Research Paper

Mechanical behavior and microstructure of compressed Ti foams synthesized via freeze casting

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Abstract

Pure Ti and Ti-5%W foams were prepared via freeze casting. The porosity and grain size of both the materials were 32–33% and 15–17 μm, respectively. The mechanical behavior of the foams was investigated by uniaxial compression up to a plastic strain of ~0.26. The Young's moduli of both foams were ~23 GPa, which was in good agreement with the value expected from their porosity. The Young's moduli of the foams were similar to the elastic modulus of cortical bones, thereby eliminating the osteoporosis-causing stress-shielding effect. The addition of W increased the yield strength from ~196 MPa to ~235 MPa. The microstructure evolution in the grains during compression was studied using electron backscatter diffraction (EBSD) and X-ray line profile analysis (XLPA). After compression up to a plastic strain of ~0.26, the average dislocation densities increased to ~3.4 × 10^{14} m^{-2} and ~5.9 × 10^{14} m^{-2} in the Ti and Ti–W foams, respectively. The higher dislocation density in the Ti–W foam can be attributed to the pinning effect of the solute tungsten atoms on dislocations. The experimentally measured yield strength was in good agreement with the strength calculated from the dislocation density and porosity. This study demonstrated that the addition of W to Ti foam is beneficial for biomedical applications, because the compressive yield strength increased while its Young's modulus remained similar to that of cortical bones.

1. Introduction

Metallic materials have significant advantages over ceramic and polymer materials as orthopedic implants owing to their excellent properties such as superior strength, fracture toughness and ductility (Geetha et al., 2009; Ryan et al., 2006). Particularly, significant attention has been paid to Ti and Ti-based alloys owing to their relatively low modulus,
high strength, superior corrosion resistance, and excellent biocompatibility (through the formation of an oxide layer upon contact with air) (Yamamoto et al., 2012; Long and Rack, 1998; Choi et al., 2014).

Despite the increasing reputation of Ti and Ti-based alloys as orthopedic implants, they still suffer from stress-shielding effect when used in the bulk form because they have significantly greater elastic moduli than that of bone, thus eventually resulting in osteoporosis and loosening of the implant (elastic modulus for natural bone: 3–20 GPa; elastic modulus for Ti and Ti-based alloys: 55–117 GPa) (Geetha et al., 2009; Li et al., 2004; Krishna et al., 2007). Therefore, their porous counterparts with lower elastic moduli values are often preferred for orthopedic implant applications. Moreover, the porous structure of the implant plays an important role in bone integration, i.e., the porous surface facilitates strong interlocking with the bone tissue around the implant, resulting in high resistance to fatigue loading and biomechanical compatibility (Geetha et al., 2009; Sauer et al., 1974; Niinomi, 2008).

Several manufacturing methods have already been proposed for porous Ti. One of the most common methods is the space-holder technique. In the space-holder method, Ti powder is mixed with organic solvents and carbamide as space-holder, which is removed later by heat-treatment to leave hollow spaces (Niu et al., 2009). A gel-casting is somewhat similar to the space-holder method. A mixture of Ti powder and some solvents forms a porous structure through casting and gelation, subsequently followed by drying and sintering (Erk et al., 2008). Another interesting process is the printing processing in which Ti powder and solvent are mixed to produce Ti ink and fabricate a 3-dimensional porous structure of Ti foam through sintering (Hong et al., 2011). Finally, Ibrahim et al. also demonstrated the processing of porous Ti using spark plasma sintering (Ibrahim et al., 2011). In this study, we selected a freeze-casting method to produce Ti and Ti-5%W alloy foams, because this processing method can control the pore morphology, pore size, and porosity of Ti foams fairly reasonably. Therefore, the freeze-casting method can allow relatively easy scale-up and commercialization.

Along with the elastic modulus, we must also investigate the plastic properties and fundamental deformation mechanisms for the porous implant materials because those properties are critical for their successful use as load-bearing implant. For example, the femur bone is normally expected to support approximately 30 times the weight of a typical adult female body (Magee, 2008; D’Angeli et al., 2013). However, only a few studies have focused on comprehensive analysis of mechanical properties of porous Ti and Ti-based alloys from the perspective of their potential use in biomedical applications. For instance, the hardness, compressive strength, and stiffness (Young’s modulus) were analyzed through compressive tests on porous Ti and Ti-based alloys (Taniguchi et al., 2016; Hong et al., 2011; Muñoz et al., 2015). Additionally, a fatigue test was performed on strain accumulated Ti-6Al-4V foam with the corresponding images and modeling results analyzed on the tested samples (Zhao et al., 2016). Despite these studies on compressive strength, fatigue, and fracture, a systematic analysis is still required particularly on the variations in microstructural and physical properties such as variations in pore morphology, deformation mechanism, and elastic modulus during compression of porous Ti and Ti-based alloys.

