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A study on corrosion resistance of ISO 5832–1 austenitic stainless steel used as orthopedic implant

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Abstract: **The ISO 5832–1 austenitic stainless steel used as biomaterial is largely applied in the area of orthopedics, especially in the manufacture of implants, such as temporary or permanent replacement of bone structures. The objective of this study was to evaluate the localized corrosion resistance of the ISO 5832–1 stainless steel used in orthopedic implants by electrochemical tests in two different solutions. The results of this study are of great interest to evaluate the corrosion of metallic implants that can result in the release of corrosion products into bodily fluids causing possible adverse biological reactions. The determination of the chemical elements in the composition of the ISO 5832–1 stainless steel was performed by neutron activation analysis (NAA). The samples for electrochemical tests were grinded with silicon carbide paper up to #4000 finishing, followed by mechanical polishing with diamond paste. The open circuit potential measurements and anodic polarization curves were obtained in solution of 0.90 wt. % of NaCl and of simulated body fluid (SBF). The results indicated that the ISO 5832–1 stainless steel presented a high resistance to crevice corrosion in simulated body fluid solution but high susceptibility to this form of corrosion in the chloride solution.**

Keywords: **Metallic biomaterials. Austenitic stainless steel. Localized corrosion. ISO 5832–1 alloy.**

Introduction

Biomaterials are described as "any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body", by National Institutes of Health (NIH) from USA, according to Hastings[1]. Many definitions have been used for biomaterials, however the NIH definition is commonly the most accepted[2].

Nowadays in the biomaterials industry, there is a growing variety of devices and materials that are being developed to be used in the treatment of diseases and injuries. Consequently, the definition of biomaterials has been expanded[3].

Austenitic stainless steels (AISI 316L), mainly those produced according to ISO 5832–1[4], have been used to meet the high demands for biomaterials for use in orthopedic prostheses due to their performance, mechanical strength and corrosion resistance when compared to titanium and Cr–Co alloys[5]. In medical field, austenitic stainless steels are widely used in plates (used in fracture treatment), screws, parts of total hip replacements, among others[6].

In view of the above, there is a great interest to determine elements present in ISO 5832–1 stainless steel, as well as to evaluate the localized corrosion resistance when exposed in NaCl and simulated body fluid (SBF) solutions.

Several analytical techniques are applied in elemental analyses of metallic alloys, such as atomic absorption spectrometry (AAS)[7], inductively coupled plasma atomic emission spectrometry (ICP–AES)[8], UV–Visible spectrophotometry[9] and neutron activation analysis (NAA)[9–12].

In this study, neutron activation analysis (NAA) was used due to its several advantages, such as high sensitivity for the detection of elements, multi–elemental determination, good precision and accuracy of the results and this technique does not require the sample dissolution.

Among the studies about applications of NAA in the analyses of biomaterials, Cincu et al.[13] analyzed biomaterials used in dental clinics to verify the influence of corrosion products released of these materials on patient health. Their results of dental materials analyses indicated the presence of nickel that is an allergenic and toxic element, besides the results showed that these types of biomaterials were well tolerated by patients over a five–year period.

Giordano et al.[14] analyzed the electrochemical behavior of two biomaterials applied to orthopedic implants in 0.90 % sodium chloride (NaCl) solution. The materials analyzed were austenitic stainless steel according to ASTM F 138 and ISO 5832–9. The polarization tests presented that the ASTM F 138 steel is less corrosion resistant than the ISO 5832–9 steel. The higher corrosion resistance of ISO 5832–9 stainless steel is due to increase stability of the passive film and the high tendency to repassivate.

The objective of this study was to determine elemental concentrations in ISO 5832–1 stainless steel and to evaluate its localized corrosion resistance in 0.90 % of NaCl and body fluid simulated solutions by electrochemical tests.

EXPERIMENTAL

Neutron activation analysis (NAA) procedure

Samples of ISO 5832–1 austenitic stainless steel were purchased in the form of bar from Villares Metals S/A. For neutron activation analysis of the steel, sample was obtained in the form of chips (smaller than 1 cm).

These chips form was cleaned to eliminate eventual impurities originating from the equipment used for cutting the material.

To apply the comparative method of NAA, synthetic elemental standards were prepared. The certified standard solutions of the elements provided by Spex CertiPrep Chemical USA were diluted and single or multielement solutions were prepared. Aliquots of these solutions were pippeted onto sheets of Whatman filter paper.

NAA procedure used is described in a previous work of Braguin[15]. For irradiation, about 50 mg of the sample were weighed in polyethylene envelopes.

