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Mechanical Alloying of Ti-20Ta-20Nb-(10÷20)Mg Alloys

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In this paper preparation of new β-Ti alloys using mechanical alloying process has been shown. β-Ti alloys are the best metallic biomaterials because of their excellent properties: biocompatibility, low Young moduli and corrosion resistance. Ti-20Ta-20Nb biocompatible alloy was investigated. Mg was used as alloying element, as well (10, 15 and 20 wt%). Pure Ti, Nb, Ta and Mg powders were alloyed under argon atmosphere in shaker type mill (Spex 8000). There was no problem with cold welding in the mechanical alloying of titanium alloys containing Mg. In the paper a possibility of porous materials preparation by sintering in temperature higher than boiling temperature of Mg has been shown. This thermal dealloying method could be an alternative to space holder technique.

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1. Introduction

Titanium based materials, such as alloys, composites, or even pure Ti are the most popular materials for orthopedic and dental implants because of their superior biocompatibility, excellent corrosion resistance, and good mechanical properties [1].

By careful chemical composition and elimination of toxic elements, it is possible to prepare alloys with excellent biocompatibility. Alloys with additions of Zr, Nb, Ta or Pt show good biocompatibility and these elements belongs to the vital group in the tissue reaction (they belongs to non-toxic and non-allergic elements). That is why both $\alpha + \beta$ type and β type titanium alloys composed of non-toxic and non-allergic elements are being intensively developed since more than ten years. Another advantage of β type titanium alloys as the materials for hard tissue application is low elastic modulus [2–6].

Magnesium based materials are attracting much attentions for medical applications. They have advantages over traditional metallic materials, ceramics and biodegradable polymers. The densities of magnesium (1.738 g/cm^3) and magnesium alloys (1.75 ÷ 1.85 g/cm^3) are similar to that of human cortical bone (1.75 g/cm^3). Compared with some titanium alloys (about 110 GPa for Ti-Al-4V), stainless steels (about 200 GPa) and cobalt based alloys (about 230 GPa), the elastic modulus of magnesium based metals (about 45 GPa) is more close to that of natural bones. Magnesium alloys are attracting much attention for hard tissue implant applications owing to their easy corrosions in body environment, which can be taken as characteristics of biodegradation if the corrosion products are bio-safely absorbed or excreted. However, the application of magnesium based metals is limited by their too fast degradation rates inducing hemolysis, osteolysis and physical stimulation of gas bubble [7, 8]. Magnesium seems to be good alloying element to titanium alloys. It decreases density, could decrease the Young moduli and improves biocompatibility of Ti based alloys. Preparation of Ti-Mg alloys is difficult because of relatively low Mg solubility in Ti and its low boiling temperature (1091 °C). Non-equilibrium processing techniques such as vapor deposition and mechanical alloying (MA) can, however, be effective methods for Ti–Mg alloy design [9–13]. Suryanarayana and Froes show that MA produces nanometer-sized crystallites in the titanium-magnesium system and their Ti-3Mg alloy has a metastable fcc structure as a result of the transformation from the hcp structure. This transformation was due to the heavy deformation involved in the mechanical alloying operation [14]. Senkov et al. synthesized a low-density Ti-Mg-Si alloy via MA. They used titanium hydride, magnesium, and silicon as starting materials and find that heat treatment (1100 °C) of the mechanically alloyed powder leads to formation of six phases: Ti, Mg, Mg_2Si, Ti_5Si_3, MgO, and $TiN_{0.3}$ [15].

2. Experimental

The nanostructured Ti-20Ta-20Nb-(10÷20)Mg wt% alloys were prepared by MA under argon atmosphere using a SPEX 8000 Mixer Mill. The ball to powder weight ratio was 20:1 (ball weight 50 g — 5 item, powder weight 2.5 g). Initial powders were: Ti — 325 mesh, purity 99.5%, Ta — 100 mesh, purity 99.98% and Nb — 325 mesh, purity 99.8% and Mg — 325 mesh, purity 99.8%, all from AlfaAesar. The process batch yield was defined as the ratio of the weight of the recovered powder and the weight of the starting powder and measured using precision balance (0.001 g repeatability). To perform that, the milling process was stopped after certain time. In the next step, as-prepared powder alloys were placed into the matrix and uniaxially pressed at a pressure of 1000 MPa. The green compacts were 8 mm diameter and about 5 mm high.

