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In Vitro Bioactivity of Surface-Modified β-Ti Alloy for Biomedical Applications

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Ti-15Mo (β-Ti) alloy was subjected to chemical followed by thermal treatment for the enhancement of in vitro bioactivity and corrosion resistance. The surface-modified specimens were characterized using scanning electron microscopy (SEM) and energy dispersive x-ray analysis (EDAX). The results indicated the formation of nanoporous layer and flake-like structure developed during chemical and subsequent thermal treatments. The in vitro bioactivity of the surface-treated β-Ti alloy was evaluated by immersing in simulated body fluid (SBF) solution. The formation of apatite particles was confirmed using Fourier transform-infrared spectroscopy, SEM, and EDAX analyses. Moreover, the electrochemical behavior of surface-modified specimens in SBF solution was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopy. The results revealed that the surface-modified specimens exhibited higher potential value and lower current density when compared to untreated specimen. The EIS studies showed the formation of new layer, indicating the growth of apatite-like particles.

Keywords biomaterials, corrosion, EIS, SBF solution, SEM, β-Ti alloy

1. Introduction

Titanium and its alloys are widely used as implant materials in dental, orthopedic, prostheses and pace makers. The success of titanium and its alloys as an implant material is due to their good mechanical properties, corrosion resistance and biocompatibility. But, its main drawback is that the implant material and the living tissue doest not form a direct chemical bond with the bone i.e. the ability to bond directly and tightly to the surrounding hard tissue through the formation of apatite like layer (Ref 1, 2).

Various techniques such as plasma spray, dip-coating, electrophoretic deposition and electrochemical deposition have been adopted to induce the direct bone bonding ability of the material. Among various methods, Kokubo et al (Ref 3) introduced chemical treatment as a method of surface modification on titanium and its alloys to improve the bioactivity. It was reported that titanium and its alloys when subjected to alkali treatment produces amorphous sodium titanate layer, which in turn induces the apatite formation (Ref 4). Thus, numerous reports are available on the alkali and alkali heat treatment over α and α + β titanium alloys (Ref 5-7).

Growing interest has been observed in the development of a new generation materials such as β type titanium alloys composed of non-toxic elements such as Mo, Nb, Ta, Zr, and Sn of biocompatible and wear resistant materials (Ref 8, 9). Recently, Oliveria et al (Ref 10, 11) developed β-Ti alloy with various compositions and studied its microstructure. They also characterized the surface of β-Ti alloy electrochemically in Ringer's solution. Karthega et al (Ref 12) studied the electrochemical behavior of β-Ti alloy in Hank's solution. Though various reports are available on the properties and behavior of β-Ti alloy, the surface modification of β-Ti alloy using chemical treatment for the enhancement of bioactivity and its corrosion properties have not yet been reported. Hence, the present investigation aimed toward the surface modification of β-Ti alloy using alkali and alkali heat treatment. The in-vitro bioactivity of β-Ti alloy was analyzed by immersing the specimens in SBF solution. Further, the corrosion behavior of the specimens was characterized using potentiodynamic polarization and electrochemical impedance spectroscopy.

2. Materials and Methods

2.1 Specimen Preparation

The specimen used for this study was Ti-15Mo (β-Ti) alloy with surface area of 1 cm^2. The specimen was polished using abrasive silicon carbide (SiC) paper up to 1200 grade. Final polishing was done using alumina powder to obtain scratch-free surface, followed by rinsing with distilled water and degreased with acetone and ultrasonically cleaned for 20 min. Finally, the specimens were rinsed in distilled water and dried.

2.2 Alkali and Alkali Heat Treatment

Chemical treatment was performed by immersing the specimen in 20 mL of 10 M NaOH aqueous solution at 60 °C for 24 h, gently washed with distilled water and dried at 40 °C for 24 h in an air atmosphere and the specimens were subsequently heat treated at 600 °C at a rate of 5 °C/min and kept hold it for 1 h and then cooled to room temperature in an electric furnace.

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2.3 Surface Morphological Characterization

Surface morphology and elemental composition of the specimens were examined using high-resolution scanning electron microscopy on a FEI Quanta FEG 200 model equipped with an energy dispersive x-ray unit. FT-IR characterization of the specimens was recorded in the range 400-4000 cm^{-1} on a Perkin-Elmer using the KBr tablet technique to determine the phosphate and carbonate groups.

2.4 Electrochemical Characterization

Electrochemical experiments were performed using a conventional three-electrode cell assembly maintained at 36.5 °C. A saturated calomel electrode (SCE) was used as a reference electrode, platinum sheet acts as a counter electrode and the test specimen (β-Ti alloy) as the working electrode. The SBF solution was used as the electrolyte and the preparation of SBF solution and the in vitro tests were carried out using an earlier report (Ref 13).

Potentiodynamic polarization studies were carried out for the untreated, alkali-treated, and alkali heat-treated specimens in SBF solution using the potentiostat (model PGSTAT 12, AUTOLAB, the Netherlands B.V), which was controlled by a personal computer. Potentiodynamic polarization studies were carried out at a scan rate of 0.001 V/s using dedicated software. In order to obtain reliable results, polarization experiments were triplicated in SBF solution. Electrochemical impedance spectroscopic measurements were carried out using an electrochemical system frequency response analyzer (FRA), with a frequency ranging from 10^4 to 10^{-2} Hz. The amplitude of the superimposed a.c. signal was 10 mV. The impedance spectra (Bode plots) obtained for alkali and alkali heat-treated specimens were interpreted and fitted using a non-linear least square (NLLS) method.

3. Results and Discussion

3.1 Surface Characterization

Figure 1(a-d) shows HRSEM-EDAX images of untreated, alkali-treated, and alkali heat-treated β-Ti alloy. The untreated β-Ti alloy exhibited smooth surface and the EDAX result showed peaks corresponding to Ti and Mo. The alkali-treated specimen exhibited a uniform porous network with the pore size of 500 nm. The alkali heat-treated specimen showed a titania gel layer with cracked surface. The cracked morphology may be due to the dehydration of a thick sodium titanate gel layer formed during heat treatment (Ref 13, 14). However at higher magnification, these titania gel layer exhibited a flake-like structure. The transformation of such porous layer into flake-like structure during heat treatment of sodium titanate layer has not been reported elsewhere. The EDAX analysis for both alkali and alkali heat-treated specimens revealed Na peak along with the Ti and Mo.

3.2 In Vitro Characterization

The in vitro characterization of the surface-modified specimens was studied by immersing the specimens in SBF solution. Figure 2(a-c) shows the HRSEM images of untreated, alkali and alkali heat-treated β-Ti alloy immersed in SBF solution for 10 days. The untreated β-Ti alloy showed a few agglomerated white colored particles. But, alkali-treated β-Ti alloy exhibited cluster of spherical particles over the entire surface of the porous layer structure. However, the alkali heat-treated specimen exhibited the presence of globular particles and these were analyzed using EDAX spectra. It can be observed that the EDAX spectra showed the peaks corresponding to calcium and phosphate for all the specimens. But, the intensity of these peaks was found to be higher for alkali-treated β-Ti alloy when compared to alkali heat-treated and untreated β-Ti alloy. This shows that the well-networked homogenous porous layer has the ability to attract more of calcium and phosphate ions when compared to flake-like structure. This may be due to the increase in surface area due to porous network structure.

Figure 3(a-c) shows the FTIR spectra of untreated, alkali, and alkali heat-treated specimens. The main absorption bands at 1466 and 1639 cm^{-1} were assigned to C-O of the CO_3 group. The absorption bands at 1032 and 562 cm^{-1} were assigned to P-O of the PO_4 group. The broad bands at 3440 and 3454 cm^{-1} due to adsorbed H_2O in the material were observed. Similar results were reported for the FT-IR analysis of apatite (Ref 15-17). From the above observations, it could be confirmed that a layer of apatite forms on the surface of β-Ti alloy after immersion in SBF solution. It has been reported that once the apatite nuclei are formed, they grow spontaneously by consuming the calcium and phosphate ions from the SBF solution, as it is supersaturated with respect to the apatite (Ref 18, 19).

3.3 Electrochemical Characterization

In order to understand the electrochemical changes during immersion in SBF solution, the untreated, alkali-treated, and alkali heat-treated specimens were subjected to potentiodynamic polarization and electrochemical impedance spectroscopy.

3.3.1 Potentiodynamic Polarization Studies. The potentiodynamic polarization studies were carried out for untreated, alkali-treated, and alkali heat-treated specimens for immediate and after 10 days of immersion in SBF solution.

Figure 4(a) shows the potentiodynamic polarization curves of untreated, alkali, and alkali heat-treated specimens for immediate immersion in SBF solution. The corrosion potential of untreated, alkali, and alkali heat-treated specimens was found to be −0.52, −0.50, and −0.42 V, respectively. It could be observed that the alkali heat-treated β-Ti alloy exhibited higher corrosion potential and lower current density when compared to alkali and untreated specimens. Such an increase in potential for alkali heat-treated specimen may due to the densification of the sodium titanate layer. The untreated β-Ti alloy exhibited almost a constant current density and extended over a wide range of potentials, which indicated the formation of a stable passive film. But, for alkali and alkali heat-treated specimens, the current density remained stable till 1 V. Beyond, 1 V there is slight increase in the current density, which may be due to the breakdown of the passive film and refilming above 1.5 V could have occurred. Similarly, breakdown and re-filming of the passive film was observed for laser-treated Ti-6Al-4V alloy (Ref 20).

Figure 4(b) shows the potentiodynamic polarization curves of untreated, alkali, and alkali heat-treated specimens immersed in SBF solution for 10 days. A marginal shift in the potential was observed for both alkali heat-treated and untreated β-Ti

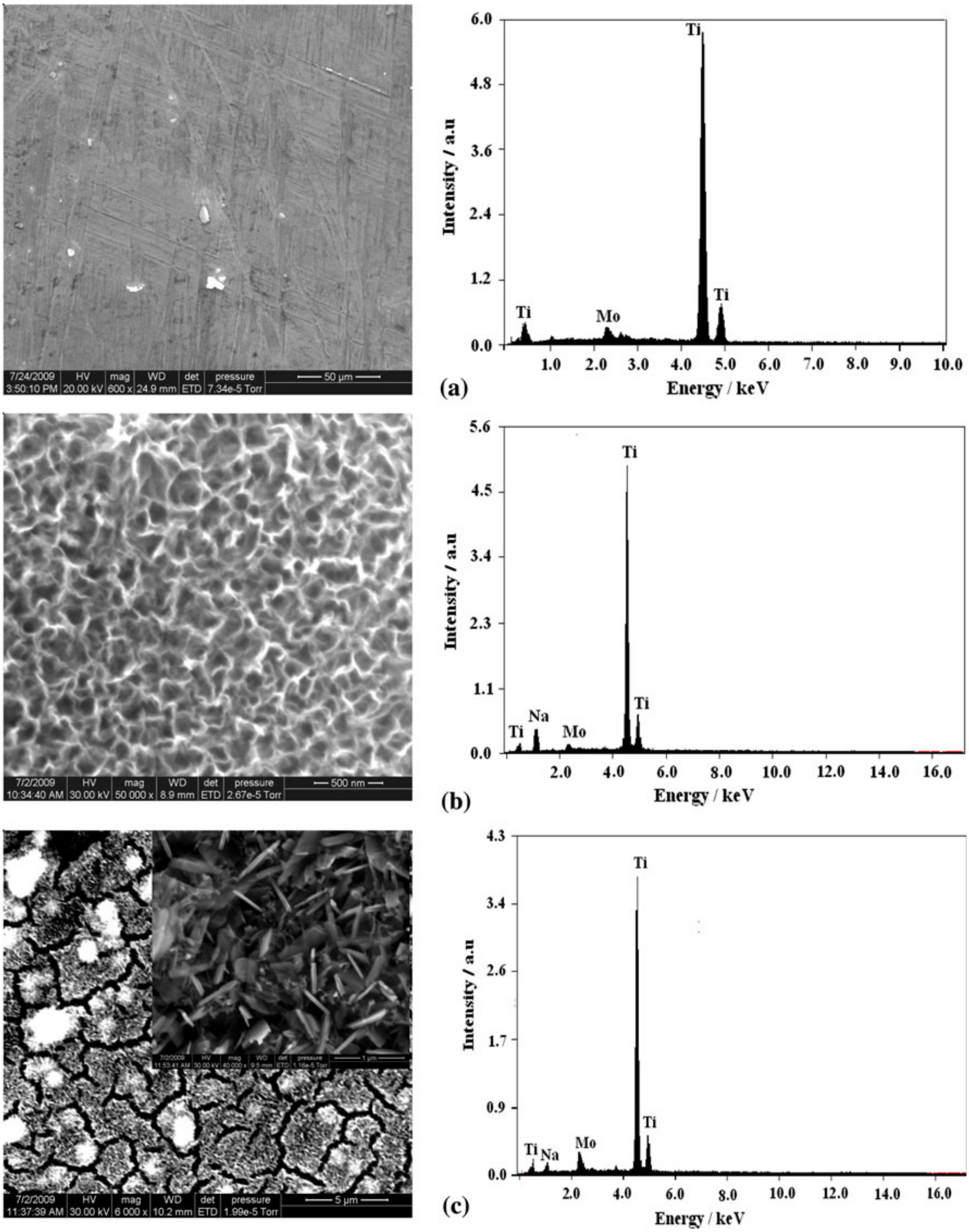

Fig. 1 HR-SEM micrographs of β-Ti alloy. (a) Untreated, (b) alkali-treated, and (c) alkali heat-treated (lower and higher magnifications)

alloy. However, the alkali-treated β-Ti alloy exhibited a significant shift in the potential and a reduction in current density, which can be attributed to the interaction of calcium and phosphate ions present in SBF solution, with the surface film formed on β-Ti alloy. Shukla et al. (Ref 21) suggested that the passive current density for the alkali-treated titanium and its alloys immersed in SBF solution was found to decrease with immersion time can be attributed to changes in surface nature of film formed.

3.3.2 Electrochemical Impedance Spectroscopic Studies. The bode plots of untreated, alkali, and alkali heat-treated β-Ti alloy on immediate immersion in SBF solution is shown in Fig. 5. The bode plot of untreated and alkali-treated β-Ti alloy showed a near capacitive behavior illustrated by the phase angle value around −80° over a wide range of frequencies, indicating the formation of compact oxide film over the surface. However, two well-defined distinct humps in the higher- and lower-frequency regions can be observed for alkali heat-treated

