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Short Communication

Laser Marked and Textured Biomaterial Evaluated by Mott-Schottky Technique

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The effect of an optical fiber laser marking and texturing techniques on the surface of the ISO 5832-1 stainless steel via the Mott-Schottky approach was evaluated in this work. This is one of the most commonly used biomaterial for permanent implants manufacture. It was found that the pulsed laser treatment increases the susceptibility to corrosion by changes on the roughness, microstructure and surface chemical composition; which affect the surface passivity, comparatively to the non treated biomaterial. In this study, the Mott-Schottky technique was very sensitive to identify the effect of the type of surface treatment, marking and texturing, according to the laser pulse frequency modification on the electronic properties of the oxide layer. The change in the semiconductors behavior was the main procedure proposed to explain the increased susceptibility to localized corrosion associated to the areas affected by the Yb optical fiber laser engraving and texturing process.

Keywords: Biomaterial, laser, marking, texturing, electrochemistry.

1. INTRODUCTION

The ISO 5832-1 austenitic stainless steel is one of the metallic biomaterials most used for implants fabrication due to its mechanical and corrosion resistance. Biomaterials find many applications, such as in the orthopedic field, for repair or replacement of the skeletal system parts. Stainless steels implantable medical devices are also used as long-term or short-term implants to help bone healing and reconstruction.

The implantable medical devices undertake a marking process before being sterilized whose function is to provide an apparent identification and traceability for the implants [1-3]. The texturing process is used to improve the surfaces hardness and roughness. One of the methods used for marking and texturing implants is the laser process. The implantable medical devices used in mobile joints of the human body require biocompatibility with the surrounding environment, mechanical strength, corrosion and wear resistance [1-3].

The laser marking process is generally used for cataloging or traceability of implantable medical and odontologic devices enabling a posterior analysis of the metallic biomaterial after its use. This method strongly affects the characteristics of the surface exposed to the aggressive human body fluids, such as microstructure, composition and surface roughness [4-6]. The surface characterization of laser marked biomaterials showed microstructure modification due to the high temperatures involved in the laser melting process [1-6]. Texture effects and great dislocation densities were associated to the laser process. These effects were evidenced by transmission electron microscopy at the interface between the melted and not melted zones [6]. These were also regions associated to higher pitting susceptibility.

Optical fiber laser texturing and marking process are largely used on martensitic stainless steels for clinical apparatus, like dental drills and piercers [7]. A recent study using the scanning vibrating electrode technique (SVET), have highlighted the areas with anodic current densities for regions with optical fiber laser incidence and cathodic to neighboring regions, which corresponds to the degradation cases obtained for autoclaving some martensitic dental tools [7].

The metallic biomaterials susceptibility to corrosion depends on the protecting characteristics of the passive layer which is formed by the interaction of the surface and the medium [4-6]. The conventional electrochemical methods allow the corrosion study correlated with surfaces finishing. An alternative or complement to these methods for the corrosion reactions evaluation is the staircase potentio electrochemical impedance spectroscopy (SPEIS), where assuming that the passive layer is a p-n hetero-junction, one can calculate the charge carriers transfer through the film [2, 8-10].

Many authors [8-13] characterize the electronic properties of its passive film using the Mott-Schottky approach, which results are reported as the inverse square of an apparent interfacial capacitance C as function of potential E, with: C =-1(/2πf Z”), where f is the test frequency and Z” is the imaginary part of the interfacial impedance. The passive film/solution interface is described by the following expression:

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 q N_q}\left(E_{FB} - E + \frac{kT}{e}\right),$$

where C is the capacitance of the oxide layer/solution interface; E, is the applied potential; ε, is the dielectric constant of the oxide; ε_0 is the permittivity of vacuum; N_q, is the density of electron semiconductor; q, is the elementary charge; k is the Boltzmann constant; T is the absolute temperature and E_{FB}, is the flat-band potential [14-16].

In the present work, the effects of the pulse frequency alteration for an Yb optical fiber laser texturing and marking techniques on the ISO 5832-1 stainless steel localized corrosion resistance have been investigated using the Mott-Schottky approach.

