CHAPTER 3

RESULTS AND DISCUSSION

This chapter deals with the results obtained after surface modification on pure titanium using various concentrations (5 wt.%, 15 wt.% and 25 wt.%) of H$_2$O$_2$ maintained at 80°C for 1 hr and followed by heat treatment at 400°C for 1 hr. Then, the surface morphologies of the specimens were characterized using Raman spectroscopy, SEM – EDAX, FTIR and electrochemical techniques. The specimens were preliminarily investigated by comparing the morphology formed before and after H$_2$O$_2$ treatment.

3.1 SURFACE CHARACTERISATION AND IN-VITRO BEHAVIOUR OF PURE TITANIUM

3.1.1 Raman Spectroscopy

The crystallographic structure of the titanium specimen formed after the surface modification using H$_2$O$_2$ followed by heat treatment was analysed by Raman spectroscopy. Figure 3.1 shows the Raman spectra for untreated and titanium treated with various concentrations of H$_2$O$_2$.

The untreated titanium exhibited no significant Raman bands may be due to the thin amorphous nature of the native oxide layer. The peaks related to anatase or rutile was not recorded, indicating that the surface oxide layer was mainly composed of amorphous TiO$_2$. Similar results were also reported earlier by Furic et al (2005).
Titanium treated with 5 wt.%, 15 wt.% and 25 wt.% of H$_2$O$_2$ exhibited peaks at 515 cm$^{-1}$ and 630 cm$^{-1}$. This indicated that titanium on treatment with H$_2$O$_2$ exhibited anatase gel layer. Earlier reports show that anatase has six Raman – active modes, among which four intense modes referred to as E$_g$ (151 cm$^{-1}$), B$_{1g}$ (409 cm$^{-1}$), A$_{1g}$ or B$_{1g}$ (515 cm$^{-1}$) and E$_g$ (633 cm$^{-1}$) are usually detected for nanocrystalline anatase (Zhang et al 2000).

![Figure 3.1 Raman spectra of untreated and H$_2$O$_2$ treated titanium](image)

Generally, the nanocrystallites possesses high chemical reactivity and large excess energy in the form of non-equilibrium defects bringing an extra driving force stored on the Ti surface, which makes it possible for the amorphous titania formed in H$_2$O$_2$ solution to change into titania with weak crystallinity (Wen et al 2007).
3.1.2 Scanning Electron Microscopic Analysis of H$_2$O$_2$ Treated Titanium

Figure 3.2 illustrates the SEM images of untreated and H$_2$O$_2$ treated titanium. The images of untreated titanium revealed uni-directional grooves formed during mechanical polish (Figure 3.2(a)).

The SEM images of 5 wt.% of H$_2$O$_2$ treated titanium (Figure 3.2(b)) showed the formation of titania layer with non-uniform pores on the surface. Further, the surface exhibited numerous bright and dark contrasting spots indicating that the layer formed over the titanium surface was not plain but was made of a number of crests and troughs. In the case of titanium treated with 15 wt.% of H$_2$O$_2$, a porous titania layer with uniformly networked pores covering the entire surface of the specimen was observed (Figure 3.2(c)). The pore diameter was found to be varying in the range from nanometer to micrometer scale. Also, the reduced number of bright and dark spots indicated a plainer surface. The presence of numerous elevations on both the specimens, indicated that the oxide layer on the surface does not grow uniformly, which may be due to the surface imperfections. Similar, sub-micrometer porous network was reported earlier by Osaka et al (2000), Wang et al (2002) and Wu et al (2002), by oxidizing commercial pure titanium plate by H$_2$O$_2$. Figure 3.2(d) shows the SEM images of titanium treated with 25 wt.% of H$_2$O$_2$, which exhibited cracked surface oxide layer. The cracked morphology may be due to the dehydration process during heat treatment of a thick layer of oxide. The formation of a thick oxide layer can be confirmed from the absence of any contrasting features as compared to the 5 wt.% and 15 wt.% treatment conditions.
Figure 3.2 SEM images of $\text{H}_2\text{O}_2$ treated titanium (a) untreated, (b) 5 wt.%, (c) 15 wt.% and (d) 25 wt.%. 
3.1.3 Fourier Transform Infrared Spectroscopic Studies

The bioactivity of a material is associated with its ability to form an apatite layer when implanted or kept in contact with a biological fluid (Kokubo et al 1990). FTIR spectroscopy is a sensitive technique to study the vibrational modes, which are characteristic of the constituent molecular groups thus permitting the detection of the hydroxyapatite and its growth on the material surface (Flowe et al 1974). The FTIR spectra of untreated and titanium treated with different concentrations of H$_2$O$_2$ on immersion in SBF solution for 7 days are shown in Figure 3.3. The broad absorption band around 3600 cm$^{-1}$ corresponds to OH$^-$ stretching and bending of H$_2$O respectively. The peak at 575 cm$^{-1}$ results from the ν$_4$ mode of O-P-O bending, while the peak at 1006 cm$^{-1}$ indicated the ν$_3$ band of P-O stretching mode. The peaks approximately at 1500 cm$^{-1}$ and 875 cm$^{-1}$ correspond to the ν$_3$ vibration mode of carbonate incorporated in the apatite (Wen et al 1998). Hence, the appearance of the phosphate and carbonate absorption bands in the spectra of the untreated and H$_2$O$_2$ treated titanium after soaking in SBF solution confirmed the formation of an apatite layer. Osaka et al (2004) reported that titanium substrates were provided with apatite forming ability after surface modification using H$_2$O$_2$. Once the apatite nuclei are formed, they grow spontaneously by consuming the calcium and phosphate ions from the solution, as SBF solution is supersaturated with respect to the apatite (Takadama et al 2001).
Figure 3.3  FTIR spectroscopy of H$_2$O$_2$ treated titanium immersed in SBF solution for 7 days (a) untreated,  (b) 5 wt.% ,  
(c) 15 wt.% and (d) 25 wt.%
3.1.4 Scanning Electron Microscopy / Energy Dispersive X-ray Analysis of Titanium After Immersion in SBF Solution

Figure 3.4(a-d) shows the SEM/EDAX results of untreated and titanium treated with different concentrations of H₂O₂ on immersion in SBF solution for 7 days. It can be observed from the figure that the surface of untreated titanium is covered with a few apatite-like crystals formed randomly. This was consistent with our previous findings for untreated titanium immersed in SBF solution (Tamilselvi 2006). However, the surface of titanium treated with 5 wt.% of H₂O₂ was partially covered with sub-micron sized apatite particles, a common morphology of apatite. The surface of titanium treated with 15 wt.% of H₂O₂ exhibited large, non-uniform, individual as well as clustered ball-like apatite particles. The growth was observed over the entire surface. In contrast, only a few ball-like particles were observed over titanium treated with 25 wt.% of H₂O₂, indicating the formation of fewer apatite particles over the surface.

The titania gel layer induces apatite formation due to the presence of abundant Ti-OH functional groups, which are effective for apatite nucleation. It has been reported that the number of surface Ti-OH groups could be increased by H₂O₂ treatment. In addition, after the heat treatment an anatase crystal structure, the porous Ti-O network and the negative surface charge density of the titania gel layer may be responsible for the apatite deposition (MacDonald et al 2004). The negatively charged units of titania are postulated to interact selectively with the positively charged calcium ions present in the solution.
Figure 3.4  SEM – EDAX analysis of $\text{H}_2\text{O}_2$ treated titanium immersed in SBF solution for 7 days  (a) untreated, (b) 5 wt.%, (c) 15 wt.% and (d) 25 wt.%
Figure 3.4 (Continued)
The EDAX spectra for untreated and titanium treated with different concentrations of \( \text{H}_2\text{O}_2 \) showed peaks corresponding to calcium and phosphate with a significant decrease in the intensity of the peak corresponding to titanium. The intensity of the peaks corresponding to calcium and phosphate were prominent for titanium treated with 15 wt.% of \( \text{H}_2\text{O}_2 \). The results revealed that more Ca and P ions were adsorbed on the porous titania gel layer formed on the surface.

### ELECTROCHEMICAL CHARACTERISATION OF PURE TITANIUM

The surface treatments have profound effect on the electrochemical behaviour during the immersion in SBF solution. In order to understand the changes in electrochemical behaviour during the apatite formation, the \( \text{H}_2\text{O}_2 \) treated specimens were characterized using OCP, potentiodynamic polarization and EIS measurements.

#### 3.2.1 Open Circuit Potential Measurements

The variation in the OCP for untreated and \( \text{H}_2\text{O}_2 \) treated titanium immersed in SBF solution for 7 days is shown in Figure 3.5. It was observed that OCP of untreated titanium was around -0.375 V, all through the immersion period, while that of the titanium treated with \( \text{H}_2\text{O}_2 \) were all nobler. The difference in OCP value for untreated and \( \text{H}_2\text{O}_2 \) treated titanium can be attributed to the nature of the surface film formed by the treatment and during the immersion in SBF solution.

Titanium treated with 15 wt.% of \( \text{H}_2\text{O}_2 \) exhibits nobler potential than treatment with other concentrations of \( \text{H}_2\text{O}_2 \) and untreated titanium. Although, the variation in the potential during the immersion period is insignificant, a decrease in potential on the 1\textsuperscript{st} day of immersion in SBF
solution can be attributed to the increased activity at the porous titania / SBF solution interface. Subsequent days show nobler potential indicating the growth of a protective layer. This is in good agreement with the results obtained from SEM-EDAX after 7 days of immersion indicating a matured growth of large ball-like apatite over the entire surface. The potentials of surface treated titanium immersed in SBF solution was found to increase with the following order 15 wt.% > 5 wt.% > 25 wt.% > untreated titanium.

