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Tantalum foams prepared by the thermal dealloying process

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ABSTRACT

The paper presents a promising method of Ta–based foams preparation by the thermal dealloying method. The concept of the foams formation was to remove one of the alloying elements from the tantalum alloy under high temperature. This element was magnesium that has a relatively low boiling temperature (1090 °C). Ta-20 wt%Ti and Ta-30 wt%Ti alloys, of the melting temperatures of approx. 2400 °C and 2200 °C respectively were investigated.

The first step of this study was the Ta-Ti-Mg alloys preparation using the mechanical alloying process. The next step was forming the green compacts by cold pressing and then sintering and dealloying at the same time.

The influence of the sintering/dealloying parameters on the porous structure formation was investigated. The sintering stage was done in vacuum at 1500 °C. During the dealloying process, the magnesium diffuses from the middle to the surface of the sample, leaving open spaces surrounded by a metallic scaffold.

The tantalum foam with high porosity and wide pore size distribution was successfully prepared. The above results clearly show a great potential of thermal dealloying in metallic foam formation.

1. Introduction

Metal foam is a class of interesting materials that can exhibit a unique combination of physical, chemical and mechanical properties. Particularly, since they are lightweight and have a low Young modulus, metallic-based foams draw much attention in medical applications from the viewpoint of bone in-growth promotion and induction of prosthesis stabilization. In the implant applications the porous materials have a significant advantage because pores (open spaces) lead to bone tissue in-growth (stronger bone/implant interface connection), enhance body fluid transport and permit drug delivery [1–6].

Tantalum is a metal that has shown excellent biocompatibility and is safe to use *in vivo* as evidenced by its current application in pacemaker electrodes, foil and mesh for nerve repair, radiopaque markers, and cranioplasty plates [7,8]. Tantalum has been shown to be corrosion resistant [9] and bioactive [10]. This metal has excellent corrosion–erosion resistance in a highly acidic environment, in comparison to titanium and stainless steel implants [9].

The oxide formed on the surface of the tantalum implants *in vivo* by self-passivation, has been found to be stable over a wide range of pH and potentials [10]. Johansson et al. have shown the excellent biocompatibility of tantalum and titanium with only subtle differences in the interfacial tissue reactions between the two metals [7]. The preparation of Ta-Ti alloys could be promising in the development of metallic biomaterials.

Preparation of porous metals can be obtained by several methods described in multiple studies. These are: the foaming processes of liquid metal [11], sintering with space holder particles [12] or, recently, new rapid prototyping methods based on selective laser sintering [13]. The above-mentioned methods provide a scaffold with tailoring size, shape and properties respective of given applications. For medical applications, however, only a tissue safe material (nontoxic) should be used, which prevents the living cells from deterioration [14].

Magnesium is an element essential to the human body. Mg^{2+} is the fourth most abundant cation in the human body and is largely stored in the bone tissues. Preparation of Ta-Mg alloys may be difficult because of the relatively low boiling temperature of Mg (1091 °C) in comparison to the melting temperature of Ta (3017 °C). Unconventional processing techniques such as mechanical alloying, however, can be an effective method for Ta-Mg alloy design. In this work, the author presents a method of preparation of tantalum-titanium alloy foams through thermal dealloying of magnesium rather than using the space holder technique.

In his last work [15] the author has shown the possibility of Ta foams preparation using saccharose particles as a space holder material dissolving in water, and leaving the Ta scaffold, which is sintered and has possible medical or catalyst applications.

In this work the author shows a new procedure of formation of Ta-based foams. Ta-20 wt%Ti and Ta-30 wt%Ti alloys, of the melting temperatures of approx. 2400 °C and 2200 °C respectively were investigated. This method can be an alternative to other Ta foams preparation techniques, achieving a wide range of pore size distribution. Several researchers have investigated porous tantalum structures produced by

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Zimmer Inc. (Warsaw, IN, USA). These foams were prepared using chemical vapor deposition/infiltration of commercially pure Ta onto earlier prepared polymer scaffolds with a high porosity of 80% [16–19]. Another example of fabrication of porous Ta structures, using LENS, has been demonstrated by Balla et al. The MTT assay showed a significantly higher living cell density (compared to Ti samples) on their material, with the total porosities between 27% and 55% [20].

