Superplasticity of nanostructured Ti-6Al-7Nb alloy with equiaxed and lamellar initial microstructures processed by High-Pressure Torsion

Jorge M. Cubero-Sesin 1,2,*, Joaquin E. Gonzalez-Hernandez 1, Elena Ulate-Kolitsky 1, Kaveh Edalati 3,4 and Zenji Horita 3,4

1 Escuela de Ciencia e Ingeniería de los Materiales, Instituto Tecnológico de Costa Rica, Cartago 159-7050, Costa Rica.
2 Centro de Investigación en Ciencia e Ingeniería de los Materiales, Instituto Tecnológico de Costa Rica, Cartago 159-7050, Costa Rica.
3 Department of Materials Science and Engineering, Kyushu University, Fukuoka 819-0395, Japan.
4 WPI, International Institute of Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka 819-0395, Japan.

E-mail: jcubero@itcr.ac.cr

Abstract. Microstructural modifications of a biomedical Ti-6Al-7Nb alloy were accomplished via heat treatment in 3 different quenching mediums and then processed by High-Pressure Torsion (HPT) at room temperature. The microstructure of the as-received condition is composed of an equiaxed duplex (α+β) structure. After the heat treatment, a combination of primary α phase and lamellar structures was obtained with an increasing fraction of the martensitic lamellar with increasing cooling rate. After HPT processing, refinement of the microstructures was observed for N=5 revolutions. Transmission electron microscopy (TEM) of the sample quenched in liquid nitrogen confirmed the nanostructure with grain sizes below 100 nm and high density of lattice defects after HPT processing for N=5 revolutions. High-temperature tensile tests were carried out at 800 °C with an initial strain rate of 2x10⁻³ s⁻¹ on specimens with different combinations of heat treatment and HPT straining. The test in the as-received condition presented a maximum elongation to failure of ~400% after HPT processing for N=5 revolutions. The highest elongation to failure in the heat-treated samples was ~580% in the sample quenched in liquid nitrogen and processed for N=5 revolutions.

Keywords: Titanium-aluminum-niobium, quenching, microstructure evolution, high-pressure torsion, superplasticity.

1. Introduction
Titanium-based alloys have been used as a biomedical material for decades due to their excellent mechanical properties, corrosion resistance and high biocompatibility [1-3]. Ti-6Al-7Nb is a practical option for medical devices and implants because of its excellent biological compatibility and good biomechanical properties. Several research works have demonstrated further potential of this alloy in
the field of bioscience, by experimenting with surface modifications in the nanoscale to improve the corrosion resistance and biocompatibility [4-8]. This suggests that the combination of grain refinement in the bulk with surface modification could improve in higher proportion both the mechanical properties and biocompatibility of this material for medical applications [9].

The microstructural evolution of duplex α+β type Ti-6Al-4V alloy has been deeply studied with different initial microstructures and methods for grain refinement [11-13]. Also, Ti-6Al-7Nb exhibited superplastic properties after HPT due to grain refinement [14,15]. It is well known that the regime for superplastic behaviour requires grain sizes < 10 μm and that this structure is stable at elevated temperatures. Also, it is necessary work with a high testing temperature, usually above ~0.5 Tm, where Tm is the absolute melting temperature of the material [14-16]. There are several conditions and other important variables during the test, such as, tensile specimen geometry, strain rate and initial microstructure of the alloy.

The objective of the current study is focused on the effects of the initial microstructure of a Ti-6Al-7Nb alloy processed by HPT over its superplasticity. The microstructure evolution due to the heat treatments and the grain refinement have been described. Finally, the deformation mechanism of the lamellae and the recrystallization of the structure has been proposed.

2. Experimental procedures

Discs of 10 mm diameter and ~1 mm thickness were cut from a commercial rod of Ti-6Al-7Nb using a wire-cutting electric discharge machine (EDM). Then, the discs were sealed in quartz tubes in an Ar atmosphere and treated at 960 °C for 2 h, followed by quenching in different mediums: (1) air at ~28°C, (2) ice water at ~5°C and (3) liquid nitrogen N201 at ~ -196°C. The specimens were further ground to a final thickness of ~0.8 mm, and then processed by HPT under a pressure of 6 GPa at room temperature, with a rotational speed of 1 rpm for N=1 and N=5 revolutions. After HPT processing, the discs were polished to a mirror-like surface and etched using Kroll’s reagent for metallographic observations at several distances from the center of the discs. High-temperature tensile tests were performed after HPT processing from tensile specimens were extracted using EDM. The length and width of the gage portion of the specimens were 1.85 mm and 0.6 mm respectively, and the thickness was kept within 0.65±0.05 mm. The tensile testing was conducted at 800 ± 1 °C with an initial strain rate of 2.0 × 10⁻³ s⁻¹.

