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Influence of Type of Alcohol as the Process Control Agent on Ti-20Ta-20Nb Alloy Preparation by Mechanical Alloying

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In this paper the influence of alcohols as the process control agents on β-Ti alloys preparation using mechanical alloying process was investigated. Three types of alcohols: methanol, ethanol and isopropanol were used in mechanical alloying of Ti-20Ta-20Nb. Pure Ti, Ta, Nb powders and process control agents were alloyed under argon atmosphere in shaker type mill (Spex 8000). Using X-ray diffraction technique, there has been observed the β phase formation after 3 h of mechanical alloying process. Using alcohols as process control agent it is possible to obtain nanocrystalline powders of titanium alloys. The milled powder was sintered in vacuum using hot pressing with high frequency induction heating. It has been shown that sintering process of powders prepared with alcohols as process control agents results in oxides and carbides formation in the alloy structure. Moreover some part of alcohol could evaporate leaving open spaces which results in relatively high porosity of the sinters.

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1. Introduction

Ti alloys are widely used in medical applications, because of their excellent corrosion resistance, biocompatibility, and mechanical properties [1]. In comparison to the pure Ti, the Ti alloys have better mechanical properties. The elements, such as Al and V are main alloying additives in the Ti alloys. Unfortunately, these elements exhibits high cytotoxicity and may induce senile dementia [2, 3]. Replacing of Al and V by Nb, Ta and Zr leads to excellent biocompatibility, because these elements belong to vital group in the tissue reaction as well as their oxides (corrosion products) [4]. β type titanium alloys are the most attractive metallic biomaterials for hard tissue application because of the lowest elastic modulus. The low modulus β titanium alloy Ti-29Nb-13Ta-4.6Zr developed by Niinomi et al. [5] is reported to be an excellent candidate for biomedical applications [5–7].

Mechanical alloying (MA) is a powerful powder processing method, which has been used to synthesize various equilibrium and nonequilibrium alloy powders with extremely fine microstructures [8, 9]. Alloying among powder particles can occur only when a balance is maintained between cold welding and fracturing of particles. If the powder particles are ductile (like most metals) they get cold-welded to each other due to the heavy plastic deformation experienced by them during milling. To reduce the effect of cold welding a process control agent (PCA) is added to the powder mixture during milling. The PCAs can be solids, liquids, or gases [10–16].

Depending on the powder type a different PCA is required. A wide range of PCAs at different level (about 1÷5 wt% of the total powder charge) has been used, include: stearic acid, palmitic acid, methanol, ethanol, stearamide, hexane, water, calcium, sodium chloride or magnesium.

The PCA can have negative effects by introducing contamination into the final alloy [17-21]. Hiraga et al. showed that methyl alcohol could be used as a process control agent in fabrication of NiTi intermetallic compounds. They found that with an increasing amount of the agent the remanence rate of powders increased and particle size decreased [22]. Krasnowski and Matyja used ethanol in an amount of 5 wt% as PCA in ball milling of the Al50Fe25Ti25. They showed that during milling Ti interacts with the dissociation products of alcohol [23]. Gabbitas et al. investigated the influence of the quantity of the PCA addition on microstructural evolution of the TiAl system. They used isopromanol. Milling without alcohol resulted in the formation of large granules (1–4 mm in diameter) and a considerable fraction of powder particles stuck onto the container wall. An addition of 1 wt% isopropanol neither decreased the granule size nor reduced the sticking problem. Increasing the quantity to 2 and 3 wt% remarkably suppressed the excessive cold welding, eliminated the powder sticking problem and improved the mixing effect [24].

In this work the influence of alcohols as the process control agents on β-Ti alloy preparation using mechanical alloying process was investigated. Three types of alcohols: methanol (CH_3OH), ethanol (CH_3CH_2OH) (simple alcohols) and isopropanol ($(CH_3)_2CHOH$) which is the simplest example of a secondary alcohol, by IUPAC nomenclature, were used in MA of Ti-20Ta-20Nb.

2. Experimental

The Ti-20Ta-20Nb wt% alloy was prepared by MA and powder consolidation process. Mechanical alloying was performed under argon atmosphere using a SPEX 8000 Mixer Mill. The mixed powders (Ti — 325 mesh, purity 99.5%, Ta — 100 mesh, purity 99.98% and Nb —

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325 mesh, purity 99.8%, all from AlfaAesar) were blended with hard steel balls for 100 h and the ball to powder weight ratio was 20:1 (ball weight 50 g, powder weight 2.5 g). Three types of alcohol were used as a process control agent (PCA): ethanol, methanol, and isopropanol. In each process the quantity of alcohol was 1.5 wt%. To check the yield of the process the milling was stopped after certain time. The process batch yield was defined as the ratio of the weight of the recovered powder and the weight of the starting powder. The weight was measured using precision balance (0.001 g repeatability).