![OCP - time graph of untreated and H\textsubscript{2}O\textsubscript{2} treated titanium immersed in SBF solution for 7 days](image)

**Figure 3.5** OCP – time graph of untreated and H\textsubscript{2}O\textsubscript{2} treated titanium immersed in SBF solution for 7 days

### 3.2.2 Potentiodynamic Polarization Studies

The potentiodynamic polarization curves for untreated and titanium treated with different concentrations of H\textsubscript{2}O\textsubscript{2} on immediate immersion in SBF solution are presented in Figure 3.6(a).

The polarization behaviour of H\textsubscript{2}O\textsubscript{2} treated specimens were appreciably different from that of the untreated specimen indicating that the
H$_2$O$_2$ treatment produces an effect on the corrosion behaviour. The untreated and titanium treated with 25 wt.% of H$_2$O$_2$ exhibited constant current density values and extend over a wide range of potentials. Thus, the potential sweep in the positive direction for the titanium specimen showed an anodic current starting at -0.5 V corresponding to the formation of titanium suboxides, TiOOH and Ti$_2$O$_3$, immediately after immersion. With an increase in the potential, the current density remained almost constant (Schmidt et al 1998). At these potentials, the layer is identified as a amorphous TiO$_2$ layer, constituted of hydrated TiO$_2$ over the surface and Ti$_2$O$_3$ sub-oxides at the metal/oxide interfaces (Pankuch et al 1993), formed according to the reactions (Pourbaix 1996):

$$2\text{Ti} + 3\text{H}_2\text{O} + 6e^- \rightarrow \text{Ti}_2\text{O}_3 + 6\text{H}^+ \quad (3.1)$$
$$\text{Ti}_2\text{O}_3 + 3\text{H}_2\text{O} + 24e^- \rightarrow 2\text{TiO(OH)}_2 + 2\text{H}^+ \quad (3.2)$$
$$\text{Ti}_2\text{O}_3 + 3\text{H}_2\text{O} + 4e^- \rightarrow \text{TiO(OH)}_2 + 4\text{H}^+ \quad (3.3)$$
$$\text{TiO(OH)}_2 \rightarrow \text{TiO}_2 + \text{H}_2\text{O} \quad (3.4)$$

The anodic current at 1.5 V refers to solution ion oxidation (oxygen evolution), which takes place via electron transfer across the oxide without transpassive dissolution of titanium (Boddy 1968).

In case of titanium treated with 5 wt.% and 15 wt.% of H$_2$O$_2$, a wide oscillation in the current density up to 1 V was observed. This indicates the partial dissolution of the surface layer, due to the hydrolysis of the titanium oxide and the equilibration of the surface with SBF solution, which results in the formation of OH$^-$ and Ti (OH)$_n$(4-n). The OH$^-$ ions formed were adsorbed on the oxide surface, while Ti (OH)$_n$(4-n) ions entered into SBF solution (Healy and Ducheyne 1992). Moreover, there was a rapid increase in the current density after 1 V for the specimen treated with 5 wt.% of H$_2$O$_2$. This may be due to the breakdown of the titania layer in SBF solution.
Figure 3.6 Potentiodynamic polarization curves of untreated and H$_2$O$_2$ treated titanium (a) immediate immersion and (b) after 7 days of immersion in SBF solution
To study the effect of immersion period on corrosion resistance of these specimens in SBF solution, potentiodynamic polarization measurements were carried out after 7 days of immersion and the results are shown in Figure 3.6(b). The polarization curves of untreated and titanium treated with 25 wt.% of H$_2$O$_2$ after 7 days of immersion exhibited similar behaviour as immediate immersion. Also, a marginal potential shift in the positive direction and a reduction in current density, can be attributed to the formation of an insulating layer over the surface. Similar, results were also observed for untreated titanium in Hank’s solution by Tamilselvi et al (2009).

The potentiodynamic polarization curves of titanium treated with 5 wt.% and 15 wt.% of H$_2$O$_2$ exhibited a decrease in the current density values by one order of magnitude and moreover, the fluctuations in the current density reduced. However, titanium treated with 25 wt.% of H$_2$O$_2$ exhibited a marginal shift in the potential and current density value. This may be due to the incorporation of Ca and P ions present in the solution over the porous surface oxide layer. A similar shift in potential was also observed for alkali and alkali heat treated titanium on immersion in SBF solution, attributing to changes in nature of the film formed over the surface (Shukla et al 2005).

3.2.3 Electrochemical Impedance Spectroscopic Studies

The electrochemical impedance spectroscopic studies were carried out for the surface modified specimens, in order to evaluate the protective properties and the formation of new apatite layer. Figure 3.7(a) shows the Bode plot of untreated and titanium treated with different concentrations of H$_2$O$_2$ on immediate immersion in SBF solution.

The spectra obtained for untreated titanium shows a phase angle value of around -80° and remained constant over a wide range of frequency.
This behaviour confirmed the highly capacitive behavior of the passive oxide film formed over the surface.

The Bode plot of titanium treated with 5 wt.% of H$_2$O$_2$ showed a phase angle value of -10° in the higher frequency region and in the intermediate frequency the phase angle shifts to -45° and in the low frequency region, the phase angle shifts slightly to -75°. This shift confirmed the presence of a thin barrier layer in the high and intermediate frequency and porous outer gel layer in the lower frequency, exhibiting two time constant. Similar behaviour was observed for titanium treated with 15 wt.% of H$_2$O$_2$ with the phase angle value shifting around -80° in the intermediate frequency and to -60° in the low frequency. In the case of titanium treated with 25 wt.% of H$_2$O$_2$, the phase angle value around -80° in the high and intermediate frequency and formation of small hump in the low frequency region was observed. It indicated the presence of two layers, with an inner barrier layer and an outer porous gel layer.

The Bode resistance plot for untreated and titanium treated with various concentrations of H$_2$O$_2$ is shown in Figure 3.7(b). The H$_2$O$_2$ treated titanium specimens exhibited higher resistance compared to untreated titanium. This may be due to the formation of a thick oxide layer formed due to H$_2$O$_2$ treatment.

When titanium is brought into contact with H$_2$O$_2$ solution, metal interface experiences two phenomena, (i) the titanium catalysed decomposition of H$_2$O$_2$ and (ii) the corrosion of the metal, which will involve the metal dissolution into the electrolyte and the formation of a titanium oxide. This oxide is far thicker than the one obtained by simple immersion of the metal in saline solutions for similar periods and is composed of two layers: an outer layer highly porous and hydroxylated, and an inner layer, much thinner and with an insulating character (Fonseca and Barbosa 2001).
Figure 3.7  Impedance spectra of untreated and H$_2$O$_2$ treated titanium on immediate immersion in SBF solution (a) Bode phase angle and (b) Bode impedance plot
The impedance spectra obtained for untreated and titanium treated with various concentrations of H$_2$O$_2$ on immediate immersion in SBF solution were fitted using equivalent circuit are shown in Figure 3.8 (a) and (b).

The fitted equivalent circuit model clearly indicated the presence of a one time constant due the passive oxide layer over the surface of untreated titanium (Figure 3.8(a)). This can be represented as $R_s(R_bQ_b)$, where, $R_s$ represents the solution resistance and $R_b$ and $Q_b$ represents the charge transfer resistance and double layer capacitance of the barrier layer. Similarly, Raistrick et al (1987) have reported the surface film to be a parallel circuit of a resistor, due to the ionic conduction through the film, and a capacitor due to its dielectric properties.

The spectra obtained for titanium treated with various concentrations of H$_2$O$_2$ were fitted using the circuit model represented as $R_s(R_gQ_g)(R_bQ_b)$, where, $R_g$ and $Q_g$ represents the charge transfer resistance and double layer capacitance of the gel layer (Figure 3.8(b)). It indicated the formation of inner barrier layer and outer porous gel layer. This type of circuit was proposed by Wang et al (2002) to simulate data for titanium in SBF solution, and can be considered as an electrical representation of a two layer model of the oxide film, consisting of an inner barrier and outer porous layer.

The above fitting procedure revealed that a good agreement between theoretical and experimental data obtained if a frequency dependent constant phase element (CPE) was used instead of pure capacitance and Warburg impedance. The impedance of a constant phase element is defined as:

$$Z_{\text{CPE}} = \left[ Q(j\omega)^n \right]^{-1}$$  \hspace{1cm} (3.5)
where, \( j \) is the imaginary number \( (j = \sqrt{-1}) \), \( Q \) is CPE, \( \omega \) is angular frequency \( = 2\pi f \) (rad s\(^{-1}\)), \( Q \) and \( n \) are frequency independent parameters, which usually depends on temperature and condition for \( n \) is \(-1 \leq n \leq 1\). CPE describes an ideal capacitor when \( n = 1 \), an ideal resistor when \( n = 0 \) and -1 for a pure inductor (Raistrick et al 1987). Generally, the appearance of a CPE is due to the presence of inhomogeneties on the electrode surface and it can be described in terms of a distribution of relaxation times, or it may arise from non-uniform diffusion whose electrical analog is an inhomogeneously distributed RC transmission line.

![ Equivalent circuit diagrams](image)

**Figure 3.8** Equivalent circuit diagrams of \( \text{H}_2\text{O}_2 \) treated titanium on immediate immersion in SBF solution (a) untreated and (b) 5 wt.\%, 15 wt.% and 25 wt.%
The impedance data of untreated and titanium treated with different concentrations of H₂O₂ on immediate immersion in SBF solution, obtained after fitting the spectra to the equivalent circuit is presented in Table 3.1. The titanium treated with 15 wt.% H₂O₂ exhibited higher corrosion resistance compared to untreated and titanium treated with other concentrations of H₂O₂. This may be due to the surface oxidation of titanium with H₂O₂ which resulted in numerous elevations and a thickened oxide layer (Walivaara et al 1993).

