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A. BIEDUNKIEWICZ[1*], E. DEMBOWSKA[2], P. FIGIEL[1], W. BIEDUNKIEWICZ[3]

ELECTROCHEMICAL BEHAVIOR OF TITANIUM IMPLANTS IN ARTIFICIAL SALIVA AFTER LASER SURFACE TREATMENT

Peri-implantitis is a pathological condition occurring in tissues around dental implants, characterized by inflammation in the peri-implant connective tissue and progressive loss of supporting bone. In the treatment of peri-implantitis, a laser surgical technique is used. Lasers are a safe and gentle alternative to traditional dental tools. They allow oral surgeons and dentists to accomplish more complex tasks, reduce blood loss, decrease post-operative discomfort, reduce the chance of wound infection, achieve better wound healing and perform some procedures in close methods without access flap. The aim of the work was to determine the impact of laser surface treatment of titanium dental implants on its electrochemical behavior in artificial saliva at 37°C. The study used an Er,Cr:YSGG laser and diode lasers 810 nm and 980 nm for debridement of titanium implant surface. In the research, the thread on the surface of implant was scanned with the diode laser beam of energy 1, 1.25, 1.5 and 2 W, cw and Er, Cr YSGG: 1,5 and 2W, pulse 30Hz

Keywords: Titanium implants, peri-implantitis, laser surgical procedure (treatment)

Introduction

Peri-implantitis is a pathological condition occurring in tissues around dental implants, characterized by inflammation in the peri-implant connective tissue and progressive loss of supporting bone. Peri-implantitis sites exhibit clinical signs of inflammation (Bleeding on Probing-BOP) and increased probing depths (PD) compared to baseline measurements. Early diagnosis and treatment are important to save the implant and return peri-implant tissues to health. The main scope of the peri-implantitis treatment is to remove the infected and necrotic tissue from the bone and from the implant surface. In this way it is possible to stop the periodontal disease and save the implant itself. It eliminates the possibility of bacterial growth in hard-to-reach places. In the treatment of peri-implantitis, a laser surgical technique is used. During this therapy, the implant surface is cleaned with aqueous saline, and then the laser surface is subjected to laser beam scanning, maintaining a continuous flow of this solution. How can peri-implantitis laser treatment improve the therapy? Lasers are a safe and gentle alternative to traditional dental tools. They allow oral surgeons and dentists to accomplish more complex tasks, reduce blood loss, decrease post-operative discomfort, reduce the chance of wound infection, achieve better wound healing and perform some procedures in close methods without access flap.

Lasers have various periodontal applications including calculus removal (Er: YAG, Er, Cr: YSGG lasers); soft tissue excision, incision and ablation; decontamination of root and implant surfaces; biostimulation; bacteria reduction; and last but not least bone removal (osseous surgery) [1,2]. Erbium, diode or Er: YAG laser combined with mechanical wound cleansing have the benefits of reducing inflammation and improving connective tissue tension. It was showed that CO_2 laser decontamination of the surface of implants allowed new bone to grow and be in contact with the implant surface (re-osseointegration) [3]. In vitro studies of osteoblasts have confirmed these effects for CO_2 and Er, Cr: YSGG lasers [4].

Serious concerns about the implant overheating followed by melting of the implant surface have been raised, along with concerns about a lack of re-osseointegration following treatment of peri-implantitis with lasers [5].

Discussions and controversies related to the risk of overheating laser disinfected implants are the subject of numerous

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[1] WEST POMERANIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING AND MECHATRONICS, DEPARTMENT OF MATERIALS TECHNOLOGY, 19 PIASTOW AV., 70-310 SZCZECIN, POLAND

[2] POMERANIAN MEDICAL UNIVERSITY IN SZCZECIN, DEPARTMENT OF PERIODONTOLOGY, POWSTANCOW WLKP. AV. 72, 70-111 POLAND

[3] WEST POMERANIAN UNIVERSITY OF TECHNOLOGY, FACULTY OF MECHANICAL ENGINEERING AND MECHATRONICS, DEPARTMENT OF MANUFACTURING ENGINEERING, 19 PIASTOW AV., 70-310 SZCZECIN, POLAND

* Corresponding author: anna.biedunkiewicz@zut.edu.pl

discussions and studies [6-10]. There is limited information available about laser-assisted decontamination of implant surfaces. Information on the clinical use of lasers in the treatment of peri-implantitis is limited, but their use seems promising [11-14]. In this process, it is important to choose the laser surface treatment conditions to obtain a high rate of bone root regeneration after laser treatment of the surface of the implant affected by peri-implantitis, as well as the bone implant site. Surfaces of materials after treatment should be able to interact with the surrounding tissue to induce direct contact of the bone with the implant.

