Corrosion Analysis of a Marked Biomaterial

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Abstract- **Marking is one of the last steps of manufacturing an implantable biomaterial. The marks on its surface constitute a permanent set of information in order to provide identification and traceability of the biomedical device. These markings become stress concentrators and regions with probability for the occurrence of failures that can lead to fracture; besides damaging the passive layer, naturally formed on stainless steels surfaces, favoring the beginning of several forms of degradation. This work presents the effect of two metal implant marking techniques on the corrosion resistance of ISO 5832-1 austenitic stainless steel, one of the most used surgical biomaterials used in Brazil. Engraving was carried out with mechanical and laser beam marking techniques were prepared. The electrochemical behavior was characterized by cyclic potentiodynamic polarization curves and indicate that the laser marking technique is the one that most affects the passive layer of the material when compared to the mechanical engraving.**

Keywords- **Biomaterials, engraving, traceability, laser, corrosion.**

I. INTRODUCTION

Biomaterials are used in prostheses or implantable medical devices in order to replace or assist certain parts of the human body so that they can properly perform their functions [1]. These materials must have a strict chemical composition and adequate surface finishing so that they are not rejected by the body during the lifespan period [2].

For hundreds of years, people have been looking for alternatives to relieve pain, reduce suffering and prolong life with greater quality. Reports on the use of synthetic materials have been found since the year 1550, with the use of gold thread for sutures [1]. Currently, advances in the biomedical engineering field have allowed the reconstruction of various parts of the human body using biomaterials.

Biomaterial is defined as a material, except drugs, of natural or synthetic origin, which can be used for a certain period of time, in order to treat, increase or replace any tissues, organs or functions of the human body in a biocompatible way, that is, without rejection [2]. Considering the biological response caused by biomaterials in body tissues, these can be classified into: bioinert, biotolerates, bioactive, resorbable [1, 3, 7].

Based on their chemical composition, they can be classified into: metallic, polymeric, ceramic or composites [1].

The biomaterial selection must take into account its physical, chemical and biomechanical properties. The main properties that must be taken into account are: mechanical strength, modulus of elasticity, flexion and torsion, fatigue resistance, corrosion susceptibility, roughness and permeability [3, 4]. Among these, metals are preferred biomaterials for orthopedic applications due to their higher mechanical properties [1-6].

Metals are widely used in orthopedic and neuromuscular stimulation areas. Orthopedic applications involve the use of biomaterial for the restoration or replacement of some part of the skeletal system. In neural stimulation, metallic biomaterials are used in an electronic system in order to provide electrical stimulation for tissues, which would otherwise be impossible due to the degree of tissue deterioration [4].

The development of biomaterials proves to be fundamentally important, in the sense that it provides an improvement in people's standard of living, represented by an increase in life expectancy, in general health and in the well-being of the population.

Many metals alloys have a thin oxide layer that provides corrosion protection. This is formed by a reaction of the metallic surface and the medium and is responsible for the passivation phenomenon. Failure in the passive film, often in a localized form, results in attack or localized corrosion that can occur as pits, crevices, under stress and associated with fatigue [7].

Although all metallic biomaterials currently used have well-characterized electrochemical properties, many manufacturing processes can alter the corrosion resistance of finished products [7, 8]. In addition, devices with complex shapes, with corners, edges, recesses, tips and other design irregularities, may have their resistance to localized corrosion affected [9-12]. Surface finishing steps, as well as surface marking, can cause increased susceptibility to localized corrosion due to surface changes [13-17].

Metallic implantable medical devices are subject to some markings in accordance with current standards; which aim to promote the traceability and after use identification. These markings become stress concentrators and places potentially subject to be the origin of failures that can lead to fracture; causing damage to passive layer and favoring the corrosion onset [7-17]. Degradation by corrosion or wear shortens an implantable medical device lifespan [17,18].

This work aims to contribute to the knowledge dissemination in the areas of engineering and health. In this way, it is intended to present the effect of two different marking techniques, *via* laser beam or pantographic, on the resistance to pitting corrosion of metallic biomaterials specimens.

II. Materials and methods

The starting material for this study was a cold-rolled ISO 5832-1 austenitic stainless steel sheet that was initially sanded in silicon carbide sieves up to 600 mesh and polished with diamond paste up to 3μm, washed in acetone for 3 min on ultrasound, and rinsed in deionized water. Mechanical markings were performed using the pantographic process. The laser beam markings were performed using a Q-switched Nd: YAG laser equipment, pumped by nanosecond pulsed diode, with wavelength of 1064 nm, output power of 50W, and power stability of 2%. The ratio marked length over total exposed area was the same for all marked specimens submitted to electrochemical characterization. It was engraved the numeral eight “8” with the same size on both methods.

Cyclic potentiodynamic technique was employed for electrochemical characterization, which, in addition to the pitting potential, makes it possible to determine the repassivation potential. The resulting density increases from the potential at which the polarization curve was lifted to a moment when a sudden increase occurs, a certain value is reached and the potential sweep direction is reversed. The repassivation potential corresponds to the potential where the downward curve crosses the axis of the electrode potentials.

The method is intentionally designed to achieve conditions that are sufficiently severe to cause the passive layer breakdown, which may not necessarily be found *in vivo* [19].

Cyclic potentiodynamic polarization tests were carried out in Gamry PCI4 / 300 potentiostat / galvanostat equipment. The electrolyte was a phosphate buffered saline solution (PBS), with a pH equal to 7.4, at 37 ° C. The electrochemical arrangement was a glass flat cell with three electrodes, consisting of a working electrode with 1.0cm^2 exposed area, a counter electrode (platinum wire with a 2.0 cm^2 geometric area) and an Ag / AgCl (3M, KCl) reference electrode. At least ten tests were carried out for each condition, in order to ensure reproducibility.

Surface characterization was performed by scanning electron microscopy (SEM) - Philips XL30. The micrographs were obtained after the electrochemical tests, without the use of metallographic etching.

III. Results and discussion

Cyclic potentiodynamic polarization curves for laser-marked and mechanically engraved ISO 5832-1 SS specimens are shown in Figure 1. The as-polished material (without markings) was also tested for comparison. The curves represent the reproducible behavior obtained in the electrochemical test.

The marked specimens showed lower resistance to localized corrosion than the pristine specimens. This effect is due to the alteration, generated by the markings, in the surfaces finishing produced on this type of biomaterial. This result is accentuated in specimens with laser engravings [7, 8, 17].

The markings have produced discontinuities on the surfaces of the evaluated biomaterial. This fact explains the drop in corrosion resistance and can be identified by the pitting potentials shown in Figure 1, which reached values in the order of 0.6V for the laser beam marking conditions and 1.0V for pantographic marking conditions.

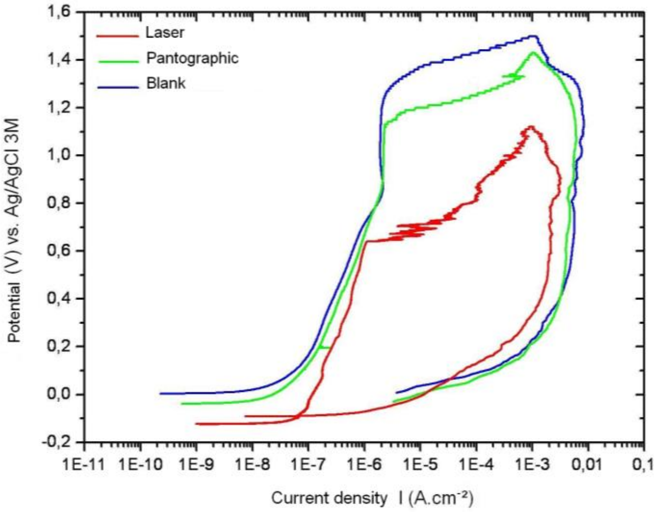

Fig. 1. Cyclic polarization curves for the ISO 5832-1 SS in three different surface finishing conditions

Knowledge of corrosion mechanisms is extremely important in the biomaterials field. Combined with biomechanical and biocompatibility tests, it enables safe use for biomedical purposes [20-25].

For comparison and better identification, all the presented images were captured in SEM - Philips XL30 equipment, using secondary electrons mode, with the same magnifications, namely: 50x and 200x magnitude for both types of marking. The specimens with laser marks are shown in Figures 2, 3 and 4, and the samples with mechanical marks, in the images of Figures 5, 6 and 7. All images were obtained after cyclic polarization tests.

Scanning electron microscopy (SEM) was used to characterize the corrosion morphology obtained after the corrosion test. Clearly, pits associated with marked regions can be observed on the evaluated surfaces. In some specimens treated by laser beam, crevice corrosion was also found, which is caused by differential aeration. The appearance of crevice corrosion mechanism in laser marked specimens can be explained by the topography changes generated by the coherent laser beam, which produced protuberance and grooved regions on the surfaces [7, 17].

The differences in surface finish between the two marking conditions are apparent. In the case of pantographically marked specimens, the finish is smoother, as there was only the removal of material using a mechanical tool. In the case of laser-marked specimens, the resulting finish, in the engraving region, has a much rougher appearance, since localized fusion of the biomaterial's metallic surface occurs, followed by extremely fast solidification.

The markings consisted of numerical characters generated on ISO 5832-1 SS specimens. In Figure 2, corrosion pits around laser markings are observed. Note the rough appearance produced by the laser pulses.

