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Original Article

Electrochemical assessment of laser-treated titanium alloy used for dental applications at acidic pH condition (*in vitro* study)

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ABSTRACT

Background: Titanium alloys are widely used in dental applications as they have good mechanical and biological properties. Implant failure is more likely to occur in inflammatory diseases related to acidic pH. The aim of the present study was to assess the effect of erbium chromium-doped yttrium-scandium-gallium-garnet 2780 nm laser surface treatment on the electrochemical behavior of titanium alloy (Ti-6Al-4V) at acidic pH.

Materials and Methods: In this *in vitro* study, a total of 20 discs of titanium alloy (Ti-6Al-4V) were used. First group, ten discs were irradiated with Er, Cr:YSGG laser which was operating in a normal room atmosphere and temperature at power 2W for 20 s at a constant distance of 0.5–1 mm with the laser system. The second group, ten discs untreated. The electrochemical behavior for both groups was investigated in simulated body fluid at pH 5.20 for up to 864 h at 192, 360, 696, and 864 h intervals using potentiodynamic polarization test and electrochemical impedance spectroscopy to evaluate the corrosion resistance.

Results: Laser-treated Ti-6Al-4V showed higher corrosion resistance at pH 5.20 compared to the untreated alloy. Immersion time affected the electrochemical behavior.

Conclusion: Er, Cr:YSGG laser could improve the corrosion resistance of Ti–6Al–4V at acidic pH.

Key Words: Corrosion, electrochemical, laser therapy, Ti–6Al–4V

INTRODUCTION

Titanium and its alloys are suitable for biomedical materials due to their superior qualities, such as low specific gravity, high corrosion resistance, low elasticity modulus, and good biocompatibility.[1] The high corrosion resistance of titanium and its alloys is partly due to a protective titanium dioxide passive film spontaneously formed on the titanium surface.[2]

In the event of damage, Titanium oxide has the ability to spontaneously reform under normal physiological conditions. However, events such as abnormal cyclic loads, implant micromotion, acidic environments, and their conjoint effects, can result in the permanent breakdown of the oxide film, which may consequently lead to exposure of the bulk metal to an electrolyte. The active dissolution of metal ions

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can occur on exposure of the bulk metal.[3] Titanium dental implants are generally surface modified to reduce corrosion, improve osseointegration, and increase the biocompatibility. To achieve this, surface treatments, such as surface machining, sandblasting, acid etching, electropolishing, anodic oxidation, plasma spraying, and biocompatible/biodegradable coatings are used to improve the quality and quantity of the bone-implant interface of titanium-based implants. Laser is now being used in implant applications.[4]

Erbium lasers are solid-state lasers categorized in the mid-infrared range of the electromagnetic spectrum, with light emitted as invisible, nonionizing thermal radiation. They are free running pulsed lasers. Wavelength is a major factor in the absorption of the laser light by biologic tissue. The largest absorption peak for water is just below 3000 nm, which is at the erbium wavelength. Erbium is also well absorbed by hydroxyapatite. Pulsed mid-infrared lasers have high tissue absorption so that they are effective ablating lasers.[5,6] Hard-tissue lasers erbium chromium-doped yttrium-scandium-gallium-garnet (2780 nm) and erbium-doped yttrium aluminum garnet (Er: YAG 2940 nm) were valuable for laser-assisted osteotomies, and for the improvement in early osseointegration after fixture placement. They also could be used for the treatment of peri-implantitis.[7-10] Er, Cr: YSGG laser exhibit almost no absorption of laser irradiation in titanium and thus prevent excessive energy transformation in the form of heat development. It can be used safely on implant surfaces with adequate water spray without increase in temperature.[11] The aim of this study was to present a better understanding of the effect of Er, Cr: YSGG (2780 nm) laser surface treatment on electrochemical behavior of titanium alloy (Ti-6Al-4V) at acidic pH condition.

