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Impact of surface treatment on the corrosion resistance of ASTM F138-F139 stainless steel for biomedical applications

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Abstract

AISI 316 LVM stainless steel type considered in ASTM F138 and F139 standards for implant devices is widely used, in particular for orthopedic surgery, because it combines good biofunctionality and acceptable biocompatibility at low costs. Adequate interaction of these materials with the human body and its capability to reach the desired service level are determined by the surface preparation. The goal of the present work is to relate the surface roughness parameters with the localized corrosion resistance of AISI 316 LVM stainless steel grit blasted for different times and passivated with nitric acid. At intermediate blasting times the roughness parameters attain an extreme value and this surface condition corresponds with the maximum pitting corrosion resistance.

Keywords: 316 LVM stainless steel; glass beads blasting; roughness parameters; corrosion; nitric acid passivation.

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1. Introduction

There are different procedures established for the surface treatment of biomaterials, some of which depend on the particular application, like orthopedic surgery. The biofunctional behavior of these implant materials are generally governed by volume properties but the interaction with the biologic medium is determined by the characteristics of the surface films. Then to obtain the best performance of these biomaterials with different surface treatments and/or coatings it is necessary to initially characterize chemistry composition, micro and/or nanostructures, roughness, film thickness of the surface layers, and then correlate the information with physicochemical properties, biocompatibility, corrosion resistance, etc.

Bead blasting is widely used and studied as surface treatment for Ti c.p. and Ti6Al4V implants (Aparicio et al., 2003, Arvidsson et al., 2006, Barranco et al., 2007, Barranco et al., 2010). For stainless steel as biomaterials there are comparatively less number of studies of its use (Multigner et al., 2010, Multigner et al., 2009) although there are several studies for different applications (Faller et al., 2005, Otsubo et al., 2003, Rhouma et al., 2001).

Glass bead blasting uses small abrasive particles propelled by an air stream to impact on the surface at fixed pressure and blasting time. Generally speaking, the process generates several surface and subsurface modifications (ASM International Metals Handbook 1996). They could be of a chemical nature (Barranco et al., 2007), related to microstructure like grain refinement (Multigner et al., 2010, Multigner et al., 2009) or associated with mechanical properties like hardness or compressive residual stress (Multigner et al., 2010, Multigner et al., 2009, Otsubo et al., 2003, Rhouma et al., 2001). Considering that shot peening enhance fatigue resistance (Azar et al., 2010, Mahagaonkar et al., 2009) and the surface modifications mentioned before, it is expected that blasting could achieve a beneficial impact as in Ti c.p. (Javier Gil et al., 2007, Jiang et al., 2006). Another effect related to blasting is the increase in surface roughness. The extent of these modifications depends on the following process parameters: glass bead size, shape and chemical composition, pressure and blasting time (ASM International Metals Handbook 1996). After blasting, either chemical passivation or electropolishing are applied as final treatment on the blastinized surface to achieve an effective cleanness and increase corrosion resistance (Faller et al., 2005).

Moreover, biomaterials surface finish or final surface topography, impacts on interaction with tissues (Wennerberg et al., 2009) and on corrosive degradation by biological fluids (Ratner et al., 1996). Biological environment is considered corrosive for metallic implants. Corrosion also plays an important role in biocompatibility since release of corrosion products or metallic ions of a non biocompatible nature could cause adverse reactions to the host organism, like hypersensitivity, inflammation or cytotoxicity (Ratner et al., 1996, Singh et al., 2007). Furthermore, corrosion could cause integrity lost of the implant rendering it no longer functional and decreasing its service life (Ratner et al., 1996, Singh et al., 2007).

Analysis of surface finish is based on the determination of a parameters set that characterize surface topography. These parameters give information about amplitude properties (for example, average roughness Sa or Sq) and functional properties (contact area, fluid retention, among others). Relevance of each parameter has to be considered in the frame of each new situation or interaction. In general, results obtained by different researchers are difficult to compare when surface characterization is improperly performed (Wennerberg et al., 2009).

Regarding to the electrochemical behavior, establishing the link between blasting parameters and corrosion resistance still requires decisive experimental evidence. There are works from the literature dealing with medical devices in Ti c.p. (Aparicio et al., 2003) and Ti6Al4V (Barranco et al., 2010) and for other applications in AISI 304 (Faller et al., 2005) and AISI 316 (Rhouma et al., 2001). In vitro electrochemical studies allow carrying out tests in controlled environments and provide methods to predict corrosion behavior and design materials for surgical applications (ASM International Metals Handbook 1987).

The aim of this work is to evaluate the relationship between roughness parameters and pitting corrosion resistance. To this end we use AISI 316 LVM stainless steel samples with different surface preparations that are based on blasting with silica spherical particles.

