Surface modification of highly porous titanium by plasma treatment

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A R T I C L E   I N F O
Article history:
Received 3 September 2014
Accepted 15 November 2014
Available online 26 November 2014

Keywords:
Porous materials
Titanium
Space holder
Metal injection moulding
Plasma treatment

A B S T R A C T
For titanium implants, a final porosity in the range of 60–65 vol% is required to achieve a network of interconnected macropores, which enables adequate fixation of the implant to the bone tissue and suitable mechanical properties. In addition, an open porosity at the implant surface is crucial for the success of the implant. In the present study, highly porous titanium foams were produced by warm compaction of MIM feedstock with the addition of space holder in a heatable die. Plasma treatment was performed on the Ti foams before the final sintering step aiming to increase the open pores at the surface. The results obtained so far demonstrate that plasma treatment is a promising technique for increasing open porosity at the surface. It even improved the dimensional accuracy of highly porous samples.

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1. Introduction

Highly porous titanium is an attractive material for biomedical implants because of titanium’s unique combination of specific properties such as strength, lightness and high resistance to corrosion. Furthermore, the introduction of well-defined porosity enables manufacturing porous titanium with an elastic modulus similar to that of human bone and suitable pores sizes to promote bone ingrowth [1].

Recently, it was shown that metal injection moulding (MIM) in combination with the space holder method (SHM) is a promising technology for manufacturing titanium implants with well-defined porosities. It enables a higher degree of automation and cuts costs in the case of large-scale production compared to the current method (SHM in combination with green machining) [2,3]. Up to now, the success of the new technology has been limited by the fact that there is a partial closing of the surface pores by a dense titanium layer, probably caused by separation of Ti powders and space holder during injection [2]. Another limitation of this technology is that no stable MIM processing conditions have yet been found when the temporary space holder amount exceeds 55 vol% [4,5]. However, a space holder content above 65 vol%, which results in a final porosity in the range of 60–65 vol%, is required to achieve a network of interconnected macropores, which enables bone ingrowth, while maintaining adequate mechanical properties for bone implants [3,5].

The application of plasma-based techniques in processing biomedical devices is quite diverse. Plasma treatment has been successfully performed on polymeric materials like polyethylene and polyethylene terephthalate in order to improve blood compatibility [6,7], wettability, roughness, cell adhesion, spreading and proliferation [8], as well as on metals like titanium implants, where its potential to improve mechanical resistance and biocompatibility has been demonstrated [9].

In the present study, warm compaction of MIM feedstock in a heatable die was used for sample production of highly porous titanium as reported in the literature [5,10]. The advantage of warm compaction compared to MIM is that small amounts of feedstock are sufficient for sample preparation. Plasma treatment was applied to samples before the final sintering step in order to remove the outer shell, aiming at an open surface porosity. The effect of plasma treatment on the Ti foams was investigated in detail and specific properties of samples after plasma treatment were analysed accordingly.

2. Experimental

A feedstock composed of 80 vol% powders and 20 vol% binder was produced. Powder loading consisted of 70 vol% rounded KCl particles (fraction 355–500 μm, Sigma-Aldrich), which were used as temporary space holders and 30 vol% gas-atomized spherical titanium powder (fraction < 45 μm, TLS). The organic binder
system consisted of 70 vol% paraffin, 25 vol% polyethylene (Hostalen GA 7260G) and 5 vol% stearic acid.

Feedstocks were produced by mixing powders and the binder system in a Haake HKD-T 0.6D kneader (IKA Werke GmbH) and warm compacting in a modified pressing die (P/O/Weber GmbH), as described in the literature [5,10]. Twenty cylindrical compacts of 12 mm diameter and approximately 13 mm height were produced. These samples were immersed in n-hexane bath (40 °C, 24 h) to remove paraffin wax and stearic acid; afterwards, desalination (water, 60 °C, 24 h) was conducted to remove space holder particles.

Plasma treatment was introduced before the final sintering step. Samples were treated in a microwave plasma device (Type nano, Diener Eletronics GmbH), under argon atmosphere at 75 Pa, 150–294 W for 30–240 min.

Thermal debinding and sintering were performed in a vacuum furnace (Type 121212WM, Thermal Technology GmbH). Prior to sintering, samples were heated up to 500 °C under argon atmosphere to remove residual binder. Afterwards, all samples were sintered at 1300 °C for 3 h in vacuum (10^{-5} mbar).

Samples were characterized by scanning electron microscope (TM3030, Hitachi High Technology America Inc.) and optical profilometry (CyberScan CT300, Cyber Technologies). Surface porosity was calculated by image analysis of the topography of 5 samples. Bulk porosity was calculated from the average of weight-dimension measurements of 5 samples. The uptake of interstitial elements was investigated by chemical analysis using IR spectroscopy (LECO TCH/CS 600). Furthermore, polyethylene pellets were plasma treated and analysed by IR spectroscopy (Bruker Tensor 27, Bruker Optik GmbH) to investigate the plasma effect on binder.

