CHAPTER 5

CORROSION STUDIES ON HEAT-TREATED AND LASER-NITRIDED Ti-13Nb-13Zr ALLOY

5.1 INTRODUCTION

The biomedical implants made out of Stainless Steel, Cobalt Chromium and Titanium and its alloys, which have been extensively used so far, have been subjected to in vitro and in vivo studies (Lemons 1986). Many workers have shown that titanium remains passive in chloride environments similar to body fluids (Ronald et al 1979) and exhibits superior corrosion behavior. However, with the passage of time titanium ions and its alloying elements have been found in the tissues adjacent to the implants (Lausmaa et al 1991). As the presence of titanium ions and its alloying elements were observed even in the absence of wear, it was confirmed that either the metal or its passive film is dissolving. The release of metal ions due to dissolution of oxide layer can cause tissue damage, even at very low levels, and this passive current rate can be still be of significance (David et al 1992).

To enhance the corrosion and wear behavior of the surgical implants, several surface modification techniques such as Plasma nitriding, Plasma Vapor Deposition (PVD), Chemical Vapor Deposition (CVD), ion implantation and Laser nitriding are being employed (Muraleedharan et al 1992, Bordji et al 1996). Further, as discussed in the chapter one, the corrosion resistance of an alloy varies with the microstructure that is attained under various heat
treatment. A microstructure obtained by a particular thermomechanical procedure may be superior with respect to the mechanical property, but may result in the inferior corrosion behavior (Charles et al 1985 and Raja et al 1993). Hence, it is often necessary to select an appropriate heat treatment procedure, which will yield a microstructure that may be superior in respect to both the mechanical and electrochemical properties. The effect of the microstructure on the corrosion behavior of the titanium alloys in physiological environment has yet not been well understood. Though, there are scattered reports on the corrosion behavior of the heat-treated α+β titanium alloys, corrosion behavior of the heat-treated β rich titanium is still to be investigated in detail.

Hence, in the present study we have carried out an extensive investigation on the corrosion behavior of the Ti-13Nb-13Zr alloy that has been subjected to various heat treatments. In addition, the corrosion behavior of this alloy nitrided at two different environments has also been investigated thoroughly. Thus, this chapter presents the results of the corrosion behavior of the heat-treated and laser nitrided Ti-13Nb-13Zr alloy in Ringer’s solution at 37°C. Only one alloy was chosen for the investigation, to have an overall understanding on the effect of the alloying elements on corrosion. The variation in the corrosion behavior of the solution treated samples due to alloying element partitioning during diffusional transformation from β phase to α+β microstructure is elucidated in detail. The corrosion behavior of the solution treated samples in Ringer’s solution is studied using Open Circuit Potential-Time measurement (OCP) and Cyclic Anodic Polarization methods.
5.2 EXPERIMENTAL TECHNIQUES

5.2.1 OCP - Time Measurement

Open Circuit Potential-time (OCP) measurements were carried out to understand the corrosion behavior of the specimens under equilibrated conditions in the simulated body environment. As soon as the molded sample was immersed in the electrolyte, the initial potential of the specimen was noted and monitored as a function of time up to 60 minutes.

5.2.2 Anodic Cyclic Polarization Measurement

Electrochemical potentiodynamic cyclic polarization study of the specimens were carried out in Ringer's solution at pH 7.4 and temperature 37.4 ± 1°C. Nitrogen gas was continuously purged into the electrolyte throughout the study to eliminate the dissolved oxygen. All the potential measurements were made with reference to a saturated calomel electrode (SCE). A platinum foil was used as a counter electrode and a Solartron made Electrochemical interface SI 1287, operated through Corrware software was used for conducting the polarization experiments. When the specimen attained a constant potential, cyclic polarization was started from an initial potential of 250 mV below the corrosion potential, $E_{\text{corr}}$. The specimen was scanned in the positive direction at a sweep rate of 1 mV/sec, and then the scan was reversed in the negative direction after reaching a potential of 2.0 V and the current was monitored with respect to the potential.
5.3 CORROSION BEHAVIOR OF THE HEAT-TREATED Ti-13Nb-13Zr ALLOY

The Ti-13Nb-13Zr alloy was hot rolled in $\alpha+\beta$ field and subjected to solution treatment above and below its beta transus temperature (735°C). The solution treated specimens were cooled in three different rates (WQ, AC, FC) and subsequently aged at a lower temperature. The corrosion studies of heat-treated Ti-13Nb-13Zr alloy were carried out in simulated body fluid (Ringer’s solution). This solution was used as the corrosion cell electrolyte, as it simulates majority of the inorganic chemical species of human extra cellular fluids (Ronald et al. 1979). The heat-treated samples were cut into small pieces of size 1 x 1 cm$^2$ for corrosion studies and molded with epoxy resin. The molded specimens were polished up to 1000 grit SiC emery paper. Final polishing was done with three steps of alpha alumina of size 1µm, 0.3µm and 0.05µm. The samples were degreased with trichloroethylene followed by ultrasonic cleaning with deionized water. The influence of microstructure on the corrosion performance of the alloys is discussed in detail based on the Open Circuit Potential (OCP), passive current density and area of repassivation loop obtained from the cyclic polarization test.