The hypothesis was that laser treatment could improve the corrosion resistance of Ti-6Al-4V at acidic condition.

MATERIALS AND METHODS

In this *in vitro* study, cylindrical rod 6 mm diameter of conventional biomedical titanium alloy Ti–6Al–4V (Bredent, Germany-GmbH) was used. The rod was cut into 20 discs with a thickness of 2 mL using a silicon carbide cutoff wheel at 3800 rpm, under continuous flowing coolant. The discs were divided into two groups: laser-treated and untreated groups (ten discs each).

Twenty Teflon molds of 10 mm diameter and 10 mm thickness were prepared for mounting the discs. A hole of 6 mm diameter and 2 mm depth was drilled from upper side of the mold to allow the disc to be secured in it exposing 0.28 cm^2 of the disc's surface. Another hole of 3 mm in diameter and 8 mm depth was drilled and screwed in the opposite side of the mold to allow for placement of 3 mm diameter copper rod. The exposed surface of the samples was finished with different grades of silicon carbide grit papers up to 2400-grit in a single direction to achieve regular and similar morphology for all samples. The final polishing was carried out with alumina paste 0.06 μm. All discs were washed with distilled water, dried, and then sterilized in alcohol before the experiment.

Laser treatment

Laser surface treatment of ten discs was carried out using Er, Cr: YSGG laser, 2780 nm (Waterlase MD, Biolase Technology, USA) which operated in a normal room atmosphere and temperature at power 2W for 20 s. The delivery system consists of a fiber optic tube terminating in a zirconia tip 600 μm in diameter. A water cooling system of 40% water and 60% air was used. The titanium samples were irradiated and hand guided at constant distance of 0.5–1 mm with the laser system Figure 1.

Each disc was irradiated in parallel movements moving the laser beam continuously and not staying too long in one spot. The disc was scanned once to standardize the treatment time. The angle created by the laser beam and the disc surface was approximately 90°.

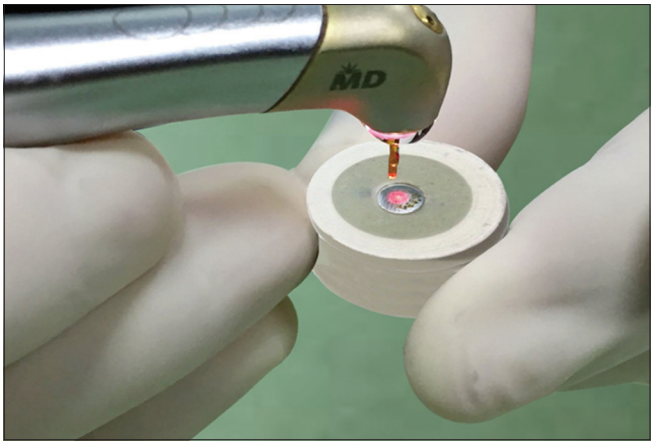

Figure 1: Titanium disc irradiated and hand guided at constant distance of 0.5–1 mm with the laser system.

Electrochemical testing procedure

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed using IviumStat potentiostat (Ivium technologies; Eindhoven, Netherlands) scanning unit controlled by a personal computer and a software. IviumStat potentiostat connected to three-electrode cell assembly consisting of titanium alloy disc as the working electrode and platinum wire as the counter electrode. The reference electrode that all potentials are referred to is $Hg/Hg_2Cl_2/Cl$- SCE of E_o = 240 mV versus NHE. To prepare the working electrodes, the samples were joined at one end to insulated copper rods, which were screwed in the Teflon molds to be in contact with the titanium alloy discs.

In order to simulate the physiological conditions of the human body, Hank's solution was used for *in vitro* corrosion studies, and its chemical composition was given in Table 1. It is prepared with double distilled water and analytical grade reagents. The prepared Hank's solution of pH 5.20 was poured into clean cell. The electrodes were immersed in Hank's solution. The fresh solution was used for each experiment. Measurements were performed at various intervals of 192, 360, 696, and 864 h at room temperature.

