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Corrosion Behavior of Thermohydrogen Processed Ti6Al4V

C.Y. Yu¹, L.X. Yang², C.C. Shen¹, B. Luan², and T.P. Perng^{1,3,*}

¹Department of Materials Science and Engineering, National Tsing Hua University
Hsinchu 300, Taiwan

²Integrated Manufacturing Technologies Institute, National Research Council
London, Ontario N6G 4X8, Canada

³Department of Chemical Engineering and Materials Science, Yuan Ze University,
Chung-Li 320, Taiwan

The corrosion behavior of thermohydrogen processed (THP) Ti6Al4V was evaluated in simulated human body environment (0.15M NaCl at 37°C). Compared with the β -solution treated specimen, the grain refined specimen A exhibited higher hardness and similar corrosion resistance, which implies better performance as a bio-implant material. At 65°C and 80°C, a decrease in corrosion resistance was observed for both A and B specimens, that might be ascribed to the increased grain boundaries and α_2 precipitates.

Key words: Ti6Al4V, thermohydrogen process, corrosion, grain refinement

*Corresponding Author:

Tel: +886-3-5742634

Fax: +886-3-5723857

E-mail: tpperng@mx.nthu.edu.tw

Ti6Al4V is widely used as a structural material for applications such as hip stems in total hip replacement due to its excellent mechanical and corrosion properties [1]. Recently, extensive studies have been reported on refinement of the grain size of titanium alloys using a thermohydrogen process by employing hydrogen as a temporary alloying element. The refinement is achieved based on the modifying effect of hydrogen on phase composition and transformation of metastable phases. While most research has focused on improvement of grain refinement resulted from THP and the corresponding change in mechanical properties [2-9], there has been no report on the electrochemical corrosion behavior of grain-refined Ti alloys resulted from THP. Our previous study showed that the grain size of Ti6Al4V could be refined to a nanoscale after the THP treatment [10]. Interestingly, this treatment also resulted in formation of a new phase (α_2 , with a stoichiometric composition of Ti_3Al), which was distributed within the α matrix [10].

The present study therefore focuses on the corrosion behavior of Ti6Al4V treated with the THP. The effects of grain refinement and α_2 phase formation resulting from the THP treatment are examined. The starting material for the THP was Ti6Al4V ELI alloy [10]. Prior to the THP treatment, the samples used in this study were subjected to β -solution treatment at 1000°C in vacuum for 0.5h, followed by furnace cooling [10]. A Sievert's volumetric apparatus [11] was used for the THP treatment. The effective hydrogen pressure was calculated via the ideal gas law, and the amount of hydrogen dissolved in the specimen was then calculated by a volumetric method where a resolution of 8×10^{-6} mole of hydrogen in the specimen could be obtained. In order to control the different microstructures, two hydrogenation treatments were conducted at different temperatures and hydrogen loadings, and subsequently dehydrogenation was carried out in vacuum at proper temperatures for 1 or 2h, followed by air cooling in about 0.5h to room temperature. There was no residual hydrogen left in the dehydrogenated specimens [10]. The specimen conditions are given in Table 1. The phases were determined by X-ray diffraction (XRD) using Cu K α radiation. Microstructural characterization was carried out by scanning electron microscopy (SEM, JEOL-5410 and JEOL-6500F) and transmission electron microscopy (TEM, FEI G2).

Prior to the electrochemical test, the sample was sealed in epoxy resin with an exposed area of 1.13cm². The sample was then ground and polished to obtain a strain free

surface. The potential dynamic polarization test was conducted using 0.15M NaCl solution as the electrolyte for assessment of corrosion resistance of bio-materials for human body [12]. This standard is adopted for corrosion evaluation for potential applications in hip prosthesis. The electrolyte was deaerated with N₂ during the entire test. An electrochemical cell fitted with three electrodes, a working electrode, a reference electrode (saturated calomel electrode, SCE) and a platinum counter electrode, was employed for the electrochemical experiment. The electrochemical measurement was performed using a potentiostat of Solartron 1287A electrochemical interface.

The XRD patterns of Ti6Al4V with different treatments are presented in Figure 1. The XRD pattern of the β -solution treated specimen shows very different relative peak intensities from those of standard pattern, indicating a strong texture [10]. After the THP treatment, the peak positions of α phase in specimen A are similar to those in the β -solution treated specimen. However, a shift of β phase peaks to the lower angle was observed, indicating that ~~a~~ high internal stress²⁵ existed in specimen A. Based on the shift, the expansion in lattice parameter is approximately 2.2%, i.e., a volume expansion of 6.9%. Since the amount of β phase in specimen A is below 15%, this contributes to ~1% expansion of the whole specimen. For specimen B, a group of additional peaks corresponding to α_2 phase are present [10], which is not observed in specimen A.