### Table 3.1  Electrochemical impedance data of untreated and H₂O₂ treated titanium on immediate immersion in SBF solution

<table>
<thead>
<tr>
<th>Titanium</th>
<th>R_s / Ω cm²</th>
<th>R_g / KΩ cm²</th>
<th>Q_g / µF cm⁻²</th>
<th>n</th>
<th>R_b / MΩ cm²</th>
<th>Q_b / µF cm⁻²</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.41</td>
<td>2.82</td>
<td>0.88</td>
</tr>
<tr>
<td>5 wt.% of H₂O₂</td>
<td>59</td>
<td>278</td>
<td>3.08</td>
<td>0.85</td>
<td>3.45</td>
<td>2.37</td>
<td>0.94</td>
</tr>
<tr>
<td>15 wt.% of H₂O₂</td>
<td>66</td>
<td>417</td>
<td>1.79</td>
<td>0.86</td>
<td>8.69</td>
<td>1.98</td>
<td>0.95</td>
</tr>
<tr>
<td>25 wt.% of H₂O₂</td>
<td>125</td>
<td>172</td>
<td>13.66</td>
<td>0.95</td>
<td>2.54</td>
<td>2.50</td>
<td>0.93</td>
</tr>
</tbody>
</table>

The Bode plot of untreated and titanium treated with various concentrations H₂O₂ after 7 days of immersion in SBF are shown in Figure 3.9 (a) and (b).

Figure 3.9 (a) shows a gradual shift in the phase angle value in the low frequency region for untreated titanium, it indicated the formation of a new layer over the surface. The formation of a new layer may be due to the interaction of calcium and phosphate ions present in the solution, as deduced from SEM images.

In case of titanium treated with H₂O₂, the spectra appear significantly different and vary extensively. It was observed that two humps appear at phase angle around -50° at the high and intermediate frequency and it shifts to -80° in the low frequency region. This indicated that the spectra exhibited three time constant, with inner barrier layer, outer porous gel layer
and formation of a new layer. The formation of new a layer is characteristic of a phase angle shift in the low frequency region. The shift in the phase angle can be attributed to the growth of apatite over the surface modified titanium.

The Bode resistance plot for untreated and titanium treated with various concentrations of H$_2$O$_2$ on immersion in SBF solution after 7 days of immersion is shown in Figure 3.9(b). Titanium treated with 5 wt.% and 15 wt.% of H$_2$O$_2$ exhibited higher resistance compared to resistance obtained for untreated and titanium treated with 25 wt.% of H$_2$O$_2$. It was also be observed that, solution resistance was high for 5 wt.% and 15 wt.% H$_2$O$_2$ treated titanium, which indicates the adsorption of solutions ions over the surface, creating a high solution resistance. This also suggest that repair of the defects in the barrier layer during the period of immersion might have occurred by the incorporation of mineral ions from the solution into the defects/pores or to the film thickening during immersion time. Pan et al (1996) suggested that a H$_2$O$_2$ addition can lead to an increased corrosion rate (titanium release) and also enhanced film thickening. The pronounced porous outer layer may be expected to facilitate the incorporation of mineral ions such as phosphate groups from biological fluids.

Figure 3.10(a) shows the equivalent circuit used to fit the spectra of untreated titanium after 7 days of immersion in SBF solution. The model is represented as $R_s(R_aQ_a)(R_bQ_b)$, where, $R_a$ and $Q_a$ represent the charge transfer resistance and double layer capacitance of the apatite layer, it indicated the presence of a two time constant, which corresponds to the barrier layer and formation of a new layer. The equivalent circuit consisting of three parallel combination of resistor and capacitor in series with solution resistance was used to fit the spectra obtained for titanium treated with 5 wt.% 15 wt.% and 25 wt.% of H$_2$O$_2$ after immersion in SBF solution for 7 days and is represented as $R_s(R_aQ_a)(R_bQ_b)(R_bQ_b)$ (Figure 3.10(b)). It indicated the formation of a new layer which may be due to the adsorption of Ca and P ions over the gel layer, as evinced from SEM-EDAX analysis (Figure 3.4(c)).
Figure 3.9  Impedance spectra of untreated and H$_2$O$_2$ treated titanium after 7 days of immersion in SBF solution (a) Bode phase angle and (b) Bode impedance plot.
Figure 3.10 Equivalent circuit diagrams of H$_2$O$_2$ treated titanium after 7 days of immersion in SBF solution (a) untreated and (b) 5 wt.%, 15 wt.% and 25 wt.%.
Table 3.2 shows the impedance data for untreated and H$_2$O$_2$ treated titanium after 7 days of immersion in SBF solution. For untreated titanium, the resistance value increased as the immersion time increased. The increase in the resistance value can be attributed to increase in the passive film thickness (Ibris and Rosca 2002). This suggests that there is a change in the passive film behaviour of the titanium due to the newly formed layer that accounts for higher protection. In case of the titanium treated with 5 wt.% and 15 wt.% of H$_2$O$_2$, the resistance values for immediate immersion were higher compared to immersion in SBF solution for 7 days, indicating the formation of a defective oxide layer over the surface due to H$_2$O$_2$ treatment. The decrease in capacitance values of both the layers may be due to partial recovery of the barrier and outer porous gel layer (Lavos – Valereto and Wolynec 2004). This is in agreement with the result obtained from OCP and potentiodynamic polarisation, where there is a decrease in the potential values and oscillations in the current density as the immersion time increased.

Pan et al (1996) suggested that when the titanium oxide layer becomes thickened and the pores are sealed, the corrosion resistance can reach to high level and prevent dissolution. This may explain the fact that the amount of titanium in the biological surroundings can reach a stable level after a long period of implantation.

Further, the low capacitance ($Q_a$) values of the apatite layer are indicative of the growth in the layer. The titanium treated with 5 wt.% and 25 wt.% of H$_2$O$_2$ exhibited higher capacitance value compared to the titanium treated with 15 wt.% of H$_2$O$_2$. This result clearly revealed that 5 wt.% and 25 wt.% of H$_2$O$_2$ treated titanium have low apatite forming ability compared to 15 wt.% of H$_2$O$_2$ treated titanium. This result was further confirmed by surface morphological analysis as described earlier.
Table 3.2  Electrochemical impedance data of untreated and H$_2$O$_2$ treated titanium after 7 days of immersion in SBF solution

<table>
<thead>
<tr>
<th>Titanium</th>
<th>$R_s$/Ω cm$^2$</th>
<th>$R_a$/KΩ cm$^2$</th>
<th>$Q_a$/µF cm$^{-2}$</th>
<th>n</th>
<th>$R_g$/KΩ cm$^2$</th>
<th>$Q_g$/µF cm$^{-2}$</th>
<th>n</th>
<th>$R_b$/MΩ cm$^2$</th>
<th>$Q_b$/µF cm$^{-2}$</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>91</td>
<td>4.10</td>
<td>0.005</td>
<td>0.61</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>51.5</td>
<td>14.67</td>
<td>0.79</td>
</tr>
<tr>
<td>5 wt.% of H$_2$O$_2$</td>
<td>117</td>
<td>5.51</td>
<td>1.54</td>
<td>0.81</td>
<td>0.22</td>
<td>4.84</td>
<td>0.73</td>
<td>2.01</td>
<td>1.14</td>
<td>0.87</td>
</tr>
<tr>
<td>15 wt.% of H$_2$O$_2$</td>
<td>136</td>
<td>8.48</td>
<td>1.28</td>
<td>0.85</td>
<td>1.39</td>
<td>0.003</td>
<td>0.78</td>
<td>6.31</td>
<td>0.56</td>
<td>0.91</td>
</tr>
<tr>
<td>25 wt.% of H$_2$O$_2$</td>
<td>128</td>
<td>4.78</td>
<td>1.09</td>
<td>0.75</td>
<td>0.18</td>
<td>7.76</td>
<td>0.65</td>
<td>1.28</td>
<td>2.46</td>
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</table>
3.3 SURFACE CHARACTERISATION AND IN-VITRO BEHAVIOUR OF Ti-6Al-4V ALLOY

3.3.1 Raman Spectroscopy

Figure 3.11 shows the Raman spectra of untreated and Ti-6Al-4V alloy treated with various concentrations of H$_2$O$_2$. The Raman spectrum of the untreated Ti-6Al-4V alloy is quite featureless, exhibiting hardly any peak. Thus, no significant Raman peaks related to the crystalline structure of the oxide layer was observed for untreated Ti-6Al-4V alloy. This indicated the amorphous nature of the passive film formed due to the naturally formed oxide layer. Ong and Lucas (1995) analysed the Raman spectra for passivated titanium specimen. They reported that no distinguishable vibrational mode was observed on the titanium surfaces, due to the amorphous oxide layer even on the passivated titanium surface. Raman spectra collected on Ti-6Al-4V alloy treated with various concentrations of H$_2$O$_2$ and with subsequent heat treatment resulted in an anatase TiO$_2$ phase as
evinced from the Raman peaks approximately at 399 cm\(^{-1}\), 515 cm\(^{-1}\) and 630 cm\(^{-1}\). The peak at 630 cm\(^{-1}\) is assigned to the anatase \(E_g\) mode and the peak at 399 cm\(^{-1}\) to the \(B_{1g}\) mode of the anatase phase (Turkovic et al 1991). The peak at 516 cm\(^{-1}\) is a doublet of \(A_{1g}\) and \(B_{1g}\) modes of TiO\(_2\) anatase phase (Alam and Cameron 2002). This indicated that an anatase layer was formed on the surface of Ti-6Al-4V alloy treated with all concentrations of H\(_2\)O\(_2\).

