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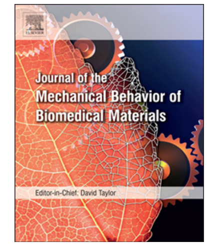

Research Paper

Synthesis of Ti–Ta alloys with dual structure by incomplete diffusion between elemental powders

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ABSTRACT

In this work, powder metallurgical (PM) Ti–Ta alloys were sintered using blended elemental powders. A dual structure, consisting of Ti-rich and Ta-rich zones, was formed due to the insufficient diffusion between Ti and Ta powders. The microstructure, mechanical properties and in vitro biological properties of the alloys were studied. Results indicated that the alloys have inhomogenous microstructures and compositions, but the grain structures were continuous from the Ti-rich zone to the Ta-rich zone. The Ta-rich zone exhibited a much finer grain size than the Ti-rich zone. The alloys had a high relative density in the range of 95–98%, with the porosity increasing with the content of Ta due to the increased difficulty in sintering and the formation of Kirkendall pores. The alloys had a good combination of low elastic modulus and high tensile strength. The strength of alloys was almost doubled compared to that of the ingot metallurgy alloys with the same compositions. The low elastic modulus was due to the residual pores and the alloying effect of Ta, while the high tensile strength resulted from the strengthening effects of solid solution, fine grain size and α phase. The alloys had a high biocompatibility due to the addition of Ta, and were suitable for the attachment of cells due to the surface porosity. It was also indicated that PM Ti–(20–30)Ta alloys are promising for biomedical applications after the evaluations of both the mechanical and the biological properties.

1. Introductions

Titanium (Ti) and Ti alloys have been widely used as implanting materials due to their high mechanical strength, large strength to density ratio, low specific gravity, high corrosion resistance in physiological media and high biocompatibility (Geetha et al., 2009). Low modulus and non-toxicity are the two major considerations in the development of new biomedical Ti alloys. The high Young's modulus of Ti implants may lead to the resorption of adjacent bone tissues and premature failure of the

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prosthetic devices. Besides, some alloying elements in conventional Ti alloys, such as V, Al, Ni and Cr, are harmful to the human body (Domingo, 2002; Steinemann et al., 1980). Therefore, the development of more corrosion resistant, low modulus and biologically friendly titanium alloys is very important. Nb (Kim et al., 2006), Zr (Correa et al., 2014), Mo (Ho et al., 1999) and Ta (Zhou et al., 2004) elements are usually added in Ti alloys. Most biomedical Ti alloys are fabricated by ingot metallurgy. However, the high melting points of Ti and refractory metals lead to high cost in the manufacturing process, and the segregation of some alloying elements is usually hard to eliminate (Mitchell, 1998).

Tantalum (Ta) exhibits excellent chemical stability and better biocompatibility than that of Ti (Balla et al., 2010). Therefore, pure Ta has been used as dental and orthopedic parts such as radiographic bone markers, vascular clips, and repairing components for cranial defect (Levine et al., 2006). However, Ta has a very high modulus of 200 GPa (Geetha et al., 2009). Due to the stress shielding effect and high cost, Ta is not considered for large implants in human body. There are some reports on lowering the modulus and weight of Ta by introducing porous structures (Sevilla et al., 2007; Bobyn et al., 2004). By depositing pure Ta onto a vitreous carbon scaffolding, Sevilla et al. (2007) prepared Ta foam with an open porosity ranging between 65% and 73%. The fatigue endurance limit of the foam at 10^8 cycles was only 13.2 MPa and the Young's modulus was 1.15 GPa (Sevilla et al., 2007). Therefore, the existence of high porosity and large pores is detrimental to the mechanical property of Ta, especially the dynamic fatigue resistance.