Figure 2 shows the microstructures of Ti6Al4V with different treatments. The β -solution treated specimen exhibits a lamellar structure with a low dislocation density (Figure 2a). For specimen A, the lamellar feature is maintained, but grain refinement within the α matrix exhibiting parallel nanoscale elongated grains is observed (Figure 2b). For specimen B, the grain refinement is less pronounced. Instead, some coarse α_2 platelets are observed within the α matrix (Figure 2c). There is no obvious structural change in the β phase after the THP treatment [10].

The Vickers microhardness values of Ti6Al4V before and after the THP treatment are given in Table 1. The hardness of Ti6Al4V increases from 306 Hv to 339 Hv after the grain refinement in specimen A. In contrast, specimen B exhibits lower hardness. The variation in hardness may be controlled by the evolution of nanostructure and the presence of α_2 precipitate.

The potential dynamic polarization measurements were conducted in 0.15M NaCl solution at 37°C to simulate the human body conditions. All samples exhibited spontaneous passivation (Figure 3), as indicated by the absence of active-passive transition peak. It is interesting that the corrosion behavior of the samples after the THP treatment is not significantly changed, although the changes in microstructure are significant as observed from Figure 2. This is a different phenomenon as compared to the commonly reported results, where grain refinement was found to be either beneficial [13-16] or deleterious [17-19], while α_2 phase was always deleterious [20-23] to corrosion resistance. This implies that the grain refined specimen A with higher strength and comparable corrosion resistance has better potential application for bio-implant.

Figure 4 shows the surface morphology for the β -solution treated Ti6Al4V after the potential dynamic polarization measurement in 0.15 M NaCl at 37°C. The white line indicates the location where the line-scan of EDX was performed. The β phase is Ti-deficient and enriched with V, and is almost free of pitting. Pitting corrosion initiated and developed primarily within the α phase. This might be due to the two phase microstructure ($\alpha+\beta$) of the Ti6Al4V, where a galvanic cell is established across the grain boundary, and α phase acts as the anode and is more susceptible to corrosion [24]. This implies that the corrosion resistance of the two-phase Ti6Al4V is primarily determined by the α phase.

The potential dynamic polarization measurement was also extended to 65°C and 80°C. The results are shown in Figure 4. The passive currents derived at potential 1.0V (vs. SCE) in the passive region are also given in Table 1. It indicates that the corrosion resistance in terms of passive current remains the same for the β -solution treated specimen, consistent with those reported previously [25-27]. However, a significant decrease in corrosion resistance is observed for both specimens A and B, particularly at 80°C. With regard to specimen A, the α matrix is considerably refined. As a result, the area of grain boundaries is increased, leading to poorer corrosion resistance than the β -solution treated specimen at higher temperatures [16, 17]. For specimen B, the existence of α_2 phase within the α matrix further enhances such galvanic corrosion due to its higher concentration of Al than in the α matrix [20-23]. This suggests that the α_2 phase formed

during the THP is detrimental to the corrosion resistance of Ti6Al4V and needs to be eliminated. The reason why the corrosion resistance of specimens A and B is so sensitive to the high temperature is not clear and requires further study.

In summary, this study examined the corrosion resistance of Ti6Al4V after the THP treatment. With grain refinement, specimen A exhibits higher hardness and comparable corrosion resistance at 37°C. It may have better performance when used as a bio-implant material. Both A and B show decreased corrosion resistance at 65°C and 80°C, that might be ascribed to the increased grain boundaries and α_2 precipitates.

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Table 1. Process conditions and the corresponding properties of Ti6Al4V.

Specimen	Process Condition	Hv	i_p ($\mu\text{A}/\text{cm}^2$)		
			37°C	65°C	80°C
β -solution	1000°C, 0.5 hr, FC	306	3.7	3.9	3.7
A	H at 200°C with hydrogen loading of 12.55at%, DH at 600°C, 1 cycle, AC	339	4.6	6.2	13
B	H/DH for 5 cycles at 750°C with hydrogen loading of 34at%, AC	280	5.1	23	32

H: hydrogenation, DH: dehydrogenation, FC: furnace cooling, AC: air-cooling.

i_p : passive current, derived at potential 1.0V (vs. SCE) in Figure 4.

Figure captions

- Figure 1 XRD patterns of Ti6Al4V after THP treatment.
- Figure 2 TEM micrographs of Ti6Al4V. (a) β -solution, (b) specimen A, and (c) specimen B.
- Figure 3 Potential dynamic polarization curves of Ti6Al4V in 0.15M NaCl solution at 37°C.
- Figure 4 Microstructures of the β -solution treated Ti6Al4V after corrosion test in 0.15 M NaCl solution at 37°C. The white line indicates the location where the line-scan of EDX was performed.
- Figure 5 Potential dynamic polarization curves of Ti6Al4V in 0.15M NaCl solution at three different temperatures. (a) β -solution, (b) specimen A, and (c) specimen B.