3.3.2 Scanning Electron Microscopy / Energy Dispersive X-ray Analysis of H\(_2\)O\(_2\) Treated Ti-6Al-4V Alloy

The surface morphology and composition of the untreated and H\(_2\)O\(_2\) treated Ti-6Al-4V alloy is shown in Figure 3.12 (a)-(d). The SEM micrograph of untreated Ti-6Al-4V alloy showed oriented grooves formed during mechanical polishing and the corresponding EDAX peaks revealed well defined peaks of Ti, Al and V. The surface of Ti-6Al-4V alloy treated with 5 wt.% of H\(_2\)O\(_2\) exhibited many white colored particles as can be seen in Figure 3.12 (b). The observed white colored particles were found to be V as evinced from EDAX analysis. The surface of untreated Ti-6Al-4V alloy comprised \(\beta\)-phase grains surrounded by \(\alpha\)-phase grains. But the treatment of Ti-6Al-4V alloy treated with 5 wt.% of H\(_2\)O\(_2\) resulted in surface topographies that reflect local difference in passivity / dissolution of the elements. Hence in this case, \(\beta\)-phase grains were preferentially removed and were observed on the top surface. This can be attributed to the higher dissolution rate of \(\beta\) phase grains compared to \(\alpha\) phase grains and also due to the difference in electrochemical properties of the two phases (Variola et al 2008). But, this result differs from that of, Ti-6Al-4V alloy treated with the mixture of acids (Sittig et al 1999).
Figure 3.12 SEM - EDAX images of $\text{H}_2\text{O}_2$ treated Ti-6Al-4V alloy (a) untreated, (b) 5 wt.%, (c) 15 wt.% and (d) 25 wt.%
Figure 3.12 (Continued)
In that case, α phase grains were attacked more rapidly than β phase grains. It was reported that such phenomena can be related to differences in electrochemical potential, with the β phase grains being more anodic than the α phase grains. Hence, this discrepancy may be due to the difference in both pH and the nature of the chemical oxidants, which modify the kinetics and thermodynamics of the process. The treatment of Ti-6Al-4V alloy with 15 wt.% and 25 wt.% of H₂O₂ resulted in the formation of cavities, with the pores in the sub-micrometer scale (Figure 3.12(c) and (d)). The EDAX results showed the peaks corresponding to Ti and Al only. The peak corresponding to V is absent. This indicated that V which was present on the top surface of the specimen dissolved during treatment of Ti-6Al-4V alloy with 15 wt.% and 25 wt.% of H₂O₂. The dissolution of these vanadium oxides resulted in the generation and diffusion of vacancies in the oxide layer (Metikos – Hukovic et al 2003), forming micro-pores on the surface of Ti-6Al-4V alloy treated with higher concentrations of H₂O₂.

3.3.3 Fourier Transform Infrared Spectroscopic Studies

The FTIR spectra of untreated and Ti-6Al-4V alloy treated with various concentrations of H₂O₂ after immersion in SBF solution for 7 days is shown in Figure 3.13. In order to assess the biocompatibility of the H₂O₂ treated Ti-6Al-4V alloy, the specimens were immersed in the SBF solution for 7 days. The result revealed the presence of hydroxyapatite growth on the H₂O₂ treated specimens.

The spectra of untreated, 15 wt.% and 25 wt.% H₂O₂ treated Ti-6Al-4V alloy showed the PO₄³⁻ band consisting of P-O stretching vibrations at 595 cm⁻¹ and 1083 cm⁻¹. The band at 870 cm⁻¹ and 1457 cm⁻¹ corresponds to the C-O stretching vibration. This mode of vibration revealed that CO₃²⁻ had incorporated in the apatite. The broad absorption band around 3500 cm⁻¹ – 3600 cm⁻¹ corresponds to OH⁻ stretching and bending vibrations of H₂O respectively (Wen et al 1989). The peaks corresponding to phosphate
and carbonate functional groups could be identified on the spectra which confirm the formation of apatite layer. Wang et al (2002) reported that H$_2$O$_2$ treated titanium can induce the apatite deposition on the surface. The surface of Ti-6Al-4V alloy treated with 5 wt.% of H$_2$O$_2$, no particles were obtained to characterize for FTIR. As a result no significant results obtained for this specimen.

![FTIR spectra of H$_2$O$_2$ treated Ti-6Al-4V alloy immersed in SBF solution for 7 days](image)

Figure 3.13 FTIR spectroscopy of H$_2$O$_2$ treated Ti-6Al-4V alloy immersed in SBF solution for 7 days (a) untreated, (b) 15 wt.% and (c) 25 wt.%. 
3.3.4 Scanning Electron Microscopy / Energy Dispersive X-ray Analysis After Immersion in SBF Solution

In applications of implants as bone plates for internal fixation, one key requirement for successful osseointegration, that is bone bioactivity, is determined by the apatite forming ability of the implant surface in body fluids. In-vitro evaluation of apatite forming ability is commonly carried out using immersion test in SBF solution for a soaking period of the order of few weeks (Shi et al 2006).

Figure 3.14 (a)-(d) shows the SEM/EDAX results of untreated and Ti-6Al-4V alloy treated with various concentrations of H$_2$O$_2$ after immersion in SBF solution for 7 days. The surface of untreated Ti-6Al-4V alloy was partially covered with few apatite like particles. Ti-6Al-4V alloy treated with 5 wt.% of H$_2$O$_2$ exhibited no appreciable changes even after immersion in SBF solution for 7 days. This indicated that the specimen had poor apatite forming ability. This may be due to the formation of a thin titanate layer at low concentration of H$_2$O$_2$. Wang et al (2002) reported that the minimum thickness of the oxide layer must be in the order of 0.2 µm to induce apatite deposition. However, in case of Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of H$_2$O$_2$, the surface was covered by a new layer of mineral precipitate. This newly formed mineral layer showed many globules on the surface. This morphology is commonly seen in other studies with SBF solution. The in-vitro bioactivity study shows that this new layer corresponds to an apatite-like structure and is constituted by small crystallites.

The formation of the bioactive material could be induced by the presence of Ti-OH groups, which reveals a negative charge to interact with calcium ions in the SBF solution. The amorphous calcium titanate is postulated to reveal a positive charge, thereby interacting with the phosphate
ions in the fluid to form the amorphous calcium phosphate, which eventually crystallized into hydroxyapatite like particles (Hench 1999).

The EDAX analysis was carried out for untreated and Ti-6Al-4V alloy treated with various concentrations of H$_2$O$_2$ after immersion in SBF solution for 7 days. When comparing with Figure 3.12(a)-(d), the untreated, Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of H$_2$O$_2$ exhibited new peaks corresponding to the elements of calcium and phosphate. This indicated that the microporous formed on Ti-6Al-4V alloy due to H$_2$O$_2$ treatment could induce the nucleation and growth of bone like apatite formation over the surface. However, Ti-6Al-4V alloy treated with 5 wt.% of H$_2$O$_2$ exhibited peaks related to Ti and Al only.

The presence of Ca and P in the EDAX spectra indicated the formation of an apatite layer. The apatite forming ability of Ti implants are related to a number of factors of the surface layer, namely morphology (Peltola et al 2000), oxide phase (Lu and Leng 2005) and thickness (Wang et al 2002). Moreover, with the formation of the apatite layer on the surface, the supersaturation of a simulated physiological solution may promote preferential nucleation of apatite on the already formed apatite than in the solution. This may be due to the higher activation energy for the homogenous nucleation of apatite in human body fluid. Thus, formation of apatite coating continues only on the initial apatite layer by spontaneous growth consuming calcium and phosphate from the surrounding body fluid. A theoretical analysis also indicated that formation of hydroxyapatite exhibits a higher thermodynamic preference than that of octacalcium phosphate (OCP) and dicalcium phosphate (DCP), thus further formation of the coating proceeds in the form of hydroxyapatite, rather than OCP or DCP (Lu and Leng 2005).
Figure 3.14 SEM–EDAX analysis of H$_2$O$_2$ treated Ti-6Al-4V alloy immersed in SBF solution for 7 days (a) untreated, (b) 5 wt.%, (c) 15 wt.% and (d) 25 wt.%. 
Figure 3.14 (Continued)
3.4 ELECTROCHEMICAL CHARACTERISATION OF Ti-6Al-4V ALLOY

3.4.1 Open Circuit Potential Measurements

The potential – time measurements were carried out for untreated and Ti-6Al-4V alloy treated with various concentrations of H$_2$O$_2$ immersed in SBF solution for 7 days and the results are shown in Figure 3.15. The Ti-6Al-4V alloy treated with 15 wt.% of H$_2$O$_2$ exhibited higher corrosion potential value compared to Ti-6Al-4V alloy treated with other concentrations and untreated alloy. This indicated the formation of thick oxide layer due to the higher concentration of H$_2$O$_2$. Ti-6Al-4V alloy on oxidation with H$_2$O$_2$ leads to increased oxide content through the formation of peroxide complexes that convert into Ti(IV)O$_2^-$, Ti(IV)O$_2^{2-}$ and Ti(III)O$_2$ (Walivaara et al 1993).