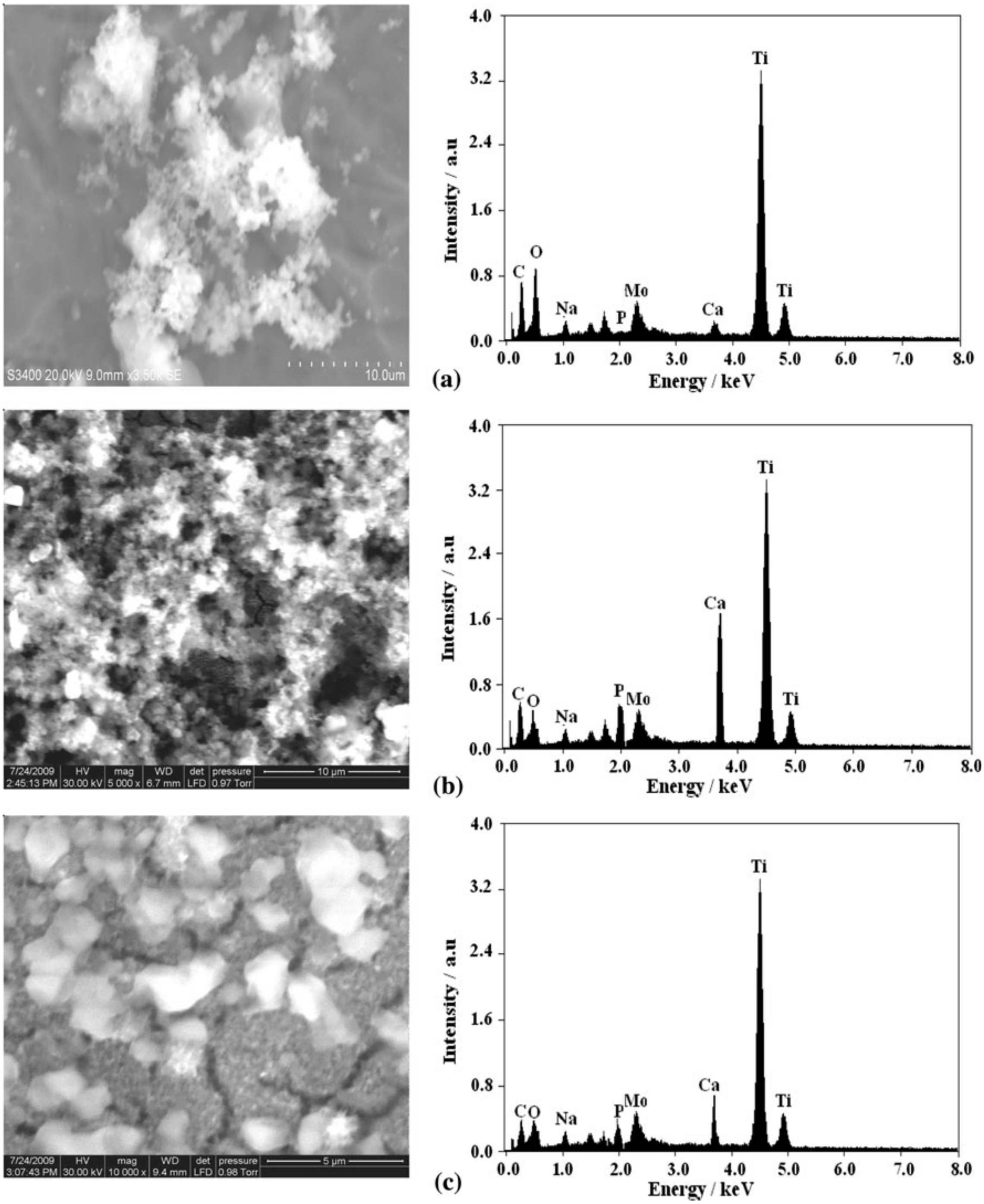

Fig. 2 HR-SEM micrographs of β-Ti alloy immersed for 10 days in SBF solution (a) Untreated, (b) alkali-treated, and (c) alkali heat-treated

β-Ti alloy. This shows that apart from barrier layer, a new layer has been formed due to alkali heat treatment. The formation of new layer may be attributed to the flake-like structure, as deduced from SEM image (Fig. 1c).

The obtained spectra for untreated, alkali, and alkali heat-treated β-Ti alloy on immediate immersion in SBF solution was fitted using equivalent circuit and is shown in Fig. 6(a, b). The spectra obtained for untreated β-Ti alloy was fitted using an equivalent circuit model represented as $R_s(R_bQ_b)$, where R_s represents the solution resistance and R_b and Q_b represent the charge transfer resistance and double layer capacitance of the barrier layer. This circuit model indicated the presence of one time constant due to the passive oxide layer over the surface. The spectra of alkali and alkali heat-treated β-Ti alloy was fitted using an equivalent circuit model (R_gQ_g) (R_bQ_b), where R_g and Q_g represent the charge transfer and double layer capacitance of the gel layer. Tamilselvi et al. (Ref 22) used similar type of equivalent circuits to fit the spectra of untreated and alkali-treated titanium in Hank's solution.

The electrochemical impedance parameters of untreated, alkali-treated, and alkali heat-treated β-Ti alloy for immediate immersion in SBF solution is presented in Table 1. For the untreated β-Ti alloy, it was observed that the resistance and capacitance of the barrier layer was high for the immediate