In the short irradiation procedure, sample and elemental standards were placed in a new polyethylene envelope positioned inside a polyethylene device and irradiated at the IEA–R1 reactor of the Institute for Energy and Nuclear Research for a period of 5 s under a thermal neutron flux of 1.9×10^{12} n cm^{-2} s^{-1}.

In the irradiations of 1 h, samples and synthetic standards were

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individually wrapped in aluminum foil, and irradiated in an aluminum device at the IEA–R1 reactor under a thermal neutron flux of 4.5 x 10^{12} n cm^{-2} s^{-1}.

Gamma ray activity measurements of radioisotopes were carried out using a GC3020 Model hyperpure germanium semiconductor detector coupled to a digital spectrum analyzer (DSA 1000), both from Canberra and a microcomputer. For data acquisition and its processing, the software Genie 2000 version 3.1 from Canberra was used. This program provides data of counting rates and gamma energies. The radioisotopes of the gamma spectra were identified by gamma ray energies and half–life. The elemental concentrations were calculated using the Equation (1)[16].

$$C_s = [m_{st}. A_s. e^{0.693(tds - tdst)/t1/2}] / [M_s A_{st}] \quad (1)$$

where the indices s and st refer to sample and standard, respectively; Ms = total sample mass; mst = mass of the element in the standard; Cs = concentration of the element in the sample; t1/2 = half–life of the radioisotope considered; td = decay time; As = counting rates of the considered radioisotope in the sample for decay time tds; Ast = counting rates of the considered radioisotope in the elemental standards for decay time tdst.

The quality control of the results was evaluated by the analysis of two certified reference materials, SRM 363 Steel Cr–V Modified, from the National Institute of Standards and Technology (NIST), USA[17] and the B.C.S/ S.S No. 467 Austenitic Stainless Steel from the BCS[18]. These results were presented in previous publication[15] and they showed good precision and accuracy, with relative standard deviations below 15.0% and values of | Zscore | $\leq$ 2 for most of elements.

Treatment of the data obtained by neutron activation analysis

The results of the elemental concentrations in the alloy were evaluated calculating statistical parameters of arithmetic mean (), standard deviation (SD) and relative standard deviation (RSD).

Corrosion test procedure

For the corrosion study, the ISO 5832–1 austenitic stainless steel was cut to obtain the sample with the dimensions of 38 mm x 18 mm x 6 mm (length, width and thickness, respectively).

The sample for electrochemical tests was grinded with silicon carbide paper up to #4000 finishing, followed by mechanical polishing with 1 µm diamond paste. After applying this polishing process, the sample was cleaned with alcohol, and then dried with a hot air jet.

The corrosion testing of ISO 5832–1 stainless steel was performed using the Gamry Reference 600+ equipment. The experimental arrangement of the electrochemical cell consisted of three electrodes, a platinum counter electrode, an Ag/AgCl (KCl 3M) reference electrode and a working electrode with exposure area of 0.5 cm^2. A rod of polymeric material was placed to increase susceptibility to crevice corrosion.

The stainless steel sample was immersed in a volume of 40 mL of each type of electrolyte solution at room temperature. The electrolytes used were 0.90 % mass of NaCl solution and simulated body fluid (SBF) solution. The preparation of the SBF was performed according to the procedure described by Kokubo and Takadama[19], but with the use of purified water instead of distilled water. The NaCl and SBF solutions were placed in polyethylene bottles and kept in a refrigerator.

The electrochemical tests used in this study were open circuit potential (OCP) measurements as a function of time of exposure to test solution and anodic polarization tests. The surface of stainless steel exposed to the corrosive medium was later analyzed by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Table 1 presents the results obtained from the analysis of ISO 5832–1 stainless steel using NAA. In this Table the mean elemental concentrations with their standard deviations, relative standard deviations, and sample specification data[4] are presented.

The concentrations of the elements Cr, Cu, Mn, Mo and Ni obtained in the ISO 5832–1 alloy are within of their specification range presented by ISO[4]. In this study As, Co, V and W elements not presented in the specification of this material were also determined. The results obtained for this alloy presented a relative standard deviation lower than 13.7 % indicating a good precision of the results.

Table 1. Concentrations of elements obtained for ISO 5832–1 austenitic stainless steel.

Element	(± SD)[a]	RSD[b], %	ISO 5832–1[4]
As, µg g–1	15.0 ± 1.5	10.2	
Co, µg g–1	213.8 ± 4.3	2.0	
Cu, %	0.0427 ± 0.0025	5.8	0.5 max
Cr, %	17.06 ± 0.61	3.6	17.0 – 19.0
Fe, %	62.6 ± 2.1	3.3	
Mn[c], %	1.60 ± 0.12	7.6	2.0 max
Mn[d], %	1.764 ± 0.025	1.4	2.0 max
Mo, %	2.49 ± 0.33	13.3	2.25 – 3.00
Ni, %	13.3 ± 1.3	9.5	13.0 – 15.0
V, µg g–1	352.5 ± 7.9	2.2	
W, µg g–1	110 ± 15	13.7	

a. arithmetic mean and standard deviation from 3 to 5 determinations, b. relative standard deviation, c. results of five–second irradiation, d. results of one–hour irradiation.