Then in the final stage the green compacts were heated through 30 min up to 700 °C for first series and 1300 °C for the second, and kept at this temperature for 1 h. After that, the sinters were slowly cooled down to room

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temperature (RT) together with the furnace. The sintering was done at 10^{-2} Pa vacuum.

Phase constitution of the new alloys was analyzed by X-ray diffraction with Cu K_{α_1} radiation and the crystallite size was estimated by Williamson–Hall method [16, 17]. Microstructure of the prepared alloys was characterized by optical microscopy (OM) and atomic force microscopy (AFM), as well. The samples were etched by Kroll's reagent. The grain size distribution was determined from measurements along random lines. Data from OM was analyzed by Olympus software and data from AFM by Quesant software (3–5 images per sample). Optical microscopy and the dual tone image method [18] was used to characterize the pore size distribution and average porosity (5 images per sample was analyzed).

3. Results and discussion

In this work the preparation of β-Ti containing magnesium by mechanical alloying was shown. The process and phase transformation was controlled by X-ray diffraction technique (XRD). Figure 1 shows data obtained for Ti-20Ta-20Nb-15Mg alloy during MA. After one hour of milling there are well visible peaks of Ti, Ta, Nb, and Mg on the XRD spectra. Such a short time results in a mixture of the initial powders. Increasing milling time results in the intensity of the XRD peaks of initial powders decreased and new XRD peaks corresponding to appearing βTi. After 8 h of MA we can observed only βTi peaks. According to the Williamson–Hall method, the average crystallite sizes of prepared alloys were 15±2, 16±5, 15±4 nm after 8 h for 10, 15 and 20% of Mg content, respectively. Further milling was ineffective on grain size refinement. The crystallite size was 15±3, 15±2, 15±4, 15±4 nm after 15, 30, 50 and 100 h, respectively, for Ti-20Ta-20Nb-15Mg. The same trend was observed for other alloys.

Figure 2 shows the process yield characteristics which are very important data from the MA process. Mg is sometimes used as a PCA. Zadra shows that using small amount (0.5%) of Mg results in about 65% yield after 2 h of milling [19]. Using Mg as a alloying element (higher amount — in this work 10, 15, 20%) we can achieve excellent yield results, even after relatively long time of milling. After 100 h of MA process more than 90% powder yield was achieved for all chemical composition. The yield increased with increasing Mg content.

As-prepared powders were sintered at temperature of 700 °C and 1300 °C. Figure 3 shows XRD spectra of the Ti-20Ta-20Nb-10Mg, Ti-20Ta-20Nb-15Mg and Ti-20Ta-20Nb-20Mg after sintering in different temperature. Sintering in 700 °C leads to obtaining of βTi structure for all chemical compositions. If the temperature rises to 1300 °C, the βTi structure is still predominant, but there are also visible peaks corresponding to αTi. Sintering in temperatures higher than boiling temperature of Mg leads to $\beta + \alpha$ structure.

The microstructure of the prepared alloys was studied using AFM and OM for alloys sintered at 700 °C