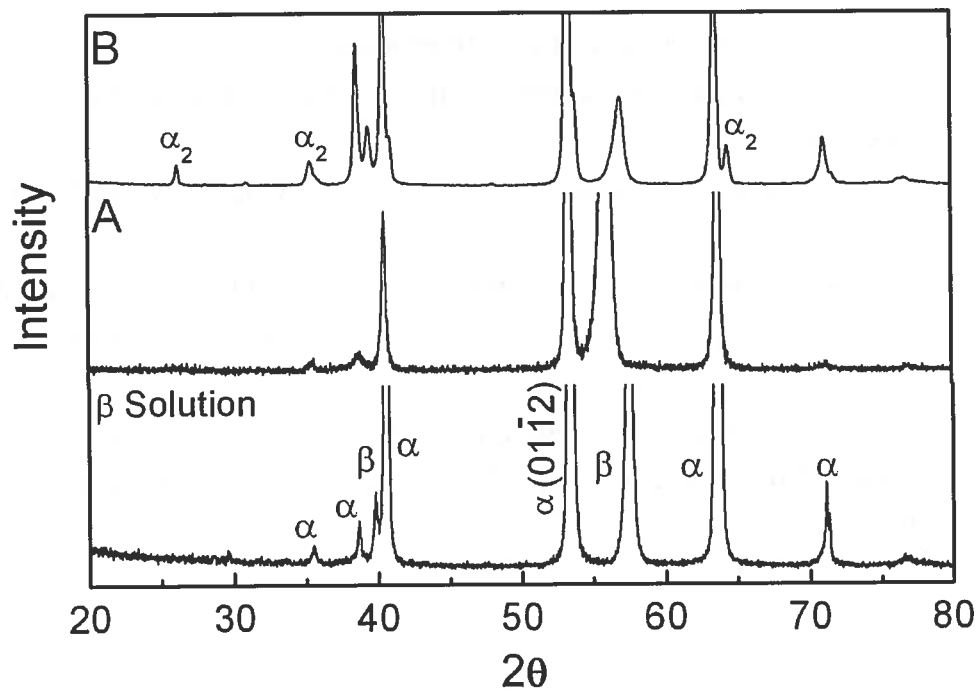
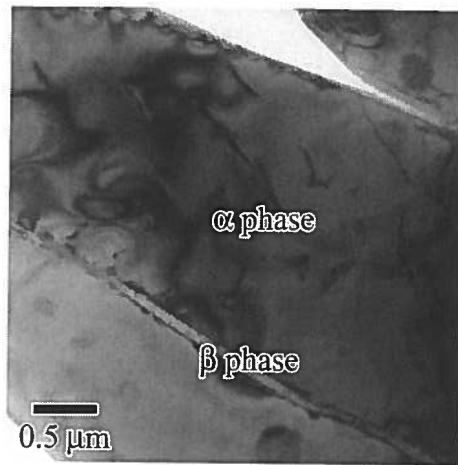
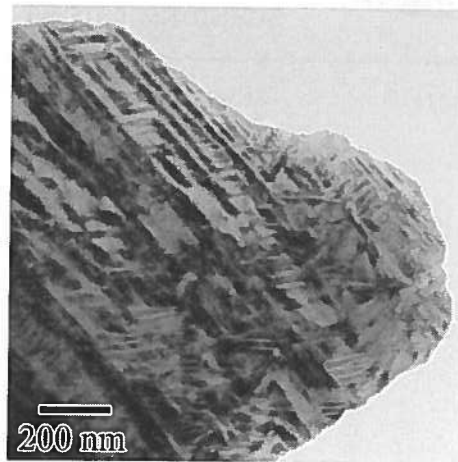


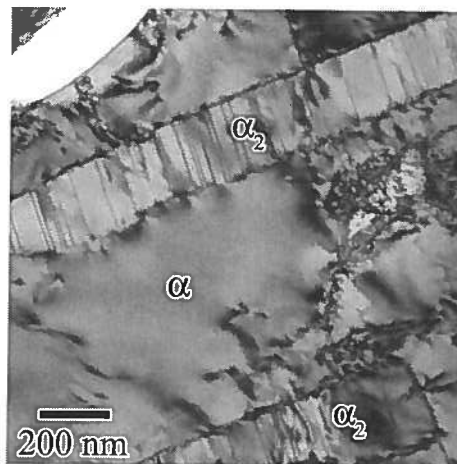
Figure 1



(a)



(b)



(c)