![Figure 3.15 OCP – time graph of untreated and H$_2$O$_2$ treated Ti-6Al-4V alloy immersed in SBF solution for 7 days](image_url)
3.4.2 Potentiodynamic Polarization Studies

Figure 3.16(a) shows the potentiodynamic polarization curves of untreated and H\textsubscript{2}O\textsubscript{2} treated Ti-6Al-4V alloy for immediate immersion in SBF solution. The untreated Ti-6Al-4V alloy exhibited a stable passive film extending over a wide range of potentials with constant current density. Ti-6Al-4V alloy treated with various concentrations of H\textsubscript{2}O\textsubscript{2} resulted in wide fluctuations in the current density throughout the passive region. These fluctuations were up to 1 V, after which there was a reduction in the fluctuations of the current density. This behaviour may be due to the presence of unstable, repetitive dissolution and refliming of the surface oxide layer (Khaled 2003). Beyond 1 V of potential, a sudden increase in the current density was observed for all the specimens. This may be due to the localised breakdown of the oxide layer. But, it has been reported that Ti alloys exhibit very high anodic potentials even in chloride solution, without forming any pit. Hence, increase in current density may be due to changes in the valence state of one of the cationic species present in the oxide film or may be associated with the oxygen evolution reaction (Baker et al 2009).

Figure 3.16(b) shows the potentiodynamic polarization curves of untreated and H\textsubscript{2}O\textsubscript{2} treated Ti-6Al-4V alloy after immersion in SBF solution for 7 days. It can be observed that for untreated alloy, the nature of the curve remains almost constant with a significant shift in potential towards positive direction and a slight decrease in the current density. This behavior can be attributed to the slow growth of the oxide film, indicating the stability of the passive layer. A decrease in the potential value was observed for Ti-6Al-4V alloy treated with 5 wt.% of H\textsubscript{2}O\textsubscript{2}. This can be attributed to the structural changes in the passive film or changes in the ionic or electrical conductivity of the film.
Figure 3.16 Potentiodynamic polarization of untreated and \( \text{H}_2\text{O}_2 \) treated Ti-6Al-4V alloy (a) immediate immersion and (b) after 7 days of immersion in SBF solution
It has been reported that the vanadium oxide formed on the surface of Ti-6Al-4V alloy dissolves and the dissolution of vanadium oxide is further enhanced by the presence of chloride ions in Hank’s solution (Metikos et al 2003). In case of Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of H$_2$O$_2$, it was observed that the current density decreased by one order of magnitude and moreover, the oscillations in the current density were reduced, which may be due to the formation of new layer over the surface.

### 3.4.3 Electrochemical Impedance Spectroscopic Measurements

Figure 3.17(a) and (b) shows the electrochemical impedance response of untreated and surface modified Ti-6Al-4V alloy on immediate immersion in SBF solution. It can be observed that the untreated alloy on immediate exposure to SBF solution, exhibited a near capacitive response illustrated by a phase angle close to $-80^\circ$ over a wide range of frequency. It indicated a typical behaviour of a thin passive oxide film. In case of Ti-6Al-4V alloy treated with 5 wt.%, 15 wt.% and 25 wt.% of H$_2$O$_2$, the impedance spectra displayed two time constants that is they were divided into two distinct frequency regions: the time constant in the high-frequency part, which arises from the uncompensated ohmic resistance due to the electrolytic solution and the impedance characteristics resulting from the penetration of the electrolyte through a porous film, and the low-frequency part accounting for the processes taking place at the substrate/electrolyte interface. Such a behavior is typical for a metallic material covered by a porous film which is exposed to an electrolytic environment, and can be described in terms of an equivalent circuit which accounts for the different electrochemical processes occurring in the system.
Figure 3.17  Impedance spectra of untreated and H$_2$O$_2$ treated Ti-6Al-4V alloy on immediate immersion in SBF solution (a) Bode phase angle and (b) Bode impedance plot

The spectrum obtained for untreated Ti-6Al-4V alloy was fitted using the circuit $R_s(R_bQ_b)$, where, $R_s$ represents the solution resistance, $R_b$ and $Q_b$ represents the charge transfer resistance and double layer capacitance of the barrier layer. The fitted equivalent circuit model (Figure 3.18(a)) clearly
indicated the presence of passive oxide layer on the metal surface possessing resistance as well as capacitance. Figure 3.18(b) shows the equivalent circuit used for fitting the impedance spectra of H₂O₂ treated Ti-6Al-4V alloy. The circuit $R_s(R_pQ_p)(R_bQ_b)$ where, $R_p$ and $Q_p$ represents the charge transfer resistance and double layer capacitance of the porous layer, and is characterized by two parallel combination of resistance and capacitance in series with solution resistance. It indicated the formation of two time constant with inner barrier layer and outer porous layer.

![Equivalent circuit diagrams of H₂O₂ treated Ti-6Al-4V alloy on immediate immersion in SBF solution](image)

The impedance data obtained after fitting the spectra is given in Table 3.3. It was observed that Ti-6Al-4V alloy treated with 15 wt. % of H₂O₂ was found to exhibit a dense inner layer of higher corrosion resistance and an outer porous layer of relatively low resistance, in comparison with Ti-6Al-4V alloy treated with other concentrations of H₂O₂.
Table 3.3  Electrochemical impedance data of untreated and H₂O₂ treated Ti-6Al-4V alloy on immediate immersion in SBF solution

<table>
<thead>
<tr>
<th>Ti-6Al-4V alloy</th>
<th>$R_s$ / Ω cm²</th>
<th>$R_p$ / KΩ cm²</th>
<th>$Q_p$ / µF cm⁻²</th>
<th>$n$</th>
<th>$R_b$ / MΩ cm²</th>
<th>$Q_b$ / µF cm⁻²</th>
<th>$n$</th>
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</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>92</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.13</td>
<td>1.18</td>
<td>0.90</td>
</tr>
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<td>5 wt.% of H₂O₂</td>
<td>115</td>
<td>24.48</td>
<td>19.02</td>
<td>0.62</td>
<td>16.63</td>
<td>2.67</td>
<td>0.82</td>
</tr>
<tr>
<td>15 wt.% of H₂O₂</td>
<td>124</td>
<td>144.20</td>
<td>8.35</td>
<td>0.87</td>
<td>37.37</td>
<td>6.42</td>
<td>0.93</td>
</tr>
<tr>
<td>25 wt.% of H₂O₂</td>
<td>145</td>
<td>130.03</td>
<td>9.22</td>
<td>0.74</td>
<td>29.52</td>
<td>3.97</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Figure 3.19(a) and (b) presents the Bode plot of untreated and H₂O₂ treated Ti-6Al-4V alloy after 7 days of immersion in SBF solution. It was observed that the untreated Ti-6Al-4V alloy showed a shift in the phase angle value of -65° in the high frequency region and -80° in the low frequency region. This shift in the phase angle value could have been due to the formation of new layer. The shift in the phase angle can be attributed to the growth of a hydrated compact outer oxide layer and/or the adsorption of solution ions on the TiO₂ surface (Pan et al 1996). The spectra of Ti-6Al-4V alloy treated with 5 wt.% of H₂O₂, with immediate immersion showed a decrease in the phase angle value in the high frequency region, indicating the presence of a two time constant. This suggested that no additional layer was formed over the surface. Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of H₂O₂ exhibited three phase angle maxima in the high, medium and low frequency regions. This indicated that the spectra exhibited a three time constant with inner barrier layer, outer porous layer and formation of a new...
layer. The formation of a new layer is characteristic of a phase angle shift in the low frequency region. The formation of a new layer can be attributed to the adsorption of calcium and phosphate ions present in the solution. The formation of Ca and P ions was confirmed from FTIR analysis.

Figure 3.19 Impedance spectra of untreated and H₂O₂ treated Ti-6Al-4V alloy after 7 days of immersion in SBF solution (a) Bode phase angle and (b) Bode impedance plot
The spectra obtained after immersion in SBF solution were fitted using the equivalent circuit presented in Figure 3.20. The circuit, $R_a (R_a Q_a) (R_b Q_b)$ model was used to fit the EIS data obtained for untreated Ti-6Al-4V alloy after immersion in SBF solution (Figure 3.20(a)). The suffix ‘a’ refers to the formation of an apatite layer and electrical elements associated with apatite layer are given as $R_a$ and $Q_a$. It has also been reported that nucleation and growth of bone-like apatite takes place on untreated Ti-6Al-4V surface on prolonged immersion in SBF solution (Wang and Wang 2002). The spectra obtained for Ti-6Al-4V alloy treated with 5 wt.% of $\text{H}_2\text{O}_2$ was fitted using the equivalent circuit presented in Figure 3.18(b), since there was no change in the nature of the spectra even after 7 days of immersion. The circuit consisting of a three parallel combination of resistor and capacitor was used to fit the spectra obtained for Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of $\text{H}_2\text{O}_2$ after immersion in SBF solution for 7 days (Figure 3.20(b)) and the circuit was represented as $R_a (R_a Q_a) (R_p Q_p) (R_b Q_b)$. It indicated that the new layer formed after 7 days of immersion which may be the due to the formation of apatite layer. The obtained results were also evident from SEM-EDAX analysis.

The impedance data obtained by fitting the spectra to an equivalent circuit are presented in Table 3.4. It was observed that the resistance value of the barrier layer increased with the immersion time for untreated Ti-6Al-4V alloy. This may be due to the insulating properties of the film with ageing in SBF solution. In the case of Ti-6Al-4V alloy treated with 5 wt.% of $\text{H}_2\text{O}_2$, a decrease in the resistance values of both the outer porous and the inner barrier layer was observed. It indicated the dissolution of the vanadium oxide film, resulting in a decrease of the corrosion resistance of the material (Ho-Jun Song et al 2007). The Ti-6Al-4V alloy treated with 15 wt.% and 25 wt.% of $\text{H}_2\text{O}_2$ resulted in decrease of the $R_b$ value, which suggests the dissolution
behaviour of the barrier layer. But, an increase in the resistance of the porous layer can be attributed to adsorption of solution ions over the porous layer.

