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Synthesis of porous Ti–50Ta alloy by powder metallurgy

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ABSTRACT

The aim of the present study was to assess the possibility of producing porous Ti−50Ta (wt%) alloys using powder metallurgy by characterizing the material properties. The influence of the sintering time on the microstructure, mechanical properties, and corrosion behaviour of the produced alloy was investigated. The samples were examined using scanning electron microscopy (SEM), transmission electron microscopy (TEM), optic microscopy, X-ray diffraction (XRD) and nanoindentation methods. The XRD results confirmed that nanocrystalline α and β phases were formed during high-energy ball milling. A longer sintering time of 72 h allowed complete interdiffusion of the elements in the pre-milled initial powders. The sintering time significantly influenced the microstructure and porosity. Additionally, the corrosion resistance of the Ti-Ta samples in Ringer's solution was characterized and differences were observed between the samples sintered at different temperatures. The open-circuit potential (E_{OCP}) and the corrosion potential (E_{CORR}) of all samples were similar. The sintered Ti−50Ta (wt%) alloy showed better corrosion resistance than equivalent Ti or Ta reference samples. We concluded that these alloys had suitable properties for medical implant applications in the future.

1. Introduction

The previous efforts of scientists and researchers have resulted in the development of implants which still fully do not meet the requirements of a human body. This is particularly important for long-term bone implants, the demand for which is increasing due to the higher prevalence of modern diseases such as diabetes, atherosclerosis, and osteoarthritis. The most important criteria from medical application point of view for biomedical alloy lies not only on non-toxicity of alloying elements, but also on its corrosion resistance. Furthermore, materials for an ideal biomedical implant should possess high strength and low Young module, most closely related to human bones. In orthopedic applications most useful parameter is a flexibility, defined as the strength to module ratio [1,2]. The higher the permissible strain, the more desirable materials are for such applications. However, metallic materials currently used in implantology do not fully replicate the behaviour of natural bone. Major disadvantages of implants include the presence of toxic elements and a significant mismatch between the mechanical properties of human bone and the implant material [3–7]. Based on previous research [8–15], it could be concluded that tantalum is one of the most promising additives for titanium alloys. The excellent biocompatibility and superior corrosion resistance of pure Ti and pure Ta have been extensively evaluated and recognized by many medical researchers. Ti–Ta alloys are promising materials for substitution of Ta as they are lighter and cheaper in comparison to “pure” Ta. Moreover, we expect that they have a higher corrosion resistance than pure Ti in reducing acids [1,13,14]. Ti–Ta alloys also have the lowest Young's modulus compared to currently used implant materials [3]. In addition, the strength of these alloys is comparable to cobalt-based alloys (e.g., Co-Cr-Mo). Zhou and Niinomi [11,16] showed that Ti–Ta alloys produced in a tri-arc furnace had strengths of 510–690 MPa depending on the percentage of added tantalum. The changes in the mechanical properties with increasing Ta content are not linear and have local maxima as they are strongly related to the specific phase of the material, which is highly dependent on the Ta content. Quenched Ti–Ta alloys containing < 20% Ta exhibit a hexagonal structure (α′), while the orthorhombic structure (α″) is observed for a Ta content of 30–50%. The microstructure characteristic for β phase was observed when the Ta content was > 60% [11]. The Young's modulus is a critical mechanical property, showing a minimum (67 GPa) for 70 wt% Ta and 69 GPa for 30 wt% Ta additions [11]. Zhou et al. [16] presented related results for Ti–Ta alloys.

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Another factor requiring further attention is the confirmation of the shape memory effect in Ti–Ta alloys. Buenconsejo et al. [17] and Miyazaki et al. [18] confirmed the existence of a permanent shape memory effect for alloys with 32 at.% Ta. For Ti-35Ta (at.%) the martensite start (Ms) temperature was 373 K and decreased by about 30 K when increasing the Ta content by 1%. The most important criteria from medical application point of view of Ti–Ta alloy lies not only on the non-toxicity of alloying elements, but also on its corrosion resistance. Corrosion studies [12,19] carried out in different environments simulating those encountered in the human body (e.g., artificial saliva and acidified saliva) showed higher corrosion resistance of Ti-Ta alloys compared to currently used alloys such as Ti-6Al-7Nb or Ti-6Al-4V. This was attributed to the spontaneously formation of a TiO_2 and Ta_2O_5 oxides, which stabilizes the titanium passivation layer and suppressed the dissolution of Ti and Ta as ions and also provide a bioneutral layer in aggressive body fluids [20,21]. However, only a few investigations of this alloy exist, most of which focus on the phase changes in bulk samples [9,21,22]. Hence, the microstructural evolution and resulting mechanical properties of porous alloys are not yet well understood.