The two main factors that influence the biocompatibility of a material are the host response induced by the material and the materials degradation in the body environment [15]. The low wear and corrosion resistance of the implants in the body fluid results in the release of non-compatible metal ions by the implants into the body. The released ions are found to cause allergic and toxic reactions [16]. Thus, development of implants with high corrosion and also wear resistance is of prime importance for the longevity of the material in the human system [17]. The concept of research and this type of evaluation of corrosion resistance of titanium and their alloys in various technological states has already been presented earlier, among others in the works of other authors [18,19]. The physicochemical state of the implant surface is responsible for the changes occurring in the environment surrounding the implant [20]. It has been shown that laser irradiation can have a positive effect on this condition through changes in the structure of the passive layer, which in turn increases the corrosion resistance of the implant [21-23].

The purpose of this study was to evaluate the changes in the corrosion properties of titanium implants generated by the laser radiation of their surface and to obtain information on whether the surface of the implant pre-irradiated with laser will change its activity in the environment of artificial saliva. Commercial implants with a complex geometric structure were used in the research. The threaded outer layer of the implant, dedicated to contact with bone tissue, is made of commercially pure titanium (cp-Ti – grade 2). The dental implants were irradiated with these lasers, with variable power settings. The research on the impact of laser surface treatment of titanium dental implants on the electrochemical behavior of implant surfaces in artificial saliva at 37°C was conducted. The study used an Er,Cr:YSGG laser and diode lasers 810 nm and 980 nm for irradiation of titanium implant surface. A novelty of the manuscript are the results of research carried out on implants used in dental practice characterized by a complex geometric structure in the shape of a thread. The results of corrosion tests of materials used in implantology before and after laser treatment presented in the literature are carried out on flat model samples. The activity and corrosion mechanisms are affected by the material and surface condition, but the complexity of implant geometry is also very important.

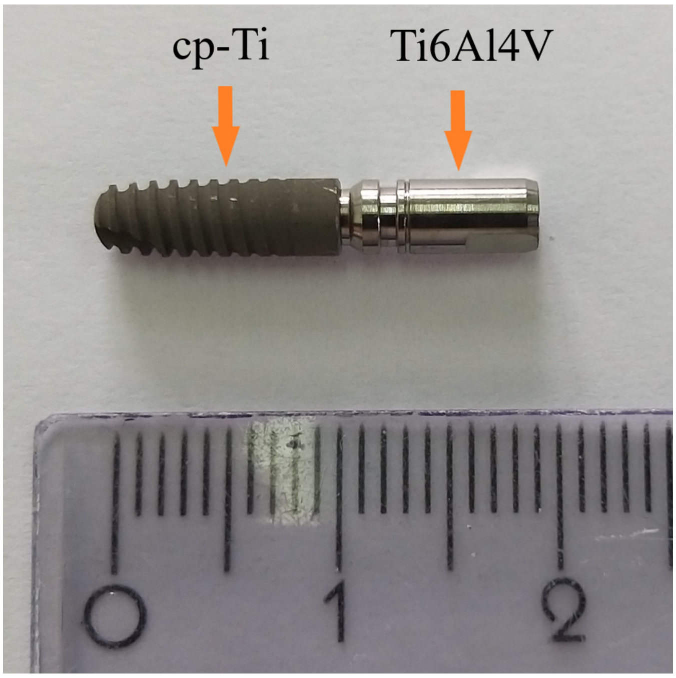

Fig. 1. Picture of the implant

1. Materials and methods

1.1. Implants

Commercial implants were used in this research (Fig. 1). The head of the implants is made of Ti6Al4V two-phase alloy and dedicated to contact with bone tissue the threaded outer layer is made of pure cp-Ti (grade 2).

The distinguishing features of the implants are, among others:

- surface of pure cp-Ti (grade 2) with high roughness (like honeycomb cells),
- connection made of Ti6Al4V alloy - ensures tight fitting of the connector to the implant surface,
- progressive thread made of pure cp-Ti (grade 2).

