Eren Yılmaz[a], Azim Gökçe[b], Fehim Findik[a,b], Hamit Özkan Gülsoy[c]
[a]Biomedical, Magnetic and Semiconductor Materials Application & Research Center (BIMAS-RC), Sakarya University, Sakarya, Turkey
[b]Metallurgy & Materials Engineering Department, Faculty of Technology, Sakarya University of Applied Sciences, Sakarya, Turkey
[c]Metallurgy & Materials Engineering Department, Faculty of Technology, Marmara University, Istanbul, Turkey

Biomedical porous Ti-16Nb-10Zr-(0–15)Ta alloys

Paper presented at the "VII International Congress of Biomaterials, BIOMAT'18", 14–16 March 2018, Havana, Cuba

To improve the properties of compact Ti alloys for biomedical applications, porous Ti-16Nb-10Zr-(0–15)Ta (wt.%) alloys were produced by the space-holding method using an ammonium hydrogen carbonate space holder. The pore size distribution, porosity ratio and mechanical properties of the obtained porous alloys were investigated. Also, the effect of Ta addition on the microstructure and mechanical properties was investigated. It has been determined that the sintered porous Ti–Nb–Zr–Ta alloys have suitable mechanical properties (elastic modulus: 36.32–38 GPa, transverse rupture strength: 154–281 MPa) for hard tissue implants.

Keywords: Porous Ti–Nb–Zr–Ta alloys; Space holder method; Elastic modulus; Implant

1. Introduction

The first-generation Ti alloys containing alloying elements such as Al, V, Ni, and Co have a higher elastic modulus (115–120 GPa) than that of bone (5–30 GPa). This mechanical incompatibility with the bone and the implant causes bone resorption and implant loosening [1, 2]. In addition, the elements Al, V, and Ni have a toxic effect through ion release in the aggressive body environment. To overcome these drawbacks, beta titanium alloys containing non-toxic elements such as Nb, Zr, and Ta have been extensively studied in recent years. The addition of Nb and Ta to Ti alloys increases the beta phase stability and reduces the elastic modulus [3]. It is also known that the alloying of Ti with elements such as Nb, Zr, and Ta increases corrosion resistance due to oxide formation on the surface [4].

Beta stabilizing elements can reduce the elastic modulus to a certain level (60–100 GPa). Porous alloy production is recommended to avoid mechanical incompatibility between implant and bone. The porous structure promotes the growth of bone tissue into the implant pores, thereby providing better biological fixation [5]. The pores allow for body fluid transport and nutrient delivery. Therefore, porosity is important for both mechanical properties and biological activities [6].

Although casting methods are widely used in implant technology, the production of Ta-containing Ti alloys is difficult due to the difference in the melting temperatures of the elements Ti and Ta. The powder metallurgy (PM) method allows for the production of such alloys with net-shape and controlled porosity and without segregations [7]. Previous works on the properties of the Ti–Ta and Nb–Ti–Ta alloys revealed that the mechanical values of these alloys are higher than that of bone [7, 8].

In this study, porous Ti-16Nb-10Zr-*X*Ta ($X = 0$, 5, 10, 15 wt.%) Ta alloys were produced by PM, using NH_4HCO_3 as a space holder. The effect of Ta on microstructure, mechanical properties and porosity characteristics has been investigated.

2. Experimental procedure

Ti (purity 99.5 %, particle size 45 μm), Nb (purity 99.8 %, particle size 45 μm), Zr (purity 98.8 %, particle size 45 μm) and Ta (purity 99.6 %, particle size 45 μm) powders were weighed according to the nominal compositions of Ti-16Nb-10Zr-*X*Ta Ta (X = 0,5,10,15 wt.%) alloys. Then the metallic powders were mixed in a Turbula mixer for 2 h and were stirred with NH_4HCO_3 (with content of 50 vol.%) for 40 min. The mixture was cold pressed with dimensions of $13.60 \times 33.66 \times 5$ mm^3 using 200 MPa pressure. Space holder removal was conducted at 250 °C for 2 h under Ar atmosphere. Thereafter, sintering was performed at 1 300 °C for 3 h under vacuum.

The densities of the porous alloys were calculated according to the ASTM B-962 standard. Kroll solution was used as an etchant. Emerging pores were characterized using a Nikon Eclipse L50 optical microscope coupled with Clemex Image Analysis software. A scanning electron microscope (SEM) (Jeol JSM-6060LV) was used to examine the microstructural properties. X-ray diffraction (Rigaku D/Max-2200) analysis was performed to determine the phase components.

Elastic modulus measurements and transverse rupture strength (*TRS*) tests were performed to investigate the mechanical properties. Following the ASTM E494-15 standard, the transverse and longitudinal ultrasonic sound velocities of dense alloys were measured using an ultrasonic flaw detector (Olympus Epoch 650). Details about the method used to calculate the elastic moduli of the alloys are given elsewhere [9].

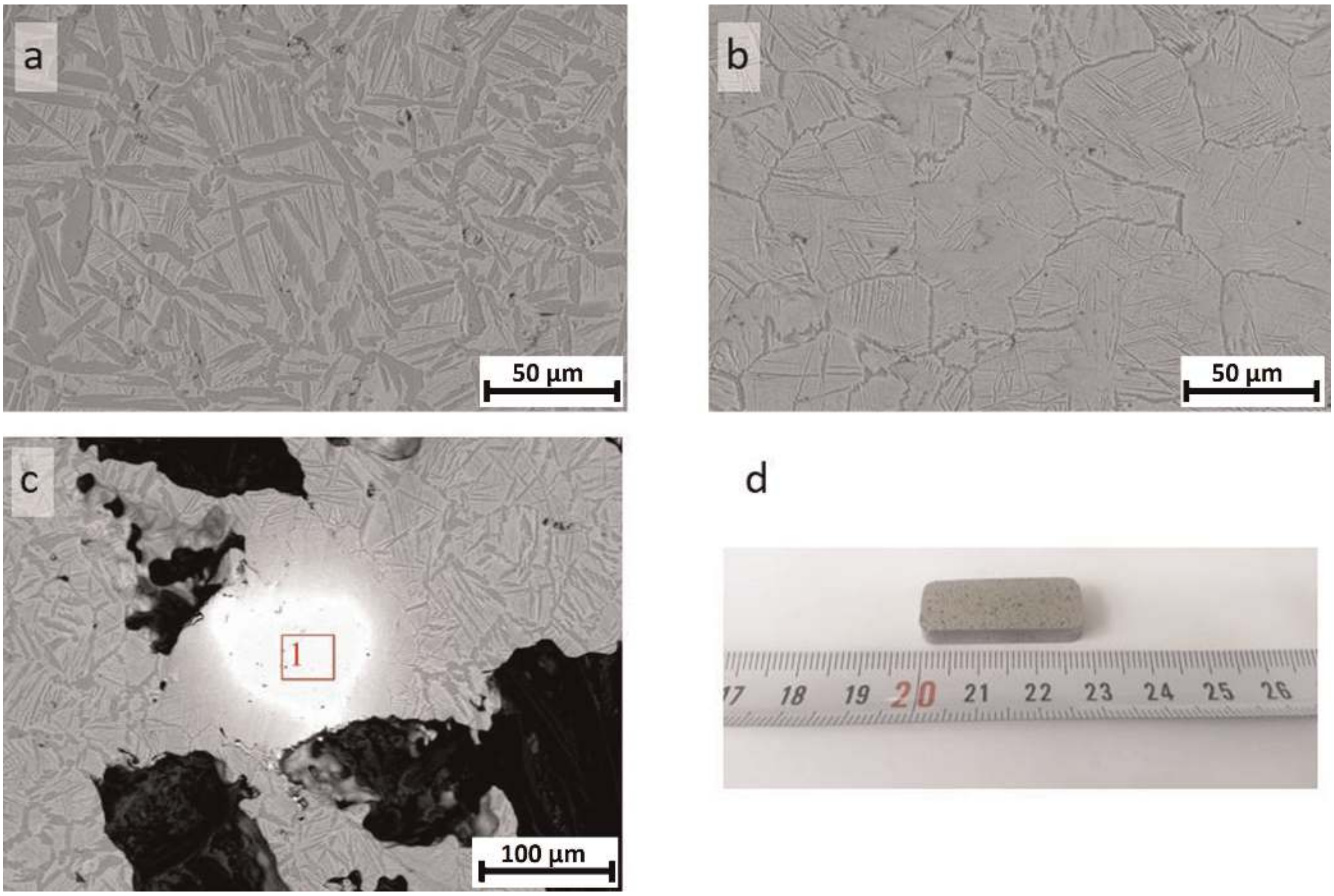

Fig. 1. SEM images of sintered (a) Ti-16Nb-10Zr, (b) Ti-16Nb-10Zr-15Ta, (c) Ti-16Nb-10Zr-5Ta, and (d) macrograph of sintered compact.