In the next step, powder was placed into the creep resistant steel die and uniaxially pressed at a pressure of 100 MPa. Then in the final stage the green compacts were heated during 2 min up to 700 °C and kept at this temperature for 10 min using high frequency induction heating equipment. After that, without the pressure, the sinters were slowly cooled down to room temperature (RT) together with the furnace. The sintering was done at 10^{-2} Pa vacuum. The compacts were 8 mm diameter and 5 mm high. Phase constitution of as-prepared alloys was analyzed by X-ray diffraction (XRD) with Cu K_{α_1} radiation. The crystallite size was estimated by Williamson–Hall method [25, 26].

Optical microscopy (OM) was used to characterize the pore size distribution. According to the dual tone image method, the average porosity was estimated [8] (5 images per sample was analyzed). Microstructure of the prepared sinters was characterized by atomic force microscopy (AFM) — the samples were etched by Kroll's reagent. The grain size was determined from measurements along random lines using Quesant AFM software (15 lines per image, 3 images per sample). Microhardness of the materials was measured using InnovaTest hardness machine (parameters: 300 g, time 10 s).

3. Results and discussion

In this work the influence of ethanol, methanol, and isopropanol on β-Ti alloys preparation using mechanical alloying process is shown. The Ti-20Ta-20Nb wt% alloy was prepared in Spex 8000 mills. The phase transformation was examined by X-ray diffraction. Figure 1 shows data obtained for Ti-20Ta-20Nb (with ethanol as PCA) alloy during MA. After one hour of milling there are still visible peaks of Ti, Ta and Nb on the XRD spectra (scanning electron microscopy (SEM) images of initial powders are presented in Fig. 2). Such a short time results in a mixture of the initial powders. Increasing milling time results in the intensity of the XRD peaks of powders mixture decreased to zero and new XRD peaks corresponding to β-Ti appeared. There has been seen the β phase formation after 3 h of MA. There were no peaks corresponding to oxides or carbides on the spectra even after 100 h of milling. According to the Williamson–Hall method, the average crystallite size of obtained alloys was 17±3 nm after 8 h. Further milling was ineffective on grain size refinement independently of PCA type. The crystalline size was 17±3, 17±4, 17±2, 17±4 nm after

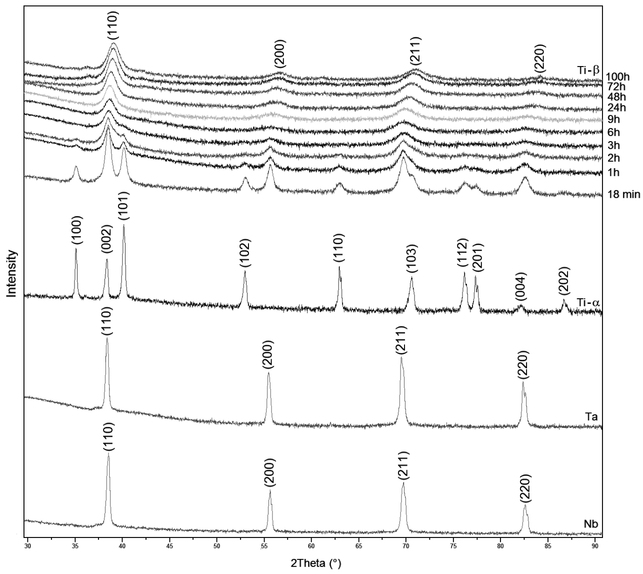

Fig. 1. XRD spectra of Ti-20Ta-20Nb alloy (with ethanol as PCA) during MA and for initial powders.

15, 30, 50, and 100 h, respectively. Such a long time of milling was ineffective, but was carried out to check the influence of alcohols on process yield. Powder after milling consists of agglomerates with size in the range of 10 to 100 μm. There was no significant changes in XRD data of the mechanical alloying of Ti-20Ta-20Nb with different alcohols.

