Electrochemical behaviour and microstructural characterization of different austenitic stainless steel for biomedical applications

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Abstract
Austenitic stainless steels, specified as ASTM F138, ASTM F1586, and ASTM F2581, underwent a comparative study, including the analyses of microstructure, crystalline phases, and Vickers microhardness. The corrosion resistance was investigated by anodic polarization curves and electrochemical impedance spectroscopy using the 0.9% NaCl solution and simulated body fluid (SBF). All samples exhibited only the austenite phase and the Vickers microhardness was influenced by high nitrogen content addition. Independent on the electrolytic solution type, the ASTM F1586 and ASTM F2581 steels had better corrosive resistance performance from the anodic polarization results. However, ASTM F2581 steel presented the passive film with better protective capacity in the saline solution while ASTM F1586 had better performance in the SBF.

1. Introduction

Metallic biomaterials have been extensively used in biomedical applications as joints replacements, bone plates, screws, stents, intramedullary nails, spinal fixations, and spacers, wires, and dental implants [1–4]. When compared to other materials (namely polymers and ceramics), they own superior properties required for structural elements. However, long-term use is still a challenge once these materials should bear the aggressiveness of the environment. The degradation could come from different conditions as corrosion, wear, tribocorrosion, and stress [5–8]. The main materials used for the manufacture of metallic bone implants are titanium and its alloys, Co–Cr alloys, and austenitic stainless steels. Therefore, metallic materials should have exceptionally high corrosion resistance, compatibility with the biological environment, low modulus of elasticity, wear-resistance, and the absence of ferromagnetism [9–11].

Austenitic stainless steel is the most popular metallic biomaterial used as biomedical implant due to its low cost, easy processing, stiffness, and reasonable chemical stability than the Co–Cr alloys, pure Ti, and Ti alloys [12]. However, stainless steels are considered inferior to Ti and Co alloys regarding biocompatibility, osseointegration and corrosion resistance [13]. Due to the good mechanical and ductility properties, the austenitic stainless steels are still widely used as screws, nails, and fracture plates to provide temporary support, being later surgically removed after the bone fracture healing process. The main problem linked to the stainless steel is the harmful effect of metal ions and fretting debris, which may be released from the implanted device due to the occurrence of corrosion and wear processes [6, 14, 15]. In this case, nickel is considered as the main harmful element released into the human body, leading to allergic reactions, teratogenicity and carcinogenicity [16–19].

Different austenitic stainless steels were considered overtime to surgical devices and implants applications. The 316 L steel has been replaced by the ASTM F138 steel due to its best mechanical and corrosion performance [20]. Then, the ASTM F1586 steel was developed, which has lower levels of nickel to minimize the undesirable
The high corrosion resistance of the austenitic stainless steels is owed to the formation of a thin oxide film on its surface. Nevertheless, this protective layer, known as passive film, is highly susceptible to localized corrosion such as pitting, crevice and stress corrosion cracking [15]. The protection capability of the passive film depends on the chemical composition of the stainless steel and electrolytic environment [32–34]. At contact with body fluids, the implanted device surface reacts with water, complex organic compounds, and dissolved gases, leading to degradation and corrosive failure [33, 34]. Increasing nitrogen content in stainless steels improves the corrosion resistance by pitting and crevice [10, 20].

This work aimed to correlate the microhardness, microstructure, and corrosion resistance of three stainless steel (ASTM F138, F1586, and F2581), used as biomaterials in conditions that mimic the use in the human body. For this, a study of the electrochemical behaviour in 0.9% NaCl and simulated body fluid (SBF) was conducted by anodic polarization and electrochemical impedance spectroscopy at 37.0 °C.

2. Materials and methods

Three commercial austenitic stainless steel for orthopaedic implant applications were studied. The VI 138 and VI 58329 samples were manufactured by Villares Metals S.A. (Brazil), which were labelled as equivalent to the ASTM F138 and ASTM F1586 steels, respectively. The P558 (PANACEA) sample was produced by Bohler Edelstahl GmbH (Austria) and was labelled as equivalent to the ASTM F2581 steel. The metallurgical processing of these samples involved vacuum induction melting, electro slag remelting, solubilization, cold working and annealing. Samples had a bar-shaped with diameters between 14 and 16 mm. The bar was cut in disc-shaped and then the cross-section was subjected to a metallographic preparation.

Metallographic sample preparation involved the sanding steps using the silicon carbide (SiC) sandpapers with 150, 220, 320, 400, 500, 600, 1200 and 13 μm grain sizes. Shortly after that, they were cleaned in an ultrasonic bath with distilled water for 15 min and subsequently electrolytically polished in an oxalic acid solution 10% (H2C2O4, 2H2O) for 5 s under sulfuric acid solution (H2SO4), phosphoric acid (H3PO4) and glycolic acid. The electrolytic attack was carried out with a potential of 12 volts D.C. in Lectropol-Struers equipment following ASTM E 407-99. Microstructural analysis was conducted on the polished surface by scanning electron microscopy (SEM, TESCAN, model VEGA3 SBU). The average grain size was determined by the intercept method (ASTM E 112-10) using optical microscopy (Olympus CX 51).

