Materials and Design 91 (2016) 340–347

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Microstructure and metallic ion release of pure titanium and Ti–13Nb–13Zr alloy processed by high pressure torsion

Ivana Dimić [a,*], Ivana Cvijović-Alagić [b], Bernhard Völker [c], Anton Hohenwarter [c], Reinhard Pippan [d], Đorđe Veljović [e], Marko Rakin [e], Branko Bugarski [e]

[a] University of Belgrade, Innovation Centre of the Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia
[b] University of Belgrade, Institute of Nuclear Sciences "Vinča", P.O. Box 522, Mike Petrovića Alasa 12–14, 11001 Belgrade, Serbia
[c] Montanuniversität Leoben, Department of Materials Physics, 8700 Leoben, Austria
[d] Austrian Academy of Sciences, Erich Schmid Institute of Materials Science, Jahnstrasse 12, 8700 Leoben, Austria
[e] University of Belgrade, Faculty of Technology and Metallurgy, Karnegijeva 4, 11120 Belgrade, Serbia

ARTICLE INFO

Article history:
Received 20 August 2015
Received in revised form 22 November 2015
Accepted 24 November 2015
Available online 2 December 2015

Keywords:
High pressure torsion
Ultrafine-grained
Titanium
Ti–13Nb–13Zr alloy
Microhardness
Metallic ion release

ABSTRACT

Significant enhancement of mechanical properties of metallic biomaterials can be achieved by grain refinement obtained by severe plastic deformation. The purpose of this study was to determine metallic ion release from commercially pure titanium (CPTi) and Ti–13Nb–13Zr alloy processed by high pressure torsion (HPT). The materials microstructures, in the initial state and after HPT deformation, were examined by scanning and transmission electron microscopy. The microhardness was determined along the radius of the disc-shaped samples of ultrafine-grained (UFG) CPTi and Ti–13Nb–13Zr alloy in order to evaluate homogeneity of HPT-processed materials. The quantities of released ions were determined using inductively coupled plasma-mass spectrophotometer for samples immersed in artificial saliva at 37 °C for 7 days. Also, the effect of artificial saliva pH value on metallic ion release was estimated. Obtained results revealed that the quantities of released ions from UFG CPTi and Ti–13Nb–13Zr alloy obtained by HPT process were higher than the quantities of released ions from CPTi and Ti–13Nb–13Zr alloy produced by traditional casting. This behavior can be explained by the fact that metallic ions are easily released from microstructure with smaller grains achieved by HPT process.

1. Introduction

1.1. Titanium and its alloys as implant materials

Over the last few decades, commercially pure titanium (CPTi) and titanium-based alloys have been extensively used in dental practice due to several benefits such as low elastic modulus, high corrosion resistance and outstanding biocompatibility [1,2]. In fact, most of the currently-used dental implants are made of CPTi and Ti–6Al–4V alloy, but CPTi is considered to be a better choice because its production is cheaper and it does not contain any allergic elements [1]. One of the several disadvantages of dental implants made of stainless steel or Co–Cr alloys is their high elastic modulus (from 210 to 240 GPa), while in the case of CPTi and Ti-based alloys elastic modulus varies between 80 and 120 GPa [2–4]. However, CPTi and Ti-based alloys still possess much greater elastic modulus than human bone which causes non-homogeneous stress transfer between the metallic implant and the bone, and thus leads to bone atrophy, metallic implant loosening and/or re-fracturing of the bone [4–6]. In order to avoid the mentioned "stress shielding effects" and failure of the implant caused by the modulus mismatch between the implant and the bone, the elastic modulus of dental implant materials is desired to be close to that of human bone (from 10 to 30 GPa) [3,4,7]. Furthermore, it should be noted that the mechanical strength of CPTi is lower than the threshold required for hard tissue replacement. Since the high mechanical strength and low elastic modulus are very important factors for the long-term use of metallic materials as implants, it is necessary to further develop CPTi and Ti-based alloys [8–10]. In order to improve mechanical properties of CPTi and Ti-based alloys, different thermomechanical treatments have been examined [4,11,12]. It is interesting to note that some of these treatments increase the mechanical strength, but also increase the elastic modulus [13]. Also, for the same purpose, different alloying elements have been added to Ti [8]. It should be mentioned that some of alloying elements, such as aluminium (Al) and vanadium (V), can cause allergic reactions in the human body and different neurological disorders, making it necessary to carefully choose the alloying elements [4,14]. In addition, V is toxic both in the elemental state and oxide

* Corresponding author.
E-mail addresses: idimic@tmf.bg.ac.rs (I. Dimić), ivanac@vin.bg.ac.rs (I. Cvijović-Alagić), bernhard.voelker@unileoben.ac.at (B. Völker), anton.hohenwarter@unileoben.ac.at (A. Hohenwarter), reinhard.pippan@oeaw.ac.at (R. Pippan), djveljovic@tmf.bg.ac.rs (Đ. Veljović), marko@tmf.bg.ac.rs (M. Rakin), branko@tmf.bg.ac.rs (B. Bugarski).

http://dx.doi.org/10.1016/j.matdes.2015.11.088

(V_2O_5) present on the surface of implants made of Ti–6Al–4V alloy [4]. Thus, concerns about possible toxicity of some alloying elements have favored the development of CPTi as an alternative to Ti-based alloys for medical and dental applications. However, in order to expand the applications of Ti-based alloys as implant materials, it is essential to choose alloying elements that will enhance the mechanical strength, reduce the elastic modulus and minimize the toxic effects of the released ions. Recently, new beta Ti alloys with low elastic modulus which contain non-toxic alloying elements, such as niobium (Nb), zirconium (Zr), tantalum (Ta), and molybdenum (Mo), have been developed [8, 9,15]. One of these contemporary Ti alloys with low elastic modulus is Ti–13Nb–13Zr alloy.

1.2. Grain refinement through severe plastic deformation (SPD) process

An alternative and very attractive method for enhancement of mechanical properties of CPTi and Ti-based alloys is severe plastic deformation (SPD) [16–19]. SPD process is defined as a process in which ultra-large plastic strains are introduced into a bulk material in order to achieve significant grain refinement [19]. The metallic materials obtained by SPD are ultrafine-grained (UFG) (grain size in the range of 100–1000 nm) or nanostructured (NS) (grain size less than 100 nm) [18, 20]. It should be noted that grain refinement through SPD process is an effective method for strengthening metals and alloys, but the precise mechanisms of grain refinement is still under discussion [17,18,21]. In comparison with other strengthening methods, grain refinement is expected to achieve high mechanical strength while maintaining a low elastic modulus of CPTi and Ti-based alloys [22]. In fact, the main reason for using Ti-based alloys for medical and dental applications has been their superior mechanical strength compared to CPTi. Therefore, in the case of CPTi, the aim is to improve the mechanical strength in order to replace the currently-used Ti-based alloys and thus avoid potential toxicity of the alloying elements. Accordingly, the reduction of grain size in the case of CPTi made it possible to attain strength levels which are comparable to those of Ti alloys [23]. For instance, Azushima et al. [19] showed that CPTi can achieve a mechanical strength which is similar to the strength of its alloys when CPTi is subjected to SPD followed by thermomechanical treatment. Furthermore, many authors have pointed out that UFG metals and alloys produced by SPD have better mechanical and physical properties compared to their coarse-grained (CG) counterparts [19,20,22]. A large number of different SPD methods, such as high pressure torsion (HPT), equal channel angular pressing (ECAP) and accumulative roll-bonding (ARB), have been developed and extensively studied [16–22].