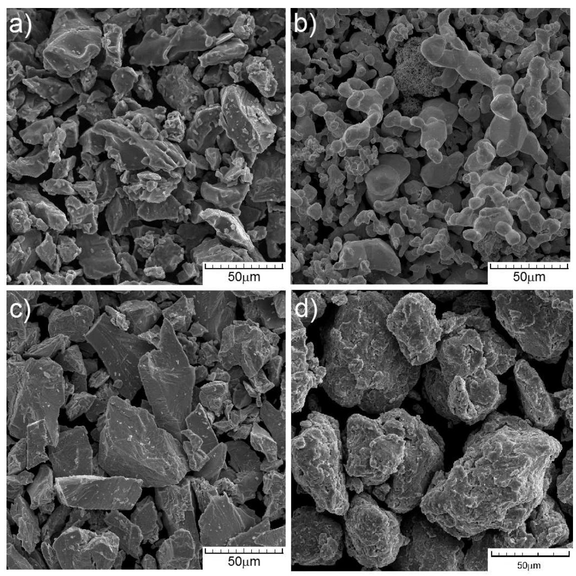

Fig. 2. SEM images of initial powders: titanium (a), tantalum (b), and niobium (c). Image (d) shows agglomerates of Ti-20Ta-20Nb alloy (with ethanol as PCA) after 100 h of milling.

Very important data from the mechanical alloying process is the yield results. Figure 3 shows the process yield characteristics. Using alcohols as a PCA we can achieve excellent yield results, even after relatively long time of milling. Independently of the alcohol type, after 100 h of MA process more than 75% powder yield was achieved and for ethanol it was almost 80%. These are very good results if compared them with solid PCA like calcium or magnesium. Zadra shows that using small amount (0.5%) of Ca or Mg results in about 85 and 65% yield but after only 2 h of milling [10].

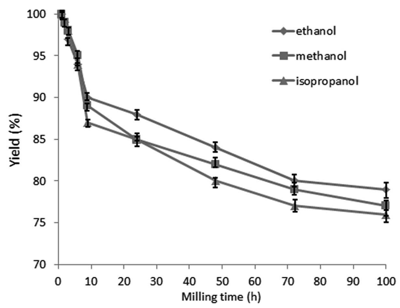

Fig. 3. Process yield characteristics.

As-prepared powders were uniaxially pressed and heated in vacuum using high frequency induction heating machine. After that, the sinters were cooled down to RT together with the die. Figure 4 shows XRD spectra of the Ti-20Ta-20Nb after sintering. Sintering at 700 °C leads to obtaining of β-Ti structure for all used alcohols. For all PCA's there are also peaks corresponding to titanium carbide and titanium oxide on the XRD data. There are no peaks corresponding to niobium or tantalum oxides. It shows that the chemical reaction between alcohols deals mainly with titanium.

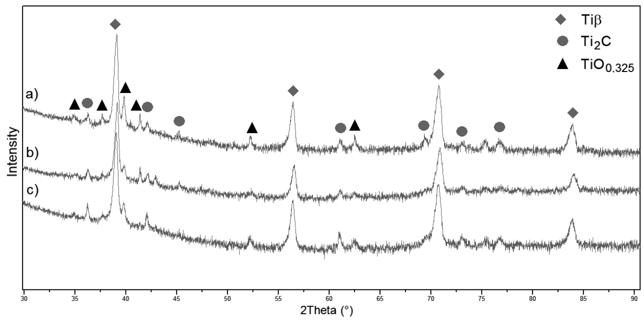

Fig. 4. XRD spectra of the Ti-20Ta-20Nb prepared with ethanol (a), methanol (b), isopropanol (c) after sintering.

The microstructure of the prepared alloys was studied using AFM. The grain size for as-prepared alloys was in range of: 0.3–0.7, 0.25–0.7, and 0.3–0.75 μm for the methanol, ethanol, and isopropanol, respectively (Fig. 5 shows grain size distribution).

Porosity is a very important factor from the biomaterials point of view because it is useful in tissue growth and strong fixing to implant and improving mechanical properties by decreasing Young modulus. The pores on the surface act as anchors for the tissue, improving bonding, decreasing osseointegration time [27, 28]. Figure 6 shows mechanically polished surface of all prepared alloys. There are well visible dark areas which are pores.