Table 1: The composition of Hank's solution (g/l: gram/liter)

Reagent	Composition (g/l)
NaCl	8.00
KCl	0.40
NaHCO3	0.35
CaCl2	0.14
MgCl2 6H2O	0.10
Na2HPO42H2O	0.06
KH2PO4	0.06
MgSO4.7H2O	0.06
C6H12O6	1.00

Potentiodynamic polarization measurements

Open-circuit potential (OCP) was measured in aerated conditions in each sample. After the stabilization of OCP, the potentiodynamic scans were started at 250 mV below OCP, at a rate of 0.5 mV s^{-1}. The results were analyzed in terms of geometric surface area. The metal corrosion behavior was studied by measuring the potential between the specimen (working electrode) and the reference electrode and plotting the E-log I (Voltage– Current) diagram.

Electrochemical impedance measurements

They were carried out for the different samples of untreated and treated titanium alloys in Hank's solution at pH 5.20 with the applied frequency ranges from 35 kHz to 100 mHz. The impedance behavior of the specimens was expressed in Nyquist plots of Z" as a function of Z'.

RESULTS

Potentiodynamic polarization curve (Tafel curves)

The metal corrosion behavior was studied by measuring the potential between the specimen (working electrode) and the reference electrode by plotting the E-log I (Voltage–Current) curves. Table 2 summarizes the mean values of the corrosion parameters derived from these Tafel lines for untreated and laser treated Ti–6Al–4V alloy for these intervals 192, 360, 696, and 864 h at room temperature. Table 2 illustrates the polarization resistance (Rp), corrosion potential (E_{corr}), corrosion current densities (I_{corr}) and corrosion rates in mm/y for all the investigated samples. As shown in Table 2, a clear shift is observed of the E_{corr} value from more negative direction in case of untreated titanium alloy toward more positive direction in case of the laser treated alloy indicating the noble behavior.

Table 2: The mean corrosion parameters for Tafel analysis of laser treated and untreated Ti-6Al-4V at various time intervals

Laser treatment	pH	Immersion time (H)	E_{corr} (V) + OCP	I_{corr} (A/cm^2)	R_p (Ω)	ba (V/dec)	bc (V/dec)
Untreated sample	5.2	192	−0.24	8.19E-07	117250	0.09	0.18
		360	−0.20	1.26E-06	72447.5	0.10	0.15
		696	−0.19	6.69E-06	14667.5	0.11	0.16
		864	−0.19	1E-05	10439	0.11	0.17
Treated sample	5.2	192	−0.20	7.77E-7	59470	0.06	0.06
		360	−0.20	1.03E-6	45985	0.07	0.06
		696	−0.18	1.15E-6	49750	0.08	0.07
		864	−0.17	1.24E-6	129000	0.14	0.42

E_{corr}: Corrosion potential; I_{corr}: Corrosion current density; R_p: Polarization resistance; ba: Slope of anode branch; bc: Slope of cathode branch; OCP: Open circuit potential

Electrochemical impedance spectroscopy measurements

The results of EIS data are displayed as typical Nyquist (Z_{re} vs. Z_{img}) for time intervals of 192, 360, 696, and 864 h at room temperature. The mean values of EIPs derived from EIS curves for untreated and treated Ti–6Al–4V alloy for various intervals are summarized in Table 3.

The equivalent electrical circuit used to fit the impedance spectra was shown in Figure 2 in which solution resistance, R_s, R_p and R_b represent the solution, porous layer and barrier layer resistance, respectively. C_p and C_b are the capacitances of the porous layer and the barrier layer.

