Corrosion Behavior of Bioactivated Titanium Dental Implant Using Different Chemical Methods

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ABSTRACT

In the past, damaged tissue was removed from the patient's body. But now tissue regeneration using scaffolds and implants are used to repair the damaged tissue and organs. Besides the mechanical properties of metallic biomaterials, they suffer from bioinertness. Using some surface treatment techniques, the bioactivity and also corrosion resistance of titanium implants could be improved. In this study, the effect of H_2O_2 and alkali treatments on the corrosion behavior of titanium implant in the artificial saliva, surface morphology and phases formed on the surface, was investigated using electrochemical corrosion test, scanning electron microscopy (SEM) and thin film x-ray diffractometry (TF-XRD), respectively. The results indicated that on the surface of H_2O_2 and alkali treated titanium samples, fine particles of anatase and fine wires of rutile were formed, respectively. The results revealed that the corrosion resistance of alkali treated titanium in the artificial saliva was higher than that of the H_2O_2 treated titanium sample. The corrosion current density for the untreated, H_2O_2 and alkali treated titanium samples was about 0.6×10^{-8}, 5×10^{-8}, $3\times10^{-8} A/cm^2$, respectively.

1-Introduction

After clean surgery innovation by Lister in 1886, biomaterial implantation was developed faster. Surgery operations before that time were not completely successful. Fixation to the surrounding bone and having a stable interface (between the bone and the implant) is one of the major problems of orthopedic implantation. Some problems of inconstancy are something such as infection, wear and related debris, loosening and bone tissue death [1]. Many researchers attempted to use bioactive materials for implantation to improve bone bonding ability. Despite the advantages of metallic biomaterials, they have some *in vivo* disadvantages such as ion release, corrosion, high density, higher elastic modulus than the surrounding bone, and bioinertness which leads to no bone bonding ability [2]. However, metallic biomaterials are widely used for some clinical applications such as load bearing implants, dental implants, bone plate and cardiovascular applications [2]. Because of superior chemical and mechanical properties of

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titanium, many researchers are interested in improving surface bioactivity of titanium to improve cell response and adhesion on its surface. For these purposes, titanium coating by bioactive bioceramics or chemical surface treatment [3] were used. Generally speaking, surface treatment of titanium is used to improve cell adhesion on the surface of titanium implant [4], corrosion resistance [5], and bioactivity of titanium surface [3, 6]. The clinically used techniques for bioactivity improvement of titanium implants are sand blast, acidic etch and hydroxy apatite plasma spray on the surface of the titanium implant [7]. Although improving the bioactivity of the surface of titanium implants is an important topic in many researches, and also the released ion from titanium is bioinert [8], but different surface properties of the titanium implants at *in vitro* conditions can affect some clinical parameters such as bone healing time [9]; so it has to be investigated. The corrosion behavior of Ti15Mo alloy in the 1.5 M NaCl solution containing different amounts of fluoride ion was investigated by Kumar et al., indicating that with increasing the fluoride ion in the solution, the corrosion resistance of the Ti15Mo alloy decreased, so the amount of fluoride ion affects the current and potential of corrosion of Ti15Mo alloy in NaCl solution [10]. Karthega et al. modified the surface of the Ti15Mo alloy using H_2O_2 treatment; it seemed that a nano porous layer of anatase was formed on the surface of the titanium alloy. The results of their corrosion study indicated that surface modification of titanium alloy using H_2O_2 treatment improved the corrosion resistance of the titanium alloy and the surface treated sample had higher corrosion potential [5].

According to the literature review, the corrosion behavior of the alkali treated titanium was not compared to the other surface treatments. So the main purpose of the present study is to investigate the corrosion resistance of surface treated titanium dental implants using H_2O_2 in alkali treatments in artificial saliva.

2-Materials and methods
2-1- Surface treatment
After polishing and washing the surface, commercially pure titanium plates (grade 2: Ti, O_2 0.25 wt.%, Fe 0.30 wt.%, C 0.08 wt.%, N_2

0.03 wt.%, H_2 0.015 wt.%, others; combined 0.4 wt.%) with the dimensions of $1\times1\times0.2$ cm were treated using two different chemical methods: alkali treatment and H_2O_2 treatment. For alkali treatment, the titanium samples were immersed in 10 (ml/per sample) of an aqueous solution of 5 M NaOH solution at 60 °C for 24 h, washed gently with distilled water, immersed in doubly distilled water at 40 °C for 24 h and dried at room temperature for 24 h. The titanium samples were then heated to 600 °C at a rate of 5 °C/min, kept at 600 °C for 1 h, and subsequently allowed to be cooled in the furnace [6]. For H_2O_2 treatment, the samples were chemically treated with a solution containing 8.8 M H_2O_2 and 0.1 M HCl at 80 °C for 25 min and heated to 500 °C at a rate of 5 °C/min, kept at 500 °C for 1 h, and subsequently allowed to be cooled in the furnace [6, 11].

