Materials Science and Engineering C 60 (2016) 446–457

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Fatigue behavior of highly porous titanium produced by powder metallurgy with temporary space holders

Sedat Özbilen [a,b], Daniela Liebert [a], Tilmann Beck [a,c], Martin Bram [a,*]

[a] Forschungszentrum Jülich, Institute of Energy and Climate Research (IEK), 52425 Jülich, Germany
[b] Gazi University, Faculty of Technology, Department of Metallurgical and Materials Engineering, Teknikokullar, Ankara, Turkey
[c] University of Kaiserslautern, Lehrstuhl für Werkstoffkunde (WKK), D-67663 Kaiserslautern, Germany

ARTICLE INFO

Article history:
Received 25 August 2015
Received in revised form 29 October 2015
Accepted 18 November 2015
Available online 1 December 2015

Keywords:
Porous titanium
Powder metallurgy
Interstitial content
Fatigue behavior
Fatigue limit
Failure mechanisms

ABSTRACT

Porous titanium cylinders were produced with a constant amount of temporary space holder (70 vol.%). Different interstitial contents were achieved by varying the starting powders (HDH vs. gas atomized) and manufacturing method (cold compaction without organic binders vs. warm compaction of MIM feedstocks). Interstitial contents (O, C, and N) as a function of manufacturing were measured by chemical analysis. Samples contained 0.34–0.58 wt.% oxygen, which was found to have the greatest effect on mechanical properties. Quasi-static mechanical tests under compression at low strain rate were used for reference and to define parameters for cyclic compression tests. Not unexpectedly, increased oxygen content increased the yield strength of the porous titanium. Cyclic compression fatigue tests were conducted using sinusoidal loading in a servo-hydraulic testing machine. Increased oxygen content was concomitant with embrittlement of the titanium matrix, resulting in significant reduction of compression cycles before failure. For samples with 0.34 wt.% oxygen, R, σ_{min} and σ_{max} were varied systematically to estimate the fatigue limit (~4 million cycles). Microstructural changes induced by cyclic loading were then characterized by optical microscopy, SEM and EBSD.

1. Introduction

Porous titanium is a well-established material for bone implants, enabling improved implant fixation by bone ingrowth combined with reduced risk of stress-shielding by adaption of Young's modulus. Powder metallurgy (P/M) with temporary space holders is a proven method for net-shape manufacturing of implants like spine cages, acetabular cups, dental implants and bone augments. Shaping can be done either by green machining of titanium powder/space holder compacts [1] or by metal injection molding (MIM) [2]. In both cases, uptake of interstitial elements like carbon, nitrogen, and especially oxygen, which are introduced during powder production and by contact with organic binders and sintering atmosphere during processing, must be carefully controlled. Oxygen in solution can significantly affect mechanical properties like yield strength, ductility, fatigue and hardness, while the oxide layer mostly affects surface properties like corrosion resistance, biocompatibility, surface energy and wetting behavior. The oxide layer is primarily TiO_2, generally has a non-uniform thickness of ≤100 nm, covers irregular surfaces, and provides biocompatibility and corrosion resistance. Although its contribution to the total oxygen content can be considerable in materials with large surface area, its influence on mechanical properties in compression is minimal [3].

While the effect of interstitials on the properties of dense titanium has been widely studied, the impact on the properties of titanium foams is less documented, and a systematic evaluation of the effect on the properties of foams with different compositions and structures does not exist. Baril [4] suggested that interstitial contents be kept below distinct levels (oxygen equivalent below 0.34 wt.%) to maintain ductile behavior in titanium foam biomaterials. Pattanayak et al. [5] reported that porous titanium is prone to contamination with oxygen gas during fabrication, possibly adversely affecting bioactivity and mechanical properties. For example, the strength of pure titanium increases and ductility decreases with increased oxygen content, as described in ASTM standard (B265-07), an undesirable trait for biomedical applications. Chino et al. [6] reported that because of high powder oxygen content, foams displayed high compressive strengths and signs of embrittlement. Lower contamination was achieved by using relatively coarse powders with low specific surface. They also reported that even powders coarse enough to prevent pyrophoric reactions may still form surface oxides in air during handling, reducing tensile ductility up to an oxygen content of ~0.8 wt.%, where titanium becomes brittle in tension. Lefebvre et al. [3] showed that the surface oxide can be an important contributor to the oxygen content in the foam, but its effect on the monotonic compression was minimal, at least for the oxide thicknesses investigated (up to 75 nm). Oxygen and nitrogen content in solution, however, significantly reduced the ductility and increased the compressive yield strength of cold-pressed titanium foams [7]. Baril et al. [8] and