Titanium and tantalum have different melting points (Ti: 1953 K; Ta: 3273 K), density (Ti: 4.51 g/cm^3, Ta: 16.6 g/cm^3) and the segregation of Ta during the solidification. Due to those differences it is difficult to fabricate Ti–Ta alloys by ingot metallurgy [16,23]. For example, Ti–Ta alloy had to be melted more than ten times to ensure the homogeneity [1]. The difficulty in the manufacturing process by melting method has hindered the applications of Ti–Ta alloys. It suggests that preparation of the alloy by powder metallurgy (PM) is a reasonable choice. PM is a comprehensive and simple technique involving fragmentation and synthesis of the material. This method allows the production of amorphous materials, solid solutions, or intermetallic phases from components with different melting points [24]. In addition, PM can fabricate porous materials using methods such as conventional element powder sintering [25], hot isostatic pressing (HIP) [26], mechanical alloying (MA) [27], and metal injection moulding (MIM) [28]. An advantage of PM is its ability to control porosity by adjusting the composition and the sintering parameters. The use of high energy ball milling leads to, obtaining the powder with different distribution of the grain size. This, in turn, with the use of different pressure of isostatic hot pressing can lead to obtaining the material with different degree of porosity, which can be used as a frame for bone restoration [29,30]. In implant applications, porous Ti alloys are expected to provide better surface interaction with cells by providing mechanical anchoring sites, facilitating cell growth [14]. It has been reported by many authors that the Ti–Ta alloys have higher strength-to-modulus ratios than other implant materials [1,21]. Besides, the PM Ti–Ta alloys have an even lower elastic modulus, and higher tensile strengthen than the ingot metallurgical alloys due to the presence of different types of pores [14].

Unfortunately, the synthesizing by sintering blended Ti and Ta elemental powders can lead to inhomogeneity of the alloys despite the use of high (from 1200 °C to 1500 °C) sintering temperatures [14]. 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 by blended powder metallurgy method of both elements is not possible or significantly difficult. Hence, insufficient diffusion occurs during the sintering of Ti–Ta powders which results in this that the alloys consist of alternated distributions of Ti-rich and Ta-rich zones. Based on the above, it seems interesting to use the method of initial mechanical alloying with subsequent sintering at a temperature much lower than the melting point of titanium [14].

In addition, the benefits of using powder metallurgy to obtain the alloys results from the interesting observations of the influence of the synthesis method on the corrosion resistance of the titanium- tantalum alloy. As demonstrated by Gill et al. the corrosion resistance exhibited by powder metallurgy and arc-melting Ti-30Ta alloys revealed that the manufacturing process had a direct effect on the obtained values. Ti-30Ta alloy manufactured by powder metallurgy method was more resistant to localized corrosion as compared with that manufactured by arc melting [31].

The aim of the present study was to characterize the properties of the porous Ti-50Ta (wt%) alloy and assess the possibility of producing this alloy using combined mechanical alloying and sintering methods The use of high energy ball milling will be helpful to initial synthesis of Ti and Ta elements and obtain a powder with different grain size distribution what will be effect on presents of pores in alloy. Additionally, the influence of different sintering times on the microstructure, mechanical properties, and corrosion behaviour of the produced alloy were investigated.

2. Experimental Details

2.1. Sample Preparation

The nominal Ti–50Ta (wt%) alloy composition was prepared using commercial powders; Ti (99.7% purity; < 20 μm particle size) and Ta (99.8% purity; < 5 μm particle size), both supplied by Atlantic Equipment Engineers. The alloy was prepared by high-energy milling in a Fritsch Pulverisette 7 premium line planter-ball mill in an Ar protective-gas atmosphere. The containers and milling balls were made of hardened steel and the process parameters were: 250 rpm milling speed, 10:1 weight ratio of the balls to metal powder, and 20 h milling time (samples labelled Ti50Ta 20 h). Then, the green compacts were prepared by cold isostatic pressing and then sintering at 1000 °C for either 24 or 72 h (labelled Ti50Ta-24 and Ti50Ta-72, respectively). For comparison of the microhardness and corrosion behavior were fabricated reference samples. The samples labelled Ti-24 and Ta-24 were prepared from the starting powders of titanium and tantalum, respectively. The powders were cold isostatic pressed and sintered at 1000 °C for 24 h.

2.2. Phase Composition Analysis

The crystal structure and phase content of the obtained milled powders were studied by X-ray diffraction (XRD) using a Phillips X-ray X'Pert diffractometer with a copper anode lamp ($Cu_{K\alpha}$ − λ = 1.54178 Å) at an electric current of 30 mA and voltage of 40 kV. The wavelengths emitted from the copper anode were passed through a curved graphite monochromator. The powder diffraction patterns were recorded by scanning at steps of 0.04° (2θ) over the angular range from 10 to 140°2θ. NIST standard SRM660a (LaB_6 powder) was used as a line profile standard for determining instrumental broadening. An accuracy of the unit-cell parameters of ± 0.02% was determined using an alumina plate standard (SRM 1976). The profile parameters of individual diffraction lines were determined using the Toraya PRO-FIT method [32], which applies the Pearson VII function to describe the line profiles. The Rietveld analysis was performed applying DBWS-9807 program that is an update version of the DBWS programs for Rietveld refinement with PC and mainframe computers [33]. The pseudo-Voigt function appeared to be the most useful in describing the diffraction lines profiles at Rietveld refinement. The R_{wp} (weighted-pattern factor) and S (goodness-of-fit) parameters were used as numerical criteria of the quality of the fit of calculated to experimental diffraction data [34,35]. The quantitative phase analysis was performed using the relation proposed by Hill and Howard [36,37]. The X-ray diffraction lines are broadened mainly due to (a) instrumental effect, (b) small crystallite size and (c) lattice distortion. The crystallite sizes and the lattice distortion of the α and β phases were estimated using Williamson-Hall method [38]. Phase verification and microstructure analysis were conducted using transmission electron microscopy (TEM; JEOL JEM 3010) operating at an accelerating voltage of 300 kV