1.2. Laser surface treatment of titanium dental implants

The experiment was carried out *in vitro* on 11 titanium implants. The subject of the study was only the surface of pure cp-Ti (grade 2). The surfaces of the implants selected for testing were characterized by the same chemical and phase structure and composition, and did not show noticeable morphological and geometric structure differences. Two diode lasers and a Er,Cr:YSGG laser were sequentially used. Diode lasers were used consecutively at wavelengths of 980 nm and 810 nm. The Er:Cr:YSGG laser used had a wavelength of 2780 nm. Irradiation of the implant surface with laser beam was carried out by setting specific parameters separately for each implant. The connector was screwed to each implant. The implant was captured through the connector with a special tweezers and fixed.

Laser radiation was applied in the presence of aqueous saline. The following parameters have been used when using a diode lasers: energy 1, 1.5 and 2W, cw and Er, Cr YSGG: 1, 1.25, 1,5 and 2W, pulse 30Hz. The lasers were applied along the thread of implants, at a speed of 2 mm per second. After this laser treatment, the implants were transferred to a desiccator. Dry implants were subjected to both microscopic and corrosion tests.

1.3. Characterization of microstructure

Irradiation effects of Er, Cr YSGG, diode 810 nm and 980 nm lasers on the morphology and chemical composition of the implant surface were determined by scanning electron microscopy (SEM) using Hitachi SU-70 apparatus equipped with Thermo Fisher Noran 7 microanalysis adapter.

1.4. Corrosion tests

Open-circuit corrosion potential (OCP) measurements were carried out in the separate cell for 24 hours while potentiodynamic polarization measurements (LSV) were performed using a scan rate of 1 mV/s at a potential initiated at −1000 mV to +2500 mV. The measurement was carried out on the Atlas-Sollich 9833 potentiostat in a three-electrode system. The calomel (reference) and graphite (auxiliary) electrodes were used. The analysis of the results has been carried out by means of the AtlasLab software. All corrosion tests were carried out in artificial saliva fluids at 37°C with a pH of 6.7 – Table 1. The corrosion tests were performed in the aerated solution. During the measurements, the mutual orientation of electrodes and the selected implant surface were normalized.

2. Results and discussion

Using the scanning electron microscope (SEM) equipped with the microanalysis adapter, the surfaces of the implants after laser treatment were observed. The microstructure of the surface of titanium has not changed under the influence of laser processing. Within the range of applied laser power of 1÷2 W, after irradiation of the implant surfaces, distinct morphological changes were not observed. There were no melting, chemical or structural changes were observed. On the surface of the implants, deposits from the saline solution were visible. Sodium chloride was most frequently observed, and potassium chloride was less frequent. Images of implant surfaces after laser treatment are shown in Figures 2. Any salt deposits or crystals were not ob-

TABLE 1

Chemical composition of Fusayama-Meyer artificial saliva solution in H_2O; pH = 6.7

Reagent	Quantity [g/dm^3]
$(NH_2)_2CO$, urea	1.0
NaCl	0.4
KCl	0.4
$CaCl_2$ $2H_2O$	0.795
NaH_2PO_4	0.69
Na_2S $9H_2O$	0.005
KSCN, Potassium thiocyanate	0.3

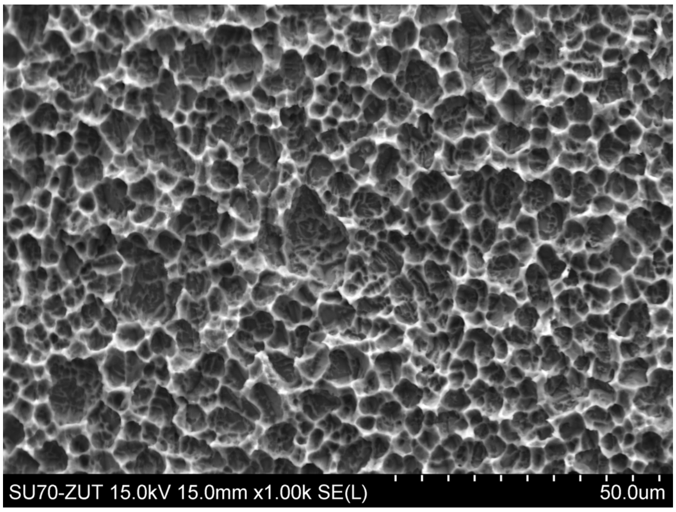

Fig. 2a. SEM image of the implant (cp-Ti) irradiated with Er,Cr: YSGG laser beam of energy 1 W