### 3. Results

Plasma treatment was performed on samples in the non-sintered state after partial debinding as well as after the desalination step. During subsequent sintering, this treatment improved the dimensional accuracy and shape stability of samples compared to untreated samples. The topography of the samples treated at 294 W for 240 min, where the plasma effects were mostly pronounced, clearly confirms this observation (Fig. 1). Furthermore, plasma treatment also increased the open pores at the surface (Table 1). Overall, plasma treatment after partial debinding resulted in higher dimensional accuracy and bulk porosity, while plasma treatment after desalination resulted in more open pores at the surface.

The preferred plasma parameters were 294 W for 60 min. Higher dwell times resulted in strong heating, leading to sample deformation during plasma processing, while shorter dwell times were not enough to open the surface porosity.

The improvement in dimensional accuracy is thought to be related to modifications of binder constituents, binder evaporation as well as possibly an initial stage of sintering at the sample surface.

![Fig. 1. Appearance and topography of the sample's face in the sintered state: (a) untreated, (b) plasma-treated after debinding (294 W, 240 min) and (c) plasma-treated after desalination (294 W, 240 min).](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bulk porosity (vol%)</th>
<th>Open surface porosity (%)</th>
<th>Shrinkage in diameter (%)</th>
<th>Shrinkage in length (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>56.0 ± 1.3</td>
<td>22.7 ± 3.2</td>
<td>24.7 ± 3.3</td>
<td>19.0 ± 1.2</td>
</tr>
<tr>
<td>Plasma-treated after debinding</td>
<td>66.8 ± 0.1</td>
<td>26.1 ± 5.2</td>
<td>13.3 ± 0.15</td>
<td>11.4 ± 1.3</td>
</tr>
<tr>
<td>Plasma-treated after desalination</td>
<td>64.6 ± 0.4</td>
<td>32.8 ± 6.4</td>
<td>15.1 ± 0.2</td>
<td>13.6 ± 1.1</td>
</tr>
</tbody>
</table>

Table 1

Resulting porosity and shrinkage of samples related to plasma treatment.
during plasma processing. The IR spectrum (Fig. 2) of plasma-treated polyethylene showed several new features compared to untreated polyethylene. The overlapping signals at 1740–1500 cm⁻¹ indicated the presence of C=O and C–C functionalities. The increase in base line intensity at 1400–1000 cm⁻¹ is typical for C–O stretching vibrations and O–H bending vibrations. These modifications in the polyethylene structure are related to the breakdown and thermal/chemical degradation of polymeric chains. SEM analysis (Fig. 3) indicated sintering neck formation and reduction in the binder amount in the plasma-treated samples. These results suggested that the collisions between the energetic plasma particles and the sample surface caused a fast heating and thermal degradation of binder constituents, which promoted the breakdown of polyethylene chains. Moreover, the low pressure employed facilitated binder evaporation, allowing titanium particles to come into direct contact at the surface, which initiated sintering at low temperatures. This sintering at the surface ensures that samples keep their external shape during thermal debinding and sintering, reducing shrinkage and improving dimensional accuracy.

Improved open porosity might be explained as follows. The occurrence of high intense plasma in some regions of the samples during the first minutes of treatment leads to high local heating, which result in degradation of residual binder, causing the formation of volatile hydrocarbons with lower molar mass and consequently producing high gas expansion. During the gas expansion, the weakly attached Ti particles from the superficial layer are removed. The effect was support by partial evaporation of remaining binder due to sample heating, which eases to remove weakly attached Ti particles from the surface further enlarging the open porosity. This effect was indicated by the loose Ti particles at the sample surface after plasma treatment.

The interstitial content of the starting powder (0.18 wt% oxygen, 0.010 wt% carbon and 0.001 wt% nitrogen) was increased to 0.343 wt% oxygen, 0.0027 wt% nitrogen and 0.0435 wt% carbon after the sintering of untreated samples and increased to 0.371 wt% oxygen, 0.0032 wt% nitrogen and 0.0430 wt% carbon after the sintering of plasma-treated samples (treatment after desalination at 294 W for 240 min). Similar contaminations were reported for spine implants manufactured by the established technique [2].

Additional characterizations of samples and plasma processing will be carried out in the ongoing work in order to further investigate and understand the plasma effect on MIM samples.

4. Conclusions

Plasma treatment was applied to warm-compacted samples in the non-sintered state after partial debinding as well as after desalination. The treatment performed at 294 W for 60 min was found to be suitable for removing the thin layer of titanium particles partly covering the macropores on the sample surface, increasing the open pores at the sample surface. This layer is usually formed in the case of processing feedstock with a large amount of space holder particles and is caused by titanium/space holder separation during feedstock injection. Furthermore, plasma treatment improved the dimensional accuracy of Ti foams, which is also a promising result, since it enables sintering of highly porous samples, with the porosity range suitable for bone implant application (around 65 vol%), without shape deformation. Overall, plasma treatment after partial debinding resulted in a higher dimensional accuracy of samples, while plasma after desalination resulted in a higher amount of pores at the sample surface. As open porosity at the surface and higher dimensional accuracy are required for implant application, plasma treatment of highly porous samples produced by MIM in combination with space holder has the potential to be applied as a standard manufacturing process for porous titanium implants.

Acknowledgements

The financial support of the Brazilian research funding agency CAPES and the German Academic Exchange Service DAAD is acknowledged.

References