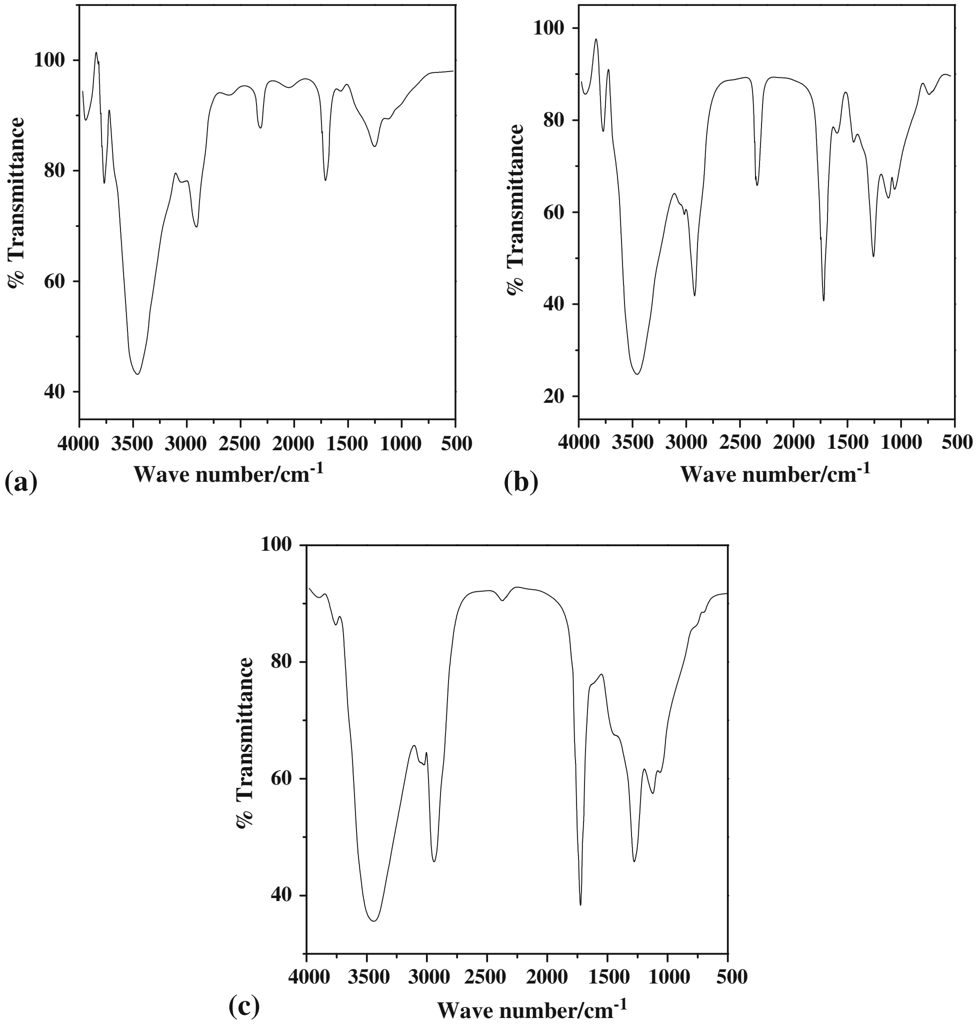

Fig. 3 FT-IR spectrum of β-Ti alloy immersed for 10 days in SBF solution. (a) Untreated, (b) alkali-treated, and (c) alkali heat-treated

immersion and this indicated a compact passive film formation on the metal surface. It can be observed that the resistance of the barrier and the gel layer is lower for alkali heat-treated β-Ti alloy when compared to alkali-treated β-Ti alloy. This may be due to the densification of the gel layer during thermal treatment.

To study the effect of immersion time in SBF solution, EIS spectra was carried out for untreated, alkali, and alkali heat-treated β-Ti alloy immersed in SBF solution for 10 days are shown in Fig. 7. A gradual shift in the low-frequency region could be observed for untreated and alkali-treated β-Ti alloy, indicating the formation of new layer. The formation of new layer may be due to the adsorption of calcium and phosphate ions over the metal surface. The alkali heat-treated β-Ti alloy exhibited two distinct behaviors with slight variation in phase angle values, this shows that there has been a gradual development of an additional layer which can also be deduced from SEM image (Fig. 2c).

Figure 8 shows the equivalent circuit model R_s (R_aQ_a) (R_bQ_b) used to fit the untreated, alkali, and alkali heat-treated β-Ti alloy after 10 days of immersion in SBF solution. The suffix "a" represents the apatite layer. The absence of gel layer in the equivalent circuit model for alkali and alkali heat-treated β-Ti alloy may be due to the total dissolution of the gel layer into the SBF solution with the formation of the apatite layer (Ref 22).

The electrochemical impedance parameters of untreated, alkali-treated, and alkali heat-treated β-Ti alloy after 10 days of immersion in SBF solution is presented in Table 2. For the untreated β-Ti alloy, it was observed that the resistance of the barrier layer decreased on comparison with immediate immersion, which indicates the thinning of the barrier layer. Moreover, the formation of apatite layer was observed for all the specimens. However, the resistance offered by the apatite layer for alkali-treated β-Ti alloy was higher when compared to alkali heat-treated and untreated β-Ti alloy. This indicates the surface of alkali-treated β-Ti alloy is more favorable for apatite deposition when compared to alkali heat-treated β-Ti alloy.