Chemical composition was determined by optical emission spectrometry (OES, SPECTROMAXx). The crystalline phase was identified by X-ray diffraction analysis (XRD, Philips-PANalytical, Empyrean model) using the JCPDS card of Fe-γ n° 310619. The Vickers microhardness was determined by ASTM E92 standard, performing 30 measurements for each sample and using a load of 0.05 kgf (0.49 N) for 30 s (microhardness Shimadzu HMV-2). These three analyses were carried out on the polished surface without electrolytic attack.

The anodic polarization curve was determined by the anodic potentiodynamic polarization test using a typical three-electrode cell configuration. In this study, the austenitic stainless steel specimen acted as a working electrode, platinum as a counter electrode and the saturated calomel electrode as reference. Potentiodynamic polarization was performed at a scan rate of 0.333 mV·s⁻¹ in range among the corrosion (Ecorr) and pitting (Epit) potentials (Autolab potentiostat, μAutolab type III/FRA 2). Besides, the region of the polarization curve with current density values less than 10⁻⁵ A.cm⁻² was considered as a passive band.

The Nyquist diagram was determined by electrochemical impedance spectroscopy (Autolab potentiostat, PGSTAT 128 N) using the same typical three-electrode cell configuration employed in the anodic potentiodynamic polarization test. The measures were performed with frequencies varying from 10 mHz to 100 kHz and a perturbation amplitude of 10 mV. The Nyquist diagram and anodic polarization curve used working electrodes prepared according to the ASTM G 5-94 standard. That electrode consisted of a disc-shaped austenitic stainless steel sample embedded in epoxy resin and with a brass electrical contact. The cross-section of the electrode was sanded with a SiC sandpaper (grain size 600), aiming to the formation of an exposed metallic region with an area close to 1 cm².

reactions at the human body [6, 21, 22]. The low-nickel and high-nitrogen austenitic stainless steel, as the ASTM F2581 steel, has been considered an alternative important for orthopaedic applications [23, 24]. Nitrogen is an effective alloying element to increase the mechanical properties when is added bellow its solubility limit in the austenite phase [15, 19, 25]. This alloying element is a strong austenite phase stabilizer, as well as it reduces stacking fault energy and avoids the strain-induced martensite formation [15, 23, 24, 26–30]. Due to high austenitizing potential of nitrogen, the nickel amount in stainless steels may be reduced significantly, which is very important, since nickel ions lead to medical complications [19]. Though, the low-nickel stainless steel need high manganese content in its chemical composition to increase the nitrogen solubility and limits the Cr2N formation [28, 31].

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Two electrochemical solutions were used for the anodic potentiodynamic polarization and electrochemical impedance spectroscopy tests. The first solution is equivalent to saline (0.9% NaCl) with pH 8.4, which was prepared by the addition of distilled water and sodium chloride (Synth, 99% purity). The second solution with pH 7.3 is a simulated body fluid (SBF) proposed by Kokubo [35], where the chemical components were reagent grade. Table 1 describes the chemical composition of the SBF solution [35]. The corrosion tests were conducted with 250 ml of electrochemical solution at 37.0 ± 2 °C to simulate the human body temperature.

### 3. Results and discussion

#### 3.1. Chemical composition, microstructure, crystalline phase, and Vickers microhardness

The chemical composition of the ASTM F138, ASTM F1586 and ASTM F 2581 samples are shown in table 2. The first one was constituted mainly by Cr, Ni, Mo, and Mn elements, which corresponded to the austenitic stainless steel with the ASTM F138 specification. The Cr–Ni–Mo–Mn system also was observed in the second sample, but its Mn, Nb and N quantities were higher than that seen in the first sample (table 2). The chemical composition of this sample is equivalent to the austenitic stainless steel with the ASTM F1586 specification. For the third sample, the Ni content was reduced significantly compared to the first and second samples (table 2). Furthermore, this sample presented Nb absence, as well as high Mn and N quantities compared to the two first described samples. The chemical composition of such sample was associated with the austenitic stainless steel with the ASTM F2581 specification.

Figure 1 shows the SEM images of the ASTM F138, ASTM F1586 and ASTM F2581 samples with metallography preparation (polished surface and electrolytic attack). Grain boundaries and annealing twins were observed in the three samples, but carbides and other precipitated phases were not identified. The absence of carbides and other precipitated phases was supported by XRD analysis (figure 2), that identified only the austenitic phase (Fe–γ) in all samples. The solubilization heat treatment caused the dissolution of alloying elements.
elements into the austenitic matrix, while cold mechanic working, and annealing heat treatment led to the formation of a microstructure characterized by narrow grain distribution and annealing twins.