2. Experimental

AISI 316 LVM stainless steel plates (0.019 %C, 1.86 %Mn, 17.29 %Cr, 2.77 %Mo, 14.34 %Ni, 0.36 %Si, 0.017 %P, 0.001 %S, 0.14 %Cu, 0.086 %N) were bead blasted for 30 sec, 2 min and 5 min with silica particles ranging from 30 to 160 µm in diameter at 5 Kg/cm^2 pressure. These samples were then chemically passivated in 20% HNO_3 (v/v) for 60 min (BP30s, BP2m, BP5m, respectively). Results were compared with those of samples subjected to mechanical polishing with 6 µm diamond paste with and without the same passivation treatment (MPP and MP, respectively). Cyclic potentiodynamic (CP) polarization curves were recorded at a scan rate of 13.8 mV/s between -1.2 V and 1.2 V. A conventional three electrode cell was used with a platinum foil as counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Before each measurement, the samples were painted with epoxi paint exposing ca 0.4 cm^2 uncovered area. Current density was calculated using the geometric area because the real area varies between different superficial treatments. Electrochemical experiments were performed in deaerated Ringer's solution: 8.6 g/L NaCl, 0.3 g/L KCl, 0.33 g/L $CaCl_2$ thermostated at 37 ± 1ºC. After each measurement optical microscopic observations were made to guarantee data free from crevice corrosion attack. Pitting potentials (Ep) were considered as the potential at which the current density reached 200 $\mu A/cm^2$.

Roughness analysis was performed using a scanning electron microscope (SEM) Philips SEM 505 equipped with a digital scanning interface ADA II and a Scandium SIS Image Analysis Software. The working voltage was 25 kV and the spot size was 200 nm. Ten stereo pairs were obtained at 203X magnification on each blasted and passivated sample and were processed to obtain roughness parameters (RP) with EZEImage Program (Ponz et al., 2006).

3. Results and Discussion

Figure 1 shows typical curves according to CP polarization measurements that confirm, in every case, initiation and propagation of pitting corrosion during the forward scan and repassivation during the reverse scan. Nitric acid treatment (MPP) that enhances pitting corrosion resistance compared to samples without passivation treatment (MP) exhibits more anodic pitting potentials (Ep) (Table 1). Blasted and passivated samples show the following sequence according to their pitting potentials: BP2m>BP5m>BP30s. The surface condition showing highest pitting corrosion resistance was MPP. Blasting and chemical passivation treatment does not generate a significant reduction in pitting corrosion resistance of 316 LVM samples for conditions BP2m and BP5m since the reduction in Ep in comparison with condition MPP amounts to 12 and 49 mV, respectively. These values are within the standard deviation range for the measurement (Table 1).

There is a large variety of parameters that can be used to describe surfaces but because many of them are not wholly reliable to use and interpret, we decided to use in this work only the most relevant ones. Table 2 shows parameters included in EZEImage Program and their meaning. Except for Sigma, all the parameters were measured from the least squares mean plane. Sa (Ra in the one-dimensional case) was included because is widely used for describing surface roughness (Aparicio et al., 2003, Arvidsson et al., 2006, Barranco et al., 2007, Faller et al., 2005, Multigner et al., 2010, Multigner et al., 2009, Otsubo et al., 2003, Rhouma et al., 2001). However, it is important to emphasize that the use of this parameter alone does not always allow thorough quantification of the surface roughness.

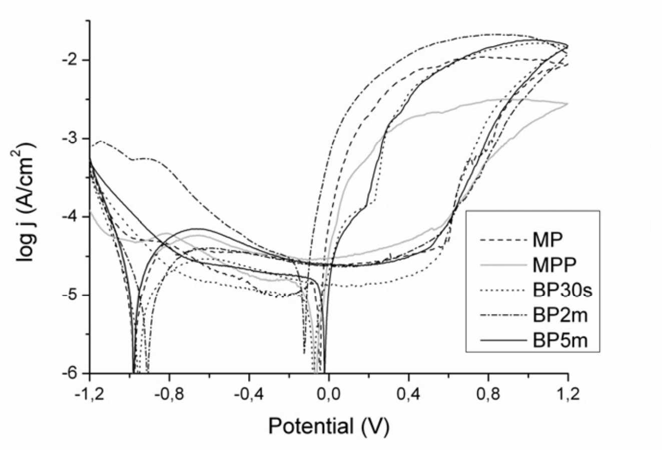

Fig. 1. CP polarization curves for the different surface treatments employed (see text for the definitions of the abbreviations in the inset).

Table 1. Pitting potential values (Ep/V) and standard deviations for the different surface treatments employed (see text for the definitions of the abbreviations in the column headings).