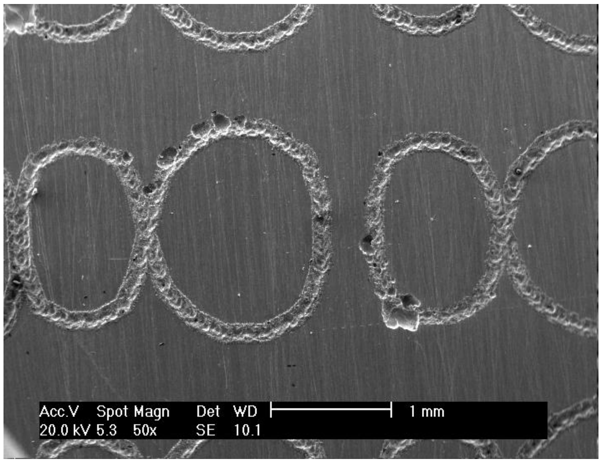

Fig. 2. SEM image of pits at the laser marked region biomaterial specimen, after electrochemical test

Figure 3 shows pitting and crevice corrosion on the laser marked biomaterial surface. The pits are identified as "holes" with more circular shapes, at the top of the central engraving shown in this figure; and the crevice, like a large and irregular crater, at the bottom of the same character in this figure. The crevice is more evident at higher magnification, as shown in Figure 4. The difference in the relief imposed by the laser beam incidence induced this type of corrosion degradation. Inside this crevice, it is possible to notice the aggressiveness caused by the laser conditions, as the microstructure was revealed and some SS grains were pulled out.

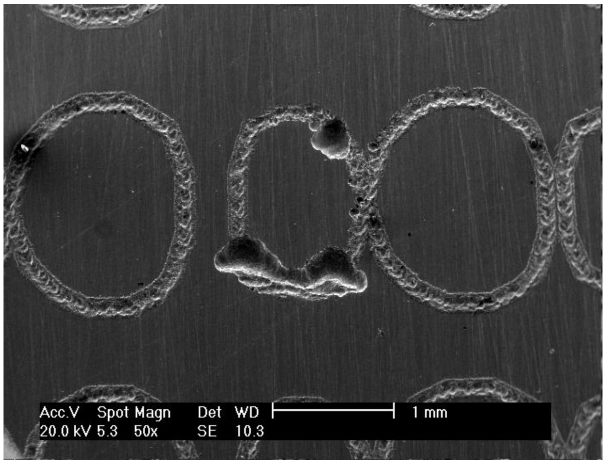

Fig.3. SEM image for laser treated surface, after electrochemical test. Emergence of pits and crevices are shown

The roughness produced by the laser beam pulses caused changes in the topography of the samples, forming regions of peaks, valleys, recesses, protuberances, and essentially anodic places with differential aeration [7, 16, 25].

Corrosion pits formed on the markings produced by the pantographic method are observed in Figure 5. The less rough appearance generated by the pantograph in the marking is noted. In the mechanical process, material is removed in order to produce the desired image on the surface. In this technique, the pits are also formed in the places with markings, however not as many pits as in laser process were found.

In Figure 5, pits of different sizes and rounded shapes are shown, associated with the marking rings; that is, despite the "smoother" appearance produced on the surfaces by the pantograph, the markings constitute discontinuities and become regions prone to initiation of localized corrosion attack.

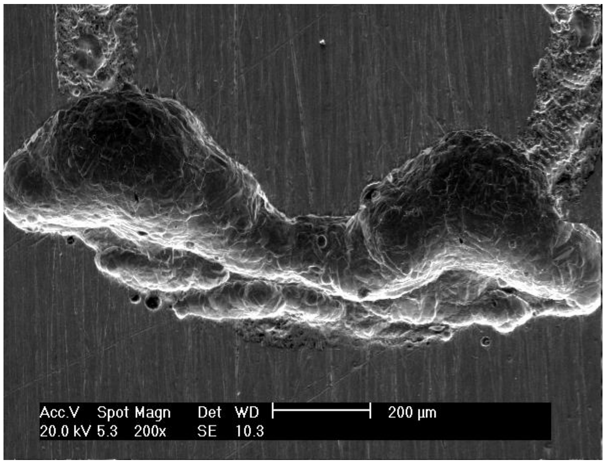

Fig. 4. Crevice magnification for Fig.3 at the laser marking ring

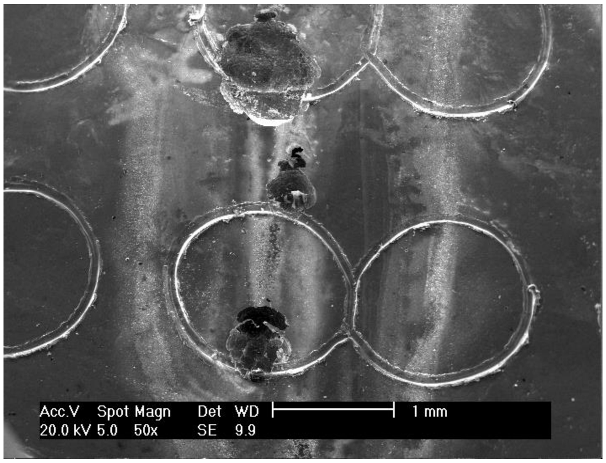

Fig. 5. SEM image of pantographic marked specimen, after electrochemical test, showing pits in the engravings

