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Surface modification of highly porous titanium by plasma treatment

N.F. Daudt [a,b,*], M. Bram [a], A.P. Cysne Barbosa [b], C. Alves Jr. [c]

[a] Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[b] Department of Materials Engineering, Universidade Federal do Rio Grande do Norte, 59078-970 Natal, Brazil
[c] Universidade Federal Rural do Semi-Árido, 59625-900 Mossoró, Brazil

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ABSTRACT

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.

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

* Corresponding author at: Institute of Energy and Climate Research, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany. Tel.: +49 2461 61 42 17.
E-mail address: n.daudt@fz-juelich.de (N.F. Daudt).

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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

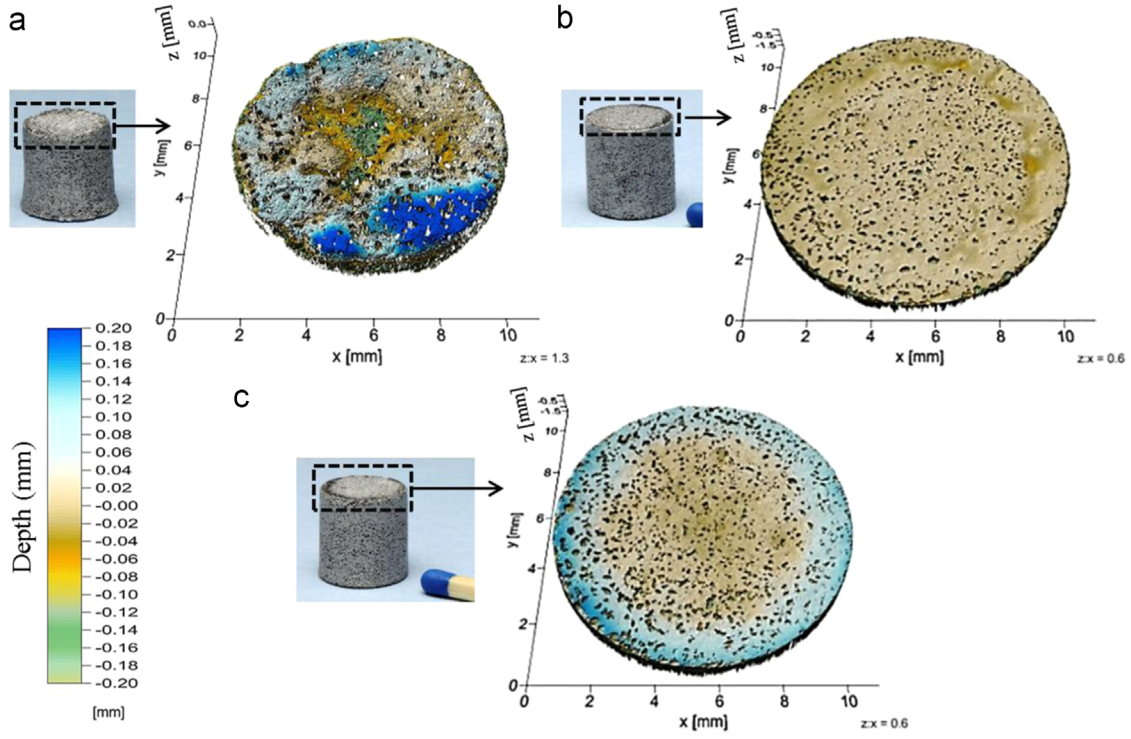

Fig. 1. Appearance and topography of the sample's face in the sintered state: (a) untreated, (b) plasma-treated after debinding (294 W, 240 min) and (c) plasma-treated after desalination (294 W, 240 min).

Table 1
Resulting porosity and shrinkage of samples related to plasma treatment.

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