Figure 2

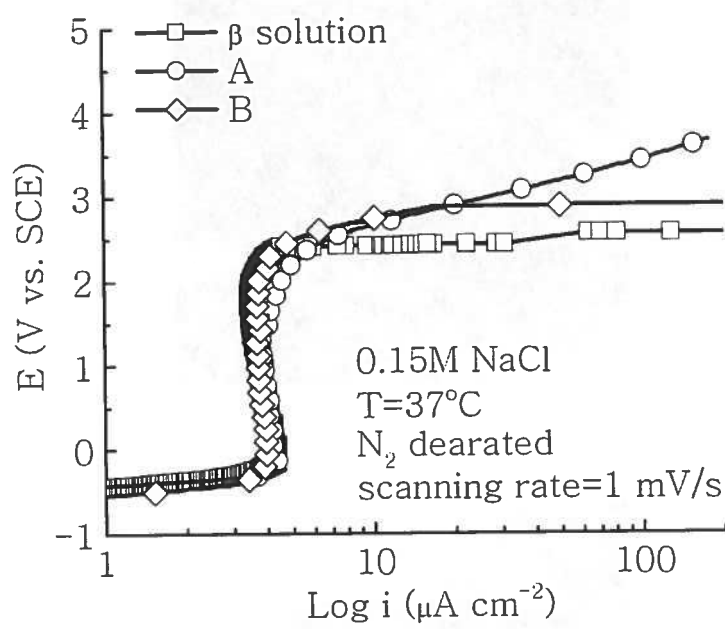


Figure 3

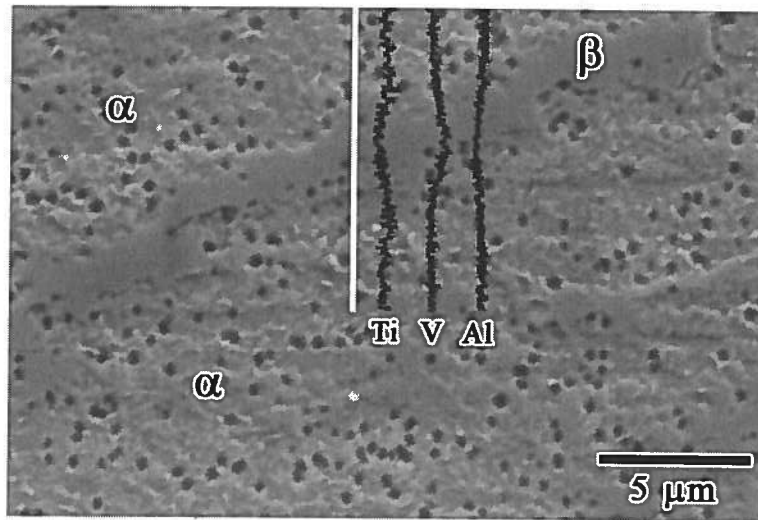
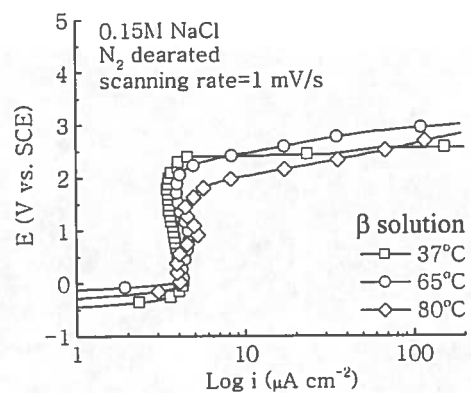
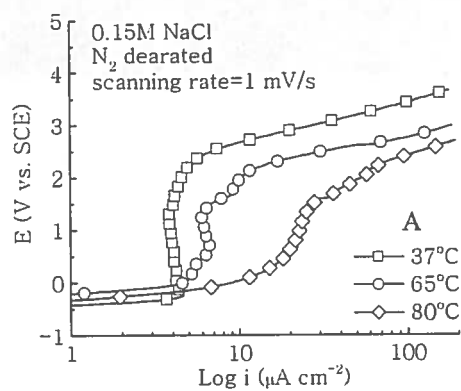


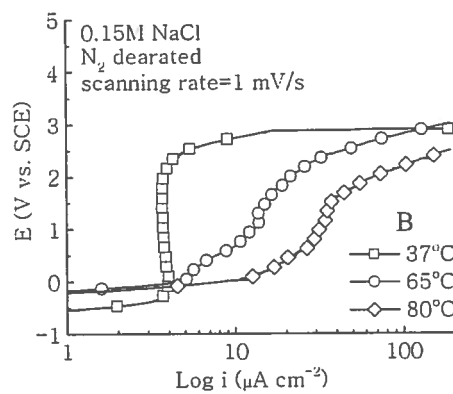
Figure 4



(a)



(b)



(c)

Figure 5