* Corresponding author.
E-mail address: m.bram@fz-juelich.de (M. Bram).

http://dx.doi.org/10.1016/j.msec.2015.11.050
0928-4931/

Lefebvre et al. [9] also reported that increasing the oxygen content from 0.24 to 0.51 wt.% in solution significantly increased yield strength and reduced ductility of foams.

Ebel et al. [10] reported a strong decrease of elongation at fracture for tensile samples produced by MIM when oxygen equivalent exceeded 0.35 wt.%, the content of titanium grade 3 for ISO 5832-2. When producing porous titanium by P/M with temporary space holders, interstitial contents usually range between titanium grade 3 (0.35 wt.% O) and titanium grade 4 (<0.4 wt.% O), but oxygen levels up to 0.8 wt.% have been found when fine titanium starting powders (e.g. <25 μm) were used.

Several studies exist [3,7–9,11–32] on the mechanical properties of titanium foams. Although there are studies on the effect of oxygen on yield strength and ductility of porous titanium, few studies exist on the fatigue of pure titanium foams and the effect of oxygen content. The limited information available can be attributed to challenges associated with the production of materials with similar structures but different oxygen contents. Difficulties also arise from differentiating oxygen in solution from oxygen in the foam surface oxide. Due to the high specific surface area, the contribution of oxygen content in the foam surface oxide must be taken into account when determining the effect of oxygen on properties [9]. Lefebvre et al. [9] reported that oxygen content impacts deformation during cyclic loading and specimen rupture was more brittle and cracks more apparent after cyclic deformation when the amount of oxygen increased.

Kashef et al. [33,34] reported that there is an urgent need to understand the failure behavior of titanium foams because of their promising use as load-bearing implant materials for biomedical applications. They showed that in a sample pre-cracked using ASTM E647-08, fatigue cracks grow along the direction of pre-cracks, following the weakest path throughout the foam. Even though titanium foams have a reasonable crack growth resistance rate for biomaterials, this may be improved by maintaining titanium powder purity during foam production [33,34], also increasing other mechanical properties.

This study focuses on the influence of interstitials, especially oxygen, on the fatigue of porous titanium. For this purpose, porous titanium parts were produced by cold compaction (CC) without binder and warm compaction (WC) with binder, in both cases starting from titanium powder/space holder mixtures with constant ratio 30/70 (in vol.%). Different interstitial contents were achieved by varying the starting powders (HDH vs. gas atomized) and by adding organic binder for WC samples. Mechanical properties were systematically investigated by static and cyclic compression tests. Microstructure was characterized using optical microscopy, scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) to determine the failure mechanisms.

2. Experimental

Starting powders: Spherical, argon atomized titanium powder (TLS Technik GmbH, Bitterfeld, Germany) and irregular shaped, dehydrided HDH titanium powder (GfE, Nuremberg, Germany) were used. Table 1 summarizes powder particle-size distribution and interstitial content. To create well-defined macropores, NaCl particles were applied as a temporary space holder. The desired space holder particle-size fraction (355–500 μm) was obtained by sieving. This particle size is known to result in macropore sizes of 100–500 μm, which enables consistent tissue response and bone ingrowth for implants.

Table 1
Properties of titanium starting powders.