2. EXPERIMENTAL

Samples of the ISO 5832-1 austenitic stainless steel, with the chemical composition (wt. %): 18.32 Cr, 14.33 Ni, 2.59 Mo, 2.09 Mn, 0.38 Si, 0.026 P, 0.023 C, 0.0003 S, and Fe balance, were marked and textured by pulsed Yb - optical fiber laser at four different pulse frequencies, as Table 1 shows.

Table 1. Optical fiber laser pulse frequencies used for marking and texturing.

Sample	1	2	3	4
Pulse Frequency (kHz)	80	188	296	350

The marking technique consisted of engraving a sequence of numerical symbols on the samples surfaces. The texturing consisted in the production of juxtaposed lines in order to cover the largest area of the samples.

The electrochemical technique used to evaluate these surfaces treated by Yb optical fiber laser was the staircase potentio electrochemical impedance spectroscopy (Mott-Schottky approach) (SPEIS). The electrochemical tests were performed using a Biologic EC-Lab V10.33 – SP-150 potentiostat - galvanostat, with a three electrodes flat-cell of composed of a working electrode with 1.0 cm^2 exposed area, a platinized platinum as the counter-electrode of and Saturated Calomel Electrode (SCE) (3M) as reference.

A naturally aerated phosphate buffer solution (PBS) was used as the electrolyte, at 37°C, with the chemical composition: NaCl 8.0 g/L, KCl 0.2 g/L, Na_2HPO_4 1.15 g/L, KH_2PO_4 0.2 g/L, with a pH of 7.4. Staircase potentio electrochemical impedance spectroscopy (SPEIS) tests of marked, textured and non treated specimens were carried out after 12 h of immersion in the electrolyte and the capacitance measurements were performed at 1 kHz of frequency. Polarization was conducted in the cathodic direction from 500 mV to -1000 mV (SCE) at successive steps of 50 mV.

3. RESULTS AND DISCUSSION

The corrosion resistance of the ISO 5832-1 stainless steel specimens, marked and textured by optical fiber laser, and as received samples (non treated) was evaluated by staircase potentio electrochemical impedance spectroscopy (SPEIS) analyzing an area corresponding to 1 cm^2.

Figure 1 shows the Mott-Schottky results for samples marked by laser, varying its pulse frequency as: (1) = 80 kHz, (2) = 188 kHz, (3) = 296 kHz, (4) = 350 kHz, and non treated samples (blank).