5.3.1 Results and Discussion

5.3.1.1 Microscopic Observations

Inspite of the fact that we have reported in detail, the microstructural development under various heat treatment of the Ti-13Nb-13Zr alloy in the previous chapter, in the following paragraph we briefly present the results of the heat treatment studies in terms of microstructure and XRD analysis. This is done inorder to have a better understanding of the corrosion behavior of the
various microstructures obtained under different heat treatment. The microphotographs of β ST specimens with different cooling rates are shown in Figure 5.1. The water-quenched specimen exhibits a martensitic microstructure (α') while the FC specimen shows a basket-weave type of microstructure. The microstructures of the α+β solution treated specimens are shown in Figure 5.2. The overall microstructural features in WQ, AC and FC specimens appear to be similar. The microstructure consists of equiaxed α (primary α) and transformed β phases. The most striking observation from the XRD studies of WQ and AC of α+β ST specimens is the presence of the three phases α, α'', and β (Figure 5.3). The presence of α'' in WQ and AC specimens of α+ β ST conditions as opposed to hexagonal α' being formed under β ST condition is due to the enrichment of the β phase in Nb.

The aged microstructures of β ST and (α+β) ST specimens are shown in Figures 5.4 and 5.5. It was observed that the aging of the β ST /WQ sample at 500°C reduced the sharpness of α' plates and resulted in the formation of fine globular α phase.
Figure 5.1 Micrographs of Ti-13Nb-13Zr alloy (a) WQ, (b) AC, and (c) FC at 760°C/1hr.

Figure 5.2 Micrographs of Ti-13Nb-13Zr alloy (a) WQ, (b) AC, and (c) FC at 680°C/4hrs.
Figure 5.3 XRD analysis for $\alpha+\beta$ ST/WQ and $\alpha+\beta$ ST/AC 
Ti-13Nb-13Zr alloy
Figure 5.4 Micrographs for β ST at 760°C/1hr and aged
(a) WQ  (b) AC  (c) FC

Figure 5.5 Micrographs for α+β ST at 680°C/4hrs and aged
(a) WQ  (b) AC  (c) FC
The α′ phase is known to transform to α and β phases (α′ → α+β) during aging which leads to compositional change in the α phase. The aging treatment on α+β ST samples does not appreciably alter the microstructure, at the optical level (Figure 5.5). XRD studies of these specimens as shown in third chapter, reveal the presence of only α and β phases. An important observation to be noted is that the orthorhombic phase which appeared under α+β ST/WQ and α+β ST/AC conditions disappeared during aging. On aging, α" phase transforms either to α + β or β only depending on the amount of the alloying elements and this transformations are discussed in detail elsewhere (Geetha et al 2001).

5.3.1.2 OCP-Time Measurement for β ST Samples

The major characteristic of titanium surgical alloys that are presently used, is their passivity in body fluid. The stability of passive condition of the as rolled, solution treated and aged Ti-13Nb-13Zr alloy at different temperatures are illustrated by the potential-time curves in Figure 5.6. The results obtained from OCP-time measurements and cyclic anodic polarization studies for βST and βST/aged samples are given in Table 5.1 The OCP of the βST/WQ sample is found to shift towards active direction with time (from -350 mV to -467mV) with a high positive shift in the beginning. On the otherhand, OCP-time measurements of FC and AC specimens did not exhibit potential drops during 1 hr exposure in the Ringer’s solution. This kind of behavior strongly suggests that surface activation is not occurring and the air-formed native oxide consisting of TiO₂, ZrO₂ and Nb₂O₅ are kinetically resistant to chemical dissolution in the simulated physiological solution.
Figure 5.6  OCP - time measurement on β ST + aged specimens of the alloy Ti-13Nb-13Zr in Ringer’s solution
Table 5.1 Heat treatment details and passive current density of $\beta$ solution treated and $\beta$ solution treated + aged Ti-13Nb-13Zr alloy in Ringer’s solution