2. Materials and methods

The procedure of foam preparation is carried out in two steps. The first step is the alloy preparation using the mechanical alloying process followed by sintering/dealloying as a second step. A mixture of powders: Ta (325 mesh, Alfa Aesar), Ti and Mg (both: 325 mesh, Sigma-Aldrich) was used for the preparation of alloys. It was performed in argon atmosphere using a SPEX8000 shaker type mill with balls to powder ratio of 15:1, for 54 and 64.8 ks, depending on chemical composition. Mechanical alloying allows getting powder form of nanocrystalline Ta-Ti-Mg alloys. The MA process is very useful in unconventional material preparation. Using MA we can achieve unequilibrium alloys or alloys composed of metals with very different melting temperatures such as Ta and Mg. In this work the author presents the possibility of preparation of tantalum-based alloys containing a relatively high amount of magnesium. The Ta-20Ti-30Mg, Ta-20Ti-40Mg, Ta-30Ti-30Mg and Ta-30Ti-40Mg was prepared. In the current study, a highly flammable amorphous/nanocrystalline powder was prepared. For safety reasons, all actions with the powder were performed in a glove box in Ar atmosphere. The weight of all substances was measured using precision balance (0.001 g repeatability). Magnesium was one of the alloying element but the role of magnesium in those materials is to generate pores (open spaces). In the next step, the mixture was portioned, placed into the die and uniaxially pressed at a pressure of 1000 MPa. The green compacts were 8 mm in diameter and 3–4 mm height. The sintering/dealloying step was carried out in the Nabertherm furnace at the temperature of 1500 °C for 7.2 ks, in 10^{-2} Pa vacuum to remove the magnesium vapor from the material and prevent excessive oxidation. After that, the sinters were slowly chilled to RT together with the furnace.

The phase constitution of the Ti-based foams, as well as the mechanically alloyed powders, was analyzed by X-ray diffraction with Cu Kα radiation (Panalytical, Empyrean model, Almelo, Netherlands). Scanning electron microscope (SEM, VEGA 5135 Tescan, Brno, Czech Republic) with the energy dispersive spectrometer (EDS, PTG Prison Avalon, Princeton Gamma Tech., Princeton, NY, USA) was used to characterize the chemical composition of the prepared foams. SEM was also applied for the investigations of the morphology of the foams and pores. The porosity was also investigated with the use of Brucker 23KN micro-Computed Tomography.

The compressive strength was measured using a 4483 Instron mechanical testing machine of the measuring range of up to 20 kN with a constant crosshead speed (the average strain rate of 0.001 s^{-1}). The mechanical properties were measured on eight samples of each series.

3. Results and discussion

The first step of Ta foams formation was the preparation of the tantalum based alloy using mechanical alloying (MA). The process and phase transformation was controlled by X-ray diffraction. Fig. 1 shows the XRD data for powder Ta-30Ti-40Mg alloy at different times of MA. After one hour of milling well visible peaks of Ta, Ti and Mg on the XRD spectra occur. Such a short time results in a mixture of the initial powders. Increasing the milling time results in a decrease of the intensity and broadening of the XRD peaks of initial powders. The peak broadening represents a reduction in the crystallite size and increase in the internal strain in the mechanically alloyed materials. After 54 and 64.8 ks of MA for alloys containing 30 and 40% of magnesium, respectively, we can observe only the Ta peaks. It suggests that the Ti and Mg dissolved in Ta structure – the Ta alloy was developed. This was similar for all investigated alloys. According to the Williamson-Hall method, the average crystallite sizes of the prepared alloys were 15 ± 2, 16 ± 5, 15 ± 4, 15 ± 3 nm for Ta-20Ti-30Mg, Ta-20Ti-40Mg, Ta-30Ti-30Mg and Ta-30Ti-40Mg, respectively.