Microstructural studies were carried out firstly by X-ray diffraction (XRD) with the Cu-Kα (λ = 1.54016 Å) radiation in the range 2θ = 30°-80°, with a scan step of 0.01° and a scan speed of 0.06 s/step. The microstructure after HPT processing of the sample with highest elongation to failure was studied by transmission electron microscopy (TEM) with an acceleration voltage of 200 kV. For this purpose, a 3mm disc was extracted from the HPT-processed discs, and thinned to electron transparency by twin-jet electroplishing at 18°C, using a solution of 90% acetic acid and 10% perchloric acid under an applied voltage of 20 V.

3. Results and discussion

The microstructural observations before and after HPT processing are shown first. Similar metallographic observations and microhardness measurements were carried out for the as-received and the heat-treated conditions to understand the initial microhardness levels and the microstructure before HPT processing. Figure 1 shows optical micrographs of the initial microstructures, prior to HPT. Figure 1(a) shows the as-received condition, while Figure 1(b), 1(c) and 1(d) show the resulting structures after quenching from 960°C in air, ice water and liquid nitrogen N2, respectively. The as-received microstructure was composed of an equiaxed α-β duplex microstructure, the areas in bright contrast correspond to α-phase grains, with β-phase particles along the grain boundaries shown in dark contrast. After heat-treating the alloy at 960°C with different cooling rates, a bimodal microstructure composed of an equiaxed α grain matrix surrounded by very fine lamellae was produced. At low cooling rates, these lamellae should be alternating α and β lamellae, and with increasing cooling rate the lamellae are replaced by martensitic α’ and metastable β structures, because the quenching is to the temperature above the martensitic transformation (Ms) temperature of ~910°C [2]. It can be seen from the
comparison of Figure 1(b) and 1(c) that the volume fraction of lamellar phase increases with the increase of the cooling rate by quenching in ice water with respect to air cooling, but not much change occurs in the volume fraction by quenching in liquid nitrogen, as in Figure 1(d). However, it is expected that the phase fraction of α in the lamellae is replaced by α’ in a higher fraction by quenching in liquid nitrogen in comparison with cold water.

Figure 1. Optical micrographs of Ti-6Al-7Nb prior to HPT processing: (a) as-received condition. (b), (c) and (d) heat-treated samples quenched from 960°C in air, ice water and \( \text{N}_2 \), respectively.