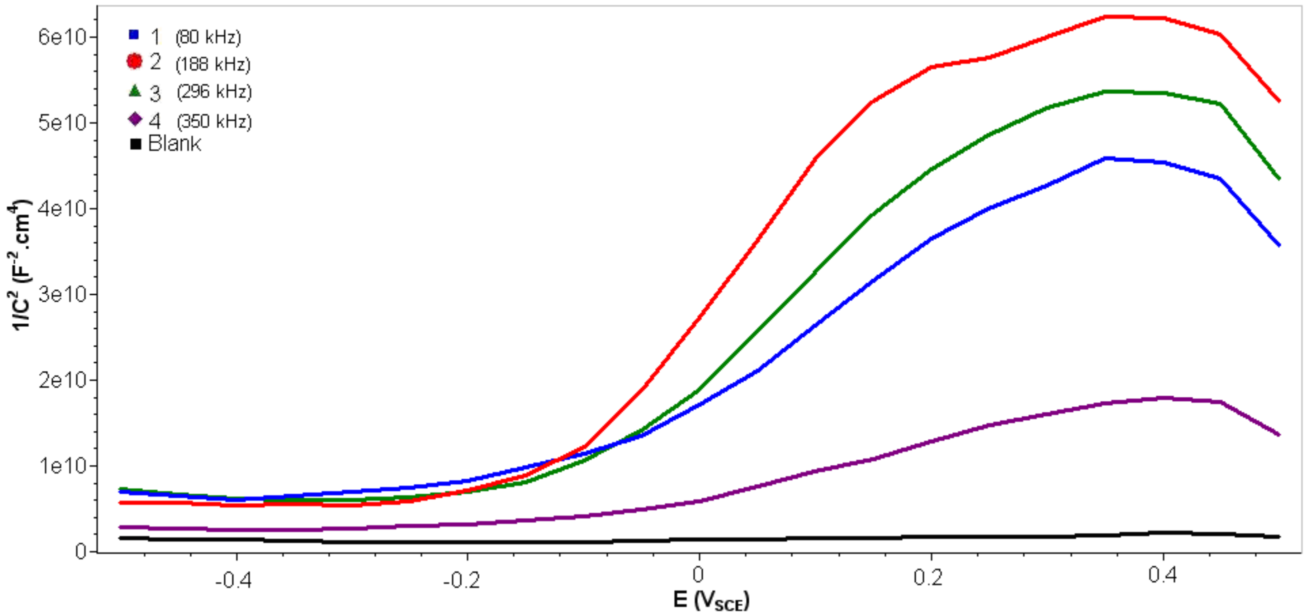

Figure 1. Mott-Schottky plots for blank and laser marked ISO 5832-1 SS specimens, measured in phosphate buffer solution (PBS), at 37 ºC, after 12 h of immersion.

Differences in the behavior of the oxides according to the surface condition of laser marking are noted. The samples corresponding to the standard steel (Figure 1) presented few slopes across the potential range evaluated.

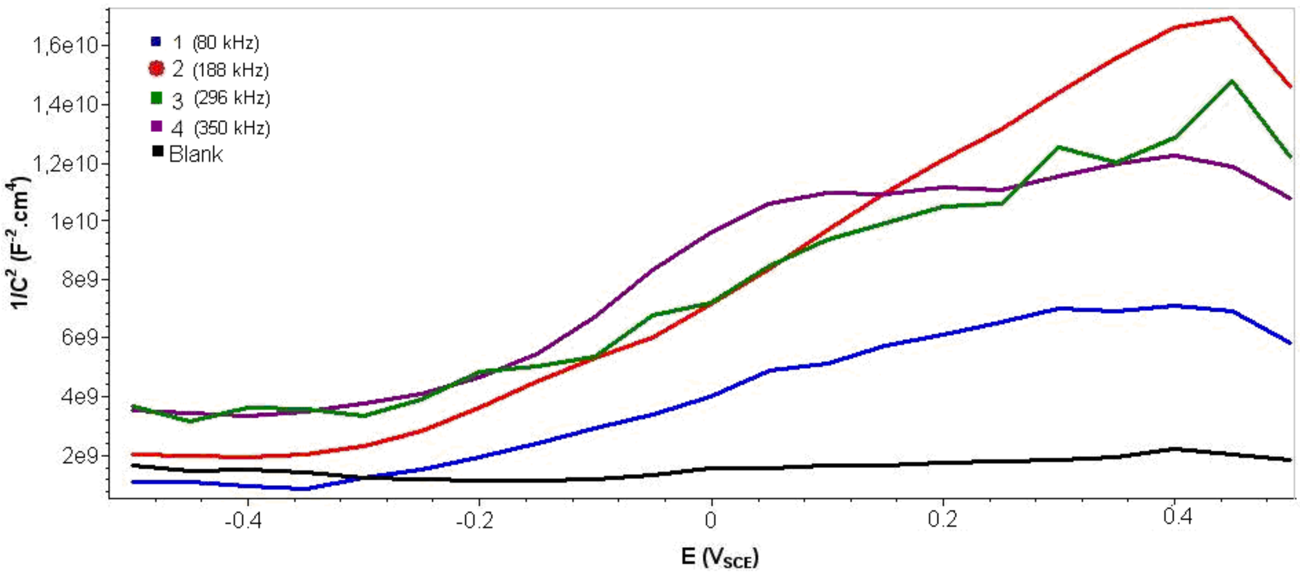

Figure 2. Mott-Schottky plots for blank and laser textured ISO 5832-1 SS specimens, measured in phosphate buffer solution (PBS), at 37 ºC, after 12 h of immersion.

The laser marked samples 1, 2 and 3 showed high slopes in the range of the potential region between -0.3V and + 0.4V corresponding to the behavior of a n-type semiconductor (positive slope of the graph of *1 / C² vs. E*), and smoother slopes in the region in the same potential region for sample 4; which reflects the duplex character of the protective film, obtained after 12 hours of immersion, according to the literature on protective oxides and their electronic properties using the Mott-Schottky methodology [8, 17, 18].