3. Results and discussion

3.1. Microstructural characterization

SEM images of the produced alloys (Fig. 1a–c) showed that as the amount of Ta increases, light-colored regions increase. This situation implies that Ta increases the amount of the β phase owing to its β stabilizing property. Also, an image of the sintered sample (Fig. 1d) revealed that samples were not distorted during sintering. It is clearly seen from the XRD analysis (Fig. 2) that Ta causes an increase in the height of the β peaks and the suppression of the α phase; such behavior is common for similar alloy systems [8]. The energy dispersive X-ray spectroscopy (EDS) analysis of the zone enclosed with a white rectangle in Fig. 1c shows that this region is rich in tantalum. It is thought that Ta was not dissolved on the Ti matrix due to its low diffusion coefficient at the sintering temperature; this caused some Ta clusters to form in the matrix. Liu et al. [8] stated that an increase in the sintering temperature is necessary to avoid such clusters.

Pore size distribution and average porosity size graphics (Fig. 3) of the produced alloys showed that the pore size distribution and average porosity size were about 9.5–87 µm and 34–38.6 µm, respectively. Although a 50 vol.% space holder was added to the produced parts, their porosity varied between 39.25–40.16 % (Table 1). It is thought that some pores shrank while others were closed during sintering [10].

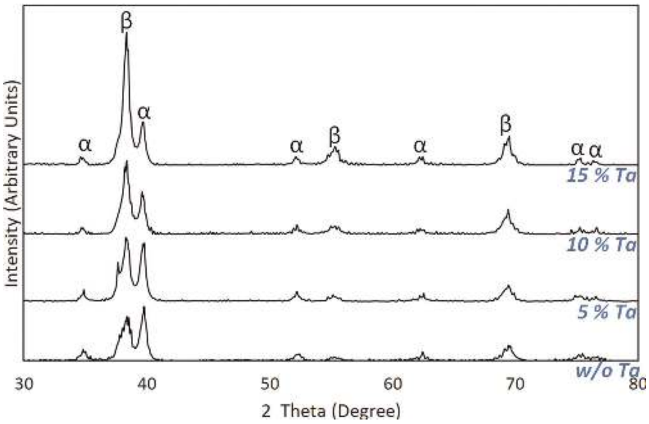

Fig. 2. XRD results for the sintered porous Ti-16Nb-10Zr-*X*Ta alloys.

Table 1. Density and mechanical properties of Ti16Nb10Zr*X*Ta porous alloys.

Property	Ta Content (wt.%)			
	0	5	10	15
Relative Density, ρ/ρ_s	0.607	0.600	0.604	0.599
Elastic Modulus, E (GPa)	38	37.90	37.61	36.32
Transverse Rupture Strength (MPa)	281	234	170	154