Figure 2 shows the XRD profiles of the as-received and the heat-treated samples with their corresponding profiles before and after being processed by HPT for \( N=5 \) revolutions. The \( \alpha/\alpha' \) and \( \beta \) phase reference diffraction positions are shown as dotted lines. The \( \alpha' \) phase has the same space group as the \( \alpha \) phase, and shares the fundamental crystallographic diffraction peaks, so it is not possible to differentiate them by XRD. The \( \alpha/\alpha' \) phases have an HCP crystal structure and their most prominent crystallographic planes are \((100)\) at \( 2\theta = 35.09^\circ \), \((101)\) at \( 40.17^\circ \) and \((110)\) at \( 62.94^\circ \). The \( \beta \) phase has a BCC crystal structure with fundamental peaks: \((110)\) at \( 2\theta = 38.84^\circ \) and \((200)\) at \( 56.11^\circ \). These peaks are consistent with the result for the as-received condition. The XRD profiles of the samples quenched from 960 °C show a significant increase in the intensity of the \((110)\) peak (\( 2\theta \approx 63^\circ \)) which suggests that it corresponds to a preferred orientation in the lamellae, associated with the increase in the fraction of the \( (\alpha+\beta) \) and \( (\alpha'+\beta) \) at the expense of the \( \alpha \) phase in the microstructure of these samples. The sample cooled in air has the lowest fraction of lamellar phase because the cooling rate was not enough to transform the whole \( \beta \) phase, and thus the \((110)\) peak corresponding to the \( \beta \) phase is still visible, which is clearly appreciable in the profile of the as-received condition at \( 2\theta \approx 38.9^\circ \). The profiles from the samples quenched in ice water and liquid nitrogen, respectively, do not exhibit this peak, probably because the \( \beta \) phase in the lamellae is very fine in structure. On the other hand, the \( \alpha \) phase peak at \( 2\theta \approx 38^\circ \) is more prominent in these two profiles, corresponding to the faster cooling, than in the air-cooled sample, where it is hardly appreciable. This suggests \( \alpha/\alpha' \) is dominant in the lamellar structure. In general, the XRD profiles from HPT processed specimens for \( N=5 \) revolutions present significant peak broadening, associated with the grain refinement in the material and the formation of large number of crystallographic defects such as vacancies and dislocations [17]. Additionally, due to the peak broadening there is a peak overlap between the \( \alpha \) and \( \beta \) phases around \( 2\theta \approx 38-39^\circ \) as a result of the high strain imposed by the HPT process. In addition, the preferred orientations defined by the initial heat treatments seem to have evolved to more random orientations. However, the significant peak broadening suggests that refinement of the microstructure is large.
Figure 2. XRD profiles of Ti-6Al-7Nb for heat-treatments before and after HPT processing for N=5 revolutions.

Therefore, TEM observations were carried out to understand the extent of grain refinement in the HPT-processed samples. Figure 3 shows TEM images from the sample quenched in liquid nitrogen from 960 °C and processed by HPT for N=5 revolutions. Figure 3(a) shows a bright-field image, where the presence of a nanostructured lamellae with thicknesses below 10 nm can be observed, along with fine crystallites with large amount of lattice distortion and dislocations at grain boundaries. Thus, in Figure 3(b) a dark-field image was taken from the diffracted beam pointed with an arrow in the inset SAED pattern, which corresponds to the (101) crystallographic plane, consistent with the highest intensity peaks at 2θ=40.2° in the XRD profiles after HPT processing, shown in Figure 2. From the dark-field image, the size of crystallites of α phase is below 100 nm. The SAED pattern in the inset corresponds to a ring pattern characteristic of a nanostructured material with a high fraction of high angle grain boundaries and lattice defects, commonly associated to metallic materials subjected to the HPT process [18].

Figure 4 shows the stress-strain curves from the high temperature tensile tests. Figure 4(a) corresponds to the samples processed by HPT for N=1 and Figure 4(b) for N=5 revolutions. The comparison shows that HPT straining results in a higher elongation to failure of the samples. The total elongation to failure measured from the samples shown in Figure 4(a) was of ~220%, ~380%, ~345% and ~325% for the as-received, air, ice water and liquid N2 quenched samples respectively. These results are all under the threshold value of 400% which is considered as superplastic behavior [16]. Also, there is an improvement in the elongation in terms of the bimodal microstructure achieved by quenching with respect to the as-received condition, but a slight decrease in the total elongation with respect to the increase in the cooling rate. On the other hand, the samples processed for N=5 revolutions exhibited higher elongations to failure as ~400%, ~455%, ~480% and ~580% for the as-received, air, ice water and liquid N2 quenched samples, respectively. In this case, the trend is clear so that the total elongation increases with the increase in the cooling rate. These elongations are all considered in the superplastic regime, achieving the best performance in the sample quenched in liquid N2.
Figure 3. TEM (a) bright-field and (b) dark-field images of sample quenched from 960°C in liquid nitrogen N₂ and processed by HPT for N= 5 revolutions. Selected-area electron diffraction (SAED) pattern shown as inset in (b).

The results in Figure 4(b) show that quenching from 960 °C in liquid N₂ in combination with HPT processing for N=5 revolutions is the best condition for superplasticity. The reason for the high elongation to failure with respect to the as-received condition can be explained from the microstructural point of view in terms of the level of microstructure refinement of an already fine microstructure that forms as a result of quenching, which favors key mechanisms for superplasticity, such as grain boundary sliding [19]. The lamellar structures achieved by quenching are already in the ultrafine-grained level, as opposed to the equiaxed structures in the as-received condition, which after HPT are further refined to form a truly ultrafine-grained structure consisting of α phase grains below 100 nm and deformed lamella of (α+β) / (α’ + β) with spacings below 10 nm, as shown in Figure 3.