4. Conclusions

Chemical and thermal treatments were performed on the surface of β-Ti alloy to improve the biocompatibility and corrosion resistance. The surface morphological studies of alkali and heat-treated β-Ti alloy showed a uniform, well-defined nanoporous layer and flake-like structure. In vitro

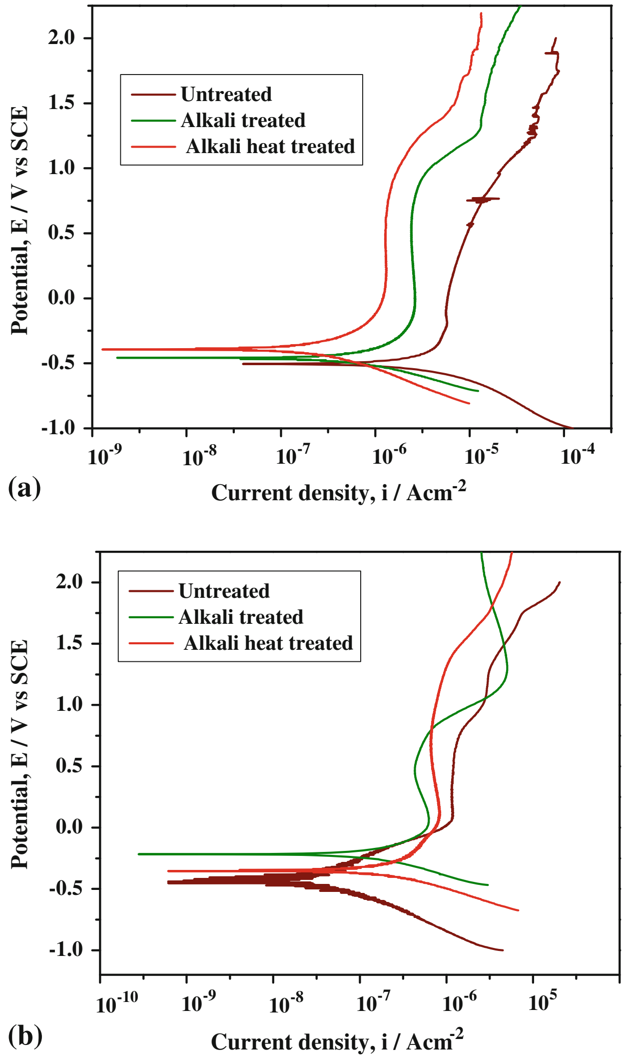

Fig. 4 Potentiodynamic polarization curves of β-Ti alloy immersed in SBF solution for (a) immediate and (b) 10 days