	MP	MPP	BP30s	BP2m	BP5m
Ep	0.640	0.705	0.624	0.693	0.656
Standard deviation	0.006	0.019	0.027	0.010	0.019

Table 2. Commonly used parameters on roughness measurements.

Parameter	Description
Sigma	Root-mean-square deviation of surface topography (measured from the plane which contain the tilt axis)
Sq	Root-mean-square deviation of surface topography (measured from the least squares mean plane)
Sa	Arithmetic mean deviation of surface topography (measured from the least squares mean plane)
Ssk	Skewness of topography height distribution
Sku	Kurtosis of topography height distribution
Sz	Ten-point height of surface topography
Sbi	Surface Bearing Index
Sci	Core Fluid Retention Index
Svi	Valley Fluid Retention Index

In the present work we studied the behavior of amplitude parameters Sq and Sa and functional parameters Sbi, Sci and Svi. Sq and Sa provide surface geometric information. Sbi, Sci and Svi describe characteristics relevant to specific applications like fluid retention, wear, lubrication, among others (Dong et al., 1994). For surgical implant surfaces, the study of the latter parameters is necessary because the volume of fluid that a surface can retain has an impact on the subsequent bone apposition.

Table 3 shows RP values obtained for blasted and passivated samples. BP2m and BP5m conditions show larger values of Sq and Sa while BP30s exhibits smaller values, being the difference between the values for conditions BP2m and BP5m smaller than between BP30s and either BP2m or BP5m. Regarding functional parameters, results show that Sbi and Sci were more sensitive to the different surface characteristics of the samples. This is in agreement with Arvidsson et al. (Arvidsson et al., 2006) although they propose that only Sci should be taken into account. Moreover, functional parameters values obtained for BP2m condition agree with values reported for two Ti c.p. commercial dental implants (Straumann SLA y Friadent XiVe) (Arvidsson et al., 2006).

Figures 2a), 2b) and 2c) show surface texture for conditions BP30s, BP2m and BP5m, respectively. BP2m and BP5m conditions exhibit similar morphological appearance while BP30s condition results in a less rough morphology.

Figure 3a) shows Sa, Sq, Sci, Sbi and Ep values normalized according to the 30 sec value as a function of the blasting time (San, Sqn, Scin, Sbin and Epn, respectively) for blasted and passivated samples. Localized corrosion resistance increases as Sa, Sq and Sci parameters increase and for BP2m all parameters take their largest values. On the other hand, Sbi varies in the opposite way, as shown in (Arvidsson et al., 2006) for blasted samples. According to the presented results, we indicate preferential use of the functional parameter Sbi for roughness characterization because it exhibits superior matching with the others parameters according to the blasting time. Figure 3b) shows the relationship between Epn and Sqn, San, Scin and Sbin and it shows that Sa and Sq variations are so similar that it is enough to use only one of them.

Studies made on blasted Ti c.p. with different particle size (Arvidsson et al., 2006, Wennerberg et al., 1996) show that surfaces with a lower Sci value (core fluid retention index) had the best bone fixation and the higher bone to metal contact in *in vivo* tests. The same research group (Wennerberg et al., 2009) established that the optimum Ra value for best bone apposition lies between 1 and 2 μm. Comparing RP values obtained in the present work with those proposed in (Arvidsson et al., 2006, Wennerberg et al., 2009) as optimum values with respect to an improved biological response, it can be seen that for condition BP2m even though Sa lies within the recommended range, Sci value is much larger than that found by Arvidsson et al. (Arvidsson et al., 2006) (1.36). The reason of this difference is that surface treatments were performed under different conditions (Giljean et al., 2010).

Table 3. Selected roughness parameters (RP) obtained with scanning electron microscope (SEM).

Parameter	BP30s	BP2m	BP5m
Sq	1.091 μm ± 0.011	1.348 μm ± 0.024	1.290 μm ± 0.034
Sa	0.860 μm ± 0.007	1.076 μm ± 0.018	1.028 μm ± 0.028
Sbi	0.619 ± 0.005	0.603 ± 0.005	0.611 ± 0.005
Sci	1.537 ± 0.015	1.575 ± 0.015	1.553 ± 0.015
Svi	0.112 ± 0.003	0.111 ± 0.003	0.112 ± 0.003