Figure 4. Stress-strain curves from samples tested at 800°C processed by HPT in as-received condition and quenched from 960°C in different mediums for (a) N=1 and (b) N=5 revolutions

Other factors that play a role in superplastic behaviour should be considered, which are not present in the as-received condition, such as the bimodal structure and the reverse phase transformation to the
equilibrium structure, as effective mechanisms to accommodate the deformation during the tensile test. Further microstructural analyses of the failed tensile specimens will allow a better understanding of the microstructural behaviour during the high temperature tensile test, so it will be the focus of the future work.

4. Conclusions

Microstructural modifications were achieved on the Ti-6Al-7Nb alloy having bimodal structures by heat treatment and HPT processing to examine the effect of the initial microstructure on mechanical properties of interest. The following conclusions were obtained:

1. Quenching from 960°C provides a bimodal structure: α’+β lamellae surrounding the α phase grains.
2. Grain refinement occurred by application of HPT processing. The prior heat treatment giving a higher fraction of (α’+β) lamellae led to a smaller grain size after processing by HPT.
3. TEM observations and SAED analyses revealed that the microstructure consists of nanograins with α grains and (α’+β) lamellae after quenching to liquid N2 and HPT processing. Such an ultrafine-grained structure results in higher superplastic elongation than the as-received state consisting of an equiaxed duplex (α+β) structure.

References

[1] Leyens C and Peters M 2003 Titanium and Titanium Alloys: Fundamentals and Applications, Wiley–VCH Verlag, USA.
[2] Donachie M 2000 Titanium: A Technical Guide. ASM International, Ohio, 2nd ed.
[3] Lütjering G and Williams J 2007 Titanium: Engineering materials and processes. Springer Berlin Heidelberg, New York, 2nd ed.
[4] Akahori T, Mitsuo K, Niimomi M, and Suzuki A 2002 Metal. Mater. Trans. A. 33A 503
[5] Huang H, Wu C, Sun Y and Lee T 2013 Thin Solid Films 528 157
[6] Mohan L, Anandan C and Rajendran N 2015 Mater. Sci. Eng. C. 50 394
[7] Huang H, Wu C, Sun Y, Yang W and Lee T 2014 J. Alloys Comp. 615 S648
[8] Rafieerad A, Bushroa A, Nasiri-Tabrizi B, Kabol S, Khanahmadi S, Amiri A, Vadivelu J, Yusof F, Basiruni W and Wasa K 2017 J. Mech. Behav. Biomed. Mater. 69 1
[9] Oliveira D, Prokofiev E, Sanches L, Polyakova V, Valiev R, Botta W, Junior A and Bolfarini C 2015 J. Alloys Comp. 643 S241.
[10] Murray J 1987 ASM Handbook: Nb (Niobium) Binary Alloy Phase Diagrams. 3 2304
[11] Matsumoto H, Nishihara T, Yohei Iwagaki Y, Tohru Shiraishi T, Ono Y and Chiba A 2016 Mater. Sci. Eng. A. 661 68
[12] Nakahigashi J and Hirofumi Y 2002 Materials Trans. 43 No.11 2768
[13] Kral P, Dvorak J, Blum W, Kudryavtsev E, Zherebtsov S, Salischev G, Kvapilova M and Sklenicka V 2016 Mater. Characterization. 116 84
[14] Cui W, Ji Z, Guo A and Zhou L 2009 Mater. Sci. Eng. A. 499 (1-2) 252.
[15] Ashida M, Chen P, Doi H, Tsutsumi Y, Hanawa T and Horita Z 2015 Mater. Sci. Eng. A. 640 449
[16] Kawasak M, Figueiredo R, Xu C and Langdon T 2007 JOM Metal. Mater. Trans. A 38A 1891
[17] Estrin Y and Vinogradov A 2013 Acta Mater. 61 782
[18] Valiev R, Islamgaliev R and Alexandrov I 2000 Prog. Mater Sci. 45 103
[19] Zehetbauer M and Zhu Y 2009. Bulk Nanostructured Materials. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim