

Hydrogen treatment of titanium based alloys

M Losertová, M Hartmann, I Schindler and J Drápala

VŠB – Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, 17. listopadu 15, 708 33 Ostrava, Czech Republic

mlosertova@vsb.cz

Abstract. The positive effect of the hydrogen on hot deformation behaviour at 700 and 750 °C was investigated after thermal hydrogen treatment of Ti6Al4V and Ti26Nb alloys. Comparing the results obtained for the non-hydrogenated and hydrogenated specimens of both alloys, it was found that the hydrogen content as high as 1325 wt. ppm has an obvious benefit effect on high temperature deformation behaviour in the Ti6Al4V alloy by stabilizing beta phase and lowering thermal deformation resistance. In the case of Ti26Nb alloy the hydrogen content of 2572 wt. ppm suppressed stress instabilities during hot compression but slightly increased thermal deformation resistance. The microstructure study was performed before and after the isothermal compression tests on the specimens in hydrogenated as well as in non-hydrogenated condition. The hydrogen amounts in the specimens were measured by means of an analyser LECO RH600.

Keywords: hydrogen effect, hydrogen embrittlement, hydrogen induced plasticity, biocompatible alloys.

1. Introduction

Titanium based materials are frequently used in surgery and orthopedics. Among them Ti6Al4V alloy belongs to the most applied alloys. As compared with 316L stainless steel, Ti6Al4V is characterized by high strength-to-weight ratio, good corrosion resistance, higher biocompatibility and lower Young's modulus [1-4]. Nevertheless, workability of this alloy at room temperature is difficult and forming must be performed at elevated temperatures, thus improving hot deformation behavior by decreasing flow stress and working temperature is desirable. The essential reason of difficulties with forming consists in the microstructure formed of $\alpha + \beta$ phases and in the relatively high temperature of $\alpha + \beta \rightarrow \beta$ transformation whereas β phase with body centered cubic structure is more malleable than α phase with hexagonal close packed lattice. The transition temperature is called β transus and for Ti6Al4V reaches 980 °C.

Although hydrogen deteriorates mechanical properties of many engineering metallic materials, titanium alloys included, and the brittleness of conventional alloys induced by the hydrogen is observed at room temperature as well as at elevated temperatures, in case of Ti alloys the hydrogen can act as a temporary alloying element in special heat treatment technology, so-called the thermo-hydrogen treatment (THT) [5-7] and shows beneficial effect in improving particular properties. Whereas the hydrogen works as β stabilizer in Ti alloys, THT technology employs the reversible reaction of hydrogen with titanium in order to modify phase compositions, kinetics of phase transformations and evolution of metastable phases in titanium alloys [8-11], that provides decreasing



flow stress and increasing hot workability of titanium alloys at lower temperatures. The temporary hydrogen alloying allows the microstructure refinement resulting in enhancement of the fatigue and strength properties [12].

Recently new candidates promising for fixation devices through the decreased Young's modulus approaching that of human bone are β alloys (or more precisely called as metastable β alloys). The alloy compositions based on non-toxic elements, as Nb, Mo, Ta and Zr, enable to reach higher biocompatibility comparing to Ti6Al4V and the other commonly used metallic alloys [1,4]. Although the refractory alloying elements mentioned above act as β stabilizers, the microstructure of β alloys may contain some α phase precipitates depending on amount of β alloying additions. Even if the β alloys are better workable, remaining α phase can cause some problems during forming processes.

The present work presents the study of hydrogen effect on hot deformation behavior at two different temperatures and microstructure evolution after the isothermal compression test performed for Ti6Al4V and Ti26Nb alloys.

2. Experimental

To investigate the hydrogen effect on the microstructure and hot deformation behavior of the non-hydrogenated and hydrogenated Ti based alloys specimens, isothermal uniaxial compression test (CT) at 700 and 750 °C was performed on Gleeble-3800 machine using basic CTA module. The experimental specimens were prepared from the forged bars of Ti6Al4V (in wt.%) alloy supplied by company MEDIN, a. s. and of Ti26Nb (in at.%) (Ti40.5Nb in wt.%) alloy prepared in own laboratories. The cylindrical samples of 10 mm in diameter and 12 mm in height exactly were machined and treated by three steps thermal treatment. In order to compare the high temperature deformation behavior with and without hydrogen in the alloy structure the same procedure of thermal treatment (TT), according to [10,13] and described in Figure 1, was performed for one group of the cylinders in flowing argon (purity 5N) and for second group in flowing hydrogen (purity 5N). Considering higher solubility of the hydrogen predominantly in β phased TiNb [11], the times of hydrogenation steps were modified [14].

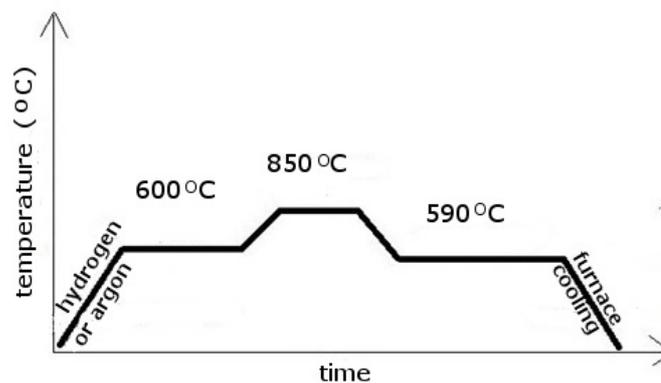


Figure 1. Three steps regime of thermal treatment with modified times at holding temperatures for both alloys (Ti6Al4V and Ti26Nb) before subsequent isothermal compression test.

After heating with the rate of 1200 °C·h⁻¹ to 600 °C in hydrogen (or in argon) the temperature was kept for 60 and 30 minutes for Ti6Al4V and Ti26Nb, respectively. Then the temperature was increased to 850 °C and held for 30 and 18 minutes for Ti6Al4V and Ti26Nb, respectively. After that the cooling to 590 °C and alloy aging was performed for 240 and 60 minutes for Ti6Al4V and Ti26Nb, respectively. Finally, the cooling was realized in the furnace to 400 and 300 °C in hydrogen (or in argon) for Ti6Al4V and Ti26Nb, respectively, and accomplished in argon to the room temperature for both alloys.

During hot deformation test, the specimens were heated with a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{h}^{-1}$ and soaked for 3.0 min at the deformation temperature before the isothermal compression. The specimens of both alloys were deformed to 50 % of their initial height with a constant initial strain rate of 0.005 s^{-1} and then air-cooled to room temperature. The flow stress during hot compression was recorded as a function of the strain. The test was stopped at the strain of 0.7.

The microstructure evolution of both alloys in different conditions of thermo-mechanical treatment was observed using optical microscopy. All metallographic specimens were ground and polished in transversal and longitudinal sections by conventional methods and then etched in solution composed of $2\text{ HF} : 4\text{ HNO}_3 : 80\text{ H}_2\text{O}$. The amount of hydrogen in the specimens was measured by means of an hydrogen determinator LECO RH 600.

3. Results and discussion

The hot deformation behavior at 700 and 750 $^{\circ}\text{C}$ during the compression test (CT) of non-hydrogenated and hydrogenated cylinders of Ti6Al4V and Ti26Nb are presented in Figure 2. Comparing the macroscopic views of hydrogenated hot compressed specimens of both alloys that are shown in Figure 3, it is clear that despite the different alloy compositions and high hydrogen contents in THT treated cylinders the hot deformation behavior is macroscopically similar. Even after the 50 % reduction in height that resulted in barrel-shaped samples, no cracks were observed on the surfaces of Ti6Al4V (Figure 3a). Unlike Ti26Nb, the presence of hydrogen in the structure decreased the peak of flow stress about by 50 and 100 MPa at 700 and 750 $^{\circ}\text{C}$, respectively. All samples exhibited dynamic recrystallization that decreased flow stress and helped to better formability. The true stress - true strain curves indicate that the mechanisms of softening are sufficiently fast to balance the rate of work hardening and are suggestive of mechanisms like dynamic recrystallization, superplasticity or dynamic recovery occurring at very high rates.

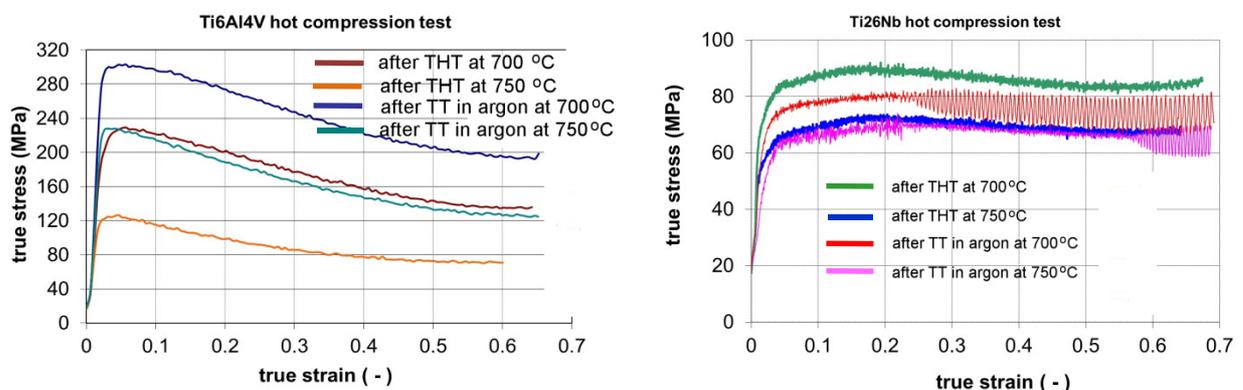


Figure 2. Comparison of CT curves at 700 and 750 $^{\circ}\text{C}$ and strain rate $5\cdot 10^{-3}\text{ s}^{-1}$ after thermal treatment in argon and hydrogen for a) Ti6Al4V and b) Ti26Nb alloys.



Figure 3. Specimens after the THT and compression test of a) Ti6Al4V and b) Ti26Nb (cracking in red boxes).

The microstructure of the as-received Ti6Al4V alloy was formed of bimodal equiaxed grains of α and ($\alpha + \beta$). After thermal treatment in Ar, the similar microstructure was observed indicating that annealing time did not affect grain growth or recrystallization (Figure 4a). The microstructure of thermo-hydrogen treated (THT) specimens was markedly changed as it can be seen in Figure 4b. During holding at 590 °C the microstructure fully decomposed after following eutectoid reaction: $\beta_H \rightarrow \alpha + \beta_H \rightarrow \beta_H + (\alpha + \gamma)$, according to [8-11], where γ is titanium hydride. The deformation microstructure after the isothermal compressive test quite differs for both testing temperatures, as seen in Figure 4. Retained amount of hydrogen after isothermal compression test resulted in the martensite microstructure with rare acicular α grains that indicated the transformation of β phase to two phase $\alpha + \beta$ microstructure processed at lower temperatures then it would be currently for hydrogen free-alloys. No hydrides were observed in all Ti6Al4V microstructures by optical microscopy.

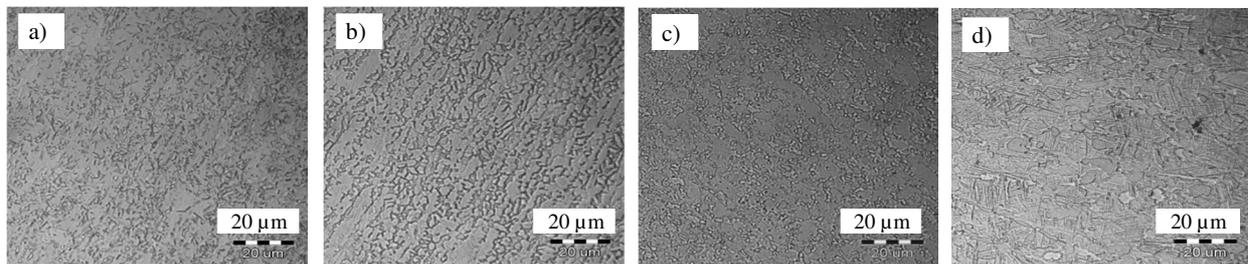


Figure 4. Microstructure of Ti6Al4V a) after TT in Ar without formability test; b) after THT without formability test; c) after TT in Ar and compressed at 750 °C and strain rate 0.005 s⁻¹; d) after THT and compressed at 750 °C and strain rate 0.005 s⁻¹

Figure 2a shows the true stress - true strain curves of Ti6Al4V specimens at 700 and 750 °C in the both thermal treatment conditions. In the case of Ti6Al4V the stress is increasing with raising strain to a maximum and then goes down, which shows that the working softening has prevailed. The deformation evolution of THT specimen shows that softening effect from dynamic recovery passed to equilibrium with the work hardening and then passed into a quasi-steady flow stage, during which the stress decreasing slowed. So compared with the non-hydrogenated state, it can be seen that hydrogen didn't delay the dynamic recovery of the deformation in titanium alloy, conversely, the steady flow stress for hydrogen containing alloy was much lower than that for non-hydrogenated specimen at the same compression temperature. This result proved that at as high concentrations of hydrogen as 1325 wt. ppm the flow stress was obviously reduced and the cylindrical sample was deformed without cracking.

The microstructure of non-hydrogenated Ti26Nb samples was formed of β grains with fine α precipitates (Figure 5a). After the hot compression tests, the microstructures of alloy were dynamically recrystallized to large β grains with very fine subgrains (Figures 5b and 5c). The hydrogen charging led to the important refining of microstructure after the THT as well as after the CT, as seen in Figure 6a. No hydrides were observed by optical microscopy.

The macroscopic view of the Ti26Nb specimens in THT condition and after the compression tests with an amount of reduction in height of 50 % is illustrated in Figure 3b. The surfaces of hydrogenated specimens were cracked (red boxes in figure) while the non-hydrogenated specimens were cracked rather rarely on the surface.

The flow stresses recorded for the Ti26Nb alloy are depending on the temperature. It is clear that niobium is β stabilizer, so the flow stresses are lower for the Ti26Nb than for Ti6Al4V due to the higher fraction of more ductile β phase. Comparing the deformation behavior at two different temperatures for hydrogen non-charged and charged specimens, it is evident that with increasing temperature the flow stress is decreasing and by reason of this the hot forming is improved for both thermal treated stages. In the case of the hydrogen non-charged specimens unusual behavior was

registered during the CT (Figure 2b). Large instabilities of flow stress were detected that can be related with lower rate of dynamic recrystallization.

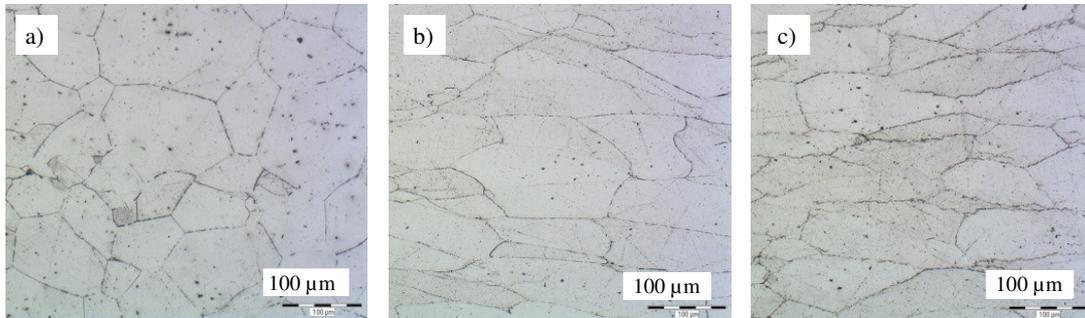


Figure 5. Optical micrograph of Ti26Nb alloy treated by three steps TT in Ar a) without compression test; b) compressed at 700 °C and c) compressed at 750 °C.

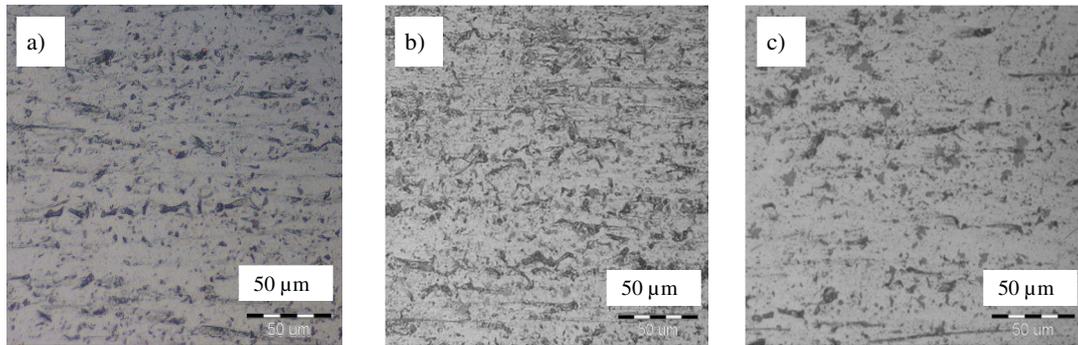


Figure 6. Optical micrograph of Ti26Nb alloy a) treated by three steps THT and deformed by compression test at b) 700 °C and c) 750 °C.

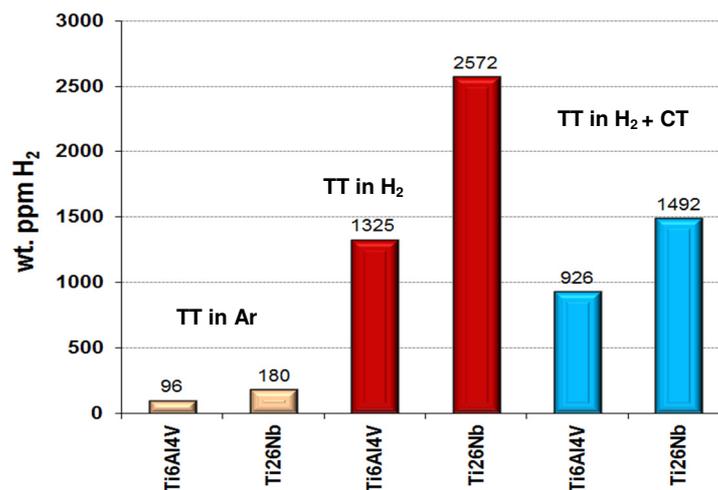


Figure 7. Amount of hydrogen in the tested specimens.

The hydrogen contents measured for four conditions of thermo-mechanical treatment (TT in argon or hydrogen, TT in argon or hydrogen + compression tested) of both Ti6Al4V and Ti26Nb alloys are summarized in Figure 7. The highest amount (2572 wt. ppm) was determined in Ti26Nb after the THT

that corresponds with higher hydrogen solubility in β phase. After the compression test, the content of hydrogen in cylinders decreased from 1325 to 926 wt. ppm and from 2572 to 1492 wt. ppm for Ti6Al4V and Ti26Nb, respectively. Nevertheless, the hydrogen concentration was sufficient for retaining β phase. The hydrogen amount decrease after the CT was more important just for the alloy with niobium (by 42 % for Ti26Nb and 31 % for Ti6Al4V). Unfortunately, the hydrogen promoted cracking on the surfaces of compression tested Ti26Nb specimens. Unlike the Ti6Al4V alloy, the hydrogen content in the Ti26Nb specimens increased the flow stress but on the other side positively influenced the flow stress instabilities observed on the true stress - true strain curves of non-hydrogenated stages (Figure 2b). Indeed, the evolution of uniaxial compressive test curves showed the stabilization of flow stress due to the hydrogen for high strains at both temperatures. The dissimilarity in hot compression behavior of both Ti alloys for hydrogen charged and non-charged stages are related with high niobium content and therefore β metastable microstructure, where hydrogen is effecting strengthening by solid solution [15]. The hydrogen effect on the development of the compression test was inconsistent for both alloy compositions.

4. Conclusion

The hydrogen effect on the hot compression behavior was investigated for two Ti alloys. The hot deformation behavior and microstructure evolution of Ti6Al4V and Ti26Nb alloys were investigated after three steps thermal treatment in flowing hydrogen or argon gases. Comparing the results obtained on the base of the isothermal uniaxial compression tests at 700 and 750 °C for non-hydrogenated and hydrogenated specimens, it can be concluded following:

- The hydrogen content has an obvious benefit effect on high temperature deformation behavior of the Ti6Al4V alloy by decreasing the β transus temperature and lowering the hot deformation resistance. Retained amount of hydrogen after isothermal compression test resulted in the martensite microstructure with rare acicular α grains that indicates the transformation of β phase at temperatures at which the hydrogen free-alloys are formed normally of two phase $\alpha + \beta$ microstructure.
- It was found that the hydrogen content as high as 1325 wt. ppm for Ti6Al4V significantly suppressed the flow stress for both temperatures of hot compression without inducing the sample cracking.
- The hydrogen content as high as 2572 wt. ppm for Ti26Nb proved an obvious positive effect on the suppression of the stress instabilities for both temperatures.
- However, the high amount of hydrogen induced increasing flow stress and resulted in cracking of the specimens.
- The benefit effect of hydrogen on increasing formability of Ti26Nb alloy at lower temperatures was not evident as it was observed in the case of Ti6Al4V alloy.
- The hydrogen amounts measured after the different thermal treatment were evaluated and the highest content (2572 wt. ppm) was determined in Ti26Nb after the THT that corresponds with higher hydrogen solubility in β phase. After the compression test the hydrogen content decreased by 42 % that was more important than in the case of Ti6Al4V alloy.

Acknowledgment

This article has been elaborated in the framework of the project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic and co-financed by the European Social Fund and of the projects SGS SP2017/77 and SGS SP2017/58 supported by Ministry of Education, Youth and Sports of the Czech Republic.

References

- [1] Niinomi M 2008 Mechanical biocompatibilities of titanium alloys for biomedical applications *J. of the mechanical behavior of biomedical materials* **1** 30-42

- [2] Enderle J D, Bronzino J D and Blanchard S M 2005 *Introduction to Biomedical Engineering* (Second ed.) Elsevier Academic Press Amsterdam 1253 p ISBN 978-0123749796
- [3] Sloten J V, Labey L, Van Audekercke R and Van der Perre G 1998 Materials selection and design for orthopedic implants with improved long-term performance *Biomaterials* **19** 1455–1459
- [4] Geetha M, Singh A K and Asokamani R 2009 Ti based biomaterials, the ultimate choice for orthopaedic implants – A review *Progress in Materials Science* **54** 397-425
- [5] Eliaz N, Eliezer D and Olson D L 2000 Hydrogen-assisted processing of materials *Mat. Sci. Eng. A* **289** 41-53
- [6] Nelson H G 2013 in: A W Thompson and N R Moody (Eds) *Hydrogen Effects in Materials* Wiley Online Library p 699 DOI: 10.1002/9781118803363
- [7] Senkov O N and Froes F H 1999 Thermohydrogen processing of titanium alloys *Int. J. Hydrogen Energy* **24** 565-576 DOI: 10.1016/S0360-3199(98)00112-8
- [8] Qazi J I, Senkov O N, Rahim J, Genc A and Froes F H (Sam) 2001 Phase Transformations in Ti-6Al-4V-xH Alloys *Metall. Mater. Trans. A* **32** 2453-2463
- [9] Murzinova M A, Mazurski M I, Salishev G A and Afonichev D D 1997 Application of reversible hydrogen alloying for formation of submicrocrystalline structure in (alpha + beta) titanium alloys *Proc. of the Selected Papers of the First Int. Conf. on Hydrogen Treatment of Materials* Int. Assoc. for Hydrogen Energy **22** 201–204
- [10] Fang T Y and Wang W H 1998 Microstructural features of thermo mechanical processing in a Ti-6Al-4V alloy *Materials Chemistry and Physics* **56** 35-47 PII S 0254-0584(98)00137-0
- [11] *Phase Diagrams of Binary Hydrogen Alloys* 2000 Ed. by F D Manchester ASM International pp 238-258
- [12] Nalla R K, Boyce B L, Campbell J P, Peters J O and Ritchie R O 2002 Influence of microstructure on high cycle fatigue of Ti–6Al–4V: bimodal vs. lamellar structure *Metall. Mater. Trans. A* **33** 899–918
- [13] Losertová M, Štamborská M and Schindler I 2014 Influence of thermo hydrogen treatment on hot deformation behavior and microstructural evolution of Ti-6Al-4V alloy *Archives of Mat. Sci. Eng.* **66** 62-66
- [14] Losertová M, Štefek O, Schindler I, Szkandera L and Kudela P 2017 Hydrogen effect on compression mechanical properties of TiNb alloys at elevated temperatures *IOP Conf. Series: Mater. Sci. Eng.* **179** 012048 doi:10.1088/1757-899X/179/1/012048
- [15] Zong Y Y, Huang S, Wang Y and Shan D B 2014 Strengthening versus softening mechanisms by hydrogen addition in beta-Ti40 alloy *Int. J. Hydrogen Energy* **39** 3498-3504