Figure 3.20 Equivalent circuit diagrams of $\text{H}_2\text{O}_2$ treated Ti-6Al-4V alloy after 7 days immersion in SBF solution (a) untreated and (b) 5 wt.%, 15 wt.% and 25 wt.%
Table 3.4  Electrochemical impedance data of untreated and H$_2$O$_2$ treated Ti-6Al-4V alloy after 7 days of immersion in SBF solution

<table>
<thead>
<tr>
<th>Ti-6Al-4V alloy</th>
<th>$R_s$/Ω cm$^2$</th>
<th>$R_a$/KΩ cm$^2$</th>
<th>$Q_a$/µF cm$^{-2}$</th>
<th>$n$</th>
<th>$R_p$/KΩ cm$^2$</th>
<th>$Q_p$/µF cm$^{-2}$</th>
<th>$n$</th>
<th>$R_b$/KΩ cm$^2$</th>
<th>$Q_b$/µF cm$^{-2}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>92.58</td>
<td>0.65</td>
<td>30.00</td>
<td>0.72</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.05</td>
<td>0.62</td>
<td>0.89</td>
</tr>
<tr>
<td>5 wt.% of H$_2$O$_2$</td>
<td>107.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>9.64</td>
<td>19.68</td>
<td>0.62</td>
<td>11.01</td>
<td>0.59</td>
<td>0.64</td>
</tr>
<tr>
<td>15 wt.% of H$_2$O$_2$</td>
<td>178.90</td>
<td>19.65</td>
<td>10.03</td>
<td>0.87</td>
<td>125.80</td>
<td>1.29</td>
<td>0.89</td>
<td>30.98</td>
<td>0.23</td>
<td>0.75</td>
</tr>
<tr>
<td>25 wt.% of H$_2$O$_2$</td>
<td>184.60</td>
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<td>15.00</td>
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<td>116.11</td>
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<td>0.80</td>
<td>20.77</td>
<td>0.37</td>
<td>0.70</td>
</tr>
</tbody>
</table>
3.5 SURFACE CHARACTERISATION AND IN-VITRO BEHAVIOUR OF Ti-6Al-7Nb ALLOY

3.5.1 Raman Spectroscopy

Figure 3.21 shows the Raman spectra of untreated and Ti-6Al-7Nb alloy treated with various concentrations (5 wt.%, 15 wt.% and 25 wt.%) of \( \text{H}_2\text{O}_2 \). The untreated Ti-6Al-7Nb alloy revealed spectral features basically corresponding to the amorphous phase. There were no characteristics peaks corresponding to either anatase or rutile. This indicated that the air formed layer is amorphous in nature. Ti-6Al-7Nb alloy treated with various concentrations of \( \text{H}_2\text{O}_2 \) and subsequent heat treatment exhibited peaks at around 390 cm\(^{-1}\), 515 cm\(^{-1}\) and 630 cm\(^{-1}\), which corresponds to anatase titania layer that formed over the surface.

![Raman Spectra](image)

Figure 3.21 Raman spectra of untreated and \( \text{H}_2\text{O}_2 \) treated Ti-6Al-7Nb alloy

Raman spectra suggest that the amorphous phase totally transformed into the anatase phase after the specimens were treated with \( \text{H}_2\text{O}_2 \) and on subsequent heat treatment.
3.5.2 Scanning Electron Microscopy / Energy Dispersive X-Ray Analysis of H₂O₂ Treated Ti-6Al-7Nb Alloy

Figure 3.22(a) shows the SEM image of untreated Ti-6Al-7Nb alloy with a relatively smooth and polished surface represents the typical morphology of mechanically polished crystalline metallic surface (Mogoda et al 2004). The EDAX analysis exhibited peak related to Ti, Al and Nb. Ti-6Al-7Nb alloy treated with 5 wt.% of H₂O₂ exhibited some clusters of flower-like particles over the surface and the corresponding EDAX analysis shows the surface enriched with niobium particles (Figure 3.22(b)). This shows that at low concentration of H₂O₂, niobium oxides are less soluble and were observed over the surface. Figure 3.22 (c) and (d) represent the SEM images of Ti-6Al-7Nb alloy treated with higher concentrations of H₂O₂ namely 15 wt.% and 25 wt.%. It can be observed that a non-homogenous surface with ridges was formed over the surface. It shows clearly that the Ti-6Al-7Nb alloy containing β phase has very low solubility compared to Ti-6Al-4V alloy in the H₂O₂ solution which was observed in Figure 3.12(c), (d) and remains unattacked on the surface, forming very sharp ridges. The corresponding EDAX analysis showed the peaks corresponding to Ti, Al and Nb.

Titanium surfaces that are treated chemically or electrochemically tend to develop specific surface topographies that reflect local differences in passivity/dissolution rate. Sittig et al (1999) reported that the surface topography formed due to treatment with the acid is highly dependent on the microstructure with the heterogenous α-β alloys, adopting a topography with the protruding β phases, due to their lower dissolution rate. Such surface treatments may be used to produce specific topographies for better osseointegration.
Figure 3.22 SEM–EDAX images of H$_2$O$_2$ treated Ti-6Al-7Nb alloy
(a) untreated, (b) 5 wt.% (c) 15 wt.% and (d) 25 wt. %
Figure 3.22 (Continued)
3.5.3 Fourier Transform Infrared Spectroscopic Studies

FTIR analysis were carried out to confirm the formation of apatite particles on the surface of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy on immersion in SBF solution for 7 days.

Figure 3.23 FTIR spectroscopy of H$_2$O$_2$ treated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days (a) untreated (b) 15 wt.% and (c) 25 wt.%
Figure 3.23 shows the FTIR spectra of untreated, 15 wt.% and 25 wt.% of H$_2$O$_2$ treated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days. All the samples exhibited similar spectra and no considerable difference could be observed among the spectra. The broad absorption bands around 3560 cm$^{-1}$ correspond to OH$^-$ stretching and bending modes of H$_2$O respectively. The presence of PO$_4^{3-}$ group was also ascertained from the FTIR peaks observed at 584 cm$^{-1}$ and 1110 cm$^{-1}$. The peak corresponding to P- OH peak was observed at 874 cm$^{-1}$ and CO$_3^{2-}$ peak was observed at 1471 cm$^{-1}$ (Wen et al 1997). Furthermore, the presence of CO$_3^{2-}$ indicates that the PO$_4^{3-}$ sites of the hydroxyapatite structure are partially substituted by carbonate ion (Kunze et al 2008). The above result confirm that the specimens are bioactive in nature. No distinguishable changes was observed for Ti-6Al-7Nb alloy treated with 5 wt.% of H$_2$O$_2$ even for 7 days of immersion in SBF solution.

3.5.4 Scanning Electron Microscopy / Energy Dispersive X-ray Analysis of Ti-6Al-7Nb Alloy After Immersion in SBF Solution

Figure 3.24 (a)-(d) shows the SEM/EDAX images of untreated and Ti-6Al-7Nb alloy treated with various concentrations of H$_2$O$_2$ immersed in SBF solution for 7 days. After soaking in SBF solution, the morphology and composition of the both untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy exhibited significant variation, confirming the materials ability to interact with the ions present in SBF solution.

The SEM image of untreated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days, exhibited few apatite like particles over the entire surface. Ti-6Al-7Nb alloy treated with 5 wt.% of H$_2$O$_2$ shows SEM image similar to H$_2$O$_2$ treated specimen on immediate immersion, which indicates that there was no formation of an additional layer, rather covered with the niobium particles over the surface. The SEM images of Ti-6Al-7Nb alloy treated with 15 wt.%
Figure 3.24 SEM–EDAX analysis of $\text{H}_2\text{O}_2$ treated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days (a) untreated, (b) 5 wt.% (c) 15 wt.% and (d) 25 wt.%
Figure 3.24 (Continued)
and 25 wt.% of H$_2$O$_2$, showed a very few apatite-like particles. This indicated that the roughness associated with the ridged surface as observed for H$_2$O$_2$ treated Ti-6Al-7Nb alloy is reduced which may be due to the extensive dissolution of the layer on immersion in SBF solution for 7 days. This makes the surface smooth and compact. This leveling of the surface makes the anchoring of bone in growth potentially less effective.

The EDAX analysis indicated the formation of new apatite layer for untreated and 15 wt.% and 25 wt.% of H$_2$O$_2$ treated Ti-6Al-7Nb alloy, which is evident from the appearance of calcium and phosphate peaks over the surface. As compared to untreated alloy, the intensity of Ca and P peaks for 15 wt.% and 25 wt.% of H$_2$O$_2$ treated Ti-6Al-7Nb alloy is less, indicating the inability of the material to induce the growth of apatite within a short period of time.

3.6 ELECTROCHEMICAL CHARACTERISATION OF Ti-6Al-7Nb ALLOY

3.6.1 Open Circuit Potential Measurements

The potential-time measurements were carried out for untreated and Ti-6Al-7Nb alloy treated with various concentrations of H$_2$O$_2$ after immersion in SBF solution for 7 days and the results are shown in Figure 3.25. This study was carried out to assess the protective ability and stability of the surface layers when exposed to a physiological solution. With an increase in immersion time, the potential values also increased gradually for both untreated and Ti-6Al-7Nb alloy treated with 15 wt.% and 25 wt.% of H$_2$O$_2$, indicating the formation of a stable film over the surface. Further, Ti-6Al-7Nb alloy treated with 15 wt.% of H$_2$O$_2$ exhibited higher potential value compared to other concentrations. This indicates that the growth of an oxide film when the surface comes in contact with a physiological solution. However, Ti-6Al-7Nb
alloy treated with 5 wt.% of H₂O₂ shows a decrease in potential values with an increase in immersion time which can be attributed to the changes occurred on the surface of the passive film during immersion in SBF solution.

