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Evaluation of Corrosion Resistance of Laser-Treated and PEKK-Coated Titanium

This research focuses on improvement of the corrosion behaviour of commercial pure titanium (Ti) grade II when exposed to Hank's solution through different surface treatments. The disc shape of titanium samples were constructed to be divided according to their surface treatment. The first experimental group the Ti sample was exposed to computer numerical control (CNC) fiber laser machine. Whereas, the other experimental group the Ti sample was only coated with Polyetherketon keton (PEKK) by using carbon dioxide (CO_2) laser technique while the last experimental group the Ti sample was treated with CNC fiber laser followed by PEKK coating by using CO_2 laser technique. All were compared with the untreated control group. The electrochemical action of the samples was tested via polarization test to assess the corrosion rate. The Results showed an improvement in corrosion resistance for all experimental groups, specifically group four showed the lowest electrical current due to the laser surface treatment followed by PEKK coating which acts as a barrier preventing electrolytic attack.

***Keywords*:** Titanium; Corrosion; Laser surface treatment; PEKK coating
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1. Introduction

Dental implant has been one of the biggest successes in modern dentistry for tooth loss replacement. Commercial pure titanium, and its alloy are the most widely used material for implant construction. That is because they embody superior qualities, may be above all, their high biocompatibilities and corrosion resistance due to the stable titanium oxide layer. This layer has two major functions in terms of electronic and physical barrier that prohibit the transportation of cations and anions to the metallic implant surface [1,2]. Hence it will not preclude corrosion attack, if for any reason the TiO_2 layer is broken or detached from the implant surface, then titanium will lose this quality and become exposed to corrosion attack as any other metal [3].

The oral cavity can resemble an electro chemical cell, due to the presence of salt and saliva, so it can be considered a hostile environment that leads to slow degradation of the material, since body fluids encompass many components for instance: chlorine, sodium, amino acids…etc. [4-6]

The corrosion level is also affected by salivary PH and buffering capacity which is shown by Chang that strong relation between the level of corrosion and the presence of bacteria and its by product. The microbial attachment on dental implant surface will lead to organic acid formation causing a reduction in PH. This reduction in PH will favour the growth of aerobic bacteria, subsequently, increase the corrosion [7].

In fact corrosion limits the fatigue life of titanium implant causing mechanical failure, which might further cause fracture in dental implant. To improve the resistance of titanium to corrosion, physical and chemical modification of titanium surface is required to increase the density of the oxide layer leading to increase the interfacial bond between the alloy and bone [8,9].

Surface modification can improve the properties of titanium and its alloys. However due to the demerits of the conventional way of surface treatment such as nitriding process or thermal spray coating which showed a weak bond between the coating and the substrate. Whereas, laser surface treatment is considered one of the promising methods for ameliorating properties, such as corrosion, furthermore, this method has unique features, for instance, highly controlled processing of the depth and width. This process can produce a very specific area of the substrate, even with complicated parts it can be reached for processing, and the high coherence and the directional pattern of the laser beam [1].

The application of lasers such as CO_2 or Nd:YAG is considered a successful method for improving implant through surface modification. Previous studies showed an increase in the corrosion resistance of titanium following CO_2 and Nd:YAG surface treatment in a nitrogen atmosphere [10,11].

Another method of surface treatment is by coating the implant with various materials and methods. The polyaryletherketone family known as thermoplastic material has widely been used as an insulator in a moisture environment. PEKK is considered one of the stronger examples of this family that has proved to have a high resistance to thermo-oxidative degradation, chemically stable, resisting hydrolysis and highly biocompatible. Therefore it is used in implant field due to the high mechanical strength and light weight. One of the mechanical properties of PEKK compared to PAEK family is the material strength which is about 80% higher than PEEK with the advantage of corrosion resistance [12,13]. All the previous properties make PEKK an attractive material for implant coating.

This study highlights the influence of treating the Ti with either fiber laser, polymer (PEKK) coating solely, or both fiber laser followed by PEKK coating on the corrosion behaviour of Ti when exposed to Hank's solution at 37 Celsius.

2. Experimental Work

Small disc shape specimens made from Ti (Orotig S rl EU Company, Italy), with 7mm in diameter and 2mm thickness were cut by a wire cutting machine (Bantam, Italy), then sandpaper was used for a smooth mirror appearance of the Ti disc. For decontamination and debridement of the specimens, they were placed for 15 minutes in an ultrasonic bath (Sonomatic/170-2-T80, Germany), followed by 10 minutes distilled water, then dried at room temperature for 15 minutes [14].