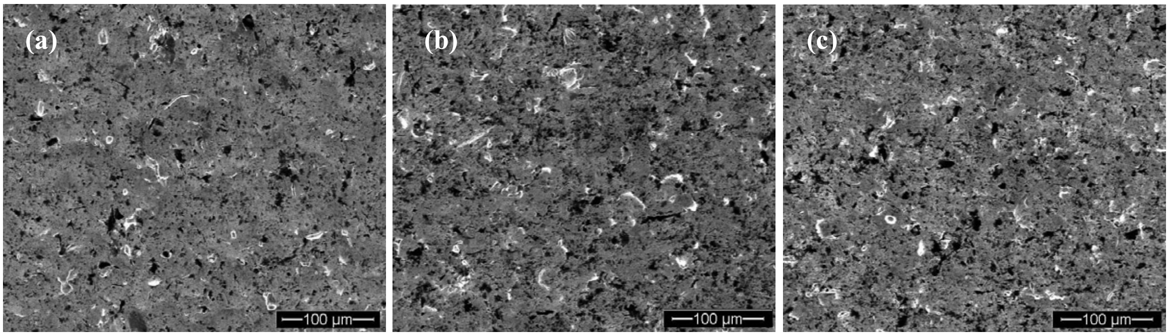

Fig. 2. SEM images of samples (a) BP30s; (b) BP2m; (c) BP5m.

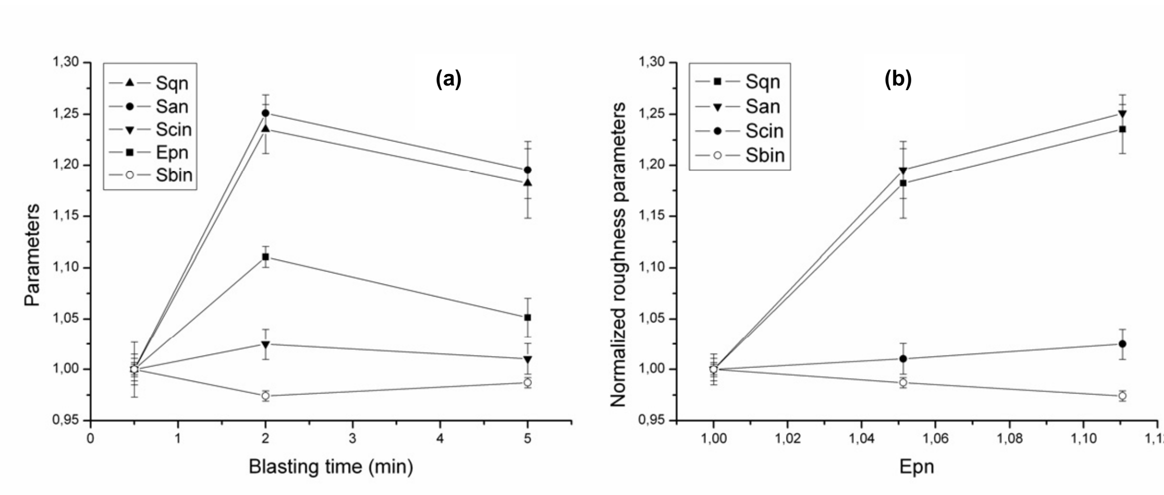

Fig. 3. Ep and RP values normalized according to 30 sec value (a) as a function of the blasting time; (b) relationship between Epn and RPn.

On the other hand, studies of the relationship between pitting corrosion and characteristics of blasted surfaces are focused on the effect of varying particle diameter and/or composition (Barranco et al., 2010, Faller et al., 2005, Rhouma et al., 2001) but not blasting time. These works show that the effect of blasting is a decrease in Ep (in all cases the samples were not passivated). In (Faller et al., 2005) the authors emphasize that the use of just amplitude parameters Ra, Rz (equivalent to Sz but related to the inclination plane of the sample) and Rmax (maximum height) do not allow correlating corrosion behavior of surfaces with different surface treatments, since for similar values of these parameters they found marked differences in Ep values.

Consequently we emphasize the importance of selecting an adequate set of roughness parameters for characterizing surface treatments of biomaterials in order to be able to correlate biocompatibility data with design parameters for the treatments. Also, bearing in mind that blasting improves some surface properties of the implant like fatigue strength, and under optimal conditions favors biocompatibility, we point out that it is possible to reach blasting plus passivation conditions leading to surfaces with corrosion resistance similar to that obtained with mechanical polishing plus passivation treatments but with improved general behavior of the implant.

4. Conclusions

Blasting time variation has a clear influence on RP (Sci, Sbi, Sa and Sq) and Ep values. Blasting times in the range 30 sec to 2 min exhibit a significant effect on the roughness parameters while within the range from 2 to 5 min it does not appreciably change Sa and Sq parameters.

Ep values of BP2m and BP5m conditions were similar to MPP condition. Thus, it is possible to obtain higher surface roughness without an appreciable loss in pitting corrosion resistance. In this sense, higher roughness could profit biofunctional behaviour of several implants.

Ep and RP showed a relationship and an extreme value at BP2m.

Roughness parameters studied show marked differences for each blasting time. Working with Sci, Sbi and Sa is suggested because Sq and Ra are quite similar but the latter is more widely used by other researchers, what, in turn, enables a comparison to be made for similar process conditions.

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