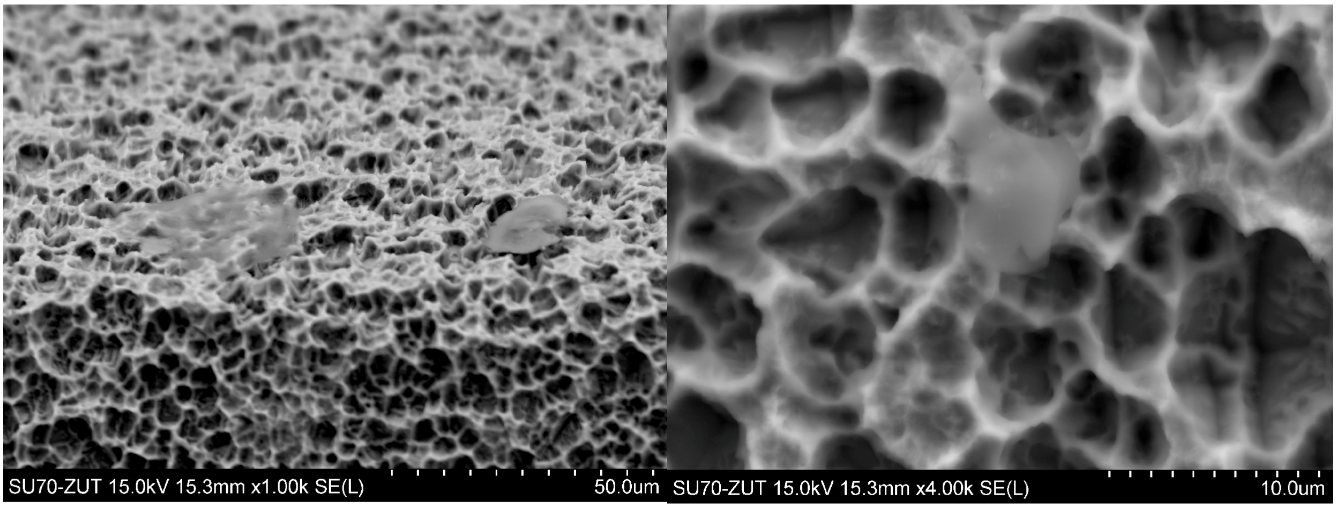

Fig. 2b. SEM images of the implant irradiated with Er,Cr: YSGG laser beam of energy 2 W; incidental deposits on titanium (cp-Ti) surface

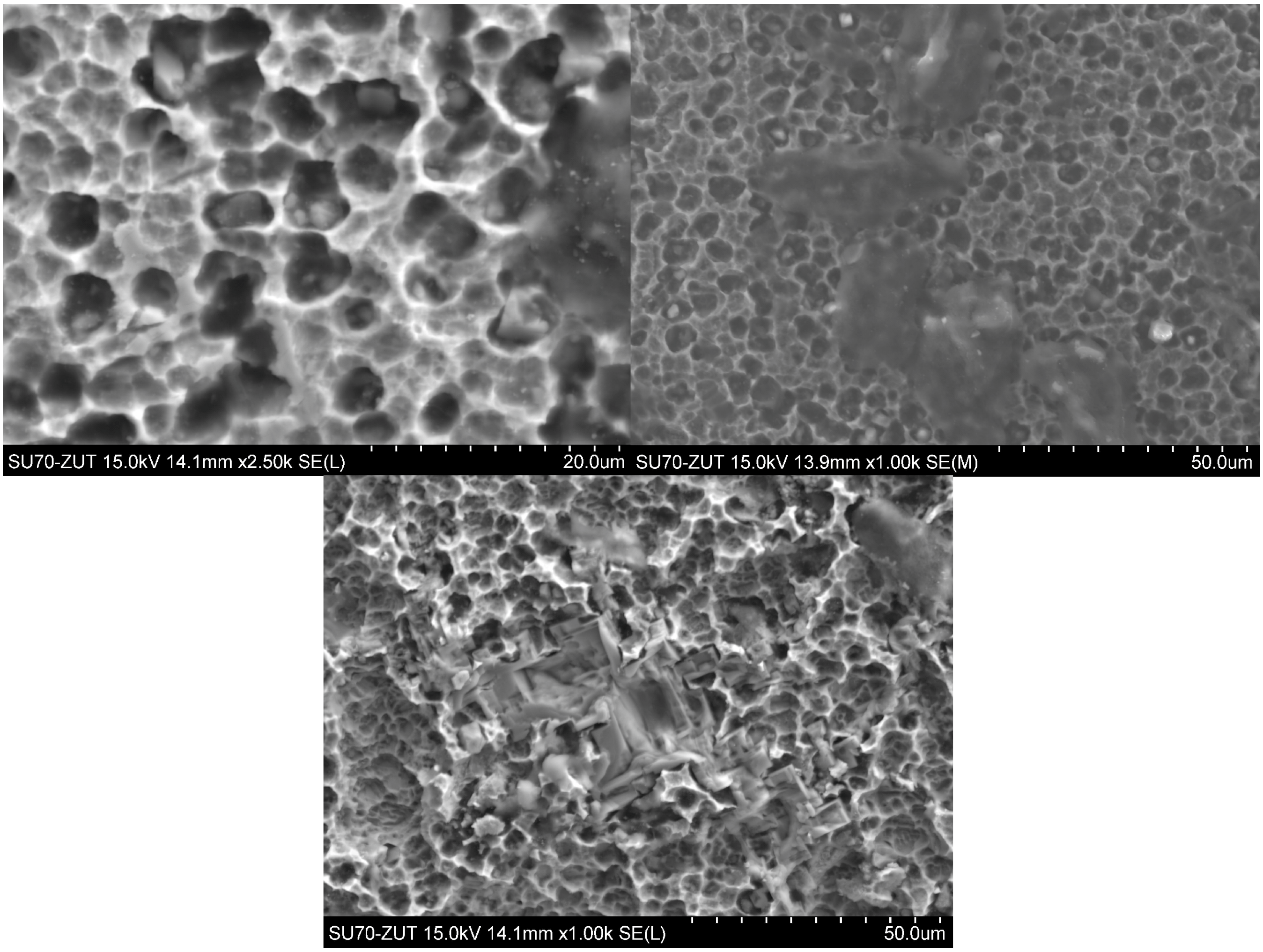

Fig. 2c. SEM images of the implant irradiated with diode 980 laser beam of energy 2 W; deposits and crystals of NaCl salt on the surface of titanium (cp-Ti)

served on the surface of the implant before and after irradiation with the Er, Cr: YSGG laser beam with 1 W energy. The surface observations of these implants did not reveal any differences (Fig. 2a). The investigation has shown that with the increase in the energy of the laser beam, the amount of the salts deposited increased. The observed deposits/crystals of NaCl and KCl salts came from the saline solution.

The comparison of the results of corrosion tests of implants after laser treatment with a reference sample (non-irradiated implant) is shown in Figures 3-5. The variation in the open circuit potentials (OCP) of the surfaces of the implants exposed to artificial saliva solution are presented in Figure 3.

It is observed from Figure 3, which presents the OCP profiles of the implants irradiated with diode 980 laser beam of energy 1 W and Er,Cr: YSGG laser beam of energy 2 W, that the open circuit potentials fluctuate continuously.

The highest potential values (in descending order) were obtained for the implants irradiated with Er,Cr: YSGG laser beam of energy 1 W, diode 810 laser beam of energy 2 W, diode 980 laser beam energy 2 W, and the non-irradiated implant (reference sample). These implants had a relatively stable OCP profile; the potential values increased slightly in time. Potential values of the surfaces of the implants irradiated with diode 810 laser beam of energy 1 W after 20 h and diode 980 laser beam of energy 1W after 9 hours showed a decreasing trend in time. These results suggest that the highest thermodynamic stability, and therefore a lower tendency to corrosion in artificial saliva solution, in comparison with other composites, show the following implants: irradiated with Er,Cr: YSGG laser beam of energy 1 W, diode 810 laser beam of energy 2 W, diode 980 laser beam energy 2 W, and the non-irradiated implant (reference sample).

The potentiodynamic polarization curves for the implants surfaces in artificial saliva solution, pH 6.7 temperature 37°C (Fig. 4 and 5) help in analyzing more thoroughly the corrosion behavior of the composites. Figure 4 shows that the implants generally displayed similar polarization curves and passivity characteristics with the exception of the implant irradiated with diode 810 laser beam of energy 1 W. The surface of this implant tends to rebuild the passive layer at higher potential values.

However, the corrosion potentials (E_{corr}) of the implants were clearly distinct and occurred in the ranges of −450 to −110 mV. Table 2 shows the corrosion potential (E_{corr}) and corrosion current density (I_{corr}) for all implants that were obtained from the data presented in Figure 4. On analysis of the implants

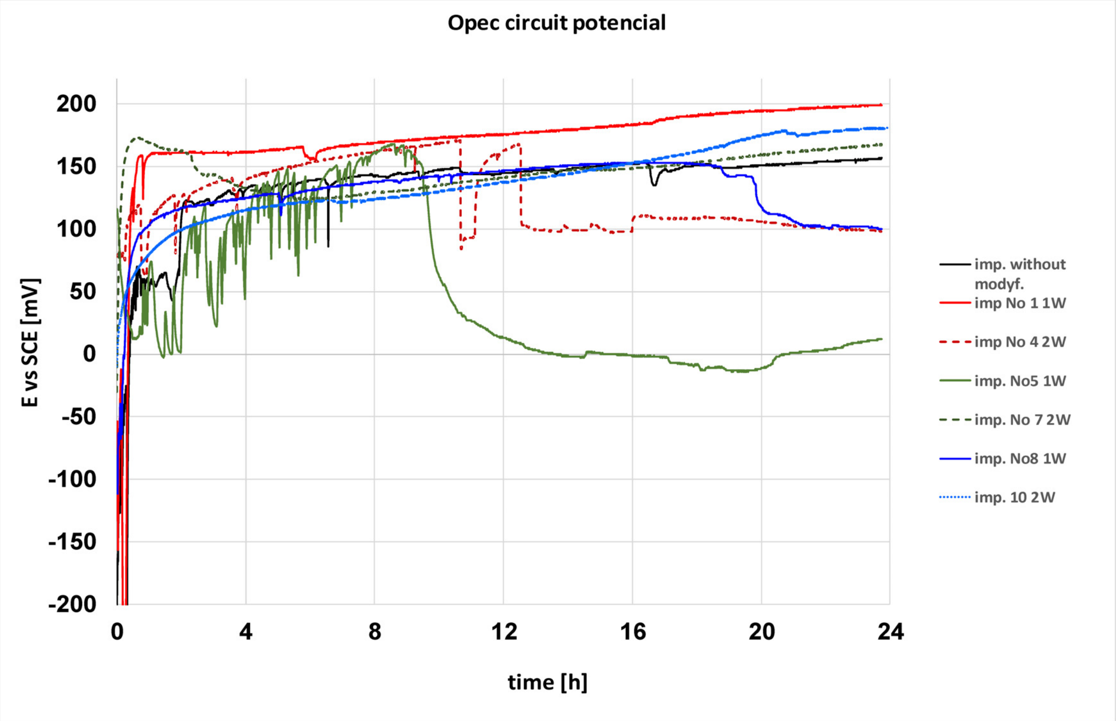

Fig. 3. The variation in the OCP of the composites exposed to artificial saliva solution, pH 6.7 temperature 37°C

in these tests, it should be noted that the values of corrosive potentials (E_{corr}) of implants show a constant tendency to decrease with the increase of the laser beam energy. An exception to this rule is the implant irradiated with Er,Cr: YSGG laser beam of energy 2 W, which has the E_{corr} value much higher than the E_{corr} of the non-irradiated implant. The highest value of corrosion potential (E_{corr}) among all the implants has been achieved by the implant irradiated with diode 810 laser beam of energy 1 W.

It should be noted that the corrosion current (I_{corr}) of implants does not show a constant tendency to change its values with the increase of the laser beam energy. It is worth noting that the corrosion current values of the implants irradiated with Er, Cr: YSGG laser are lower compared to the value corresponding to the non-irradiated implant with the exception of the implant with the energy of the beam of 1 W. The lowest value was obtained for the implant irradiated with diode 810 laser beam of energy 2 W.

