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Electrochemical Characterization of an Optical Fiber Laser-Treated Biomaterial

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<http://dx.doi.org/10.5772/intechopen.72653>

Abstract

The implant manufacturing process includes texturization to enhance its adhesion and marking the final products for their identification, long-term quality control and traceability. Marking is carried out after cleaning and prior to sterilization. These marks eventually can concentrate stress leading to premature failure. The marked areas are defective regions that affect the passive film formed on the metallic biomaterials used for implants favoring the onset of various corrosion types, such as pitting, crevice or fatigue. This study aims to evaluate the effect of a Yb optical fiber laser marking processes used for metallic implants on the localized corrosion resistance of the austenitic stainless steel ISO 5832-1. This is one of the most used materials for manufacturing implants. The electrochemical behavior of the marked areas obtained by this method was evaluated in a phosphate-buffered saline (PBS) solution with pH of 7.4 and the results were compared with unmarked samples. All tested surfaces were prepared according to the recommendations for the use in surgery. For localized corrosion resistance evaluation, electrochemical tests such as monitoring the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and cyclic potentiodynamic polarization measurements were performed. The results showed that the laser marks affect the protector characteristics of the biomaterial's passive film. Lower pitting resistance was associated to the laser marked areas.

Keywords: biomaterials, stainless steel, electrochemistry, laser, marking

1. Introduction

The increase in people's life expectancy and the rising number of accidents with serious injuries have raised the number of orthopedic surgeries worldwide. In order to help or replace injured

body parts, implants or prostheses are used to perform their duties properly. These materials must have adequate chemical composition and surface condition so they are not rejected by the body.

The material selection for biomedical application should take into consideration its physical, chemical and mechanical properties. The main properties that must be taken into account are: strength, elasticity modulus, bending and torsion, fatigue resistance, corrosion resistance and hardness [1, 2]. The manufacturing process of metallic implantable medical devices is one of the most important stages of the production of implants, and this can be via casting, forging, machining, welding or by powder metallurgy. This process also involves cleaning, surface finish, marking and sterilization, according to the strictest standards of quality control [1–3].

The implants when in contact with human tissue might suffer constant wear and corrosion, and the corrosion products may cause hypersensitivity, leading to the need for implant replacement surgery. These surgeries lead to increased costs and health risks for patients. Therefore, research and development of biomaterials with improved surfaces is of great interest [1–3].

Using materials to repair or restore damaged tissues or organs in humans is not new. The first reports of biomaterial use have 4000 years of existence, describing the use of sutures for repair of wounds. The reports of use of non-organic materials are from 1550, with the use of gold thread for sutures [1]. Earliest indications are also around this period, with the medical records of Hindu, Egyptian and Greek civilizations citing bone transplants from animals to humans.

Nowadays, advances in biomedical engineering and surgery have made possible the reconstruction of various parts of the human body with biomaterials. According to Williams [2], biomaterial is any substance or combination of substances, except drugs, naturally occurring or synthetic, that can be used during any period of time, as part of a system that treat, augment or replace any tissue, organ or body functions.

Biomaterials have many applications such as orthopedic for the repair or replacement of any part of the skeletal system. Metallic biomaterials are also used for neural or neuromuscular stimulation in electronic systems in order to provide electrical stimulation to tissues with certain degree of deterioration [4, 5]. The development of biomaterials appears to be fundamentally important in the sense that it provides an improved standard of living for the people, represented by an increase in life expectancy, general health and well-being of the population.

The metallic materials used in implants or prostheses are generally passive materials and therefore are subject to localized corrosion when in contact with body fluids. According to Lyman and Villamil [1, 6], the most common types of corrosion observed in metallic implants are: galvanic, crevice, pitting and selective corrosion.

Pitting corrosion is a localized attack on a surface covered with oxide. A pit is initiated by adsorption of anion activators, particularly chloride ions. When the pitting potential is reached, the electric field strength in the thinner parts of the film is so high that chloride ions can penetrate the film, starting localized dissolution of the oxide film. Thus, once a pit has formed, it will continue to grow autocatalytic [7–10].