2-2- Surface characterization
Surface morphology of the untreated, H_2O_2 treated, and alkali treated titanium samples was evaluated and studied using scanning electron microscopy (SEM; XL 30, Philips, Netherlands). Secondary electron detector. Also thin-film X-ray diffractometry (TF-XRD: X'pert Pro MPD 2009, PANalytical Co., Netherlands) was used to characterize the phases formed on the surface of the untreated, H_2O_2 treated and alkali treated titanium samples. This measurement was performed using a Cu-Kα X-ray source at 40 kV and 40 mA and a glancing angle of 1° against the incident beam.

2-3- Electrochemical corrosion tests
Potentiodynamic polarization test was performed using an AMETEK potentiostat/ galvanostat (model PARSTAT 2273) equipped with PowerSuite software. The scan rate was 1 mV s^{-1} in the range of +500 to +1000 mV. A platinum wire and a saturated calomel electrode were used as the auxiliary and reference electrodes, respectively. The tests were carried out in artificial saliva at 25 °C with a rest time of 60 min needed for reaching a steady-state open circuit potential (OCP).

3- Results
3-1- Surface morphology
Fig. 1 presents the SEM images of the untreated, H_2O_2 treated and alkali treated titanium samples.

Fig. 1(c) indicates the surface of the alkali treated titanium covered with nano rods (mean diameter of about 120±8 nm), while there were no nano sized particles on the surface of the untreated titanium sample (Fig. 1(a)). Also, on the surface of the alkali treated titanium samples, no crack can be observed, while the H_2O_2 treatment is a corrosive process for titanium [6] and many cracks are formed on the surface of H_2O_2 treated titanium sample.

However, when titanium is immersed in H_2O_2, two phenomena take place on the surface: 1) the Ti-catalyzed decomposition of H_2O_2 and 2) the corrosion of the titanium which will involve the metal dissolution into H_2O_2, and then solution and formation of titanium oxide on its surface. This thicker oxide layeris composed of two layers: an outerlayer highly porous and hydroxylated and an inner layer, much thinner and with an insulating character [5].
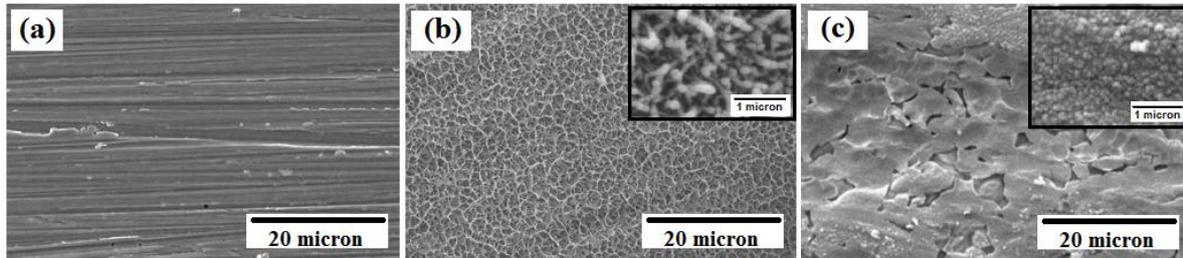
Fig. 1. SEM images of the surface of: (a) untreated, (b) H_2O_2 treated, and (c) alkali treated titanium samples