1.3. High pressure torsion (HPT) process

HPT is defined as process in which samples of metallic materials are subjected to compressive force and concurrent torsion under a high hydrostatic pressure (>2 GPa) [24]. For this synthesis process disc specimens are placed between two anvils possessing both a small cavity, see Fig. 1. Then the disc is subjected to large compressive forces inducing into the disc hydrostatic pressures in the range of several GPa [19, 24]. After this loading step one anvil is rotated against the other inducing a shear strain into the specimen. The high pressure ensures large friction forces between anvil and sample. In this way the sample becomes shear deformed and sliding between anvil and sample, which would not increase the degree of deformation in the sample, is avoided. An equivalent strain (ε), using the v. Mises criterion, imposed on the sample can be calculated using the following relation [25]:

$$\varepsilon = \frac{2\pi Nr}{\sqrt{3}t}. \quad (1)$$

According to Eq. (1), the equivalent strain depends on the number of rotations (N), the thickness (t) of the sample and on the radius (r). This simple relation shows that the strain is linear dependent on the radius. Recently, the HPT process has been widely used due to its effectiveness in grain refinement and the very simple way in which extremely high shear strain can be achieved [19,25,26]. In practice, HPT is considered to be one of the most powerful SPD processes for producing exceptional grain refinement in pure metals and alloys [27]. This can be mainly attributed to the presence of the high amount of hydrostatic pressure, which prevents the initiation of cracks and so failure of the specimen.

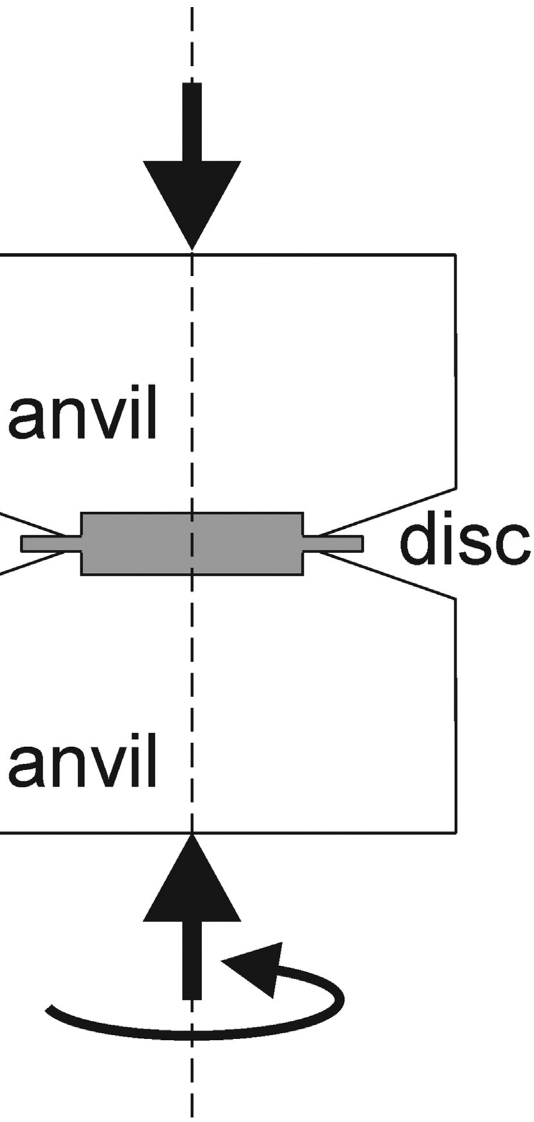

Fig. 1. Schematic overview of HPT process.

1.4. Metallic ion release

The metallic implant materials are subjected to biodegradation in the oral environment primarily by dissolution in human saliva which is an aerated aqueous solution of about 0.1 N chlorides, with varying amounts of Na, K, Ca, PO_4, CO_2, sulfur compounds and mucin [10, 28–30]. In fact, the oral environment is strongly corrosive for dental implants mainly due to bacterial activity, humidity and variation of temperature and pH value [28–30]. The average pH value of human saliva in normal conditions is between 5.5 and 7.5 [10]. It should be mentioned that the oral cavity is constantly subjected to pH value changes, but extremely low pH values (between 2.0 and 3.0) rarely occur and cannot be maintained for a long time period because of the buffering action of the human saliva. For instance, extremely acidic conditions have been