DISCUSSION

Most metal corrosion occurs through electrochemical reactions at the interface between the metal and electrolyte solution. Because corrosion occurs through electrochemical reactions, electrochemical techniques are ideal for the study of the corrosion processes using a metal sample with a surface area of a few square centimeters to model the metal in a corroding system.[12] Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, moving electrons into the metal. The other is the cathodic reaction, in which a solution species (often O_2 or H+) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs.[13] Monitoring the relationship between electrochemical potential and current generated between electrically charged electrodes is called R_p. It allows the calculation of the corrosion rate to determine the quantitative assessment of corrosion and to measure the susceptibility to localized corrosion for corrosion-resistant materials.[14] The R_p is the ratio of the applied potential and the resulting current. The rate of corrosion is directly proportional to corrosion current while inversely related to R_p.[15] Impedance measurements are useful and informative method of corrosion assessment. It can be used to follow actively corroding systems.[16]

Er, Cr: YSGG (2780 nm) is hard tissue laser used currently in dentistry. During irradiation, parameters such as output power, energy, dose, and duration should be considered. The power setting chosen was 2 Watt, 20 Hz over a period of 20 s and the energy dose 100 mJ/pulse to allow adequate dose to be delivered to the titanium alloy surface without undesirable results.[17]

In the present study, the corrosion rate increases by time for both laser treated and untreated Ti-6Al-4V alloy immersed in acidic medium. This could be due to that the oxide structure changes over time on immersion in bio-electrolyte solutions. The high concentration of chloride ions in these fluids is highly aggressive for biomaterials.[18] In acidic chloride solutions (at pH of 5.2), the concentration of H + ions will increase and enhance the rate of dissolution thereby reducing the oxide thickness. Furthermore, aggressive ions such as Cl − ions diffuse and migrate through the oxide layer, and then adsorbed on the oxide surface which is responsible for passive layer breakdown due to the formation of titanium chloride.[19] Laser treatment decreased the corrosion

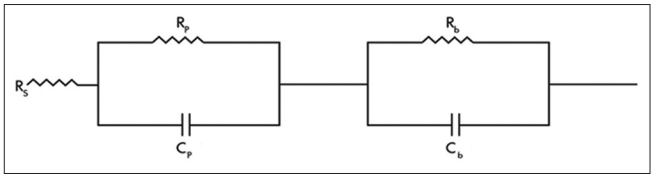

Figure 2: The equivalent electrical circuit used to fit the impedance spectra.

Table 3: Values of fitting parameters of laser treated and untreated Ti-6Al-4V at different pH for various time intervals at room temperature

Laser treatment	pH	Immersion time (H)	R_s	R_p	R_b	C_p	C_b
Untreated sample	5.2	192	4.13E+02	3.53E+03	1.15E+04	1.01E-04	9.30E-04
		360	1.20E+02	1.77E+03	1.08E+04	6.03E-05	7.74E-05
		696	4.88E+02	4.35E+02	3.49E+03	2.11E-04	5.15E-04
		864	1.95E+02	5.49E+02	3.03E+02	4.67E-04	3.58E-04
Treated sample	5.2	192	7.67E+02	1.24E+04	3.02E+04	2.30E-05	1.63E-04
		360	1.81E+04	9.32E+04	8.74E+04	4.57E-06	2.86E-06
		696	1.64E+03	7.24E+03	6.09E+02	1.91E-06	1.91E-06
		864	7.57E+03	6.40E+04	6.06E+04	1.08E-05	7.96E-06

R_s: Solution resistance; R_p: Porous layer resistance; R_b: Barrier layer resistance; C_p: Porous layer capacitance; C_b: Barrier layer capacitance

rate. This could be due to laser-treated alloy releasing electron easier thus reaching equilibrium faster and prevent electron flow (electrical current) so more noble metal was achieved. For laser-treated samples, the current density (I_{corr}) decreased compared to untreated samples at different time intervals. The E_{corr} increased with laser treatment compared to untreated samples at different time intervals which means that it acts as an electron donor to electrolyte indicating a better corrosion resistance.[16]