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Microstructure</th>
<th>OCP (mV)</th>
<th>Passive Current Density (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>760°C/1h +WQ (β ST/WQ)</td>
<td>Sharp martensitic structure</td>
<td>-467</td>
<td>3.3</td>
</tr>
<tr>
<td>760°C/1h +AC (β ST/AC)</td>
<td>Small beta grains with alpha precipitation</td>
<td>-513</td>
<td>4.8</td>
</tr>
<tr>
<td>760°C/1h +FC (β ST/FC)</td>
<td>Basket weave structure</td>
<td>-362</td>
<td>3.9</td>
</tr>
<tr>
<td>$\beta$ ST/WQ+550°C/4h/AC (β ST WQ/ A)</td>
<td>Fine globular $\alpha$ Phase +$\beta$</td>
<td>-175</td>
<td>1.6</td>
</tr>
<tr>
<td>$\beta$ ST/AC +550°C/4h/AC (β ST AC/ A)</td>
<td>Fine globular $\alpha$ phase + $\beta$</td>
<td>-693</td>
<td>3.8</td>
</tr>
<tr>
<td>$\beta$ ST/FC+550°C/4h/AC (β ST FC/ A)</td>
<td>Coarse $\alpha$ phase + $\beta$</td>
<td>-410</td>
<td>2.3</td>
</tr>
</tbody>
</table>
This result is concordant with the observations made by Cittig et al in the Ti-Nb-Ta alloy (cittig et al. 1999). Aging of the WQ specimen shifts the OCP to very high positive value (Figure 5.6). The surface oxide layer of this specimen is found to exhibit the best OCP value when compared to all the β ST samples.

5.3.1.3 Anodic Cyclic Polarization Studies for β ST Samples

The corrosion resistance of an alloy is measured on the basis of the current density value obtained from the anodic polarization studies. The lower the current density, the higher is the corrosion resistance of an alloy. Figures 5.6, 5.7 and 5.8 shows anodic polarization curves measured for heat-treated samples in Ringer’s solution at pH 7.4. From the cyclic anodic polarization studies, it is evident that there are appreciable changes in the corrosion behavior of the samples heat treated and cooled at various rates. From Figure 5.6, it is obvious that in all βST samples a stable passive layer is formed. The reason for the small increase in the value of passive current density of the βST/AC sample may be due to the presence of more number of beta grains in that structure (Figure 5.1.b). From our experimental results it is evident that aged β ST/WQ exhibits the best corrosion behavior out of all the βST samples. It recorded the lowest passive current density of value 1.6 μA. However, an increase in current density is observed at potential 1.05 V (from 2.34 μA to 5.16 μA) for this sample. The rapid increase in the current density, above 1.2V is due to oxygen evolution on the surface. The increase in the anodic potential leads to a high electrical field across the passive layer in oxidizing/acidic medium. Under these circumstances ion transport occurs and film growth continues to hundreds of nano meters. The recent investigation of Sundararajan et al also showed an increase in the current density value for Cp Ti and Ti-6Al-4V alloy in Ringer’s solution (Sundararajan et al 1998). On the otherhand,
there is no increase in the value of the current density at higher potentials for the βST/WQ sample.

The corrosion resistance of the AC and FC specimens of the currently studied alloys was found to decrease at higher potentials. A small amount of β phase will be precipitated during cooling and this results in a decrease in Nb and Zr content in the α phase. Thus, depletion of niobium and zirconium in the alpha phase of this structure has resulted in an increase in passive current density at higher potentials. Aged and unaged AC samples exhibit high values of OCP and passive current density than WQ and FC samples. As mentioned earlier it is felt that, inferior corrosion behavior is due to the presence of a large number of beta grains and uneven distribution of the alloying elements. On the otherhand, the aged AC sample is found to exhibit stable passive layer formation than the unaged one. Even distribution of the alloying elements during aging and the absence of large number of grains as compared to βST/AC sample have resulted in the formation of stable oxide layer (Geetha Manivasagam et al 2002).