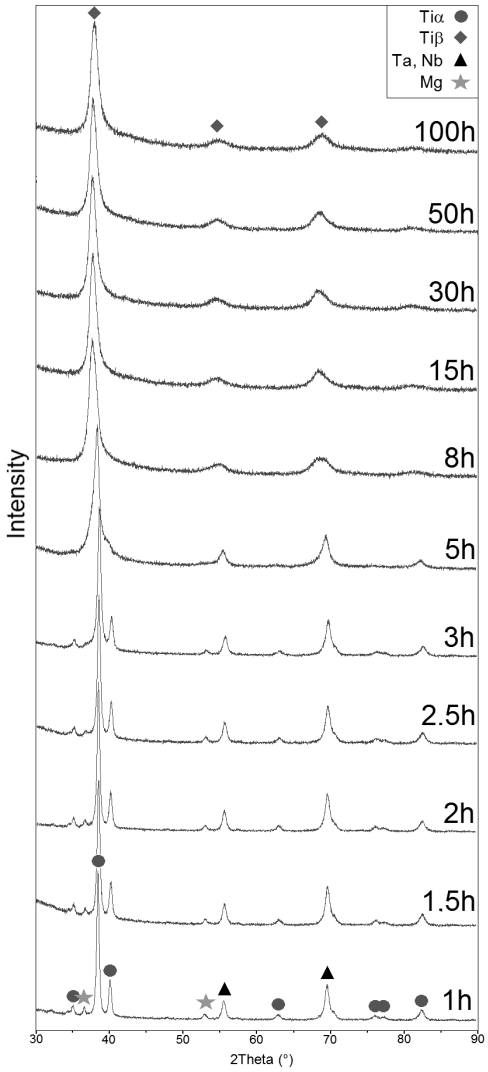

Fig. 1. XRD spectra obtained for Ti-20Ta-20Nb-15Mg alloy during MA.

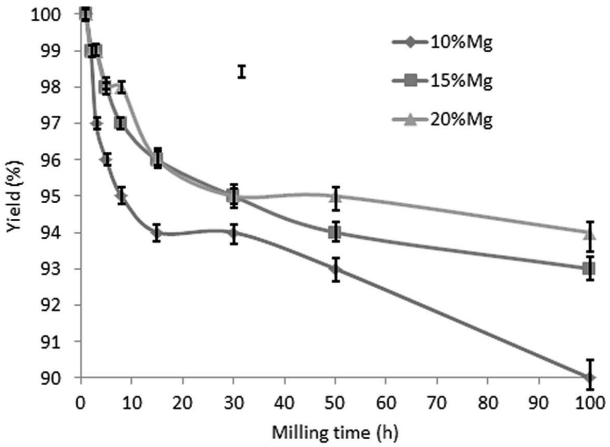

Fig. 2. Process yield characteristics.

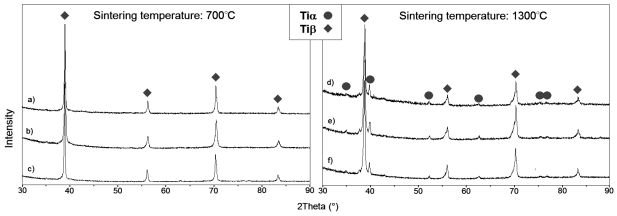

Fig. 3. XRD spectra of the Ti-20Ta-20Nb-10Mg (a), (d), Ti-20Ta-20Nb-15Mg (b), (e), and Ti-20Ta-20Nb-20Mg (c), (f) after sintering in different temperature.

and 1300 °C, respectively. The grain sizes for alloys sintered in lower temperature were in the range of: 0.3–0.7, 0.3–0.9, and 0.3–0.8 μm for the Ti-20Ta-20Nb-10Mg, Ti-20Ta-20Nb-15Mg, and Ti-20Ta-20Nb-20Mg, respectively (Fig. 4). Figure 5 shows microstructure of the

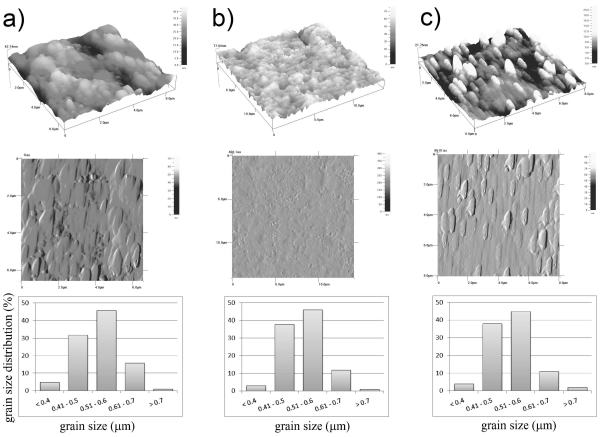

Fig. 4. AFM study on the microstructure and grain size distribution of the Ti-20Ta-20Nb-10Mg (a), Ti-20Ta-20Nb-15Mg (b), and Ti-20Ta-20Nb-20Mg (c) sintered in 700 °C.

alloys sintered at 1300 °C. The grain size, which is obvious, increased with increasing sintering temperature and in this case was 0.9–7, 1–5, and 0.8–7 μm for the Ti-20Ta-20Nb-10Mg, Ti-20Ta-20Nb-15Mg, and Ti-20Ta-20Nb-20Mg, respectively.