The mechanism of pitting corrosion occurs by nucleation and growth, which creates conditions for its propagation, which are: the chloride ions enrichment in pitting, the generation of an acidic solution inside the pit, by hydrolysis of metal ions, high conductivity of salt solution,

the limited supply of oxygen and, outside of the pit, forming a layer of hydrate, with the dilution of pits solution by diffusion and convection [11–17].

The laser marking technique is commonly used for biomaterials classification or traceability enabling posterior analysis of the implantable metallic device after its use. The laser engraving process strongly affects the biomaterials' surface properties, especially those exposed to the corrosive human body fluids, such as microstructure, composition and roughness [18–25].

Qi et al. [26] studied the effects of laser engravings on stainless steels. They have used a pulsed, Q-switched Nd: YAG laser and evaluated the influence of pulse frequency, energy and speed on the final metallic surfaces quality. They compared the depth, width and contrast generated by the laser process and observed that the pulse frequency was the parameter that most affected surface oxidation, and consequently, the contrast of the surfaces subjected to this laser beam. Similarly, Leone et al. [27] verified that the laser pulse frequency was the parameter that most interfered in the contrast obtained on the digital images of the surfaces submitted to the engravings. They have used the same type of laser and the same parameters as Qi et al. [26]. The material that underwent the markings was an AISI 304 stainless steel. They have observed that the roughness and oxidation of the etched surfaces increased as a result of increasing the pulse frequency.

Bizi-Bandoki et al. [28] studied the changes in roughness and surface tension of the AISI 316 L stainless steel and the Ti-6Al-4 V alloy. A titanium-sapphire ultra-short pulse laser was used varying only the number of pulses. The researchers have found that as the number of pulses increased, the topographic features of both materials were also altered, producing surface undulations and their changing behavior from hydrophilic to hydrophobic.

2. Experimental procedures

The material used in this study was the austenitic stainless steel, ISO 5832-1, which is largely used for orthopedic implants. Its chemical composition is shown in **Table 1**. The tested surfaces were marked via pulsed nanosecond ytterbium (Yb) optical fiber laser, at four different pulse frequencies, as shown in **Table 2**. For comparison reasons, unmarked surface of this biomaterial was also evaluated. The marking procedure consisted of recording the number 8 (eight) many times on the surface in order to cover the largest possible area of the samples.

C	Si	Mn	P	S	Cr	Mo	Ni	Fe
0.023	0.378	2.09	0.026	0.0003	18.32	2.59	14.33	Bal.

Table 1. Chemical composition of the ISO 5832-1 stainless steel (wt.%).

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

Table 2. Yb-optical fiber laser pulse frequencies.

NaCl	KCl	Na ₂ HPO ₄	KH ₂ PO ₄
8.0	0.2	1.15	0.2

Table 3. Chemical composition (g/L) of phosphate-buffered saline solution (PBS).

The aim was to evaluate the effect of the marks on the corrosion resistance of the implant. The mark is usually carried out for identification and traceability of the implant.

To evaluate the specimens' corrosion resistance, electrochemical techniques were employed such as open circuit potential *versus* time (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization. All electrochemical tests were carried out using Biologic EC-Lab V10.33 – SP-150 potentiostat-galvanostat equipment. The electrochemical test cells were composed of a three electrode setup, with the specimen as the working electrode, a Pt counter electrode (wire with geometric area of 2.0 cm²) and a saturated calomel electrode (SCE) (3 M) reference electrode. The area of the working electrode exposed to the electrolyte corresponded to 1 cm². In order to ensure reproducibility, at least four samples for each surface condition were measured. The electrolyte used was a phosphate-buffered saline (PBS) solution, pH of 7.4, with chemical composition shown in **Table 3**. The solution was prepared from high purity chemical reagents and deionized water. Potentiodynamic polarization tests were carried out at a rate of 0.167 mV/s, at (37 ± 1)°C, after monitoring the open circuit potential (OCP) for 12 h.