Laser surface structuring was performed on the Ti specimens with the aid of fiber laser CNC machine (Jinan JinQiang 20W laser– China) with1064 nm wavelength and 20-watt power to obtain a dot-like design with a 0.01 mm space between each one. The disc specimens were placed 20 cm in distance from the laser source. The designed dimensions of the sample surface profiles were drawn using (CorelDraw software version XII). When the fiber laser CNC system is triggered, the laser source starts shooting the Ti sample with a continuous series of laser pulses in an ablation process to form the required surface structure [15].

As for the coated specimens, the PEKK needs to be evenly sprayed to the Ti surface and then exposed to the CO_2 laser; this was performed by using chemical spray pyrolysis. PEKK solution was prepared by dissolving (1 gm) of PEKK and (3 grams) of para chlorophenol with (100 ml) of distilled water before spraying the (para chlorophenol + water + PEKK), the solution was stirred in a magnetic stirrer for 24 hours. After the Ti specimens were sprayed with PEKK, they were treated by CO_2 laser (I2itek, Fractional, HQ Dublin, Ireland) exposure with the following parameters (two watts, wavelength of 10.6 micrometers).

The discs of (Ti) were divided into four main groups as follows

- **Group one:** Ti discs without any treatment, this group served as the baseline and did not undergo any treatment (Control Group).
- **Group two:** Ti discs with laser surface structuring.
- **Group three:** Ti discs with PEKK coating
- **Group four:** Ti discs with both laser surface structuring and PEKK coating.

All the specimens' groups were measured using polarization technique to assess the corrosion rate.

The corrosion cell was connected with three electrodes. These electrodes are reference electrode, auxiliary electrode, and working electrode. The working electrode is responsible for measuring the current and potential of a subject. It is composed of metal wire attached to the specimen. The specimen is connected to the holder, which permits exposure to the solution. The back of each working electrode was joined with copper wire and copper tape and secured with cold epoxy resin. Before each measurement, the working electrodes were sanded with 1,200 grit sandpaper and rinsed with distilled water. To simulate biomedical conditions, a freshly formed electrolyte solution was used for each specimen. In this project, Hank's solution was used at 37 ± 2 °C temperature. To determine the corrosion rate, based on the concept of polarization, Tafel slopes extrapolation, and corrosion potential were examined. The action of the electrochemical system relies on the transfer charge reaction which happens at the interface. The rate of corrosion was measured by open circuit potential, this was accomplished by reaching the steady state between the tested specimens and the electrolytic solution. The difference in potential, based on recording the current within 30 min with 60 seconds as time step for each specimen, when the steady state has been reached, the potential obtained is the open circuit potential.

3. Results and Discussion

Titanium and its alloy are used in a wide range in the medical field specifically as implant materials because of their good properties and high biocompatibility. However, corrosion has always been a problem affecting the durability of dental implants. Owing to the passive thin oxide layer formed on the titanium surface due to air exposure. The metal can withstand the corrosive attack from the environment. That is due to the specific properties of this oxide layer that control the corrosive action of the metal [16]. However, a slight movement in the implant or exposure to an acidic media can lead to the breakdown of the oxide layer making the metal vulnerable to electrolytic attack, for this reason, the implant surface is modified by surface treatment to minimize the corrosion effect and increase the metal biocompatibility. One of the applied methods is laser surface treatment which proved to decrease corrosion rate, as stated by an earlier study from Iakovlev who found that laser exposure on steel at 1046 nm wavelength improves corrosion resistance by forming a protective layer [17]. Hence fiber laser has not yet been tested on corrosion behavior.

The choice for electrochemical technique is ideal for studying the corrosion processes since most metal corrosion occurs through electrochemical reactions at the interface between the metal and electrolyte solution. Because corrosion occurs through electrochemical reactions, it normally occurs at a rate determined by equilibrium between opposing electrochemical reactions [18]

The results in table (1) explain the corrosion rate, Icorr, Ecorr for all groups. A decrease in corrosion rate was seen in group two compared to group one (control) this could be attributed to the phenomenon explaining the transformation of alpha and beta phases to an acicular alpha phase due to the energy application which ameliorates the corrosion resistance [11]. The decrease in Icorr when Ti is exposed to fiber laser is ascribed to the formation of oxide layer which hinders the process of metal anodic dissolution and enhances the anti-corrosion properties. Additionally, the increase of Ecorr with laser treatment may be due to the easy release of electrons (act as an electron donor) in consequence reaching a more rapid balance preventing the flow of electrical current interpreting the enhancement of corrosion resistance [19].