Therefore, in the present study, we synthesized Ti and Ti-5%W alloy foams via freeze casting for a systematic analysis on the microstructural evolution of the Ti foams during compression. Tungsten (W) was added to improve the strength and wear resistance through a solid-solution strengthening effect of W in Ti grains (Choi et al., 2014, Frary et al., 2003). Moreover, we analyzed the microstructural evolution, elastic moduli, compressive strengths and deformation mechanisms of the freeze-cast porous Ti and Ti-5%W alloy foams using compression test, electron backscatter diffraction (EBSD) and X-ray line profile analysis (XLPa). In particular, we investigated the subgrain boundaries and the dislocation densities of the compressed samples using EBSD and XLPa. We also examined the effect of porosity and dislocations on the mechanical properties (e.g., elastic modulus, flow stress) of Ti foams. This systematic study using a range of analytical test methods are expected to provide valuable insights on the mechanical and deformation behavior of porous Ti and Ti-based alloy foams and other applicable porous implants under complex stress and strain states for their potential use as biomedical materials.

2. Material and methods

2.1. Preparation of Ti foams via freeze casting

Pure Ti foam was synthesized from commercially pure Ti powder (Alfa Aesar, MA, USA) with a mesh value of 325 (particle size is smaller than 44 μm). The concentration of metallic impurities was less than 0.2%. Among the nonmetallic elements, oxygen and nitrogen have the highest concentrations with values of 0.694% and 0.3%, respectively, according to the manufacturer’s analysis. Ti-W alloy foam was also synthesized. In this case, 5 wt% W powder with an average particle size of 1 μm was added to the Ti powder. A sequence of experimental procedures was performed to prepare the samples prior to freeze casting. First, polyvinyl alcohol (PVA; Mw 89,000–98,000, purity ~99%, Sigma-Aldrich Co., MO, USA) was dissolved in distilled water, and an appropriate amount of Ti or Ti/W powder mixture was then added to the prepared solution to complete the slurry. The slurry was then poured directly on top of a Cu chiller rod of 40 mm in diameter standing in a stainless steel vessel under liquid N₂. In order to ensure thermal protection along the horizontal direction and allow heat transfer through contact between the slurry and the Cu rod, the slurry was wrapped with polyethylene foil and inserted into a polymer mold. The freezing rate was ~10°C/min. The frozen green body was lyophilized in a freeze dryer (Operon, OPR-FDU-7003, Republic of Korea) to remove ice through sublimation at ~90°C and 5 × 10⁻³ Torr for over 24 h. The lyophilized green body was then sintered in a vacuum furnace at 1050°C for 6 h.
2.2  Mechanical test

Cuboid specimens with dimensions of 3 × 3 × 6 mm³ were cut from the pure Ti and Ti-W foams. Quasi-static uniaxial compression tests were conducted on these samples at a strain rate of $\sim 10^{-4} \text{s}^{-1}$ using an MTS universal mechanical testing machine. Three specimens were tested for each compression test and the results showed good reproducibility. The mechanical tests were interrupted at several selected strains in order to investigate the evolution of the defect structure during compression. The true strain was determined from the cross-head displacement as $\ln(l_0/l)$, where $l_0$ and $l$ are the heights of the initial and deformed samples, respectively. The true stress was calculated as the ratio of the force and the cross-sectional area of the compressed sample. For porous structures, the actual cross-sectional area cannot be determined from the cross-section of the initial sample and the true strain, because the sample volume may change during compression. Therefore, the cross-sectional area was measured directly at the beginning and end of deformation as well as at the strains where the compression test was interrupted. Between these strain values, the cross-section was determined by interpolation using an exponential function.