Surface characterization of the ISO 5832-1 stainless steel either with laser or without laser engravings was carried out by scanning electron microscopy (SEM).

3. Results and discussion

The corrosion resistance of the ISO 5832-1 stainless steel, greatly used for biomedical applications, was measured by electrochemical methods. **Figure 1** shows the variation of the open circuit potential as a function of immersion time for the four different types of laser marked surfaces and the blank (without laser), at 37°C, during a period of 12 h, which was reasonable time for the stabilization of corrosion potential. The tests were carried out for 10 specimens of ISO 5832-1 austenitic stainless steel, for each of the following conditions: unmarked and laser marking, changing the pulse frequencies in four levels. The analysis of **Figure 1** allows the understanding of some phenomena that have been repeated for several specimens depending on the type of surface evaluated.

The curve presented in black color, referring to the steel without markings, is representative of the amount of 10 tests performed and presents a more constant open circuit potential for the period evaluated, which suggests the existence of a more stable passive film on the steel. From the first 4000 s of immersion, there is an increase in potential, which with the passage of time, exhibits more uniform behavior until reaching a value of the order of 0.18 V (SCE) in 12 h of test.

Most of the specimens marked by laser beam with parameters 2 and 4 showed a trend of increasing in potential for nobler and more stable values. Specimen 1 showed a drop in open

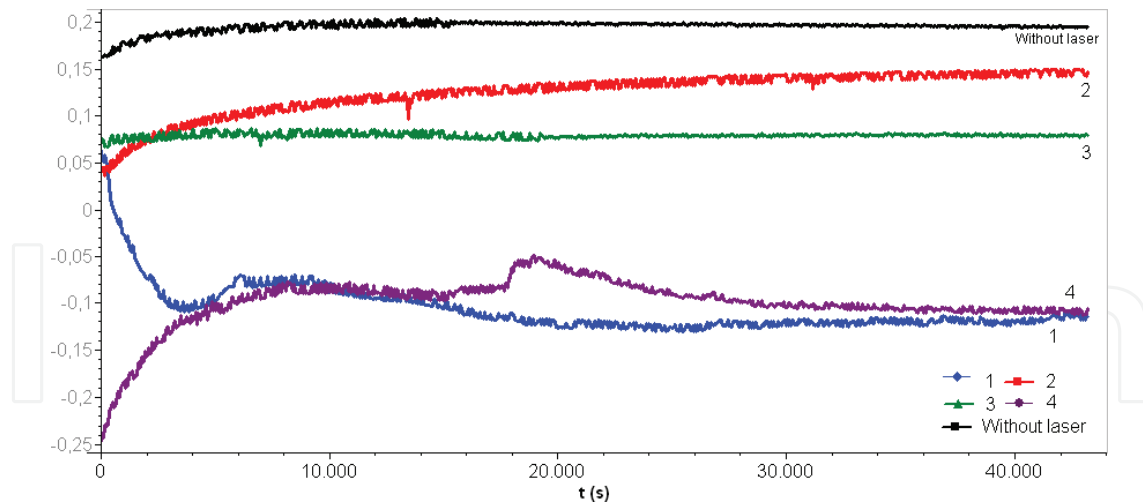


Figure 1. Open circuit potential variation with time of immersion for unmarked and Yb-optical fiber laser marked surface, in different frequencies, during 12 h of immersion in phosphate buffer solution (PBS).

circuit potential for the first immersion times, around 4000 s. This potential drop can be associated with the attack of more active regions of the surface due to the formation of microplates related to defects generated by the laser marking process. The attack of the more active regions can be considered as a partial “cleaning” of the surface by corrosive attack that is followed by a more homogeneous surface responsible for the recovery of potential in the final moments of the immersion. Specimen 3 presented values of more uniform potentials throughout the open circuit immersion period.