5.3.1.4 OCP-Time Measurement for α+β ST Samples

The OCP and passive current density values obtained for samples heat-treated in α+β field are listed in Table 5.2. The OCP’s of the α+β solution treated samples are presented in Figure 5.9. The OCP of the α+β solution treated WQ and AC specimens was found to shift towards negative value at the beginning and latter it attained a stable potential. On the contrary, the OCP of aged α+β ST samples shifted towards noble direction. No potential drops were observed for these specimens with an air-formed oxide which strongly indicates that native oxide formed on this surface is highly stable and is resistant to chemical dissolution in the simulated body solution.
Figure 5.7 Anodic cyclic polarization curves for $\beta$ ST specimens of the alloy Ti-13Nb-13Zr in Ringer's solution
Figure 5.8 Anodic cyclic polarization curves for β ST and aged specimens of the alloy Ti-13Nb-13Zr in Ringer's solution.
5.3.1.5 Anodic Cyclic Polarization Studies for $\alpha$$+\beta$ ST Samples

The results of the cyclic anodic polarization studies are presented in figures 5.10 and 5.11. The cyclic anodic polarization behavior of the $\alpha$$+\beta$/WQ sample was very striking. During the forward scan, it was seen that, a highly stable layer without any fluctuations was formed on the surface. Moreover, there was no increase in the value of the current density up to 2000 mV. In contrast, we observed an increase in the current density value above 1000 mV in most of the heat-treated samples. In addition, this sample exhibited a very small area during the reverse scan, suggesting that the repassivation behavior of this sample was also superior when compared to the other heat-treated samples.

From the cyclic anodic polarization studies, it is observed that, 1) A highly stable passive layer has been formed on this sample due to the even distribution of alloying elements in the three phases namely $\alpha$, $\alpha''$ and $\beta$. 2) The sample will repassivate very quickly even if the surface oxide will undergo dissolution due to wear or some other process. On the otherhand the passive current density of the aged WQ sample was marginally higher than the unaged one. However, as there was no increase in the current density value with increasing potential, it is evident that the aged sample also forms a very stable passive layer on the surface similar to the unaged one. Contrary to these results, the current density values of unaged and aged FC samples increases to very high values even at very low potential of 1.14 V (Figures 5.10 and 5.11). This is due to the enrichment of Nb and Zr in $\beta$ phase and their depletion in $\alpha$ phase.
Table 5.2 Heat treatment details and passive current density of $\alpha+\beta$ solution treated and $\alpha+\beta$ solution treated + aged Ti-13Nb-13Zr alloy in Ringer's solution

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Microstructure</th>
<th>OCP (mV)</th>
<th>Passive Current Density (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$680^\circ$C/4h +WQ ($\alpha+\beta$ST WQ)</td>
<td>Equiaxed $\alpha$ + transformed $\beta$ with $\alpha''$ + $\beta$</td>
<td>-405</td>
<td>2.4</td>
</tr>
<tr>
<td>$680^\circ$C/4h +AC ($\alpha+\beta$ ST AC)</td>
<td>Equiaxed $\alpha$, + transformed $\beta$ with $\alpha''$, $\beta$</td>
<td>-471</td>
<td>2.6</td>
</tr>
<tr>
<td>$680^\circ$C/4h +FC ($\alpha+\beta$ ST FC)</td>
<td>Equiaxed(coarse alpha) + $\beta$</td>
<td>-305</td>
<td>2.3</td>
</tr>
<tr>
<td>$\alpha+\beta$ST/WQ+550$^\circ$C/4h/AC ($\alpha+\beta$ STWQ/ A)</td>
<td>Equiaxed $\alpha$ + transformed $\beta$, with out $\alpha''$</td>
<td>-64</td>
<td>2.4</td>
</tr>
<tr>
<td>$\alpha+\beta$ST/AC+550$^\circ$C/4h/AC ($\alpha+\beta$ ST AC/ A)</td>
<td>Equiaxed $\alpha$ + transformed $\beta$, with out $\alpha''$</td>
<td>-391</td>
<td>2.7</td>
</tr>
<tr>
<td>$\alpha+\beta$ST/FC+550$^\circ$C/4h/AC ($\alpha+\beta$ ST FC/ A)</td>
<td>Equiaxed (coarse alpha) + $\beta$</td>
<td>-345</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Figure 5.9  OCP - time measurement for $\alpha + \beta$ ST + aged specimens of the alloy Ti-13Nb-13Zr in Ringer's solution
Figure 5.10 Anodic cyclic polarization curves for $\alpha+\beta$ ST specimens of the alloy Ti-13Nb-13Zr in Ringer's solution
Figure 5.11 Anodic cyclic polarization curves for α+β ST and aged specimens of the alloy Ti-13Nb-13Zr in Ringer's solution
5.3.1.6 Repassivation Behavior of the Heat-Treated Samples

The repassivation behavior of all the $\alpha+\beta$ ST and $\beta$ ST specimens shows (Figures 5.7, 5.8, 5.10 and 5.11) that there was no breakdown of the film during the forward scan. The specimens were polarized cathodically (i.e. reverse scan) by decreasing the potential in steps of 1 mV/min. We observed that cathodic curve is displaced to the left of the anodic curve i.e. smaller currents were observed during reverse scan. If the passive film would have disrupted or changed during the forward scan, the current would have increased as the potential is decreased (Ronald et al. 1979). Thus, it is evident from our observation, that the passive film formed during the forward scan is still intact.