2.3  Microstructure analysis by EBSD and XLPA

The EBSD analysis was performed using an FEI Quanta 3D dual beam scanning electron microscope (SEM) equipped with an EDAX type EBSD system. In order to obtain high-quality EBSD images, mechanically polished surfaces of the samples were ion milled for 25 min by a 10 keV Ar-ion beam at an incidence angle of $\sim 6^\circ$. The EBSD scans covered 200 μm × 200 μm regions with a step size of 0.5 μm between neighboring measurement positions. The grain size and misorientation distributions were determined from the EBSD scans using OIM software (version 5.3) from TexSEM Laboratories (TSL).

Moreover, XLPA was also performed to investigate the microstructure of the samples. The X-ray line profiles were measured with a high-resolution rotating anode diffractometer (Rigaku, RA MultiMax-9) using CuKα₁ ($\lambda = 0.15406$ nm) radiation. Two-dimensional (2D) imaging plates were used for detecting the Debye-Scherrer diffraction rings. The line profiles were obtained by integrating the 2D intensity distribution along the rings, and the X-ray diffraction patterns were evaluated using the convolutional multiple whole profile (CMWP) fitting method (Ribárik et al., 2004). In this procedure, the diffraction pattern is fitted by the sum of a background spline and the convolution of the instrumental pattern and the theoretical line profiles related to the crystallite size and dislocations. The instrumental profiles were measured on a LaB₆ standard sample under the same conditions as those applied for the Ti foam samples. The theoretical profile functions were calculated on the basis of a model of the microstructure having spherical crystallites and lognormal size distribution, and the lattice strains were assumed to be caused by dislocations. Approximately fourteen peaks of Ti were fitted in the evaluation of line profiles. The area-weighted mean crystallite size ($<x>_{\text{area}}$) and the dislocation density ($\rho$) were obtained from this method. In addition, the prevailing dislocation slip systems in hexagonal crystals were determined. The experimental values of parameters $q_1$ and $q_2$ in the dislocation contrast factors obtained by the CMWP method depend on the type of dislocations. The theoretical $q_1$ and $q_2$ values for the 11 possible slip systems in Ti were calculated according to Kuzel and Klimanek (1988) and are listed in Dragomir and Ungár (2002). The 11 dislocation slip systems can be classified into 3 groups on the basis of their Burgers vectors: $b_1 = 1/3[\overline{2}1\overline{1}0]$ ($<a>$ type), $b_2 = (0001)$ ($<c>$ type), and $b_3 = 1/3[\overline{2}113]$ ($<c+a>$ type). A comparison of the experimental and theoretical values of parameters $q_1$ and $q_2$ yields the fractions of $<a>$, $<c>$, and $<c+a>$ dislocations. A detailed description of the evaluation procedure can be found in Máthis et al. (2004).

3.  Results

3.1  Microstructures of initial foams

The initial microstructures of the pure Ti and Ti-W foams are shown in Figs. 1a and 2a, respectively. The black areas correspond to the pores, while the colored areas indicate the orientations of the grains. The volume fraction of pores was determined as the fraction of black areas in the SEM images. According to quantitative metallography, these two fractions are equal within error range. The pore volume fraction values for the pure Ti and Ti-W foams were 33% and 32%, respectively, thus indicating that the porosity was not altered by W alloying. The porosity was also estimated from the density obtained as the ratio of mass to volume of the samples. A direct Archimedes’ method could not be employed for determining the volume of these foams because they have a large fraction of open pores, as revealed by microscopic observations. Alternatively, the volume was calculated from the product of the three orthogonal dimensions of the cubic specimens. The porosity volume fractions for Ti and Ti-W foams obtained from the density measurement were 33% and 30%, respectively, which are in good agreement with the values obtained from EBSD analysis. The average grain size values for the Ti and Ti-W foams were 17 μm and 15 μm, respectively, therefore neither the grain size nor the porosity was significantly altered in the two foams. Electron probe microanalysis (not presented in this paper) indicated that in the Ti-W foam, $\sim 2$ wt% W was completely dissolved into Ti grains, while the other 3 wt% W remained uniformly as secondary phase particles.