For longer immersion times in this solution, around 25,000 s, all specimens with and without laser markings, exposed in **Figure 1**, show uniform behavior of the corrosion potential, indicating the formation of a stable passive film.

The electrochemical impedance spectroscopy (EIS) diagrams for the biomaterials under the conditions studied, obtained at 37°C in PBS solution, immediately after the potential monitoring corrosion are shown in **Figure 2**.

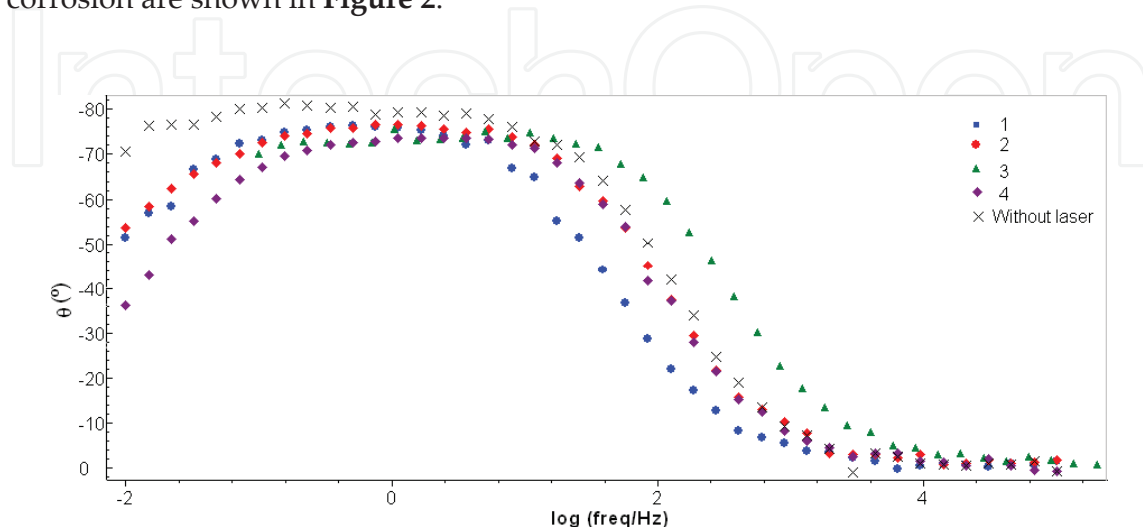


Figure 2. Bode diagram (phase angle) obtained after OCP for austenitic stainless steel ISO 5832-1 in PBS at 37°C.

Figure 2 presents the Bode (phase angle) diagram for the laser marked specimens and without marks, with phase angle values between -35° and -80° , in the low-frequency region, which corresponds to that of passive metals [18, 29–32], and the samples without laser treatment had the lowest values and the highest values were obtained for the samples marked in condition 4.

The diagram shows two constants. One is in the region of high frequencies, identified with a slope between 0.01 and 0.1 Hz. The other in the region of low frequencies, characterized by a slope between 1 and 10 Hz for the surface corresponding to specimen 1 and between 10 and 100 Hz for the other conditions of marked surfaces (specimens 2, 3 and 4) and without laser. This behavior was observed for stainless steels and associated with the constant at high frequencies at the external-medium oxide interface and the constant at mean frequencies at the internal metal-oxide interface [29–31].

The Bode diagrams, shown in **Figure 3**, represent the reproducibility obtained in 10 tests for each condition and suggest that the change in the laser beam parameters used for the markings has a small influence on the impedance in the low-frequency region, the lowest values obtained for the specimens marked in conditions 1 and 4, and the highest for the material without laser treatment, in this frequency range. This fact evidenced a slight decrease in the protective capacity of the passive film for the treated specimens.

In **Figure 2**, the Bode diagrams show a narrow plateau for the laser-labeled specimens under all conditions evaluated with phase angle values around -70° , in the medium frequency range, and a wide plateau with phase angle values close to -80° over a wide frequency range, from averages to low, for specimens without laser treatment, typical of passive materials [18, 29, 30].