The impedance behavior of laser treated and untreated Ti-6Al-4V alloy immersed in acidic Hank's solution for different time intervals was expressed by Nyquist plots. For the interpretation of the electrochemical behavior of a system from EIS spectra, an appropriate electric circuit model of the electrochemical reactions occurring on the electrodes is necessary. Many circuit models were tried, to obtain the closest fit with least Chi-square value. As shown in Figure 2, the EEC model with two RC couples was based on two contributions, R_1C_1 and R_2C_2, related to high and low frequency time constants, respectively.[20,21] According to the studied system, these time constants get different physical meaning. In this given equivalent circuit, R is attributed to the electrolyte resistance between the reference electrode and the surface of the working electrode (R_s). The first time constant (at high frequency) is attributed to the inner barrier layer (corrosion product) compounds which can be partially protective; R_1 and C_1 were associated to the inner layer impedance represented by resistive (R_b) and C_b elements. While, the second time (at low frequency) is linked with the double-layer capacitance at the electrolyte/outer surface interface and the charge transfer resistance (R_{ct}) of the outer porous surface, respectively. The total R_p is the sum of R_b, R_{ct}. The barrier layer is compact, having a high resistance, whereas, the outer layer is porous.

The nature of the alloy-solution interface did not change with immersion time. At all immersion times, the system fits into the same circuit model. The barrier resistance was high at 192 h of immersion and then slowly decreased till 864 h of immersion for untreated samples. The initial increase in the R_b could be due to the growth of the oxide layer in the solution, and the slow decrease afterward was due to attack by chloride ions from Hank's solution. The general formation of oxide layer was explained by Stern double-layer theory, which proposes that the electrical double layer is formed whenever a metal is exposed to an aqueous environment. This double-layer consists of an inner barrier layer and outer diffusion layer which were confirmed by an equivalent circuit employed in EIS modeling.[22]

For laser-treated samples, the barrier resistance showed a nonspecific trend with time which may be due to change in the characteristics of barrier layer due to laser treatment. The values of R_b in laser-treated samples were higher than the values of R_b in untreated samples which is associated to high impedance and is responsible for high corrosion resistance of laser-treated samples.[21] The porous layer resistance in laser-treated samples did not follow a specific pattern. This could be due to the incorporation of ions into the pores from the solution. The porous outer oxide layer can accommodate the adsorbed ions in the oxide film matrix and increase the biocompatibility of the implant material. This means that the protection provided by the passive layer was attributed to the barrier layer while the ability to osseointegrate could be due to the presence of the porous layer.[20] The values of porous layer resistance in the laser-treated samples were higher than the values of the porous layer resistance in untreated samples. The increase in the resistance values suggests the increase of thickening of the outer passive layer on the laser-treated samples which facilitates osseointegration and improves biocompatibility.

Biswas *et al.* reported better corrosion resistance in laser melted surfaces compared to laser nitrided surfaces. The reduced pitting corrosion provided by surface melting was possibly because of partial suppression of beta phase formation in the microstructure and the change in morphology from granular to acicular.[23] Zaveri studied treated Ti–6Al–4V alloy with pulsed-wave Nd: YAG laser under various conditions to obtain a surface oxide layer for improved corrosion resistance. Corrosion resistance studies were carried out in three different simulated bio-fluids (SBFs), namely NaCl solution, Hank's solution, and Cigada solution. Tafel analysis showed that the laser-treated Ti–6Al–4V were more corrosion resistant than bare specimens in any of the above SBFs.[24]

CONCLUSION

Implant failure is more likely to occur in inflammatory diseases related to low pH levels. The electrochemical behavior of laser treated and untreated titanium alloy

under acidic condition at 192, 360, 696, and 864 h intervals was studied. The result shows that laser treatment and immersion time had a contribution on the corrosion resistance of titanium alloy. We can conclude that Er, Cr: YSGG laser could improve the corrosion resistance of Ti–6Al–4V in the acidic medium.

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Conflicts of interest
The authors of this manuscript declare that they have no conflicts of interest, real or perceived, financial or non-financial in this article.

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