Figure 3.25  OCP–time graph of untreated and H₂O₂ treated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days

3.6.2 Potentiodynamic Polarization Studies

Figure 3.26(a) shows the potentiodynamic polarization curves of untreated and Ti-6Al-7Nb alloy treated with different concentrations of H₂O₂ followed by immersion in SBF solution. For untreated Ti-6Al-7Nb alloy, a constant current density over a wide range of potentials can be observed. It has been reported that the formation of sub-oxides such as NbO and NbO₂ occurs at E_{corr}. The passive region starting from E_{corr} can be attributed to the transformation of NbO and NbO₂ to a more stable Nb₂O₅ oxide. The current peak near the potential around 1.7 – 2.0 V is a consequence of oxygen evolution.
Figure 3.26 Potentiodynamic polarization of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy (a) immediate immersion and (b) after 7 days of immersion in SBF solution.
Thermodynamic data confirmed that oxygen evolution on titanium and niobium occurs at the same potentials (Pourbaix 1966). It can be observed that the current density pattern exhibits a distinct curve around 2V. This can be attributed to a change in the mechanism of oxide film growth at this potential. The polarization curve of surface modified Ti-6Al-7Nb alloy exhibited wide oscillations of the current density in the passive region and a sudden increase in the current density after 1.5 V. This pattern was similar to the polarization curve of H$_2$O$_2$ treated Ti-6Al-74V alloy (Figure 3.16(a)).

Figure 3.26(b) shows the potentiodynamic polarization curves of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy immersed in SBF solution for 7 days. A minimal shift in the potential towards the positive direction and a decrease in the current density by an order, throughout the potential range was observed. This behaviour can be attributed either to the formation of a stable layer over the surface or to a prolonged interaction of calcium and phosphate ions present in the SBF solution, which forms the apatite layer (Sergio Luiz Assis et al 2006).

3.6.3 Electrochemical Impedance Spectroscopic Measurements

The electrochemical impedance spectroscopic measurements of untreated and Ti-6Al-7Nb alloy treated with various concentrations of H$_2$O$_2$ on immersion in SBF solution is shown in Figure 3.27. The untreated Ti-6Al-7Nb alloy showed a phase angle around -75°, which can be attributed to a single passive film formed over the surface. Ti-6Al-7Nb alloy treated with 5 wt.% of H$_2$O$_2$ showed two time constants and was well separated in the frequency domain. In the higher frequency region, the phase angle started from -10° and continuously decreased up to -65° till the middle frequency region. This maxima corresponds to the passive film on the base metal substrate. The secondary maxima started from the middle frequency region, attained a phase angle of -80° in the low frequency region. The formation of secondary maxima may be due to the layer formed because of H$_2$O$_2$ treatment,
Figure 3.27 Impedance spectra of untreated and H₂O₂ treated Ti-6Al-7Nb alloy on immediate immersion in SBF solution. (a) Bode phase angle and (b) Bode impedance plot.
as deduced from the SEM image (Figure 3.22(b)). In the case of Ti-6Al-7Nb alloy treated with other two concentrations of H$_2$O$_2$, it exhibited a phase angle close to -75° and -70° (deviated from -80° as observed for untreated), which may be due to the compact oxide layer formed due to the chemical treatment and presence of white particles as observed from SEM images (Figure 3.22(c)).

Figure 3.27(b) shows the Bode impedance plot of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy. There were no significant changes observed in the impedance values of untreated and Ti-6Al-7Nb alloy treated with 5 wt.% and 25 wt.% of H$_2$O$_2$. However, Ti-6Al-7Nb alloy treated with 5 wt.% of H$_2$O$_2$ exhibited a higher impedance value compared to untreated and Ti-6Al-7Nb alloy treated with other concentrations of H$_2$O$_2$.

Figure 3.28(a) represents the equivalent circuit model $R_s(R_bQ_b)$ used to fit the spectra obtained for untreated and 15 wt.% and 25 wt.% of H$_2$O$_2$ treated Ti-6Al-7Nb alloy, Where $R_s$ represents the solutions resistance, $R_b$ and $Q_b$ represents the resistance and capacitance of the barrier layer, This shows that compact and dense oxide layer is formed over the surface of the Ti-6Al-7Nb alloy after H$_2$O$_2$ treatment and on subsequent heat treatment. The equivalent circuit model $R_s(R_bQ_b)(R_oQ_o)$ presented in Figure 3.28b was used to fit the spectra obtained for Ti-6Al-7Nb alloy treated with 5 wt.% of H$_2$O$_2$, where, the suffix ‘O’ represents the outer layer, which may be formed due to niobium oxide layer.
Figure 3.28 Equivalent circuit diagrams of H₂O₂ treated Ti-6Al-7Nb alloy on immediate immersion in SBF solution (a) untreated, (b) 5 wt.%, 15 wt.% and 25 wt.%

The EIS spectra were analysed with an equivalent circuit and the curve fitting was performed for all the substrates which shows a good agreement between the experimental data and the fitting of the curve. The fitted values are given in Table 3.5. Based on the above results, it could be observed that 15 wt.% H₂O₂ treated Ti-6Al-7Nb alloy possesses a high corrosion resistance property compared to Ti-6Al-7Nb alloy treated with other two concentrations.
Table 3.5  Electrochemical impedance data of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy on immediate immersion in SBF solution

<table>
<thead>
<tr>
<th>Ti-6Al-7Nb Alloy</th>
<th>$R_s$ / Ω cm$^2$</th>
<th>$R_o$ / KΩ cm$^2$</th>
<th>$Q_o$ / μF cm$^{-2}$</th>
<th>$n$</th>
<th>$R_b$ / MΩ cm$^2$</th>
<th>$Q_b$ / μF cm$^{-2}$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>101</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.30</td>
<td>4.91</td>
<td>0.93</td>
</tr>
<tr>
<td>5 wt.% of H$_2$O$_2$</td>
<td>137</td>
<td>8.24</td>
<td>8.44</td>
<td>0.76</td>
<td>10.50</td>
<td>1.63</td>
<td>0.89</td>
</tr>
<tr>
<td>15 wt.% of H$_2$O$_2$</td>
<td>160</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16.88</td>
<td>0.39</td>
<td>0.91</td>
</tr>
<tr>
<td>25 wt.% of H$_2$O$_2$</td>
<td>109</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.10</td>
<td>0.63</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Figure 3.29(a) and (b) represents the Bode phase angle and impedance plot of untreated and Ti-6Al-7Nb alloy treated with various concentrations of H$_2$O$_2$ after 7 days of immersion in SBF solution. It was observed that the untreated and Ti-6Al-7Nb alloy treated with 15 wt.% and 25 wt.% of H$_2$O$_2$ exhibited distinct behaviour with different phase angle values. This may be due to the formation of a newly formed layer after the interaction of the solution ion with the surface of Ti-6Al-7Nb alloy. The formation of a new layer is characteristic of a phase angle shift at low frequencies. This can be attributed to a physical change over the surface due to the interaction of the ions present in the electrolyte (Aziz Kerrzo et al 2001). However, the spectra of Ti-6Al-7Nb alloy treated with 5 wt.% after 7 days of immersion in SBF solution is similar to immediate immersion. This shows that no additional layer was formed over the surface. But the phase value of the spectra was found to decrease, indicating that there may be dissolution of the niobium particles in the SBF solution which were loosely clinging to the surface. A significant changes are also observed in the impedance spectra of all the specimens (Figure 3.29(b)). It was observed that the Ti-6Al-7Nb alloy treated with 25 wt. % of H$_2$O$_2$ exhibited lower resistance compared to other concentrations.
Figure 3.29 Impedance spectra of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy after 7 days of immersion in SBF solution (a) Bode phase angle and (b) Bode impedance plot.
Figure 3.30 (a) represents the equivalent circuit used to fit the spectra of untreated and Ti-6Al-7Nb alloy treated with 15 wt.% and 25 wt.% of H₂O₂ treated specimen. Since changes were observed for 5 wt.% of H₂O₂, Figure 3.30(b) was used to fit the spectra. The fitted values are presented in Table 3.6. From the table, it can be inferred that apatite layer with higher resistance was observed for 15 wt.% of H₂O₂ treated Ti-6Al-7Nb alloy. Further, the capacitance values of the apatite layer were lower, which revealed the growth of the apatite layer over the surface when compared to Ti-6Al-7Nb alloy treated with other concentrations.