3.2  Mechanical behavior of foams under compressive load

Fig. 3a and b show the true stress vs. true strain curves for the Ti and Ti-W foams during compression. The mechanical test was performed up to a total strain of approximately 0.3 for both foams (which corresponds to a plastic strain of approximately 0.25–0.28). Below this strain, the deformation was homogeneous in the samples because strain localization was not observed on the surfaces of the compressed specimens. At the end of compression tests (at the plastic strains of 0.28 and 0.25 for Ti and Ti-W foams, respectively), the plastic
Poisson’s ratio was 0.35 ± 0.03 (the ratio of the magnitudes of engineering strains measured normal and parallel to the loading axis). The mechanical tests were interrupted at plastic strains of approximately 0.06–0.07 and 0.16–0.17 to investigate the evolution of the defect structures (dislocations and grain boundaries) during compression, and the results are presented in the following section. The Young’s moduli and yield strength values of both foams were determined from the first loading curve (see Table 1). It should be noted that the compression stress–strain curves are not strictly linear in the initial stage of deformation, and a transient stage was observed for which the derivative of the curves increased with increasing strain. This nonlinear stress–strain behavior can be attributed to the nonparallel orientations of the contact surfaces of the samples and the instrument crosshead. Therefore, the Young’s modulus was determined from the linear section of the stress–strain curve after this transient stage. The elastic moduli values obtained for the pure Ti and Ti–W foams were 23 ± 2 GPa and 22 ± 2 GPa, respectively, thus indicating that W alloying has negligible influence on Young’s modulus, which is in agreement with a previous study where W dissolution in Ti matrix up to 10 wt% had little effect on the Young’s modulus of Ti-10W alloy (Choe et al., 2005). On the other hand, the yield strength is more sensitive to W alloying because its value was much higher for the Ti–W foam (~235 MPa) than for the pure Ti foam (~196 MPa).

It should be noted that the present Ti foam processed by freeze casting exhibited higher strength than the value predicted from other experiments as well as those from theoretical calculations (Siegkas et al., 2016). The previously reported experiments were carried out on Ti foams sintered with the help of a polymeric binder and a foaming agent. In the theoretical prediction, virtual foam geometries were created using a procedure based on Voronoi tessellation. Additionally, the quasi-static mechanical response was determined by finite element simulations. More specifically, the flow stress at a compressive strain of 0.05 was predicted to be 240 ± 10 MPa from the experimental and theoretical values for the foams with porosity of ~33%. For our freeze-cast Ti foam, the flow stress at the same strain was measured to be larger (~320 MPa), due most likely to the different pore morphology and structure developed in the foams caused by the different processing method.

The strain hardening behavior of pure Ti and Ti–W foams was analyzed by plotting the derivative of stress with respect
to plastic strain \((ds/d\epsilon_p)\) as a function of stress \((\sigma)\), as shown in Fig. 4 (Kocks–Mecking plot). The plastic strain was determined by subtracting the elastic strain component from the total strain, where the former quantity was determined as the ratio of actual stress to Young's modulus. Owing to the interruption of compression test and the noise of measurement, \((ds/d\epsilon_p)\) could not be directly obtained by determining the derivative of the experimental data. Therefore, the following function was fitted to the \(\sigma-\epsilon_p\) data points and the derivative of this fitted curve with respect to plastic strain.

**Fig. 2** – EBSD images showing microstructural evolution in Ti–W foam (a) in as-processed state and (b), (c), and (d) after quasi-static compression up to plastic strains of \(~0.06\), \(~0.16\), and \(~0.26\), respectively. Note that the color code is shown in the inset of Fig. 1d.

**Fig. 3** – True stress vs. true strain plots obtained with quasi-static compression tests at room temperature for (a) pure Ti and (b) Ti–W foams.
was then obtained as follows (Lademo et al., 1999):

$$\sigma = \sigma_0 + \sigma_1 (1 - \exp(-A_1 \epsilon_p)) + \sigma_2 (1 - \exp(-A_2 \epsilon_p)) + \sigma_3 (1 - \exp(-A_3 \epsilon_p)).$$

(1)

Fig. 3 shows that for both foams, strain hardening decreases gradually as stress increases, which is in accordance with the typical behavior of bulk Ti. The decrease in \((d\sigma/d\varepsilon_p)\) with increasing stress is caused by the annihilation processes of dislocations (e.g., cross-slip and climb). Irrespective of the foam state and W alloying, the \((d\sigma/d\varepsilon_p)\) versus \(\sigma\) curve can be divided into two segments. The decrease in strain hardening is much higher in the first segment than in the second segment. A comparison of the two foams shows that \((d\sigma/d\varepsilon_p)\) is larger for Ti-W than for Ti at any stress value because of the higher rate of increase in dislocation density due to the pinning effect of W on dislocations (see Section 3.3). The significantly lower stresses and strain hardening values of Ti foam than those of bulk Ti can be attributed to its porosity.