In Figure 6, an arising pit on a ring marked by mechanical technique is shown, as highlighted in the central region. In this micrograph, the association of the beginning of the pitting corrosion mechanism with the marking area is evident. The sudden change in the surface finish is a decisive factor for starting the corrosion process, which propagates autocatalytically. Figure 7 presents an enlargement of the pit shown in Fig. 6. The ring engraving constitutes a discontinuity in the surface finish for the biomaterials specimens. These two types of processing for identification cause topographic changes. In this sense, the roughness analysis produced by these techniques will be evaluated later and presented in future works.

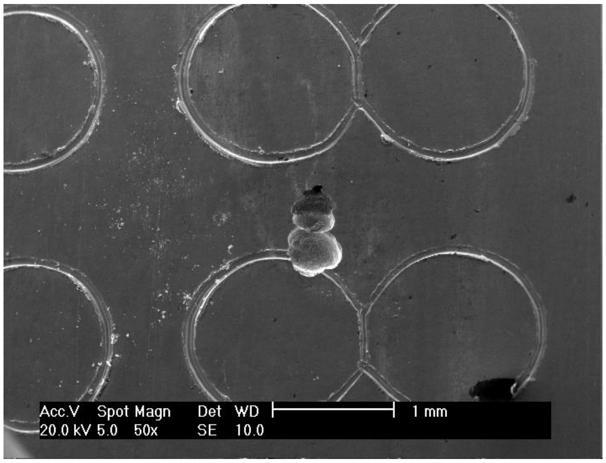

Fig. 6. Image obtained by scanning electron microscopy (SEM) for a biomaterial with pantographic markings, after electrochemical test, showing a pit located at the engraving

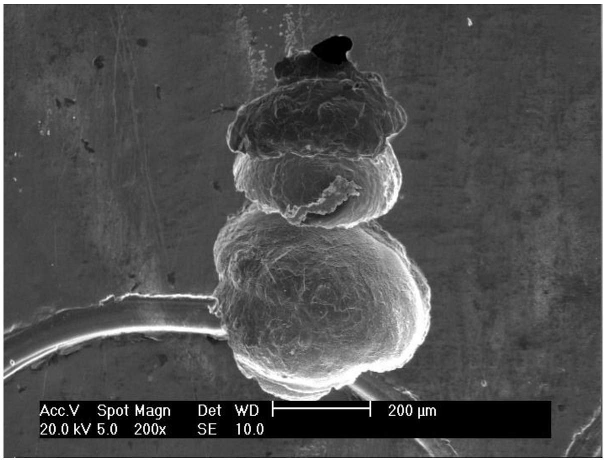

Fig. 7. Magnification of a corrosion pit found in the region of the pantographic marked ring

In this study, it was evident that the two types of markings evaluated produced a deleterious effect on the localized corrosion resistance. The decrease in corrosion resistance was more accentuated by laser beam-treated specimens. This is due to the temperatures reached by the beam, which are sufficient to melt the surface and the rapid extraction of heat from them, explained by the duration of each pulse, which is in the order of nanoseconds.

The laser beam incidence sites, in addition, have greater roughness, become essentially anodic zones [7, 8, 16], which favors the onset of corrosion processes.

The need to present qualitative results and to evaluate aspects of identification of visual alterations on the biomaterials surfaces is important because it supports the results obtained through the electrochemical techniques with accelerated tests.

According to the ABNT NBR 15613-2: 2010 standard, the tests must be accelerated to obtain responses in a timely manner, which would otherwise be impractical by conventional techniques, since, by immersion it would imply a loss of negligible mass.

The fact that the result of the biomaterial is compared with itself enables a paired analysis. There is no point in comparing with other types of biomaterials with different natures, and the comparison with other metallic alloys should consider biocompatibility, biofunction, physical, chemical and metallurgical characteristics, properties, type of processing, performance, applications, cost and market availability.

IV. CONCLUSIONS

The markings evaluated in this work represent discontinuities on the biomaterials surfaces. Electrochemical tests indicate that the pitting corrosion mechanism is accentuated in samples with laser marks, and less accentuated in samples with pantographic marks. Regions with crevice corrosion were observed in the laser marked specimens, explained by the differential aeration resulting from the topographic alteration generated by the laser beam.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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