Higher phase angles at low frequencies for unlabeled specimens suggest passive and more protective films. The drop in the phase angles at the lowest frequencies for the labeled specimens is an indicative of the deterioration of the passive film properties. In the laser-etched samples, the peak phase angle occurs at lower frequencies compared to the untreated specimens, suggesting that the outermost layer of the oxide is less protective than the others [18, 24].

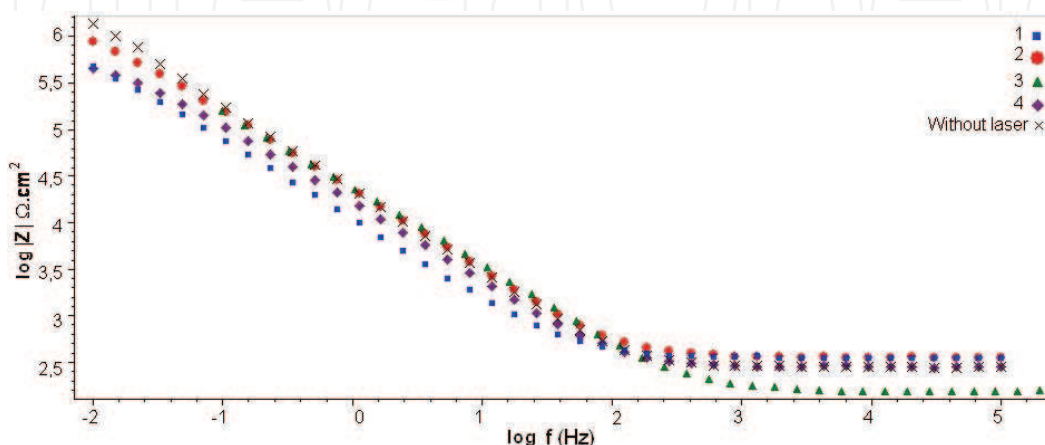


Figure 3. Bode diagram (Z-module) obtained after OCP for austenitic stainless steel ISO 5832-1 in PBS at 37°C.

For the same period of immersion from the open circuit corrosion potential, Nyquist impedance diagrams exhibit capacitive behavior, typical of passive materials, and showed lower-Z imaginary values for the specimens with laser treatment; when compared to the specimens without laser beam application. In **Figure 4**, for the same frequency value, the lower impedances were associated with the laser labeled specimen in condition 3, followed by the marking conditions with parameters 4, 1 and 2.

The EIS results were supported by the cyclic potentiodynamic polarization curves. The lower resistance to pitting corrosion was associated with the laser treated specimens; this is explained by the thermal effect of the process on the homogeneity of the microstructure of this analyzed biomaterial, which reduces the potential for breaking the passive film.

Figure 5 presents the cyclic polarization curves for specimens with and without laser marks. This result represents the laser effect on the susceptibility to corrosion of this stainless steel; the curves presented values of passive film breakdown from about +0.3 V (ECS) to +0.8 V (ECS).

This variability is expected for heterogeneous surfaces such as the specimens with markings via laser beam, where the conditions of the specimens under conditions 1 and 4 showed higher resistance to localized corrosion. It is noted that the film breaking potentials, for all laser marked conditions, are below the specimens without laser marks, that is, polished to 1 μm .

The microstructure of the ISO 5832-1 austenitic stainless steel, widely used for biomaterial application, is presented in **Figure 6**.

Figure 7 shows that pitting susceptibility is increased in the laser affected areas of the stainless steel surface.