The corrosion current values of the implants irradiated with diode 980 laser are also lower compared to the value corresponding to the non-irradiated implant. The lowest value was obtained by the implant irradiated with diode 980 laser beam of

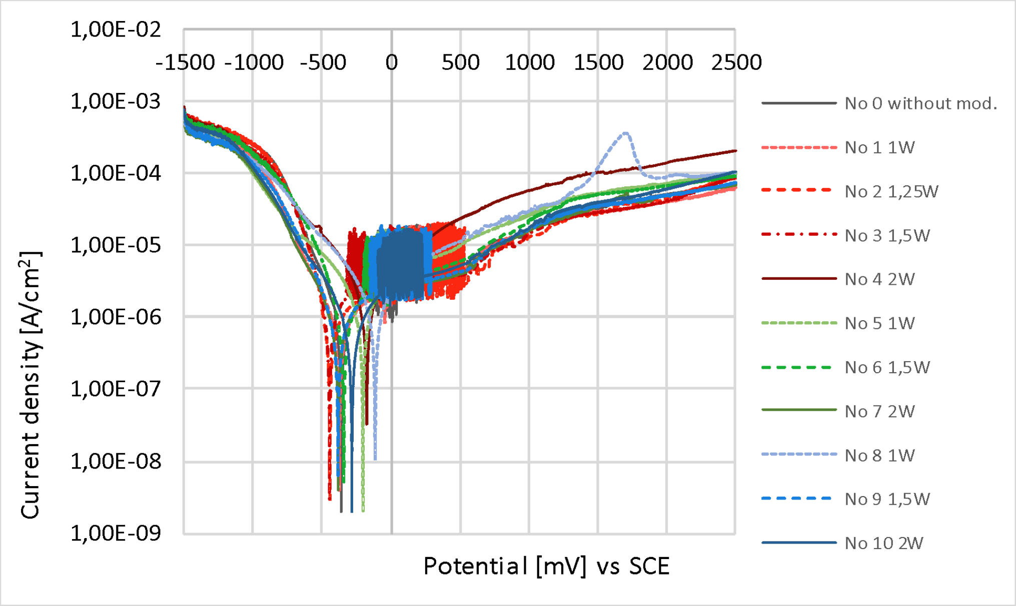

Fig. 4. Comparison of anodic polarization curves of all implants tested, pH 6.7 temperature 37°C

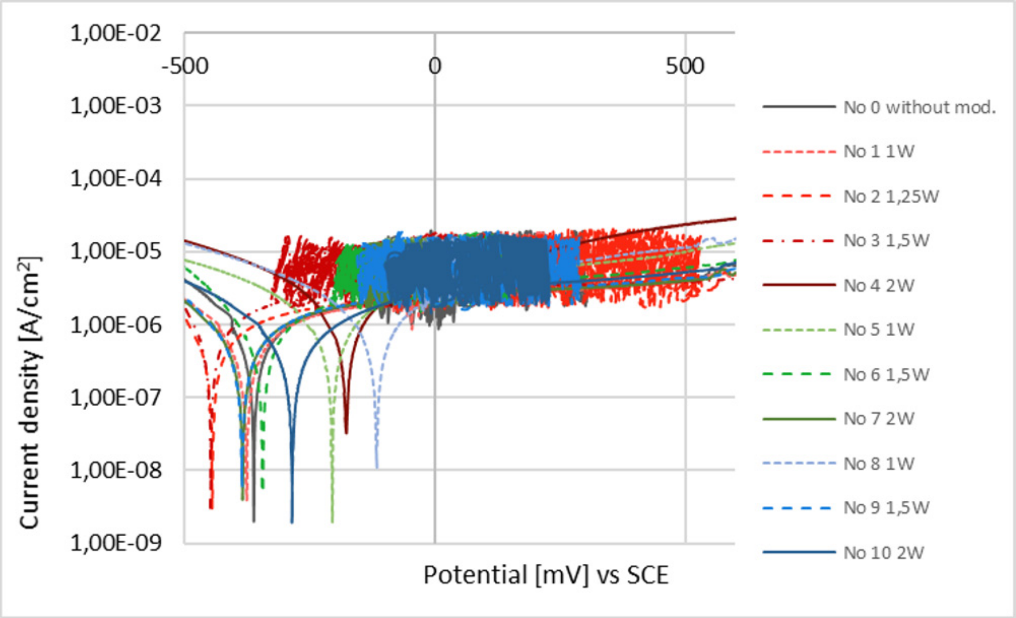

Fig. 5. The selected fragment of the comparison of the potentiodynamic polarization curves for the implants surfaces in artificial saliva solution, pH 6.7 temperature 37°C