Figure 2 shows the Mott-Schottky results for samples textured by laser, varying its pulse frequency as: (1) = 80 kHz, (2) = 188 kHz, (3) = 296 kHz, (4) = 350 kHz, and blank samples.

The duplex behavior of the oxide layer formed on this stainless steel was verified. Above -0.3 V, the graph of *1 / C² vs. E* presents a positive slope, corresponding to the behavior of an n-type semiconductor, which according to Hakiki et al. [8, 9, 15] is associated with the outer layer of iron oxides and hydroxides in passive films formed on stainless steels. Below this potential, the graph tends to change slope, suggesting a tendency to become negative, typical of a p-type semiconductor, and refers to the inner layer most chromium enriched oxide. The textured samples exhibited a duplex character, typical for passive films formed on stainless steels, as found in the literature [2].

On the range of potentials between approximately -0.5 V and -0.3 V, which corresponds to the negative slope of the curves, very smooth slopes were obtained, which are related to of a p-type semiconductor behavior and are associated to the chromium oxide, formed in the inner part of the film. However, for potentials higher than -0.3 V, positive but more pronounced inclinations were observed, corresponding to the outermost part of the film, which is basically composed of iron hydroxides and oxides.

Analyzing Figures 1 and 2, the laser outcome on the electronic properties of the passive layer formed on this stainless steel, used for biomaterials, at these laser treatments conditions is evident. It was observed that in addition to the change in inclination, also the flat band potential (E_{bp}) displacement occurred, which is obtained by extrapolating from 1 / C² to zero. The results for the dopant calculations for all surface conditions analyzed are shown in Figures 3 and 4.

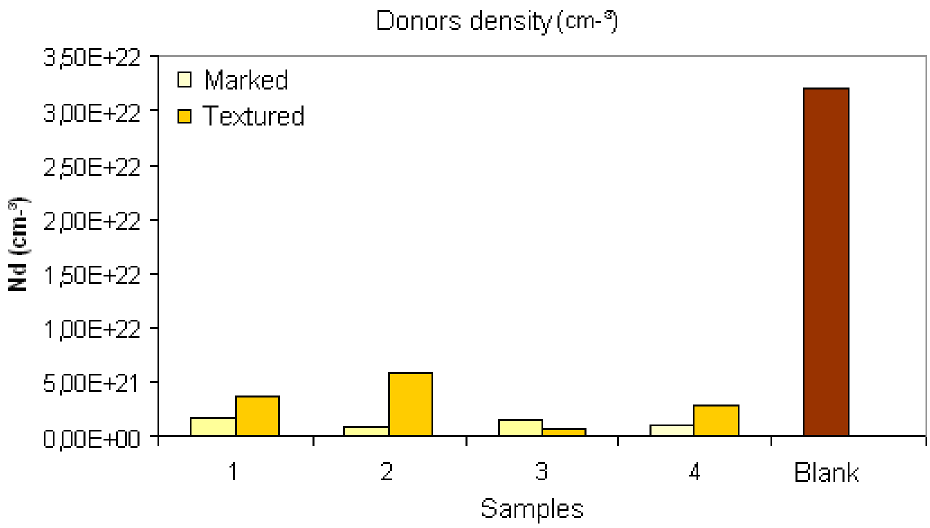

Figure 3. Donors density obtained by the Mott-Schottky graph, at the region of positive inclination potential (behavior of an n-type semiconductor), for marked, textured and blank samples.