In this work I show the possibility to increase volumetric porosity of Ti alloys by thermal dealloying. Porous materials are attractive for hard tissue implant application. Porosity is useful in tissue growth, strong fixing to implant and improving mechanical properties by decreasing Young modulus [20, 21].

Figure 6 shows mechanically polished surface of all prepared alloys. There are well visible dark areas which are pores. For alloys sintered at 700 °C the porosity level is about 2%. With increasing sintering temperature to 1300 °C some amount of Mg evaporated leaving open spaces. Depending on initial magnesium content in the alloy the porosity level was 4.1±0.2, 5.6±0.2 and 8.8±0.3 for 10, 15, 20 wt% of Mg, respectively. Using the thermal

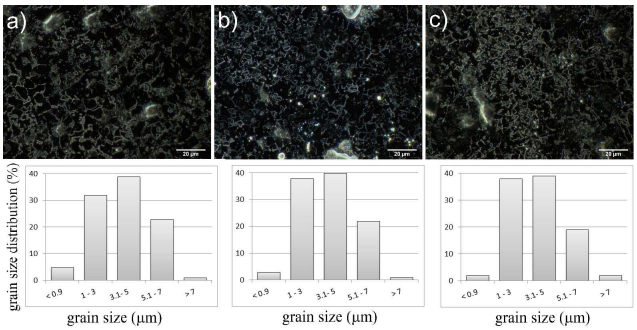

Fig. 5. Microstructure and grain size distribution of the Ti-20Ta-20Nb-10Mg (a), Ti-20Ta-20Nb-15Mg (b), and Ti-20Ta-20Nb-20Mg (c) sintered in 1300 °C.

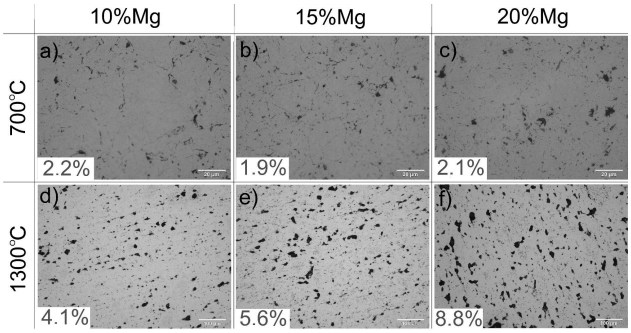

Fig. 6. OM micrographs of polished surface and porosity level of Ti-20Ta-20Nb-10Mg (a), (d), Ti-20Ta-20Nb-15Mg (b), (e), and Ti-20Ta-20Nb-20Mg (c), (f) sintered in 700 °C and 1300 °C.

dealloying it is possible to prepared porous alloys in easier way than using space holder technique. The method described in this work consists of two steps: mechanical alloying and sintering. When using space holder there are one more step: mixing the powder with space holder material. It is important to thoroughly mix the powders to get homogeneous pores distribution. Usually there is no such a problem with MA.

4. Conclusions

In this paper the influence of Mg on β-Ti alloys preparation has been shown. Ti-20Ta-20Nb-(10÷ 20)Mg wt% alloys were prepared by MA and powder metallurgy process. Based on this study, the following conclusions can be drawn:

1. Less than 10 h is enough to obtain nanocrystalline powders of titanium alloys, further milling was ineffective on grain size refinement.

2. Using magnesium as alloying element (more than 10 wt%) to titanium alloys there is no problem with cold welding using Spex8000 mill for mechanical alloying process. The yield, even after 100 h of MA, was more than 90% for all chemical compositions.

3. Sintering in temperature higher than boiling temperature of Mg leads to increase of volumetric porosity of the Ti alloys. This thermal dealloying process could be an alternative to space holder technique.

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