown of polymeric chains and increased crystallinity of polyethylene during plasma treatment were also reported by Sanchis et al. (2006). Shorter polymeric chains tend to be more easily packed, resulting in higher crystallinity, as claimed by Zhang et al. (2002).

SEM of fracture surface cross-sections (Fig. 9) and on the top surfaces (Fig. 10) of unsintered MIM samples before and after plasma treatment showed a significant reduction in binder content with increasing plasma treatment time. In addition, SEM indicated the formation of sinter-necks during plasma treatment (Fig. 10).

4. Discussion

As expected, increased powder load improved the shape retention of MIM samples during thermal debinding and sintering, with samples produced with 80 vol.% powder load best retaining their shape. However, these samples still exhibited shape distortion and reduced open porosity. To overcome this drawback, plasma treatment was used to improve shape stability and to enhance surface porosity. Plasma treatment improved dimensional accuracy, decreased shrinkage and increased total porosity for MIM 80 samples and prevented sample collapse during debinding and sintering for MIM 72 samples. Plasma treatment also had no detectable effect on the additional uptake of interstitial elements.

Raman spectroscopy, SEM and OES showed that interaction between energetic plasma particles and sample surfaces resulted in thermal degradation of organic binder constituents. Plasma treatment promotes the breakdown of polyethylene chains, consequently increasing crystallinity. Moreover, the low pressure employed during plasma treatment promotes binder removal, allowing titanium particles near the sample surface to come into contact and sinter, as demonstrated by SEM images of plasma-treated samples (Fig. 10). OES spectra (Fig. 7) show that the plasma has sufficient energy to excite titanium atoms, which sug-
suggests the plasma energy is high enough to initiate sintering at the sample surface. This initial sintering at the surface ensured sample shape-retention during thermal debinding and sintering, reduced shrinkage, and improved dimensional accuracy. Furthermore, removing binder from the sample surface caused weakly attached titanium particles to collapse, decreasing the dense superficial layer and consequently increasing open surface porosity.

Shape retention of highly-porous metals during sintering is frequently a challenge for PM manufacturing. In this context, plasma treatment has potential to increase the dimensional accuracy of parts manufactured by techniques other than MIM PM. Plasma-supported sintering on the surface of the powder samples is interesting in its own right and will be explored in more detail in future work.

5. Conclusions

Metal injection molding combined with the space holder method was successfully used to manufacture highly-porous titanium parts suitable for biomedical applications. When a constant
ratio of space holder to titanium powder of 70:30 (in vol.%) was used in the feedstock, an increase of the total powder load of up to 80 vol.% was found necessary to maintain sample shape and avoid collapse during sintering. Plasma treatment after space holder removal and prior to sintering promoted shape stability and increased surface and bulk porosity and dimensional accuracy. This was attributed to binder degradation and sintering initiation due to the plasma’s energetic action on sample surfaces. Plasma treatment did not increase sample impurity content, allowing production of parts with porosities of up to 64% and Grade 4 quality. Plasma treatment has potential for use in other powder metallurgical processes where an increase in shape stability, dimensional accuracy and open porosity is required.

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