3-2- Phases on the surface

TF-X-ray diffraction patterns of the untreated, H_2O_2 treated, and alkali treated titanium samples are presented in Fig. 2. According to this figure, the surface of the untreated, H_2O_2 treated and alkali treated titanium samples consisted of titanium, titanium+anatase (TiO_2) and titanium+rutile (TiO_2)+sodium titanate (Na_2TiO_3), respectively. All of the mentioned phases including anatase, rutile and sodium titanate are bioactive and improve apatite inducement ability of titanium samples [6, 12]. So, as reported previously, H_2O_2 and alkali treatments improve the bioactivity of titanium samples.
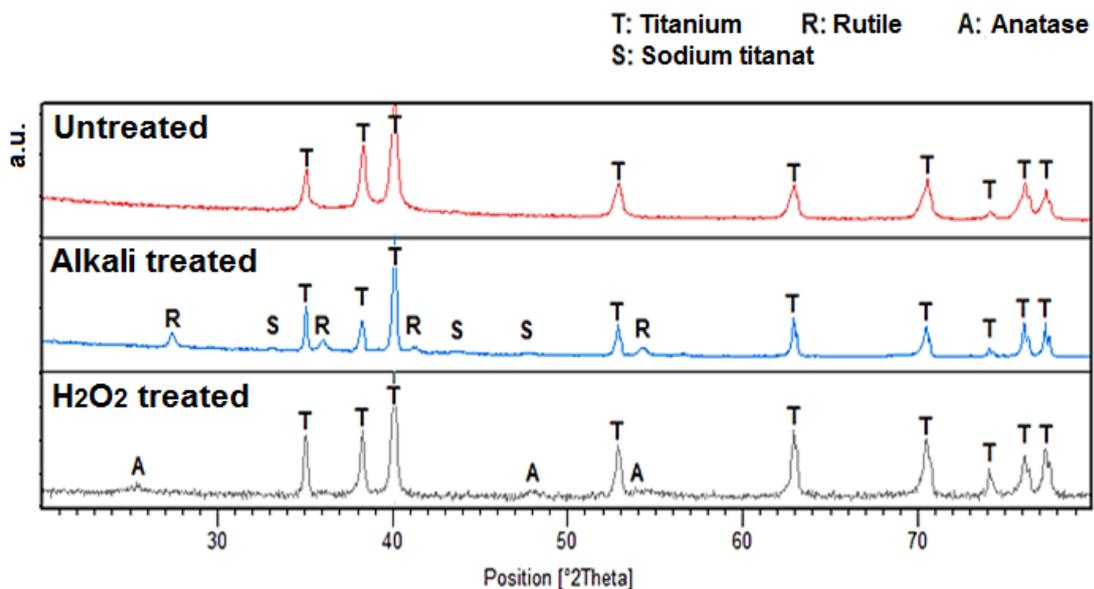
Fig. 2. Thin film X-ray diffraction patterns of untreated, H_2O_2 treated and alkali treated titanium samples

3-3- Corrosion behavior
3-3-1- Results of potentiodynamic polarization
Fig. 3 shows the potentiodynamic polarization curves for the untreated, H_2O_2 treated and alkali treated titanium samples in the artificial saliva. Also, the potential and current density of all samples were extracted using Tafel extrapolation method on these curves and the obtained values are presented in Table 1.
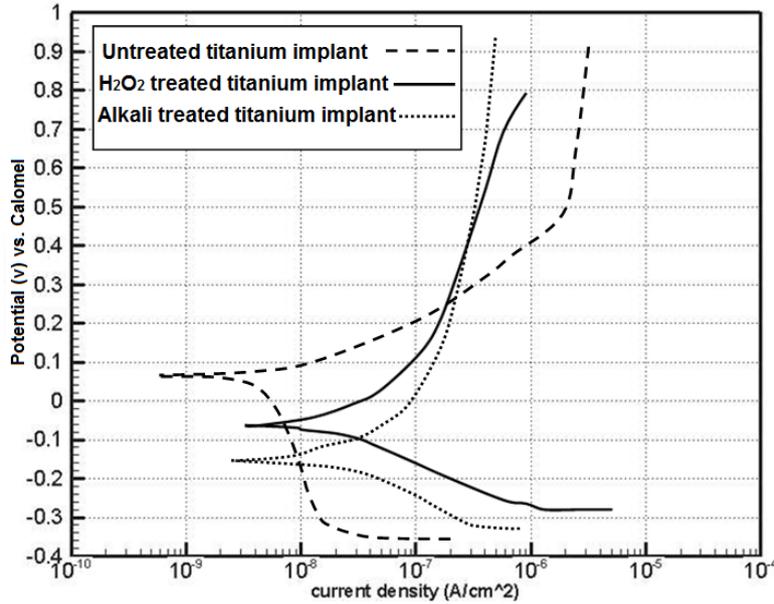
Fig. 3. Potentiodynamic polarization curves for the untreated, H_2O_2 treated and alkali treated titanium samples