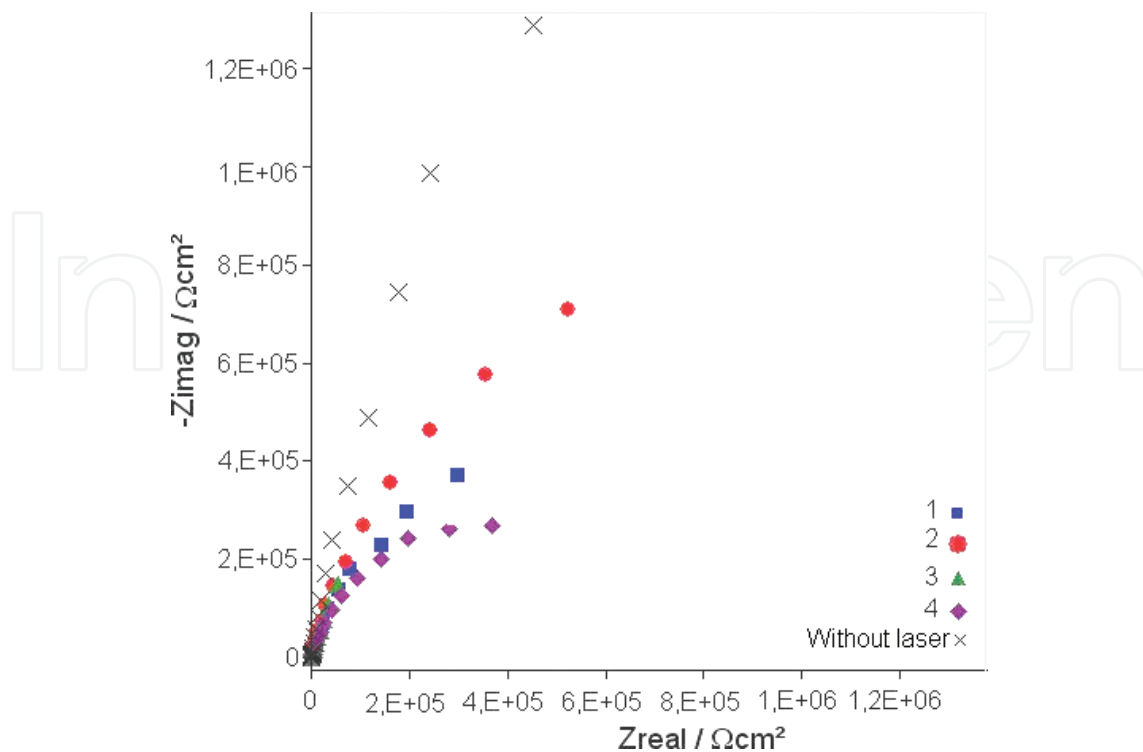


Figure 4. Nyquist diagram obtained after OCP for austenitic stainless steel ISO 5832-1 in PBS at 37°C for the specimens.