3.3. Microstructural evolution during deformation

The microstructure evolution in the two foams was investigated by interrupting the compression at plastic strains of approximately 0.06–0.07, 0.16–0.17 and 0.25–0.28 (see Fig. 3). The latter state corresponds to the end of deformation. Although, the plastic strain values at each interrupted state are slightly different for the two foams, we assume that the difference is insignificant and refer these states to the approximate plastic strain values of ~0.06, ~0.16, and ~0.26, respectively, for both foams. Figs. 1 and 2 show the EBSD images of the same area after compression at different strains for Ti and Ti-W foams, respectively. Because some grains shifted from the study surface during compression, the evaluable area decreased with increasing strain. Therefore, the black area in the images increases regardless of the variation in porosity. Hence, the porosity for the deformed samples could not be evaluated from the EBSD images. Instead, the porosity values of the compressed samples were estimated from the density obtained by measuring the mass and dimensions of the specimens.

In the as-processed foams, each grain can be characterized by a single color in the EBSD images (see Figs. 1a and 2a), indicating negligible misorientation inside the grains. On the other hand, different colors can be seen inside the grains of the plastically deformed samples, suggesting misorientations between the different parts of the grains. It should be noted that due to the uncertainty of the EBSD misorientation analysis, the threshold of misorientation angle measurement was set to be 2°, a standard value in the literature. In both the compressed foams, a majority of LAGBs (more than 95%) were characterized by misorientations less than 6°. Fig. 5a and b show the evolution of misorientation distributions in the pure Ti and Ti-W foams in an angle range of 2°–6°, respectively. The fraction of boundaries at a certain misorientation angle was calculated as the ratio of the length of these boundaries to the total length of edges of pixels inside the studied area (the possible locations of boundaries). Fig. 5a and b show that the amount of LAGBs increases with increasing plastic strain in both foams. LAGBs are typically formed by the arrangement of dislocations into low-energy configurations. Therefore, the increase in dislocation density during compression was investigated using XLPA.

The dislocation density was determined from the breadths of the X-ray diffraction peaks. The peak profiles were obtained from the Debye–Scherrer diffraction rings detected on the imaging plates. Fig. 6a and b show Debye–Scherrer rings for reflection 110 of the as-processed pure Ti-based foam sample and the sample compressed up to a plastic strain of ~0.26, respectively. The ring for the as-processed Ti foam consists of very narrow spots (see Fig. 6a) scattered from different grains. These measured peaks are as narrow as the instrumental broadening (\(\Delta(2\theta)=0.03°\)), thus suggesting a lower dislocation density and larger crystallite size when compared with the detection limits of the present diffraction setup \((10^{13} \text{ m}^{-2} \text{ for the dislocation density and } 1 \mu \text{m for the grain size})\). In the case of the compressed sample, the number of sharp spots decreased and a continuous broad ring was formed (see Fig. 6b) owing to the increase in dislocation density and/or reduction of crystallite size. The coexistence of both sharp spots and continuous broad ring segments indicates an inhomogeneous spatial distribution of lattice distortions caused by the compression of the foam. The sharp spots and broad ring segments correspond to the less and more deformed parts of the sample. Similar characteristics of Debye–Scherrer rings were observed for the Ti-W foam. Because the width of the sharp spots remained very narrow even after compression, these parts of the Debye–Scherrer rings were not evaluated. However, the continuous and broad segments of the rings were cut to determine dislocation density and crystallite size. The individual peaks as a
function of the diffraction angle ($2\theta$) were obtained by integrating the intensity along the rings (in direction $x$ in Fig. 6b), and these peaks were then used to construct the X-ray diffraction patterns for CMWP fitting. The average crystallite size values in the more deformed parts of the pure Ti and Ti-W foams were 60 and 63 nm, respectively, as obtained from CMWP fitting. It is noted that these crystallite size values are much smaller than the grain sizes observed in the EBSD images. This apparent discrepancy can be explained by the breaking of X-ray coherency due to the small misorientations inside the grains (Gubicza, 2014). Therefore, XLPA measures the size of the subgrains or dislocation cells rather than the true grain size. The dislocation densities in the more deformed parts of the Ti and Ti-W foams were $(6.2 \pm 0.7) \times 10^{14} \text{ m}^{-2}$ and $(9.3 \pm 1.0) \times 10^{14} \text{ m}^{-2}$, respectively. These values characterize only the strongly deformed parts of the material. Therefore, the average dislocation density of the whole material was calculated by considering the fraction of the less deformed parts in the foams. The latter quantity was determined as the fraction of the intensities of the sharp spots in the entire Debye–Scherrer ring. The intensity was summed in direction $2\theta$ (see Fig. 6b), and these integrated intensity values were plotted as a function of the coordinate $x$, as shown in Fig. 6c for reflection 110 of the pure Ti foam compressed up to a plastic strain of $\sim 0.26$. Thereafter, a spline was fitted to the parts of the intensity distribution that are free of sharp intensity peaks (see Fig. 6c). The area under this spline corresponds to the intensity scattered from the more deformed parts of the sample. The area under the sharp peaks but above the spline denotes the intensity scattered from the less deformed volumes. The fractions of the more deformed parts for the Ti and Ti-W foams were 55% and 63%, respectively. As the dislocation density is negligible in the less deformed volumes (it is lower than the detection limit,
The average dislocation density for the whole sample could be determined from the product of the volume fraction and the dislocation density of the more deformed parts. Therefore, the average dislocation density for the entire Ti and Ti-W foam materials (without pores) were $(3.4 \pm 0.4) \times 10^{14} \text{m}^{-2}$ and $(5.9 \pm 0.6) \times 10^{14} \text{m}^{-2}$, respectively. The higher dislocation density in the Ti-W foam is attributed to the pinning effect of the solute W atoms on dislocations formed inside the grains during compression. To the best of our knowledge, this is the first report on the dislocation density in compressed Ti foams prepared by freeze casting for biomedical applications.