5.3.1.7 Discussion

The experimental results suggest that the corrosion resistance of the Ti-13Nb-13Zr alloy changes considerably with the heat treatment. All the heat-treated Ti-13Nb-13Zr samples did not result in potential drop and remain passive at OCP in Ringer’s solution, indicating that air formed native oxide is resistant to chemical dissolution. However, $\beta$ST/WQ +aged and $\alpha+\beta$ST/WQ samples exhibit more positive OCP values than the other heat-treated samples. This strongly suggests that the oxide layer formed on these specimens were nobler than that of the other heat-treated samples. Equiaxed structure is more corrosion resistant than the other microstructures. The passive films developed over equiaxed structures are very stable and uniform as compared to structures with uneven grain sizes (Thair et al. 2002). In the present study also, the $\alpha+\beta$ ST samples with equiaxed structure is found to exhibit superior corrosion behavior. The reason for the superior behavior of the Ti-13Nb-13Zr alloy during the OCP -time measurements may be due to the alloying additions like Nb and Zr which is
reported to diminish the rate of proton reduction when compared to Cp Ti (Yu et al 1999).

Anodic polarization curve illustrates the typical passive behavior which is associated with titanium and its alloys. The passivation peak is not observed for all the heat-treated samples and the current immediately enters the passivity zone. This implies, that this alloy attains passivation like pure titanium in Ringer's solution. Titanium oxide can be present on the titanium surface at normal or slightly elevated temperatures as a rutile, a tetragonal form of titanium dioxide, and the presence of this surface film upon titanium offers excellent corrosion resistance to this alloy in a wide range of corrosive media (Prusi et al 1992). Moreover, the presence of Nb₂O₅ can reduce migration of active ions like Cl⁻ through the passive film and improves the structural integrity of the oxide film and reduce the pit initiation (Shreir 1997) The reason for this is the lower solubility of Nb ion, unlike the elements Al and V in Ti-6Al-4V alloy.

It is well known that the corrosion resistance of titanium alloys is enhanced when alloyed with Zr, Nb, Ta and Pd, as the formation of ZrO₂, Nb₂O₅, Ta₂O₅ and PdO, strengthen the TiO₂ passive film formed on the surface. Nb₂O₅ is more resistant to chemical dissolution in comparison to TiO₂ (Yu et al 1999 and Okazaki et al 1999). Thus β titanium alloys exhibit better corrosion behavior than the α+β titanium alloys. The reason for the inferior corrosion behavior of the α+β biomedical titanium alloys such as Ti-6Al-4V, Ti-5Al-2.5Fe and Ti-6Al-7Nb is due to the presence of the alloying additions such as Al and V. Depending on the heat-treatment procedure there is much variation in the distribution of the alloying elements in various phases. Several workers have observed a decrease in the corrosion resistance of these alloys due to enrichment of aluminum in the alpha phase and depletion of Nb in the beta...
phase. Any heat treatment such as aging that leads to an enrichment of aluminum in the α phase resulted in the preferential dissolution of the α phase and consequently led to increased anodic current density compared to its ST counterpart (Thair et al 2002, Yu et al 1999 and Raja et al 1993). On the other hand, the β phase enriched with niobium was highly corrosion resistant in the same environment. The preferential dissolution of α phase is also reported for a series of Ti based alloys (Yu et al 1999). The reason for the stability of β phase with Nb content is due to the high thermodynamic stability of Nb oxide which has more negative heat of formation, compared to that of Ti or Zr. In addition, the strength of the covalent bonds between Ti and the alloying element Zr estimated by Molecular Orbital calculation in various physiological saline solution shows that Ti-Zr alloy has higher bond order $B_0$ values and exhibits higher corrosion resistance of the β type alloys. Thus, the rate of ion release is decreased with Zr additions. Okazaki et al (1998) also observed that corrosion resistance of pure metals like Ti, Nb and Ta in Eagle’s medium solution at 37°C was very high through the exhibition of low current densities in contrast to the Al and V which showed high current densities. They have also confirmed the potency of Ti, Nb, Zr and Ta to develop highly protective passive layers, resulting in a much lower potential electrochemical interaction than Ti-6Al-4V and contributes in the formation of new bone tissue around these alloys in bone marrow (Mishra et al 1993, Okazaki et al 2001 and Okazaki et al 1998).