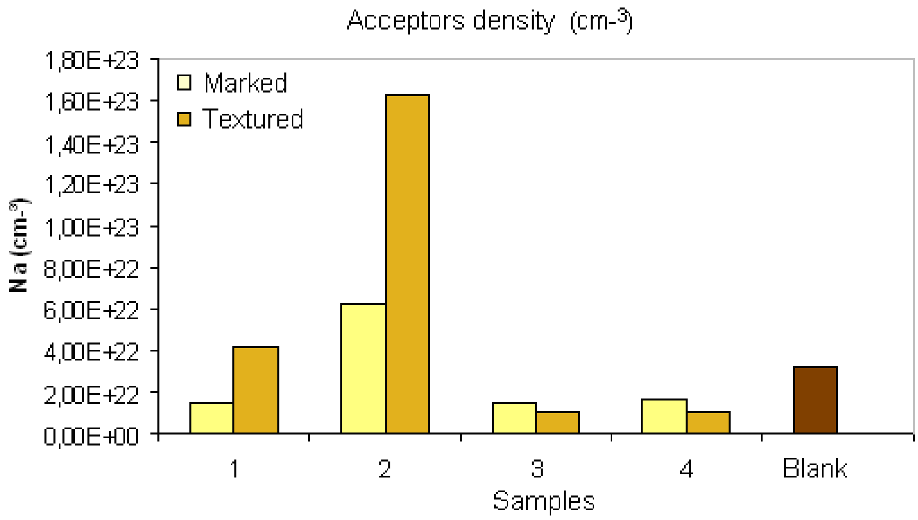

Figure 4. Acceptors density obtained by the Mott-Schottky graph, at the region of negative inclination potential (behavior of a p-type semiconductor), for marked, textured and blank samples.

The dopant density values for the marked and textured specimens are on the order of 10^{22} cm^{-3}. These values are higher than the dopant concentration found in the literature for this type of steel, which is from 10^{20} cm^{-3} to 10^{21} cm^{-3}. The acceptor densities at the oxide formed on the laser marked specimens were lower than those of the blank samples, except for sample 2. However, for the textured specimens 1 and 2, treated with the lowest pulse frequencies, (f = 80 kHz and f = 188 kHz), the acceptors density was higher than the other conditions, including the blank sample.

Figures 3 and 4 show the donors and acceptors charge densities, respectively, for each surface treatment condition relating to the change of the pulse frequency. These densities were estimated taking into account only the posterior and previous slopes to the flat band potential for all conditions tested.

The results for n-type semiconductors (donors) were higher for the texturing conditions under pulse frequencies 1 (80 kHz), 2 (188 kHz) and 4 (350 kHz), indicate that defects in this layer are probably responsible for a greater susceptibility to localized corrosion. This has been related to the outermost layer of the oxide, rich in nickel and iron [2, 8, 15, 19-20]. The external oxide, being more defective, would favor the ionic transport through this oxide layer, providing the attack and the breaking of the internal layer and the process of corrosion by pit that propagates autocatalytically.

For p-type semiconductors (acceptors), the results were higher for the texturing conditions under pulse frequencies 1 (80 kHz) and 2 (188 kHz), and for marked samples under parameters 3 (296 kHz) and 4 (350 kHz). This fact is related to electronic defects density in the innermost oxide layer, related with chromium oxides mainly [8].

Hakiki et al. [8-9] studied the electronic structure of the passive films formed on AISI 304 austenitic stainless steel applying the Mott-Schottky technique supported by Auger electron spectroscopy. It was verified the influence of chromium on the behavior of the capacitance of that stainless steel. Increasing the chromium content, the slope of the capacitance curves that responded as a p-type semiconductor also increased; which agrees with the fact that the passive film presents a duplex character, being formed by more internal regions formed by oxides of chromium and, external, formed by iron oxides and hydroxides; making it possible to compare the passive film with a p-n hetero-junction.

Both types of optical fiber laser treatment used in this work resulted in higher densities of charge acceptors and, however, lower donor densities. This suggests that the laser beam also affects the innermost oxide layer. Variation in donors (n-type) and acceptors (p-type) slopes of the Mott-Schottky graphs are related to the alteration of the charge carriers densities in the passive film due to the laser pulse frequencies used.

The SPEIS results showed that the Yb optical fiber laser texturing and marking treatments, with the parameters used in this work, had a deleterious achieve on the corrosion resistance of the ISO 5832-1 stainless steel, leading to decrease the resistance of the passive layer naturally formed at the surfaces.

4. CONCLUSIONS

The results of the present study showed that the optical fiber laser texturing and marking techniques used for biomaterials induced a high concentration of semi-conductors defects. For the same immersion period, the concentrations of charge acceptors on the passive film of the laser marked and textured samples were different from the values obtained for the charge donors. These modifications on the biomaterial's surface semiconductors properties lead to decrease the corrosion resistance, mainly the pitting and crevice resistance, which is undesirable for biomaterials applications.

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