Figure 3.30 Equivalent circuit diagrams of H₂O₂ treated Ti-6Al-7Nb alloy after 7 days immersion in SBF solution (a) untreated, 15 wt.% and 25 wt.%, (b) 5 wt.%
Table 3.6  Electrochemical impedance data of untreated and H$_2$O$_2$ treated Ti-6Al-7Nb alloy after 7 days of immersion in SBF solution

<table>
<thead>
<tr>
<th>Ti-6Al-7Nb alloy</th>
<th>$R_s$ / Ω cm$^2$</th>
<th>$R_a$ / KΩ cm$^2$</th>
<th>$Q_a$ / μF cm$^2$</th>
<th>$n$</th>
<th>$R_o$ / KΩ cm$^2$</th>
<th>$Q_o$ / μF cm$^2$</th>
<th>$n$</th>
<th>$R_b$ / MΩ cm$^2$</th>
<th>$Q_b$ / μF cm$^2$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>7</td>
<td>14.10</td>
<td>7.58</td>
<td>0.719</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>51.5</td>
<td>3.90</td>
<td>0.92</td>
</tr>
<tr>
<td>5 wt.% of H$_2$O$_2$</td>
<td>106</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.09</td>
<td>1.733</td>
<td>0.633</td>
<td>8.31</td>
<td>5.10</td>
<td>0.71</td>
</tr>
<tr>
<td>15 wt.% of H$_2$O$_2$</td>
<td>158</td>
<td>6.87</td>
<td>9.82</td>
<td>0.674</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.31</td>
<td>4.29</td>
<td>0.86</td>
</tr>
<tr>
<td>25 wt.% of H$_2$O$_2$</td>
<td>117</td>
<td>6.95</td>
<td>10.78</td>
<td>0.63</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
<td>7.14</td>
<td>0.77</td>
</tr>
</tbody>
</table>
3.7 BIOACTIVITY AND CORROSION BEHAVIOUR OF H\textsubscript{2}O\textsubscript{2} TREATED TITANIUM AND ITS ALLOYS

The mechanism of apatite formation on the surface of titanium and its alloys is a subject of much scientific interest, as it may provide fundamental understanding in bioactive surface functionalisation of non-bioactive materials. Recently, in-vitro studies of H\textsubscript{2}O\textsubscript{2} treated titanium showed that the apatite formation on the bioactive titanium metal is due to the formation of peroxy titania layer formed during H\textsubscript{2}O\textsubscript{2} treatment. The mechanism for the formation peroxy titania layer is as follows:

MECHANISM FOR THE FORMATION OF TITANIA LAYER

Generally, the reactions between the titanium and H\textsubscript{2}O\textsubscript{2} can be interpreted by three procedures: the oxidation of titanium, titania gel formation, and Ti ion dissolution during the decomposition of H\textsubscript{2}O\textsubscript{2} to O\textsubscript{2} and H\textsubscript{2}O.

Tengvall et al (1988) suggested that H\textsubscript{2}O\textsubscript{2} formed during a respiratory burst forms a TiOOH matrix, at least as an intermediate form on a TiO\textsubscript{2} layer; the matrix formation may also be the cause of the growth of oxide layer. Thus, the gel layer may be formed due to the series of reactions (Figure 3.31) leading to direct formation of titanium peroxides on the Ti-H\textsubscript{2}O\textsubscript{2} system and can be considered on the basis of Tengvall et al (1989) report. It involves some redox reactions and the equations are discussed below.
\[
\begin{align*}
\text{Ti}_{(s)} + 2\text{H}_2\text{O}_2 &\rightarrow \text{TiOOH}_{(aq)} + 1/2\text{O}_2(\text{g}) + \text{H}_3\text{O}^+ & (3.6) \\
\text{TiOOH} + 1/2\text{O}_2(\text{g}) + \text{H}_2\text{O}^+ &\rightarrow \text{Ti(OH)}_4 & (3.7) \\
\text{Ti(OH)}_4 &\rightarrow \text{TiO}_2\text{(aq)} + 2\text{H}_2\text{O} & (3.8) \\
\text{Ti(OH)}_4 &\rightarrow \text{Ti(OH)}_{4-n}^{4+} + n\text{OH}^- & (3.9) \\
\text{TiO}_2\text{(aq)} + 4\text{H}^+ &\rightarrow \text{Ti(IV)}_{(aq)} + 2\text{H}_2\text{O} & (3.10)
\end{align*}
\]

Equation (3.6) shows that TiOOH is derived from an \( \text{H}_2\text{O}_2 \) solution accompanying the formation of protons or oxonium ions. \( \text{TiOOH}_{(aq)} \) may stay either on the substrate surface or in the solution. In equation (3.7) the hydrated neutral complex \( \text{Ti(OH)}_4_{(aq)} \) is derived from \( \text{TiOOH}_{(aq)} \), consuming the oxonium ions, while equation (3.8) describes the formation of hydrated titania gel, \( \text{TiO}_2\text{(aq)} \), from \( \text{Ti(OH)}_4_{(aq)} \). Equation (3.9) shows that \( \text{Ti(OH)}_4 \) changes to the positively charged complex \( \text{Ti(OH)}_{n+4-n}^{n+} \). In equation (3.10) dissolution of the hydrated titania gel proceeds at the expense of protons or oxonium ions.

![Figure 3.31 Mechanism of titania gel layer formation on titanium substrate in \( \text{H}_2\text{O}_2 \) solution](image_url)

Figure 3.31 Mechanism of titania gel layer formation on titanium substrate in \( \text{H}_2\text{O}_2 \) solution
Thus, the pH decreases when Ti\(_{(s)}\) reacts with H\(_2\)O\(_2\) equation (3.6), while it increases in other reactions. Therefore, the decrease in the pH suggests either the release of TiOOH into the H\(_2\)O\(_2\) solutions or the formation of TiOOH\(_{(aq)}\) on the Ti substrates. The increase in the pH suggests the formation of Ti(OH)\(_4\) and Ti(OH)\(_4\)\(^{-n+}\), as well as the dissolution of TiO\(_2\)\(_{(aq)}\).

**Bioactivity of the Titania Gel Layer**

Thus produced Ti-OH groups in the titania gel were suggested to favor the deposition of calcium phosphates by providing negatively charged sites, hence being the targets of adsorbing calcium and phosphate ions to form apatite nuclei. The present chemical treatment with H\(_2\)O\(_2\) could yield a titania gel involving TiOOH\(_{(aq)}\) and TiO\(_2\)\(_{(aq)}\) on the titanium substrates. Therefore, the chemical bonding states around Ti atoms in these derived titania gels are very different from those in the sol-gel derived titania gels. For example, titanium substrates treated with H\(_2\)O\(_2\) solution developed thin titania layers, could not deposit apatite unless they were heat treated or were chemically treated with the low-temperature process for crystalline titania proposed by Wu et al (2002). Wälivaara et al (1993) reported that the chemical treatment in H\(_2\)O\(_2\) enhanced calcium adsorption onto Ti surfaces. It was reported that at least two types of negatively charged sites in the titania gels formed on titanium substrate. One is the TiOH group and the other is the TiOOH group. Wang et al (2000) suggested that thermal treatment at 400°C eliminated the Ti-O-O-Ti and TiOOH groups from the titania gel derived by H\(_2\)O\(_2\) treatment and promoted the formation of TiO\(_2\)(anatase), resulting in enhanced apatite deposition. Hayakawa et al (2001) reported that titanium treated chemically with H\(_2\)O\(_2\) containing TaCl\(_5\) and subsequently heated at 400°C for 1 h yielded titania gels involving anatase and rutile together with an amorphous phase. Those gels also favored the deposition of apatite and that their apatite forming ability was even better than gels with anatase only. Miyazaki et al (2001)
reported that the TaOH groups on tantalum metal substrate required at least one week to induce apatite nucleation in SBF solution. The apatite forming ability of the gel layer could be improved by subsequent thermal treatment which eliminates the O-O groups.

Recently, Takadama et al (2001) reported that the sodium titanate layer formed due to NaOH treatment yielded Ti-OH groups due to the exchange of ions between the sodium ions in the layer and oxonium ions in SBF solution, subsequently these Ti-OH groups induced apatite nucleation. The bioactivity of the Ti-OH groups derived from those sodium titanate layers depended heavily on both increase in the pH near the gel – SBF interface due to sodium ion release from the gel and further it increases the degree of supersaturation of the SBF solution for apatite formation.

However, the titania gel layer derived from the present chemical treatment method would not induce any extra increase in the degree of supersaturation of the SBF solution, as in the case of alkali treated titanium, because they could not increase in either pH or Ca (II) and P(V) concentrations. Eventhen, the present gel layer could deposit dense layers of apatite particles in SBF solution through the reaction shown below:

\[
\text{Ti(OH)}^{3+}_{(\text{ox})} + \text{HPO}_4^{2-}_{(\text{aq})} \leftrightarrow \text{Ti}^{4+}_{(\text{ox})}\text{PO}_4^{3-}_{(\text{ads})} + \text{H}_2\text{O} \quad (3.11)
\]

Where (ads), (ox) and (aq) denote adsorbed ions and ions in oxide and aqueous solution, respectively.

In conclusion, we can emphasize that the high apatite-forming ability of the titania gel originates from the favorable structure of the gel itself. On the basis of the structural matching between TiO\textsubscript{2} (anatase) and Ca\textsubscript{10}(PO\textsubscript{4})\textsubscript{6}(OH)\textsubscript{2} (hydroxyapatite) as proposed by Wang et al (2001), anatase favored the deposition of apatite. Therefore, the present chemical treatment
method is convenient way for providing titanium specimen with a negatively charged and microporous surface, which is very much essential for in-vitro apatite-forming ability.

From the SEM studies, the titanium and its alloys treated with different concentrations of H$_2$O$_2$ was found to produce porous titania layer. These porous layers induced the growth of matured layer of calcium phosphate over the surface of entire specimen on immersion in SBF solution for one week.

The corrosion performance of all the specimens was obtained from potentiodynamic polarization studies. The polarization curves show that a sudden increase in the potential was observed above 1 V, which shows the passivity breakdown due to increase in the local conductivity. The passivity breakdown depends mainly on the electrolyte composition, its concentration and to less extent roughness of the surface and temperature. The presence of low concentration of H$_2$O$_2$ leads to the formation of dissolution patterns, however increase in concentration of H$_2$O$_2$ leads to a continuous dissolution of the passive film and damage to the compact film. This damage to the passive film is reflected in the passivity breakdown observed electrochemically.