Additionally, XLPFA analysis was also employed for the determination of the fractions of $<a>$, $<c>$, and $<c+a>$ dislocations. The procedure was described in detail by Mátíš et al. (2004). The fractions of $<a>$, $<c>$, and $<c+a>$ dislocations for both the Ti and Ti-W foams compressed up to a plastic strain of $0.26$ were $68 \pm 4\%$, $5 \pm 3\%$, and $27 \pm 3\%$, respectively. Similar dislocation type fractions were obtained in plastically deformed bulk Ti (Gubicza et al., 2008). The abundance of $<a>$-type dislocations can be attributed to their lowest energy due to the smallest Burgers vector.

4. Discussion

The measured elastic moduli of Ti and Ti-W foams were approximately $23 \text{GPa}$ and $22 \text{GPa}$, respectively, which are much lower than that of bulk Ti (approximately $114 \text{GPa}$) owing to the uniformly distributed porosity. The relationship between the elastic moduli of the foam ($E_f$) and bulk Ti ($E_b$), and the porosity ($P$) can be expressed as follows (Luo and Stevens, 1999):

$$E_f = E_b \exp(-kP), \tag{2}$$

where the value of parameter $k$ depends on the material. For the foams used in this study, $k = 0.05$. In order to confirm the validity of Eq. (2) for freeze-cast Ti foams, an additional pure Ti sample was synthesized with a porosity of $55\%$, as determined from the EBSD images. The higher porosity was achieved by a lower sintering temperature of $1020 \degree C$. For this sample, the elastic modulus and yield strength obtained by compression were $7 \text{GPa}$ and $44 \text{MPa}$, respectively. Using Eq. (2), the same value of $k$ was obtained for this sample as for the foams with $32\%$–$33\%$ porosity.

One of the most important mechanical parameters for surgical implant materials is Young’s modulus. In the case of traditional implant materials (such as bulk stainless steel or Ti), the elastic modulus of the implant $(100-200 \text{GPa})$ is significantly higher than that of cortical bones $(19-20 \text{GPa}$ (Rho et al., 1993)). Therefore, the implant eventually bears the majority of the external load owing to its higher elastic modulus. This stress-shielding effect typically leads to osteoporosis of the bones. However, a porous structure in implant materials can reduce their elastic moduli to an appropriate value. The elastic moduli of the present Ti and Ti-W foams $(23 \text{GPa})$ are similar to that of cortical bones, thus eliminating stress-shielding effect. Therefore, these Ti foams are promising candidates as bone implant materials.