In the Figure 1 the open circuit potential variation curves for ISO 5832–1 austenitic stainless steel in 0.90% NaCl and SBF solutions are presented.

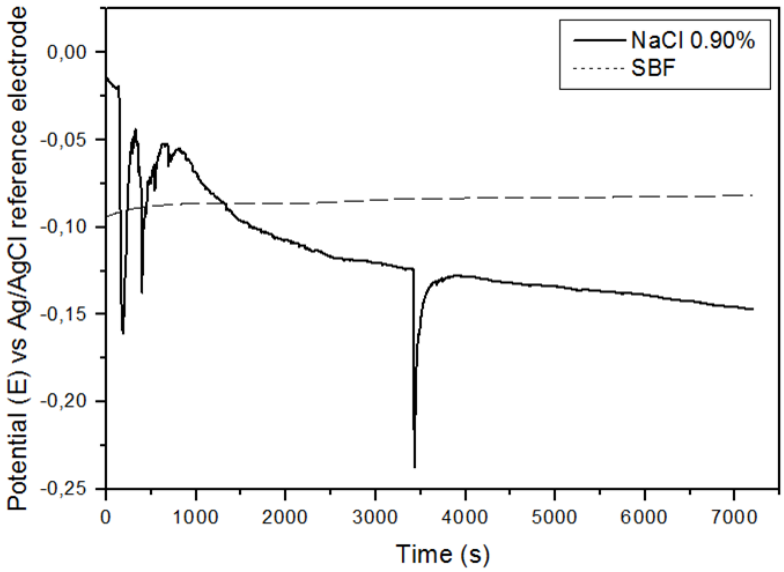

Figure 1. Variation of open circuit potential as function of the immersion time of ISO 5832–1 stainless steel in 0.90% NaCl and SBF solutions.

Figure 1 shows very stable potential values over time obtained using the SBF solution. Using NaCl solution, there were large potential oscillations, typical of localized corrosion. The tendency of potential decreasing with the time immersion indicated corrosive attack of the medium to the passive film, initially present on the steel surface.

The potential stability of the steel in SBF solution indicates that in this medium the passive film was preserved over the duration of the test and the medium was not aggressive enough to cause damage to the oxide layer.

Figure 2 shows the anodic polarization curves obtained potentiodynamically for ISO 5832–1 steel in NaCl and SBF solutions.

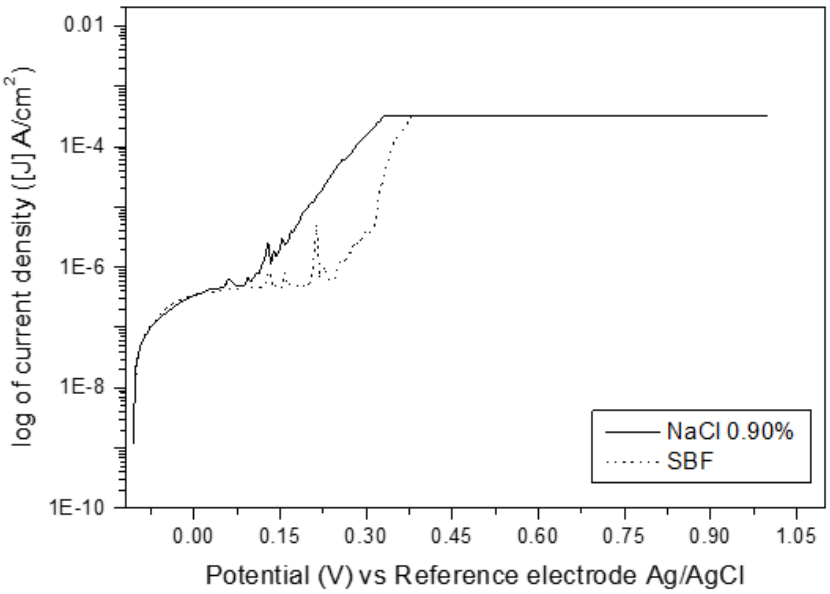

Figure 2. Potentiodynamic polarization curves of the ISO 5832–1 stainless steel in NaCl and SBF solutions.

The anodic polarization curves showed typical behaviors of passive materials from open circuit potential to passive film break potential, indicated by the gradual current increase. The passive film breaks potential were observed at potentials of about 0.12 V for NaCl solution, and of 0.25 V for the SBF solution. These results confirm that open circuit potential measurements showed a higher tendency to localized corrosion associated with chloride medium.

