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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 $\sim 3.4 \times 10^{14}\ m^{-2}$ and $\sim 5.9 \times 10^{14}\ m^{-2}$ 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,

Abbreviations: EBSD, electron backscatter diffraction; XLPA, X-ray line profile analysis; SEM, scanning electron microscope; LAGB, low-angle grain boundary

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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 N_2. 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 polystyrene 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.