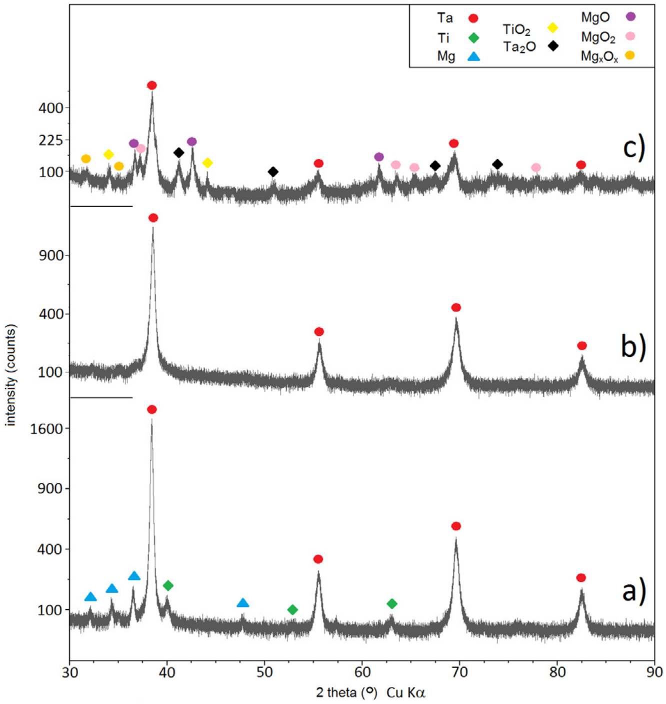

Fig. 1. XRD spectra of the Ta-30Ti-40Mg at different stages: powder after 3.6 ks a), after 64.8 ks b) and Ta-30Ti/40 Mg scaffold after sintering/dealloying c).

Fig. 2 shows the process yield characteristics. In the previous work [21] the author shows that magnesium used as the alloying element to titanium alloys results in achieving excellent yield results, even after relatively long time of milling. Here, this conclusion relating to tantalum alloys can be validated. For the investigated alloys, even after 15 h of the MA process, more than 97% powder yield was achieved and no problem with cold welding was observed. Alloys with higher amount of Mg show a bit higher yield.

As-prepared powders were uniaxially pressed (1000 MPa) and sintered at 1500 °C. The scheme of MA process and green samples preparation have been shown in Fig. 5a. Fig. 1c shows the diffractogram of the Ta-30Ti-40Mg after sintering. The only metallic phase on this curve is tantalum, which suggests that titanium is fully dissolved in the Ta structure and magnesium is evaporated. The sintering stage was performed in alumina tube in 10^{-2} Pa vacuum. These conditions were insufficient to protect the material from oxidation. On the

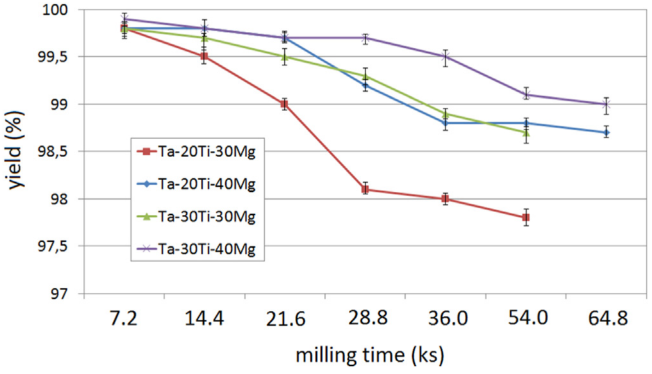

Fig. 2. Process yield characteristics.

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