Table 1. Current density and potential of corrosion for untreated, H_2O_2 treated and alkali treated titanium samples in the artificial saliva (extracted from Fig. 3 using Tafel extrapolation)

Condition of titanium sample	Potential (E_{corr} (mV) SCE)	Current density ($I_{corr}(A/cm^2)$)	OCP (mV) SCE	Pi (mm/year)
H_2O_2 treated	-68	5×10^{-8}	+255	1.14×10^{-6}
Untreated	+71	0.6×10^{-8}	+278	1.37×10^{-7}
Alkali treated	-148	3×10^{-8}	+307	6.85×10^{-7}

According to Table 1, after H_2O_2 and alkali treatments, the potential of corrosion is reduced to the minus values; also, the current density of both treated samples increased more than the untreated sample. The most important parameters which affect the current density is surface morphology: with increasing surface roughness and surface discontinuity of sample, the current density increases. According to Fig. 1, the surface roughness and discontinuity of H_2O_2 and alkali treated samples are greater compared to the untreated sample. So, the current density of H_2O_2 and alkali treated samples must be greater than the untreated one, which are in accordance with the values of Table 1.

3-3-2- Electrochemical impedance spectroscopy (EIS)
Fig. 4 presents the Nyquist plots of the untreated, H_2O_2 treated and alkali treated titanium samples which are obtained from electrochemical impedance spectroscopy (EIS) tests. The obtained data of each sample were extracted using Zview software and presented in Table 2. In Table 2, R1 and R2 present the polarization resistance of surface layer (anatase or rutile) and polarization resistance of surface layer-substrate (titanium) interface, respectively. If the surface of a sample is not facet and smooth, the phrase "cd1(capacitor capacity of twofold layer)" will be replaced by "Q". In these cases, "Q" is identified by two

parameters: "n" and "CPE", where "n" refer to the "experimental power parameter" and is related to the surface roughness and smoothness of the sample. Normally, the "n" value is in the range of 0-1, and with increasing surface roughness of the sample, "n" value decreases to zero. The "CPE" phrase is a constant phase element which is the capacity of the twofold layer in the non-homogenous condition and its unit is Farad [13].
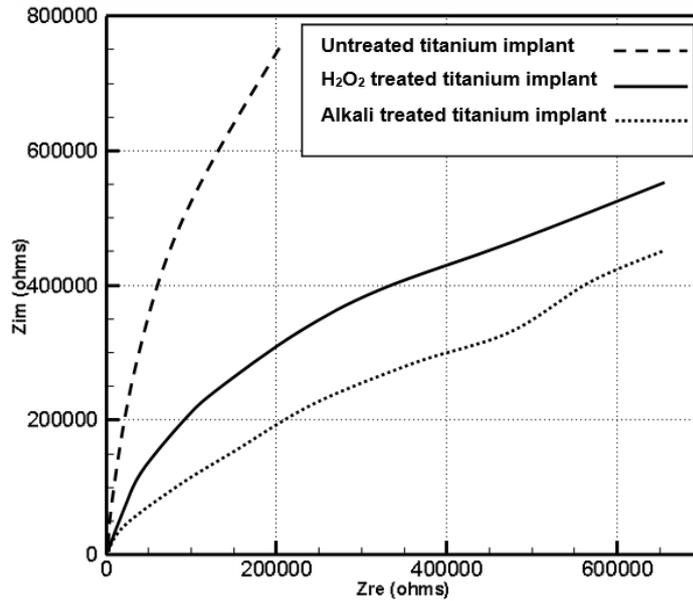
Fig. 4. Nyquist plots for the untreated, H_2O_2 treated and alkali treated titanium samples

4- Discussion

Table 2 presents the quantitative data of EIS test. In Table 2, Q1 and Q2 are capacitor constant of the twofold layer of the surface layer and the surface layer-substrate interface. The pH value and ions of corrosive media affect the corrosion resistance of titanium [14]. All the EIS tests were performed in the same artificial saliva solution, and the polarization resistances of the solutions (Rs) were almost same for all tests.