Inspite of the fact, that Ti-Nb-Zr alloys exhibit superior corrosion performance, a small variation in anodic behavior of ST and STA samples was observed from our work. The variations in corrosion behavior are observed due to either the enrichment or the depletion of the beneficial alloying elements such as Zr and Nb in a particular phase that occurs on different heat treatment. The current density of the heat-treated samples above 1.2 V increased as
the potential increased, and then decreased with further increase in the potential. Figure 5.12 shows the anodic polarization behavior of the α+β WQ samples and α+β FC and aged samples. The WQ sample is passive up to 2 V and implies that it has attained a stable passivation. The repassivation behavior of this heat-treated sample was superior amongst all the heat-treated samples as the area of the hysteresis loop was very minimum for this sample. On the other hand, in the FC sample there is a considerable increase in value of the current density above 1 V. The α phase of the FC samples is enriched with Ti and Zr, and the β phase consists of large amount of Nb. The α phase thus formed is found to undergo dissolution above 1.2 V similar to that of Cp Ti (Sundararajan, 1998).

Repassivation behavior of different heat-treated samples of Ti-BNb-13Zr alloy showed similar behavior in Ringer’s solution. The predominance of TiO₂ in all the oxide films and Ti/Ti³⁺ dissolution following repassivation will lead to this behavior (Kolman et al, 1996). Kolman et al (1996) have reported that, oxides of Mo and V in β titanium alloys Ti-15Mo-3Nb-3Al and Ti-15V-3Cr-3Al-3Sn do not contribute to repassivation. They further suggest that, the difference in composition and microstructure have little effect in repassivation behavior of β versus α titanium. Though, we were not able to observe considerable difference in the repassivation behavior of most of the heat-treated samples, the α+β ST/WQ specimen was found to exhibit extremely smaller area of hysteresis. This clearly implies the quicker tendency of the surface layers for repassivation. This sample also revealed the formation of stable passive layer formation during the forward scan in anodic polarization studies. From this observation, it seems that the repassivation behavior of the extremely stable passive layer will be superior. Thus, it is seen that the oxides of the solute
elements also influence the repassivation behavior of the passive film to some extent.

In summary, the following conclusions are arrived. The isomorphous \( \beta \) phase stabilizer such as Nb present in the alloy improved the passivity of the \( \beta \) phase, and Ti and Zr also improved the passivity and limited the active dissolution of the \( \alpha \) phase. The higher-valent oxides (e.g. \( \text{Nb}_2\text{O}_5 \)) that are usually the best passivating films, owe their protective property largely to their extreme slowness of their dissolution under many conditions rather than their thermodynamic stability. However, depletion of the beneficial alloying elements in the \( \alpha \) phase to a greater extent was not beneficial above 1.2 V. Though, there was a sudden increase in the current density above 1.2 V, it attained a constant value when the potential was increased further. This implies that, this alloy has high tendency for repassivation after dissolution. Further, the variation in the corrosion behavior of the heat-treated samples, which has beneficial alloying elements, is attributed to the distribution of the cluster of solute oxides in \( \text{TiO}_2 \) matrix. It is well known that when alloying elements (except V and Fe) form an oxide, these oxides will occur as discrete clusters embedded in a titanium matrix surface oxide (Marc Long et al 1998). If the alloying elements are evenly distributed in all the phases, then their oxide clusters also get distributed uniformly in the matrix and form a stable passive layer (Figure 5.13a). The heat treatment that leads to the uneven distribution of the alloying elements in various phases results in unstable passive layer formation (Figure 5.13b). Thus, the variation in the corrosion behavior of the heat-treated alloy Ti-13Nb-13Zr samples are attributed to the distribution of the alloying elements and their oxides to various extent in different phases.
Figure 5.12 Anodic cyclic polarization for WQ and FC + aged specimen of α+β ST Ti-13Nb-13Zr alloy

TiO$_2$ matrix

Figure 5.13 a) Clusters of solute oxides evenly distributed on the surface
(b) Clusters of solute oxides unevenly distributed on the surface
5.4 CORROSION BEHAVIOR OF THE LASER NITRIDED Ti-13Nb-13Zr ALLOY

5.4.1 Introduction

To reduce the metal ion release in the implants due to wear, several surface modification treatments have been suggested such as prepassivation, nitrogen ion implantation and TiN coating (Behrndt et al 1991). Although such treatment can substantially increase the corrosion resistance under static condition, they are hardly capable of providing long term benefits under the conditions of wear that often prevails at the implant surface. Protective oxide layers are easily torn from the surface, whereas the thinning of ion implanted layer quickly leads to their complete removal (Edward Rolinski, 1989). Hence it is advantageous, if the surface modification could simultaneously achieve the goal of wear and corrosion resistance improvements. Laser nitriding is an advanced technique used for titanium alloys to improve its wear behavior by the formation of very hard and thick TiN layer (Senthil Selvan et al 1998). The corrosion behavior of laser nitrided Ti-13Nb-13Zr alloy is presented in the following sections.