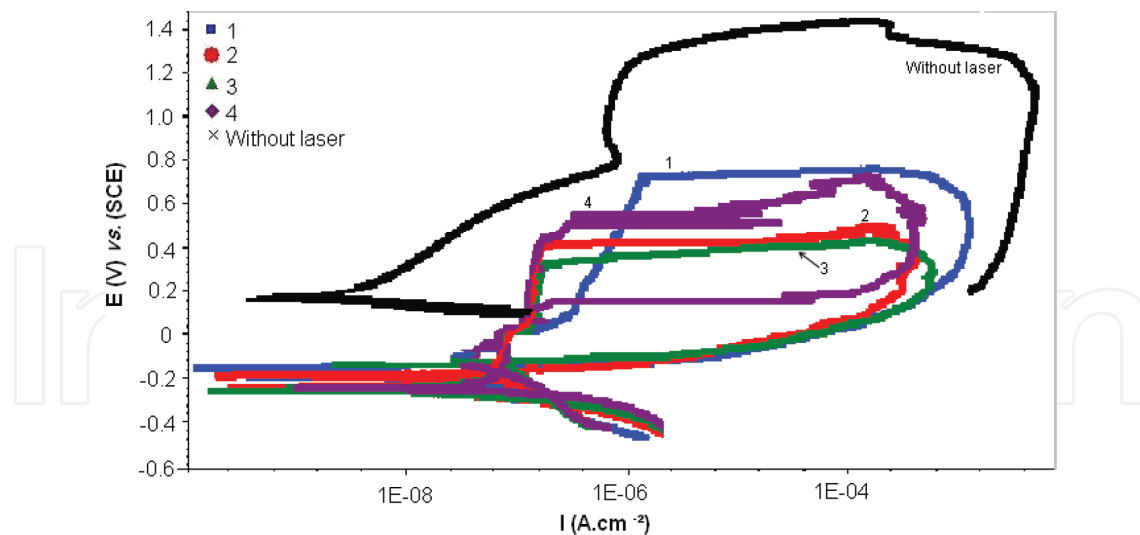


Figure 5. Potentiodynamic polarization curves for unmarked and laser marked ISO 5832-1 stainless steel samples obtained in phosphate-buffered saline solution (PBS).

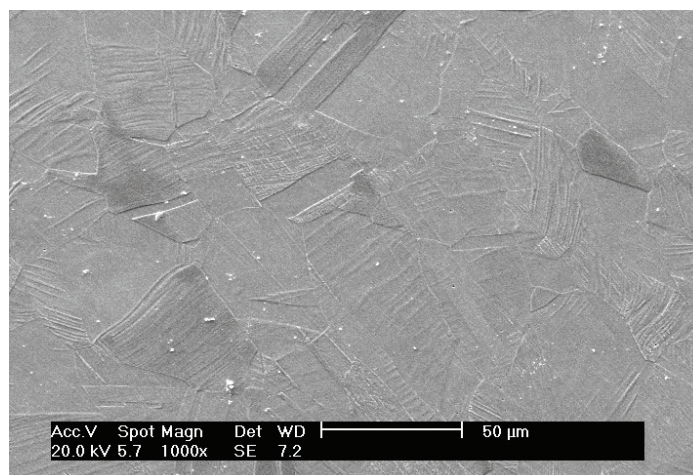


Figure 6. SEM microstructure of ISO 5832-1 austenitic stainless steel surface.

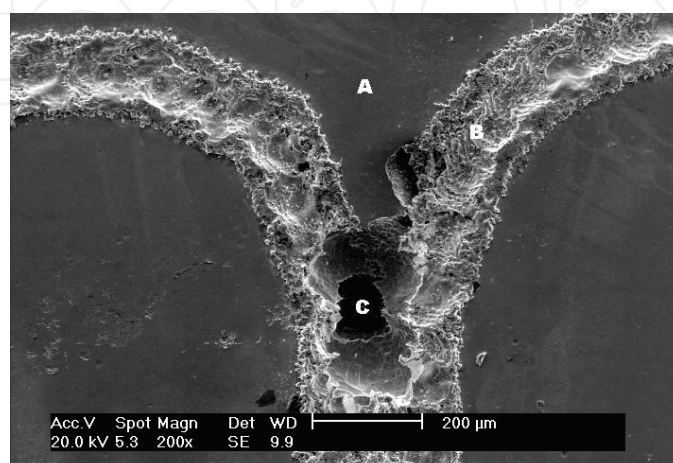


Figure 7. SEM image of the ISO 5832-1 stainless steel surface after polarization tests. (A) Region without laser, (B) laser marked region and (C) laser marked region showing pits associated to the melted areas.

4. Conclusions

The results of this study showed that susceptibility to pitting corrosion increases due to the thermal effect of the laser marking process in the surface of the stainless steel comparatively to the unmarked regions. In addition, the passive films properties are widely changed by the marking process, with the frequencies used.

The lowest pitting resistance was found for the samples with laser marks. This is explained by the thermal effect of the laser marking procedure on the stainless steel microstructure decreasing pitting resistance. The laser marking occurs by melting of the surface in order to produce the desired marks, besides that a rougher nonhomogenous surface is generated, which favors the corrosion attack.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this book chapter.

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