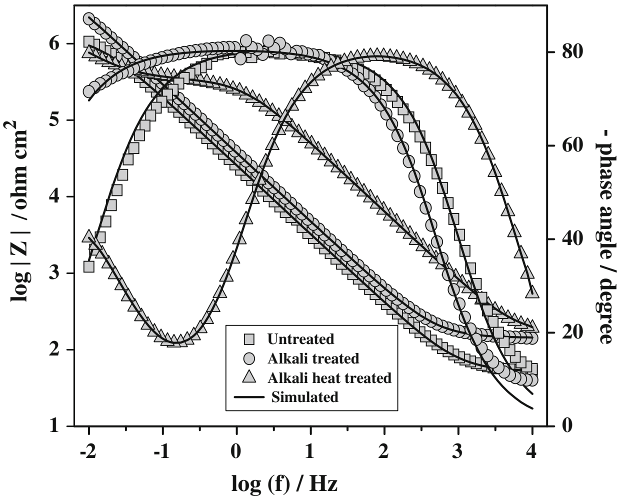

Fig. 5 Bode plot of β-Ti alloy for immediate immersion in SBF solution

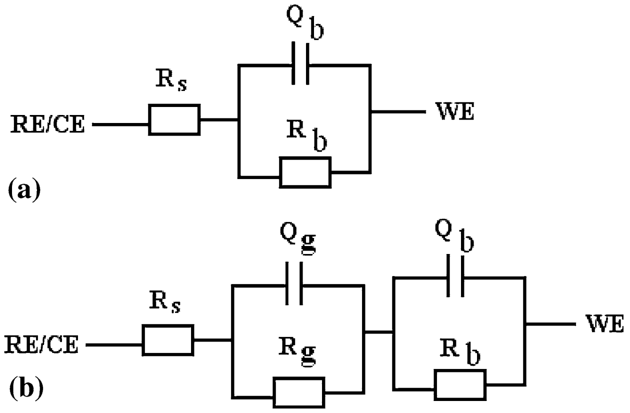

Fig. 6 Equivalent circuit diagrams fitted for β-Ti alloy for immediate immersion in SBF solution. (a) Untreated, (b) alkali and alkali heat-treated

Table 1 The electrochemical impedance parameters of untreated, alkali-treated, and alkali heat-treated β-Ti alloy for immediate immersion in SBF solution

	R_s, Ωcm^2	Q_g, µF · cm^{-2}	n_g	R_g, M · Ωcm^2	Q$_b$, µF · cm^{-2}	n_b	R_b, M · Ωcm^2
Untreated	52.1	…	…	…	7.39	0.90	1.33
Alkali-treated	142.9	5.09	0.89	1.48	4.16	0.79	8.92
Alkali heat-treated	158.8	0.46	0.91	0.32	5.32	0.78	3.26

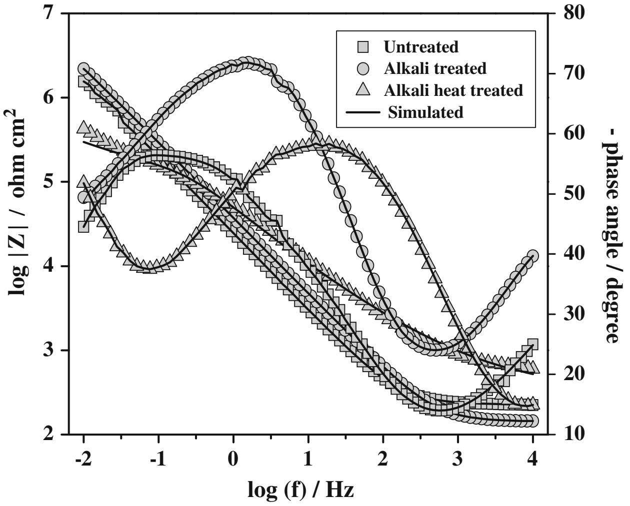

Fig. 7 Bode plot of β-Ti alloy after 10 days of immersion in SBF solution

characterization revealed the formation of apatite-like particles over the entire surface of alkali-treated β-Ti alloy. The electrochemical studies indicated that the alkali-treated β-Ti alloy after 10 days of immersion in SBF solution exhibited very low current density and excellent corrosion resistance when compared to alkali heat-treated and untreated β-Ti alloy.

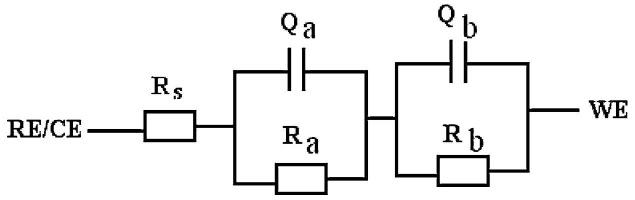

Fig. 8 Equivalent circuit diagram fitted for untreated, alkali, and alkali heat-treated β-Ti alloy immersed in SBF solution for 10 days

Table 2 The electrochemical impedance parameters of untreated, alkali-treated, and alkali heat-treated β-Ti alloy after 10 days of immersion in SBF solution

	R_s, Ωcm^2	Q_a, $\mu F \cdot cm^{-2}$	n_a	R_a, $M \cdot \Omega cm^2$	Q_b, $\mu F \cdot cm^{-2}$	n_b	R_b, $M \cdot \Omega cm^2$
Untreated	186.2	0.38	0.81	0.43	25.45	0.68	0.004
Alkali-treated	202.3	8.34	0.71	0.94	15.25	0.80	0.93
Alkali heat-treated	209.1	0.63	0.86	0.06	14.33	0.55	1.85

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