The surfaces of the ISO 5832–1 steel samples obtained after electrochemical tests were analyzed by scanning electron microscopy (SEM) to characterize the morphology and sizes of the attacked areas and these are shown in Figures 3 and 4. Surface analysis of these Figures after the polarization test confirmed crevice corrosion on these surfaces. This was explained by the oxygen gradient due to the rod presence on the exposure area, causing crevice corrosion promoted by differential aeration cells.

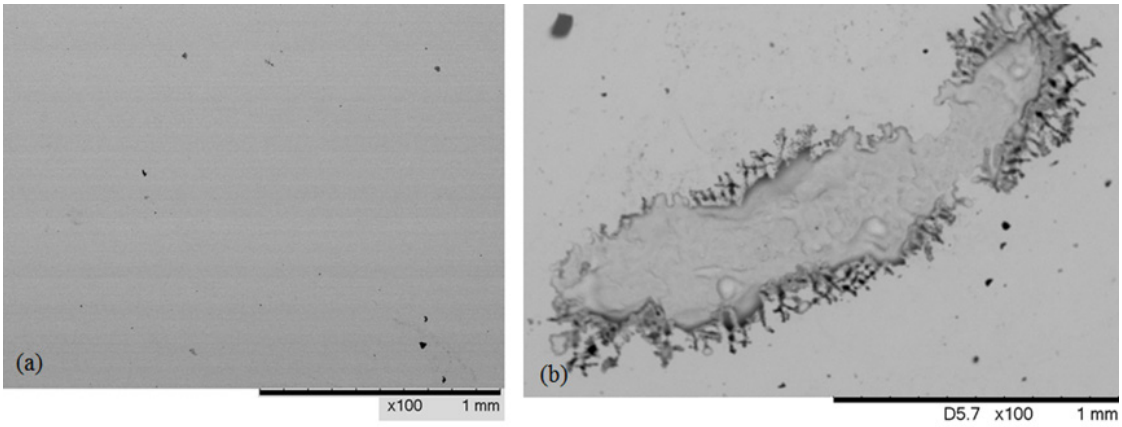

Figure 3. Micrographs obtained by SEM: (a) Surface of ISO 5832–1 steel polished before electrochemical testing; (b) Surface of ISO 5832–1 steel showing crevice corrosion after anodic polarization test in 0.90% NaCl.

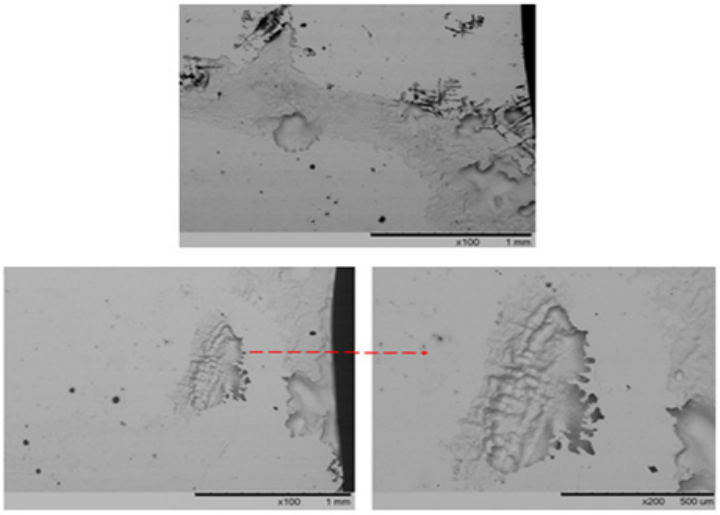

Figure 4. Micrographs obtained by SEM of the corroded region on the surface of the polished sample of ISO 5832–1 steel after polarization test in SBF solution showing crevice corrosion.

The comparison of the micrographs of the Figures 3 and 4 shows that the areas attacked by crevice corrosion were higher in the case of NaCl solution than that in SBF solution. These results are in agreement to the Figure 1 and Figure 2 of electrochemical tests.

Conclusions

The obtained results allowed concluding that the NAA technique can be properly applied in the determination of the chemical elements present in the ISO 5832–1 austenitic stainless steel. Cr, Cu, Mn, Mo and Ni results determined in this alloy are within the specification of this steel. In addition, elements As, Co, V and W that are not shown in the specification of this material were determined.

Corrosion tests have shown that ISO 5832–1 steel presents different behavior between NaCl and SBF solutions. The highest susceptibility to crevice corrosion was verified in NaCl solution, but in SBF solution this alloy showed resistance to this type of attack.

Acknowledgments

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