Ti–Ta binary alloys have attracted wide interests recently due to a good combination of high strength and low modulus (Zhou et al., 2004; Sumner et al., 1998). For example, Ti–70Ta (wt%) alloy with a metastable beta phase has a high strength of 600 MPa and low modulus of 67 GPa (Zhou et al., 2005). The martensitic transformation starting temperature (Ms) decreases by 30 °C per 1 at% Ta in Ti–Ta alloys with the content of Ta ranging from 30 to 40 at% (Buenconsejo et al., 2009). In the Ti-rich composition, Ti–30Ta alloy has an elastic modulus of 77 GPa and a tensile strength of 713 MPa (Zhou and Niinomi, 2009). The alloy has been commercialized for biomedical applications (Mareci et al., 2009). Due to the large difference in the melting points between Ti and Ta (about 1350 °C) and the segregation of Ta during the solidification, it is difficult to fabricate Ti–Ta alloys by ingot metallurgy. For example, Ti–Ta alloy was melted more than ten times to ensure the homogeneity (Zhou et al., 2004). The difficulty in the manufacturing process has hindered the applications of Ti–Ta alloys.

Through powder metallurgy, all the elements can be mixed homogeneously in the form of powders, and thus, it is convenient to fabricate alloys or composites with multiple components. So, it is suggested to fabricate Ti–Ta alloys by sintering blended elemental Ti and Ta powders. One difficulty lies in the fact that the diffusion coefficient of Ta at sintering temperatures (lower than the melting point of Ti) is so low that a complete alloying of both elements is not possible. Therefore, a gradient structure consisting of Ti- and Ta-rich zones might be formed. The structure combines the advantages of the light-weight of Ti and the high biocompatibility of Ta. Moreover, it is possible to adjust the mechanical properties of PM Ti–Ta alloys by changing the interfacial structure between the two zones. Thus, in this work, Ti–Ta composite structures were synthesized by sintering blended elemental powders. The microstructure and mechanical properties of PM Ti–Ta alloys were studied at different sintering temperatures and compositions. The biological behavior of the Ti–Ta alloys was also evaluated in order to explore the possibility of using the alloys for clinical applications.

2. Materials and methods

2.1. *Preparation of Ti–Ta alloys*

Elemental powders of Ti (purity >99.9%, particle size <45 μm) and Ta (purity >99.99%, particle size <5 μm) were blended in five nominal compositions: Ti–20Ta, Ti–25Ta, Ti–30Ta, Ti–35Ta and Ti–50Ta (at%). The mixed powders were compacted in cylinder form by the cold isostatic pressing under a pressure of 180 MPa for 2.5 min. Then, the compacts were sintered in high vacuum (10^{-4} Pa) at 1400 °C for 2 h. For Ti–30Ta alloys, temperatures ranging from 1200 °C to 1500 °C, with an interval of 100 °C, were also used during the sintering process.

2.2. *Material characterization*

The microstructures were observed using optical microscope (OM), transmission electron microscope (TEM), and scanning electron microscope (SEM) equipped with an energy dispersive X-ray analysis (EDX) unit. After sectioning, metallographic samples were ground, polished, and then etched with a solution of 10% HF, 5% HNO_3 and 85% H_2O (in volume). Thin foil specimens were prepared by mechanical milling on different emery paper to a thickness of 50–80 μm, and then by ion thinning.

X-ray diffraction (XRD) analyses were performed on a Rigaku D/Max 2500 v/pc X-ray diffractometer from 20° to 85° with a scanning speed of 4° min^{-1}. The pore features of the sintered Ti–Ta composite structures were characterized using a Leica DM2700 M optical microscope. The relative density was obtained by total area of the pores divided by the whole area. 20 optical micrographs were taken from the cross sections of each sample.

Rectangular bar specimens with a size of 10 mm × 2 mm × 42 mm were machined from the sintered specimens by electro discharge cutting, and then were ground and polished. The dynamic Young's modulus was determined by the resonance vibration method at room temperature as described previously (Zhou et al., 2004). The specimen was suspended and driven electrostatically in flexural vibration. The dynamic Young's modulus, E, was calculated from the following equation,

$$E = \frac{0.9649m\, L^3 f_r^2}{wd_3} \quad (1)$$