Table 2. Equivalent circuit's values for untreated, H_2O_2 treated and alkali treated titanium samples, obtained from Nyquist plots

Condition of titanium sample	Rs (ohm-cm^2)	R1 or Rp (ohm-cm^2)	Q1		R2 (ohm-cm^2)	Q2	
			CPE1 (µ farad)	n		CPE2 (µ farad)	n
H_2O_2 treated	71	200000	0.0000415	0.47	--	--	--
Untreated	68	200000	0.000138	0.59	--	--	--
Alkali treated	10	400000	0.0000217	0.51	520000	0.00323	0.68

According to Table 2, the alkali treated titanium had less capacitor capacity of the twofold layer; it means a strong dielectric was created at passive layer-electrolyte. So in the case of the alkali treated titanium, less ion is diffused from substrate to the passive layer, so a thinner passive layer is composed on the surface of alkali treated titanium than the H_2O_2 treated titanium. The passive layer acts as a barrier for corrosion to be continued. Results of electrochemical impedance spectroscopy are in good agreement with the results of polarization

test, because the H_2O_2 treated titanium had a higher current density than the alkali treated titanium. Also, the results indicated that the polarization resistance of alkali treated titanium is higher than the untreated and H_2O_2 treated titanium implants. It means fewer electrons passed throughout the passive layer, so the thin film formed on the surface of alkali treated titanium had a suitable effect on the reduction of the corrosion rate of titanium dental implant in the artificial saliva solution. The current density (Table 1) is affected by the surface morphology and roughness of the sample while the polarization resistance (Table 2) is affected by the properties of the coating and substrate interface. So, it seems that in the case of the alkali treated sample the properties of the interface were more effective than surface morphology. Also, according to the results of the equivalent circuits in Table 2, the 'n' value of H_2O_2 treated titanium is much smaller than that of the untreated and alkali treated titanium implants, which means that the H_2O_2 treated titanium had a larger specific surface area or more discontinuity or cracks on its surface than other samples. The values of Table 2 are in good agreement with the results of SEM study (Fig. 1).

According to Fig. 4, the spectra of alkali treated titanium exhibited two incomplete semicircles, while the spectra of H_2O_2 treated and untreated titanium exhibited just one incomplete semicircle.

So, the alkali treated titanium had the corrosion behavior with two time constants. Therefore, the polarization resistance of surface layer (rutile)-substrate (titanium) interface was significant, and this interface showed suitable corrosion resistance. In the spectra of the alkali treated titanium, the first semicircle is related to the passive layer-electrolyte interface, and the second semicircle is related to the doubled resistance of the surface layer (rutile)-substrate (titanium) interface. This behavior will result in a better corrosion resistance of the alkali treated titanium than the H_2O_2 treated titanium sample. The obtained spectra of all samples were fitted with an equivalent circuit model. The equivalent circuit model of the samples with single time constant behavior (untreated and H_2O_2 treated titanium samples) and the equivalent circuits of the samples with two time constant behavior (alkali treated titanium) are presented in Fig. 5(a) and Fig. 5(b), respectively. The experimental data were found to be in good agreement with the theoretical values. In Fig. 5, Rs (artificial saliva resistance) and Q1 (double layer capacitance) were arranged sequentially and then the equivalent capacitor was paralleled to the polarization resistance.
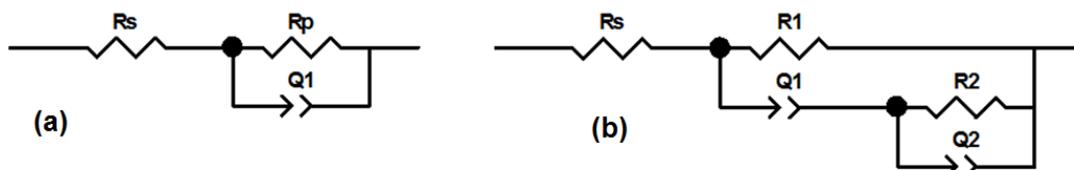
Fig. 5. Equivalent circuits for simulation of Nyquist plots of: a) untreated and H_2O_2 treated, b) alkali treated titanium samples

5- Conclusion

To improve the bioactivity of titanium implants, they were surface treated using H_2O_2 and alkali treatments. Then the corrosion behavior of untreated and H_2O_2 treated and alkali treated titaniumsamples were compared. The results

indicate that the rutile phase formed on the surface of alkali treated titanium improves the corrosion resistance of titanium sample more effectively than H_2O_2 treatment. Since less ion release is favorable for *in vivo* implantation,

alkali treatment is more appropriate for surface modification of titanium implants than H_2O_2 treatment.

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