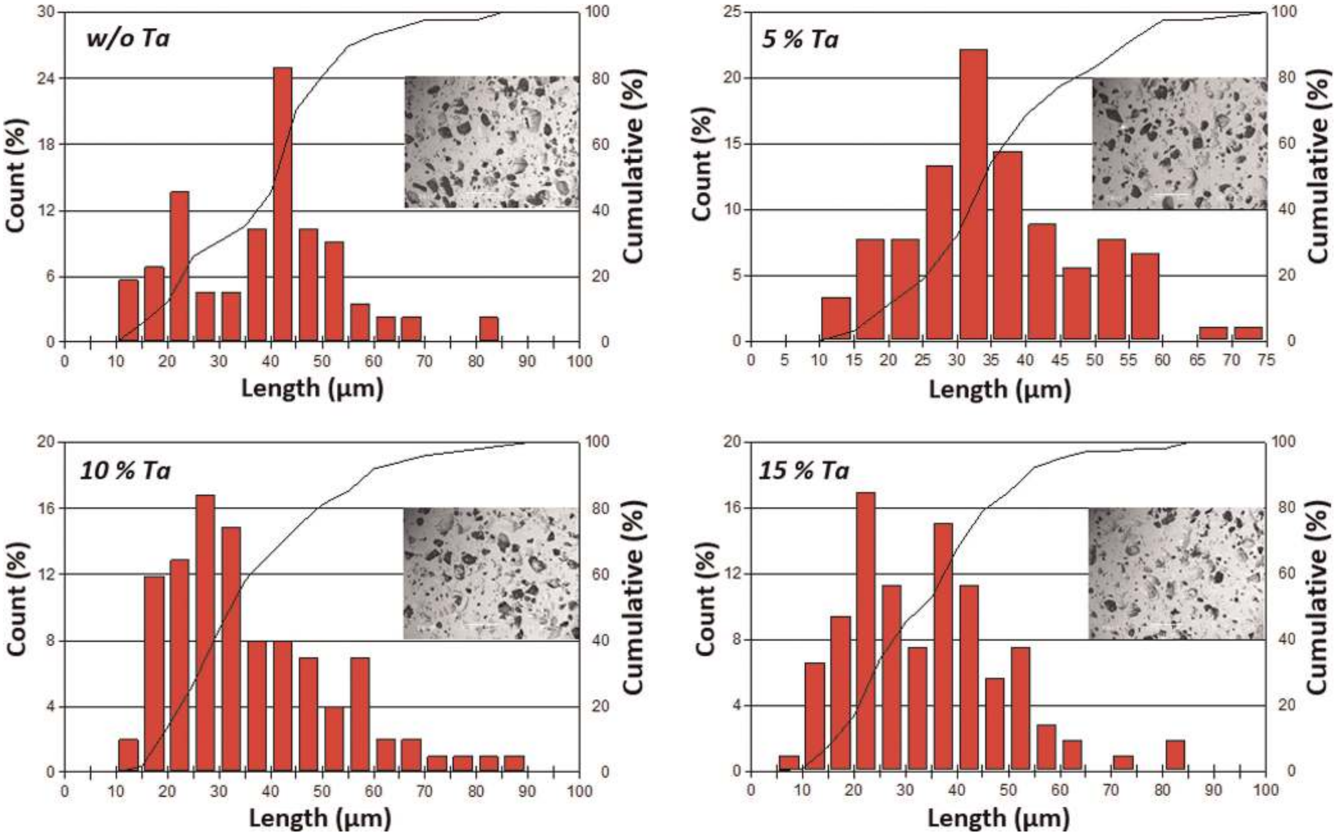

Fig. 3. Pore morphology and pore size distribution of alloys.

Sintering temperature, space holder size, and amount are all factors affecting pore morphology and porosity. The content of Ta did not have a significant effect on the amount and size of porosity. Isolated pores are observed in the produced parts while the porosity level is relatively low (30–50 %). As the size and number of space holders increase, isolated pores transform into connected pores [11].

The implant surface has significant effects on cell behavior and shear strength between bones and the implant [12]. Suitable porosity characteristics, such as porosity ratio (>40 %) and pore size (>100 μm), provide for the development of mineralization and vascularization by facilitating the access of body fluids and nutrients to the cell. Because the size of the MG63 cells is around 30 μm, the width of the hemispherical pores in the implant material must be at least approximately 30 μm for bone cell response [13]. To migrate and colonize, the cells need gaps equal to or greater than their size. If the pores are smaller than needed, the probability of fibrous tissue formation on the implant surface increases and mechanical interlocking on the bone–implant interface becomes insufficient [14]. The pore sizes of the produced parts were between 34–38.6 μm and the porosity ratio was 40 %. Although these values are in the margins for cell activity formation, it is thought that a space holder with a higher particle size should be used to obtain optimum porosity size.

3.2. Mechanical properties

Table 1 provides information about the mechanical properties of produced alloys. In Ti alloys, Ta has a β phase stabilizing effect. The addition of Ta to the Ti–Nb alloys increases the lattice parameters due to the higher atomic diameter of the Ta [7]. The relative density decreased slightly with the addition of Ta (Table 1). Recent work has shown that the Ta causes an increase in porosity [8]. These effects of Ta weaken the interatomic bond strength and consequently reduce the mechanical properties. The addition of 15 wt.% Ta to the Ti-16Nb-10Zr alloy reduced the *TRS* from 281 MPa to 154 MPa. In previous work on Ti alloys, the addition of Ta reduced the tensile strength [8]. The effect of Ta on the elastic modulus was insignificant (Table 1). A similar trend has been reported by Liu et al. in their work on the production of Ti–Ta alloys by PM [8]. The almost constant stability of the elastic modulus can be explained by the fact that, in addition to reducing strength, Ta causes solid solution hardening.

The *TRS* and elastic modulus of the cortical bone are 110–184 MPa and 4–30 GPa, respectively [15]. The elastic modulus of dense Ti-16Nb-10Zr-*X*Ta alloys is measured from 100–105 GPa. The increase in porosity leads to the reduction of the effective area carrying the load and also causes an increase in stress concentration. The mechanical properties of the produced alloys were measured as being approximate to that of the bone.

4. Conclusions

The present study obtained the following results.

- All sintered alloys are composed of α and β phases. β phase stability increased as Ta was added to the Ti-16Nb-10Zr alloy.