5.4.2 Experimental Work

The Ti-13Nb-13Zr alloy was laser nitrided in two different environments (dilute and pure nitrogen atmosphere) with 1.06 μm Nd:YAG laser. The samples were prepared for corrosion studies as mentioned in the section 2.8 and the corrosion studies were performed by using the techniques described in the section 5.2.
5.4.3 Results and Discussion

5.4.3.1 Microscopic Observation

The microstructure of the samples nitrided at dilute nitrogen environment (0.2 Bar N₂) exhibited white diffused zone, on the other hand, the samples nitrided at pure nitrogen environment reveal the formation of dendritic structure (Figure 5.14) Needle like structures were present below the dendrites and beta grains were also observed in this region. The dendrites consist of TiN as reported by several workers (Xin et al 1996) and also it was found to contain more Zr and less amount of Nb as seen from X-ray back scattered image analysis (Figure 5.15)

5.4.3.2 OCP-Time Measurement and Anodic Cyclic Polarization Studies

The OCP-Time measurement curves of laser nitrided samples and the samples polished to various depths are presented in Figures 5.16 and 5.17. The anodic polarization curves of the laser nitrided and untreated specimens are shown in Figures 5.18 and 5.19. The values of passive current density measured for all the nitrided specimens at 500 mV (SCE) are given in Table 5.3. The rapid attainment of stable potential for nitrided samples compared to the untreated specimen, the shift of OCP towards noble direction and the attainment of stable potential in a short span of time indicated the formation of noble surface layer produced by laser nitriding. The passive current density of laser nitrided samples at pure and dilute nitrogen environment measured at 0.5 V was extremely lower than the untreated alloy. This can be attributed to the fact that the protective layers formed on the surface of the alloy via laser treatment are essentially inert and resistant to the environment.
It is reported that, the surface of the ion implanted titanium alloy is removed to half of its initial thickness due to wear when implanted in the human body (Dahm et al 1995). Thus, in the present study the laser treated surface was polished to various depths and their corrosion resistance in Ringer’s solution was evaluated, to understand the behavior of various layer of the treated surface towards corrosion. The passive current density of the specimens grinded to different depths was higher than the specimen laser nitrided at 1 bar N₂ due to the removal of surface consisting of TiN dendrites. However, these specimens showed noble OCP and low values of passive current density when compared to the untreated samples as shown in Figure 5.18 and Table 5.3. This implies that, the laser treated samples will exhibit better corrosion behavior even if it undergoes some surface dissolution due to wear (Geetha Manivasagam et al 2001b).

5.4.3.3 Discussion

Laser nitriding allowed significant improvement of corrosion behavior of Ti-13Nb-13Zr alloy in the Ringer’s solution. The corrosion potential (OCP) of the nitrided sample was more positive than its untreated counterpart indicating stronger surface passivation. From the cyclic anodic polarization studies also, it is observed that the laser nitrided specimens exhibit much better electrochemical behavior than the untreated specimen by virtue of much lower passivation current density at low potentials. However, the corrosion resistance of the specimen treated at pure nitrogen environment was very high when compared to the specimen treated at dilute environment. The high corrosion resistance attained by the laser nitrided samples can be attributed to the formation of TiN compounds on the surface.
Figure 5.14 Micrographs for the laser treated Ti-13Nb-13Zr
a) at pure N$_2$ environment b) at dilute N$_2$ environment
Figure 5.15 Characteristic X-ray image showing the distribution of the alloying elements in the dendrites
Figure 5.16  OCP-Time measurement curves for Ti-13Nb-13Zr hot rolled and Laser nitrided at dilute and pure nitrogen environment
Figure 5.17  OCP-Time measurement curves for Ti-13Nb-13Zr
hot rolled and nitrided at pure N$_2$ environment
and grinded to various thickness
Table 5.3 Passive current density for untreated and laser treated Ti-13Nb-13Zr alloy at different conditions