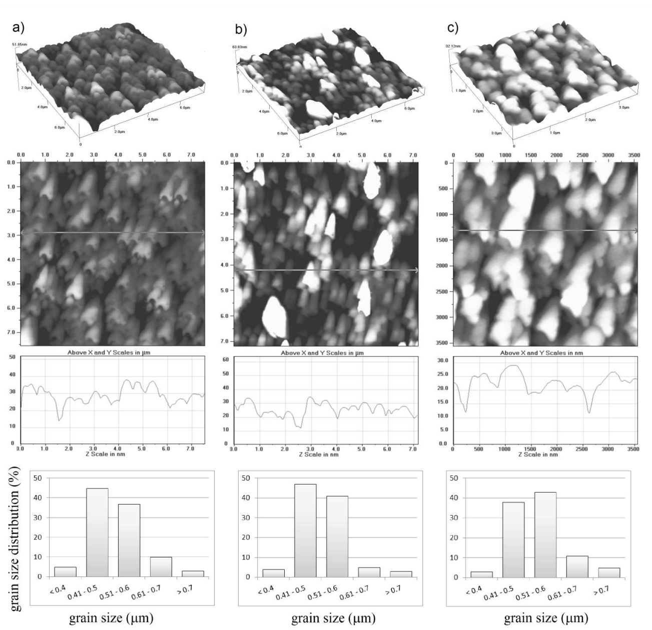

Fig. 5. AFM study of microstructure of the Ti-20Ta-20Nb prepared with methanol (a), ethanol (b), isopropanol (c).

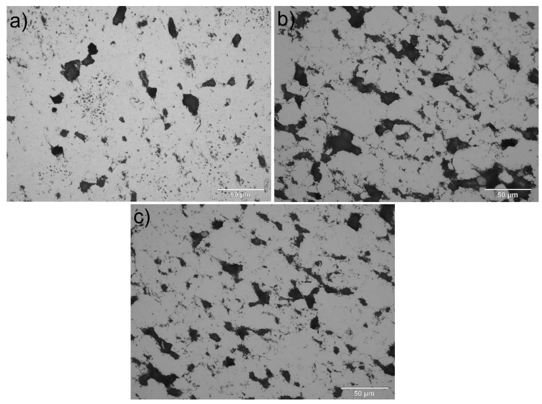

Fig. 6. OM micrographs of the Ti-20Ta-20Nb prepared with methanol (a), ethanol (b), isopropanol (c) showing porosity.

Despite using hot pressing the porosity level of sintered materials is relatively high. For alloys prepared with ethanol the porosity level is about 11.5%. Using isopropanol the porosity reached 14% and the highest level was obtained for methanol (19.2%) — Fig. 7. During the sintering some part of alcohol could evaporate leaving open spaces.

Microhardness of the sintered materials was measured using InnovaTest hardness machine. The data was taken only from areas without pores. Figure 8 shows hardness changes using different PCA. The alloy prepared with ethanol shows highest microhardness (about 520 HV0.3). Lower microhardness was obtained for Ti-20Ta-

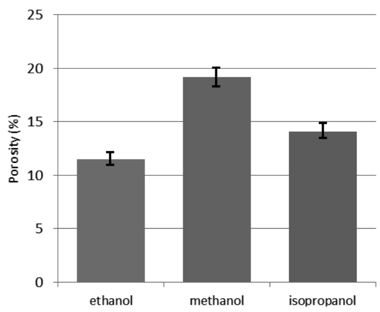

Fig. 7. Porosity level of Ti-20Ta-20Nb prepared with different alcohols.

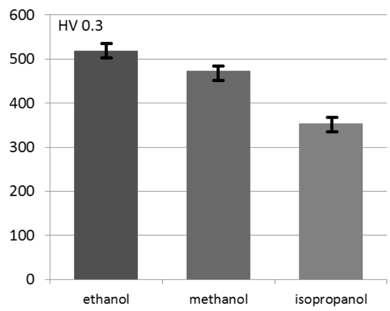

Fig. 8. Hardness of Ti-20Ta-20Nb prepared with different alcohols.

20Nb prepared with methanol (about 470 HV0.3). Using isopropanol there was no significant changes of micorhardness when compared with pure microcrystalline titanium (350 HV0.3). The reason of different microhardness could be explained by different reactivity of applied alcohols with titanium results in different quantity of oxides and carbides which change the mechanical properties of the sinters.

4. Conclusions

In this paper the influence of ethanol, methanol, and isopropanol on β-Ti alloys preparation has been shown. Ti-20Ta-20Nb alloys were prepared by mechanical alloying (MA) and powder consolidation process. Based on this study, the following conclusions can be drawn:

1. Using alcohols as PCA it is possible to obtain nanocrystalline powders of titanium alloys. Less than 10 h is enough to get $<$ 20 nm crystallites.

2. Using ethanol, methanol, and isopropanol in titanium alloys preparation results in oxygen and carbon introduced into the alloy as oxides and carbides (during sintering process) which have substantial influence on mechanical properties of the material.

3. Using alcohols as PCA in titanium alloys preparation could result in relatively high porosity of the sinters, despite using hot pressing technique. During the sintering some part of alcohol could evaporate leaving open spaces. This method of porous materials preparation could be an alternative to space holder technique.

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