Table (1) Parameters obtained from poteniodynamic curve (Tafel) polarization

No.	Sample	$E_{corr.}$ (V)	$I_{corr.}$ (A)	Corr. Rate (mm/y)
1	Group one	-0.485	$2.032*10^{-6}$	$1.651*10^{-1}$
2	Group two	-0.328	$9.534*10^{-7}$	$7.748*10^{-2}$
3	Group three	-0.315	$5.666*10^{-7}$	$4.605*10^{-2}$
4	Group four	-0.318	$4.552*10^{-7}$	$3.699*10^{-2}$

Laser-treated metal creates a surface with standard roughness, increased hardness, improved corrosion resistance and formed an oxide layer that increases the biocompatibility of titanium [15,20].

This study demonstrated a raise of the (open circuit potential) OCP with time as seen in Fig. (1) in all the experimental groups, which exhibited a shift toward more positive values over time. The positive potential development indicated the formation of a protective passivation layer on titanium. These findings were acknowledged by Gugelmin et al., the formation of an oxide layer will diminish the process of alloy dissolution in a physiological environment [9]. This behavior was more pronounced in group four, and to a lesser extent in the other groups, where group one drifted more toward negative values since group one was not surface treated so more prone to minerals attack.

For a better understanding of corrosion behavior on titanium surface with and without surface treatment and coating, a Potentio-dynamic polarization test was undertaken presented in Fig. (2). The variation in Potentio-dynamic curves indicated a behavioral change in titanium when exposed to laser, PEKK coating, or combination of both. The gradual decrease of Icorr in groups three and four showed the efficacy of PEKK as an organic barrier allowing the permeability of minimum numbers of electrolytes from reaching the metal thus protecting the titanium from corrosive attacks [21].

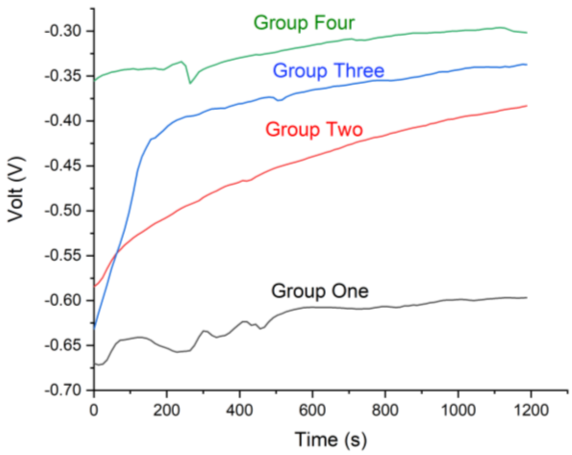

Fig. (1) The OCP plot for all tested groups

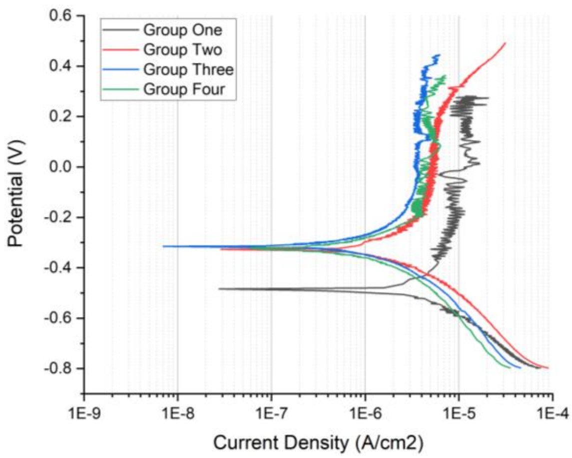

Fig. (2) The polarization curves of the four tested groups

Additionally, a rough interface profile improved adhesion and long-term corrosion protection which depends on the integrity of the coating. So the prevailing assumption is that improving adhesion extends the life of corrosion protection the underlying assumption is that strong adhesion is the primary way a coating limits access and movement of corrosive species. Since metals are generally stronger and tougher than organic coatings, it is advantageous for the mechanical integrity of the combination if the metal tips extend well into the thickness of the coating. One could notice how vertical pits would enhance the adhesion of metal and polymer providing higher adhesion to reduce external forces [22]. These findings explain the decrease in corrosion rate for group four. An earlier study by Moskalewicz found improvement in corrosion resistance after titanium alloy coating with PEEK material compared to uncoated titanium alloy [23].

This work is an *in-vitro* study that cannot mimic the actual oral environment therefore further studies are recommended to confirm the given results.

4. Conclusion

From the former results and discussion, it is apparent that treating the commercial pure titanium grade II (Ti) with fiber laser has improved the surface properties of the metal. Also coating the metal with polymer such as PEKK decreases the corrosion rate of Ti metal by acting as insulator minimizing the electrolytic attack from the environment. Moreover, treating the metal with fiber laser followed by PEKK coating presented the best result because of the good adhesion between the two materials.

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