Titanium powder	Particle size [μm]			Interstitial content [wt.%]		
	d_{10}	d_{50}	d_{90}	Oxygen	Nitrogen	Carbon
HDH, irregular	24.0	48.3	85.0	0.355	0.030	0.016
Gas atomized, spherical	19.1	33.2	51.2	0.166	0.006	0.004

Sample preparation: To adjust the interstitial content of porous titanium specimens, three different sample preparations were used. In all cases, a constant ratio of titanium powder/temporary space holder of 30/70 (in vol.%) was used.

a. Sample series A: Gas atomized and HDH titanium powders were mixed in a 50:50 (vol.%) ratio in a 3D Turbula Mixer T2C (Willy A. Bachofen AG, Basel, Switzerland) for 2 h. The binderless mixture was compacted at room temperature by uniaxial pressing at 350 MPa using a cylindrical die with a diameter of 60 mm. To reduce wall friction, a small amount of lubricant (5 vol.% PVA solved in distilled water, Sigma Aldrich, Steinheim, Germany) was added. Furthermore, a solvent (Petroleum Benzin reinst, Art. 910, Merck, Darmstadt, Germany) was used to prevent segregation of titanium powder and space holder during die filling. The height of the pressed compacts was approximately 18 mm (50 ml volume).
b. Sample series B: The same sample preparation as series A was used, but only with HDH powder.
c. Sample series C: A gas atomized titanium powder and space holder mixture was mixed with a binder system used in-house for MIM of titanium powders. A detailed description of the feedstock preparation can be found elsewhere [2]. The feedstock was warm compacted with a modified laboratory press PW 100 E with an electrically heated tool (10 H, size II) and digital thermostat TRG1 (all parts from Paul Otto Weber GmbH, Remshalden, Germany). Before compaction, the feedstock was kept for 1 min in the die, which was heated to 150 °C to melt the binder system. The feedstock was then pressed with 110 MPa in the water cooled part of the die. To avoid cracking during cooling, the pressure was held for an additional 30 s. Cylindrical compacts 12 mm in diameter and 15 mm in height were produced.

A detailed description of debinding of samples from series C by solvent extraction in n-hexane and desalination of samples from series A–C in a heated water bath (60 °C) can be found elsewhere [2,30]. After desalination, samples from series C were thermally debinded at 500 °C for 2 h under argon atmosphere. Samples from series A and B did not require this processing step. All samples were sintered at 1300 °C for 3 h in a 121212 WM horizontal vacuum furnace (Thermal Technology GmbH, Bayreuth, Germany) with heating and cooling rates of 5 K/min and a vacuum of $<10^{-3}$ Pa. Finally, porous titanium compacts from all series were shaped by electro-discharge machining (EDM). Cylindrical samples with a diameter of 8 mm and a height of 9–11 mm were used for all mechanical tests. More than 10 samples were produced from each series. The average porosity of the samples from series A was 65.1 ± 0.4 vol.% (n = 16), from series B 64.7 ± 0.3 vol.% (n = 18) and from series C 61.0 ± 0.8 vol.% (n = 14). The porosity was calculated geometrically using the sample's dimension and weight.

Chemical analysis: Interstitial contents of starting powders and of sintered samples were analyzed by oxygen combustion combined with IR-spectroscopy for oxygen and carbon, and by thermal conductivity for nitrogen. Three to five specimens were used for each sample type.

Microstructural characterization: The microstructure of sintered samples before and after mechanical testing was investigated. Samples were cut with a Sommer 2400 diamond wire saw (Sommer Präszisionstechnik, Usingen, Germany) and subsequently ground and polished. Optical

Table 2
Chemical analyses of sintered samples (3–5 samples per analysis).

Production route	Content [wt.%]		
	Oxygen	Nitrogen	Carbon
Series A	0.336 ± 0.011	0.0225 ± 0.0030	0.0058 ± 0.0008
Series B	0.443 ± 0.004	0.0461 ± 0.0045	0.0116 ± 0.0012
Series C	0.580 ± 0.137	0007 ± 0.005	0.076 ± 0.021