energy 1.5 W. The values of the corrosion current of implants irradiated with the diode laser 810 decrease with the increase in the energy of the radiation beam. The lowest value of the corrosion current (I_{corr}) among all the implants has been achieved by the implant irradiated with diode 810 laser beam of energy 2 W but the highest value of the corrosion current (I_{corr}) among all the implants has been achieved by the implant irradiated with Er,Cr: YSGG laser beam of energy 1 W.

The best corrosion resistance measured by the relatively higher values of resistance polarization (R_{pol}) characterized the implant irradiated with diode 810 laser beam of energy 2 W, then the implant irradiated with diode 810 laser beam of energy 1.5 W, the implant irradiated with Er,Cr: YSGG laser beam of energy 1 W and the implant irradiated with diode 980 laser beam of energy 2W.

Figure 5 shows the magnification of the selected fragment of the comparison of the potentiodynamic polarization curves for the implants surfaces in artificial saliva solution, pH 6.7 temperature 37°C.

During all measurements, abrupt shifts in the values of potentials were observed (Fig. 5). High surface roughness (like honeycomb cells) and specific thread geometry, and the associated differences in current density on these surfaces could have an impact on the initial stage of the passivation process and then on the stabilization of the surface condition of the implants.

3. Conclusion

In this work, the effect of laser irradiation of implant surfaces on its morphology and corrosion resistance were presented. The subject of the study was the corrosion characteristic of the cp-Ti thread after lasers treatment.

TABLE 2

Corrosion parameters of the composites exposed to artificial saliva solution, pH 6.7 temperature 37°C

Laser type	samples	E_{corr}, [mV]	I_{corr}, [A/cm^2]	R_{pol} [Ω·cm^2]	β_a [mV·dec^{-1}]	β_c [mV·dec^{-1}]
Non-irradiated	implant No 0	–362	$0.131\cdot10^{-6}$	$82\cdot10^3$	44	56
Er,Cr: YSGG 2780 nm	implant No 1, 1W	–375	$0.140\cdot10^{-6}$	$102\cdot10^3$	63	69
	implant No 2 1,25W	–445	$0.087\cdot10^{-6}$	$81\cdot10^3$	28	39
	implant No 3 1,5W	–447	$0.112\cdot10^{-6}$	$58\cdot10^3$	28	31
	implant No 4 2W	–177	$0.094\cdot10^{-6}$	$51\cdot10^3$	23	21
Diode 980 nm	implant No 5 1W	–205	$0.066\cdot10^{-6}$	$70\cdot10^3$	20	22
	implant No 6 1,5W	–344	$0.061\cdot10^{-6}$	$79\cdot10^3$	20	24
	implant No 7 2W	–384	$0.083\cdot10^{-6}$	$100\cdot10^3$	36	40
Diode 810 nm	implant No 8 1W	**–116**	$0.098\cdot10^{-6}$	$61\cdot10^3$	27	28
	implant No 9 1,5W	–384	$0.063\cdot10^{-6}$	$104\cdot10^3$	29	30
	implant No 10 2W	–285	**$0.056\cdot10^{-6}$**	**$118\cdot10^3$**	29	31

Within the range of applied laser power of 1÷2 W, after irradiation of the implant surfaces, distinct morphological changes were not observed. There were no melting, chemical or structural changes were observed. The investigation has shown that with the increase in the energy of the laser beam, the amount of the salts deposited increased.

The best corrosion resistance measured by the relatively higher values of resistance polarization (R_{pol}) and the lowest value of the corrosion current (I_{corr}) was obtained for the implant irradiated with 810 nm diode laser beam of energy 2 W. Changes in corrosion parameters may be the result of changes in the structure, phase composition of the thin passive layer Ti_xO_y, which was formed as a result of irradiation of this very expanded surface of the implants.

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