<table>
<thead>
<tr>
<th>Specimen Condition</th>
<th>Passivation current Density, μA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Hot Rolled Alloy</td>
<td>3.3</td>
</tr>
<tr>
<td>Laser Treated at 0.2 Bar N₂/Ar</td>
<td>0.7</td>
</tr>
<tr>
<td>Laser Treated at 1 Bar N₂</td>
<td>0.18</td>
</tr>
<tr>
<td>Laser Treated at 1 Bar N₂, surface grinded to 50 μm depth</td>
<td>3.9</td>
</tr>
<tr>
<td>Laser Treated at 1 Bar N₂, surface grinded to 100 μm depth</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Figure 5.18 Anodic cyclic polarization curve for the Laser nitrided Ti-13Nb-13Zr at pure N$_2$ environment and grinded to various depth.
Figure 5.19 Anodic cyclic polarization curves for Ti-13Nb-13Zr hot rolled and Laser nitrided at dilute nitrogen environment (N2/Ar)
The surface of the laser nitrided samples consists of TiN, which would possess excellent corrosion resistance by developing a thin surface layer (200 Å) of TiO₂ (Starosvetsky et al 2001). This layer forms readily and inherits good corrosion resistance and adherence to the TiN layer. Furthermore, the nitrogen incorporated in TiN may be reacting with oxygen to form oxynitrides. These oxynitrides along with oxides impede the dissolution at the surface, thus increasing the corrosion resistance. The oxynitrides formed in the passive film creates a protective layer preventing titanium coming into contact with reactive ions like O²⁻ and Cl⁻. Moreover, titanium form its oxide at the surface and this results in the formation of thin passive film, which will resist the mobility of Cl⁻ and other ions through the film (Thair et al 2002 and De Becdelievre et al 1988).

In addition, the alloying elements such as Nb and Zr have contributed to the enhanced corrosion resistance of the treated samples by the formation of titanium/niobium oxynitrides and titanium/zirconium oxynitrides. Reduction in the time and area of the repassivation loop during cyclic polarization (Figure 5.18) indicates the stability of the passive film against the corrosion attack, and the faster repassivation tendency of laser nitrided surface. But at higher potential the anodic current of nitrided samples reached higher values as compared to that of untreated specimen. The gradual increase in the anodic current of laser nitrided samples indicates a reduction in protective properties of the passive film. It should also be mentioned that increase in anodic current occurs only at high potentials and thus should not impair the materials corrosion behavior in body fluid environment maintained at a low equilibrium potentials. The behavior of the specimen during reverse scan indicates that the repasasivating tendency of the nitrided surface was much higher than the untreated samples. Thus, it may be concluded that even if the surface layers of the treated samples undergo
rapid dissolution due to wear, the nitrided surface will passivate easily than the untreated alloy and prevent corrosion of the underlying substrate.

5.5 CONCLUSION

1. Heat treatment at various temperatures resulted in microstructural changes and these changes appear to affect the corrosion resistance of the alloy.

2. The electrochemical techniques clearly reveal that, all the ST and STA specimens exhibit spontaneous passivity in the Ringer’s solution.

3. Amongst the β ST samples, the aged β ST/WQ sample exhibited the noble value of OCP and lower passive current density. However, the passive current density of this sample increased considerably at high potential due to the depletion of the beneficial alloying elements Zr and Nb in the alpha phase.

4. There was no appreciable change in the values of passive current density of the α+β ST samples. The heat treatment α+β ST/WQ resulted in very stable oxide layer formation and the area of repassivation was least for this specimen. This indicates the high corrosion resistance of the alloy for this heat treatment. The outstanding behavior of this sample is attributed to the even distribution of the alloying elements in the three phases (α, α” and β) developed during this treatment.

5. Though, the OCP and passive current density of α+β ST/FC specimen was lower than WQ and AC samples, there was a small increase in the
value of passive current density at higher potential and the area of repassivation was higher than that of the WQ sample.

6. All the air-cooled samples (β ST and α+β ST) exhibit high negative values of OCP and high passive current density as compared to the other samples. Uneven distribution of the alloying elements under this treatment result in low corrosion resistance of these samples.

7. Repassivation behavior of the alloy clearly indicates, the increasing current observed at higher potential is not due to breakdown or change in the passive layer, but rather reflects additional current related to oxygen evolution.

8. A significant lower current density was measured for Laser nitrided Ti-13Nb-13Zr alloy.

9. The improved corrosion resistance of laser nitrided Ti-13Nb-13Zr alloy in the simulated body fluids is due to the change in the nature and composition of the passive film formed after laser nitriding. This improvement arises from the formation of precipitates of TiN, which screen the underlying titanium atoms, avoiding their migration and stabilizing the growth of the oxide film.