Porosity also affects the plastic properties, i.e., yield strength and the strain hardening behavior of Ti foams. These parameters can be compared to the corresponding values for bulk Ti with Grade 2 purity with a similar grain size of $20 \mu \text{m}$ (Gubicza et al., 2008). Due to the porosity of pure Ti foam (33%), its yield strength $(196 \text{MPa})$ is lower by a factor of 1.7 when compared with that obtained for bulk Ti $(330 \text{MPa})$. At the end of the compression test (at a plastic strain of $0.26$), the flow stress of the Ti foam is primarily determined by the dislocation density in the grain interiors and the volume fraction of pores between the grains. The dislocation strengthening can be taken into account using the following Taylor equation:

$$\sigma_{\text{Y}} = aM^2Gb \sqrt{\rho}, \tag{3}$$

where $a$ is a constant $(0.5$ for Ti (Okazaki et al., 1977; Liu and Mishnaevsky, 2014)), $M$ is the Taylor factor $(3.05$ for texture-free Ti (Liu and Mishnaevsky, 2014; Panda et al., 2014)). $G$ is the shear modulus $(43 \text{GPa}$ for Ti), and $b$ and $\rho$ are the Burgers vector of dislocations ($0.37 \text{nm}$ if the population of the dislocation slip systems is taken into account; see above) and dislocation density, respectively. By substituting the dislocation density obtained via XLPFA into Eq. (3), dislocation strengthening was calculated to be $455 \text{MPa}$. Because the porosity decreased minimally during the present compression test, its effect was taken into account by dividing the value obtained from Eq. (3) by a factor of 1.7, which was determined from the ratio of the yield strength values of the bulk Ti and Ti foam. This stress value was then added to the yield strength, and a value of $464 \text{MPa}$ was obtained, which is in good agreement with the experimental flow stress value $(472 \text{MPa})$. In the case of the Ti-W foam, dislocation strengthening was greater $(600 \text{MPa})$ as obtained from Eq. (3) at a similar plastic strain value $(0.26)$ owing to the higher dislocation density. Taking the porosity effect into account, the flow stress value of the Ti-W foam was $580 \text{MPa}$, which is similar to the measured value $(525 \text{MPa})$, considering the experimental error. Therefore, we conclude that the addition of W to the Ti foam increased the flow stress by increasing the threshold stress of plasticity as reflected by the higher yield strength and by increasing the dislocation density by hindering the annihilation of dislocations. This study revealed that the addition of $5 \text{wt}\%$ W to Ti foam increased the compressive strength considerably while its Young’s modulus remained similar to that of cortical bones, thereby improving the mechanical performance of the Ti foam for its potentially promising use in biomedical applications.

5. Conclusions

In this study, we analyzed the mechanical properties and microstructural evolution during compression of Ti and Ti-W foams with the porosity of $32\%$–$33\%$ synthesized via freeze casting. The following conclusions were drawn:

1. The Young’s modulus for both Ti and Ti-W foams were $23 \text{GPa}$, which is in accordance with the predicted value from the porosity and elastic modulus values of bulk Ti.
the other hand, the yield strength was significantly affected by W content. The yield strength values for Ti and Ti–W foams were ~196 MPa and ~235 MPa, respectively. The higher yield strength for the Ti–W foam can be attributed to the solute hardening of tungsten. The Young’s modulus of the foams are similar to the elastic modulus of cortical bones, thereby eliminating the osteoporosis-causing stress-shielding effect and making the Ti foams potential candidates for use as surgical implant materials. It was also found that W addition increased the compressive strength of Ti foam considerably without changing its beneficial low value of Young’s modulus for its potential use in biomedical applications.

2. During compression up to a plastic strain of ~0.26, the dislocation densities in Ti and Ti–W foams increased to ~3.4 × 10^{14} m^{-2} and ~5.9 × 10^{14} m^{-2}, respectively. The higher dislocation density in the Ti–W foam can be attributed to the pinning effect of the solute W atoms on dislocations in Ti grains. According to the best of our knowledge, this is the first report on the dislocation density in compressed Ti foams prepared by freeze-casting for biomedical applications. It was revealed that the increase in flow stress during compression was caused by the increase of the dislocation density in the grain interiors.

3. The strain hardening behavior of the foams was investigated using the Kocks–Mecking plot. Strain hardening decreased gradually with increasing stress for both the foams and the reference bulk Ti material. At each stress value, the strain hardening rate was significantly greater for the Ti–W foam than for the pure Ti foam, most probably due to the higher rate of increase in dislocation density during compression, which was caused by the pinning effect of the solute tungsten atoms on dislocations.

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