- About 40 % porosity Ti-16Nb-10Zr-*X*Ta alloys was produced using a 50 % by volume space holder. Pore size distribution and average pore size were measured at 9.5–87 μm and 34–38.6 μm, respectively.
- The addition of Ta to the Ti-16Nb-10Zr alloy caused a decrease in *TRS* while the elastic modulus remained almost constant.
- With the addition of the space holder to the base alloy, the *TRS* and elastic moduli of the alloys decreased by 71–84 % and 42–44 % respectively compared to those of the dense alloy reported in the literature.

References

[1] Y.L. Zhou, M. Niinomi: J. Alloys Compd. 466 (2008) 535–542. DOI:10.1016/j.jallcom.2007.11.090
[2] C. Aguilar, C. Guerra, S. Lascano, D. Guzman, P.A. Rojas, M. Thirumurugan, L. Bejar, A. Medina: Mater. Sci. Eng. C 58 (2016) 420–431. PMid:26478329; DOI:10.1016/j.msec.2015.08.053
[3] L.M. Elias, S.G. Schneider, S. Schneider, H.M. Silva, F. Malvisi: Mater. Sci. Eng. A 432 (2006) 108–112. DOI:10.1016/j.msea.2006.06.013
[4] D.Q. Martins, W.R. Osório, M.E.P. Souza, R. Caram, A. Garcia: Electrochim. Acta 53 (2008) 2809–2817. DOI:10.1016/j.electacta.2007.10.060
[5] J. Rivard, V. Brailovski, S. Dubinskiy, S. Prokoshkin: Mater. Sci. Eng. C 45 (2014) 421–433. PMid:25491847; DOI:10.1016/j.msec.2014.09.033
[6] J.Y. Xiong, Y.C. Li, Y. Yamada, P. Hodgson, C.E. Wen: Mater. Sci. Forum 561–565 (2007) 1689–1692. DOI:10.4028/www.scientific.net/MSF.561-565.1689
[7] J. Liu, L. Chang, H. Liu, Y. Li, H. Yang, J. Ruan: Mater. Sci. Eng. C 71 (2017) 512–519. PMid:27987739; DOI:10.1016/j.msec.2016.10.043
[8] Y. Liu, K. Li, H. Wu, M. Song, W. Wang, N. Li: J. Mech. Behav. Biomed. Mater. 51 (2015) 302–312. PMid:26275506; DOI:10.1016/j.jmbbm.2015.07.004
[9] E. Yılmaz, A. Gökçe, F. Findik, H.O. Gulsoy, O. İyibilgin: J. Mech. Behav. Biomed. Mater. 87 (2018) 59–67. PMid:30041140; DOI:10.1016/j.jmbbm.2018.07.018
[10] A.C. Alves, I. Sendão, E. Ariza, F. Toptan, P. Ponthiaux, A.M.P. Pinto: J. Porous Mater. 23 (2016) 1261–1268. DOI:10.1007/s10934-016-0185-0
[11] X. Rao, C.L. Chu, Y.Y. Zheng: J. Mech. Behav. Biomed. Mater. 34 (2014) 27–36. PMid:24556322; DOI:10.1016/j.jmbbm.2014.02.001
[12] S.F. Hulbert, F.A. Young, R.S. Mathews, J.J. Klawitter, C.D. Talbert, F.H. Stelling: J. Biomed. Mater. Res. 4 (1970) 433–456. PMid:5469185; DOI:10.1002/jbm.820040309
[13] O. Zinger, K. Anselme, A. Denzer, P. Habersetzer, M. Wieland, J. Jeanfils, P. Hardouin, D. Landolt: Biomaterials 25 (2004) 2695–2711. PMid:14962549; DOI:10.1016/j.biomaterials.2003.09.111
[14] J. Li, H. Liao, B. Fartash, L. Hermansson, T. Johnsson: Biomaterials 18 (1997) 691–6. DOI:10.1016/S0142-9612(96)00185-8
[15] Y. Li, C. Yang, H. Zhao, S. Qu, X. Li, Y. Li: Materials (Basel). 7 (2014) 1709–1800. PMid:28788539; DOI:10.3390/ma7031709

(Received March 21, 2018; accepted October 26, 2018)

Correspondence address

Prof. Dr. Hamit Özkan GÜLSOY
Metallurgy and Materials Eng. Dep.
Technology Faculty,
Marmara University
Turkey,
Istanbul
Tel: +90 216 3365770
Fax: +90 216 3378987
E-mail: ogulsoy@marmara.edu.tr
Web: http://abys.marmara.edu.tr/hamitozkan.gulsoy/

Bibliography
DOI 10.3139/146.111749
Int. J. Mater. Res. (formerly Z. Metallkd.)
110 (2019) E; page 1–4

ISSN 1862-5282