The ASTM F138, ASTM F1586 and ASTM F2581 samples exhibited average grain sizes ($G$) of $10.7 \pm 0.1$ ($\sim 8 \, \mu m$), $8.9 \pm 0.3$ ($\sim 14 \, \mu m$) and $5.4 \pm 0.1$ ($\sim 47 \, \mu m$), respectively. Although the addition of nitrogen restrings the grain growing in austenitic stainless steels [29, 30, 36], the grain size increased with nitrogen increasing in the chemical composition of the ASTM F138, ASTM F1586 and ASTM F 2581 samples (table 2). In this case, the difference in grain size was caused by the use of different processing parameters, since the annealing increasing temperature causes a significant grain growing in austenitic stainless steels.

Vickers hardness ($H_v$) as a function of the average grain size of the ASTM F138, ASTM F1586, and ASTM F2581 samples is shown in figure 3. Disregarding the differences in chemical composition and processing routes among the three samples studied, the Vickers hardness showed a tendency to increase with the raise in grain size. Although, the hardness and strength of austenitic stainless steels decrease with an increase in grain size [28, 37], disagreeing to results shown in figure 3. The Hall-Petch model is used to analyse the grain size dependence on

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Figure 1. Micrographs of secondary electrons of austenitic stainless steels, highlighting details of the matrix and grain boundaries. Electrolytic attack with oxalic acid 10%. (a) ASTM F138 sample; (b) ASTM F1586 sample and (c) ASTM F2581 sample.

Figure 2. XRD patterns of the three austenitic stainless steel samples. Fe-$\gamma$ is the austenitic phase.
The Hall-Petch equation expresses the Vickers hardness \( (H_v) \) as a function of grain size \( (G) \):

\[
H_v = H_{v0} + kG^{-0.5}
\]

where \( H_{v0} \) is hardness when the grain size is infinite, and \( k \) is a constant that represents the grain boundary as an obstacle to plastic deformation.

Figure 4 shows the grain size dependence on the Vickers hardness of the ASTM F138, ASTM F1586 and ASTM F2581 samples, following the Hall-Petch model (equation (1)). The hardness-grain size behaviour observed in figure 4 was the opposite of that reported in the literature \[18, 28, 36\]. This absence of grain size dependence on the hardness indicated that the grain-boundary hardening was little effective to improve the mechanical properties of austenitic stainless steels, implying the activation of solid-solution hardening. This latter hardening mechanism was triggered due to the high nitrogen content addition to the ASTM F1586 and ASTM F2581 samples, once nitrogen is a strong austenite phase stabilizer, reducing stacking fault energy, and avoids the strain-induced martensite formation \[15, 18, 28\]. Even with highest grain size, the ASTM F2581 sample obtained higher hardness than other samples (figure 3), indicating that the solid-solution hardening had a more beneficial effect on the mechanical properties than the grain-boundary hardening based on the Hall-
Petch model. Nevertheless, both hardening mechanisms must be considered during the austenitic stainless steels processing.

3.2. Anodic polarizations curves in saline and SBF solutions

Figure 5 shows the anodic polarization curves of the ASTM F138, ASTM F1586, and ASTM F2581 samples immersed in naturally aerated saline solution with pH 8.4 and at a temperature around 37°C. Additionally, the corrosion potential ($E_{\text{corr}}$), breakdown potential ($E_{\text{pit}}$), and current density ($j$) values determined from these anodic polarization curves are shown in table 3. In saline solution, all samples had spontaneously passivation and achieved $E_{\text{corr}}$ values around $-0.16 \, \text{V}$. Above this $E_{\text{corr}}$ value, the current density increased with increment in potential until 0.04, 0.01, and 0.07 V for the ASTM F138, ASTM F1586, and ASTM F2581 samples (figure 5), respectively. These different potentials ranges define the active anodic regions of the austenitic stainless steels immersed in saline solution. When the referred potentials were exceeded, the current density showed a small variation with an increase of potential until reaching the respective breakdown potentials ($E_{\text{pit}}$) of the ASTM F138, ASTM F1586, and ASTM F2581 samples (figure 5). The ASTM F138 sample has lower

![Figure 5. Anodic polarization curves of the different austenitic stainless steel samples immersed in naturally aerated saline solution with pH 8.4 and at a temperature around 37°C.](image-url)

| Sample | Parameter | ASTM F138 | ASTM F1586 | ASTM F2581 |
|--------|-----------|------------|------------|------------|
|        | $E_{\text{corr}}$ (V) SCE | $-0.16 \pm 0.01$ | $-0.17 \pm 0.01$ | $0.16 \pm 0.01$ |
|        | $E_{\text{pit}}$ (V) | $0.56 \pm 0.03$ | $0.90 \pm 0.01$ | $0.93 \pm 0.01$ |
|        | $j$ ($\mu\text{Acm}^{-2}$), $E_{\text{corr}} > 0.05$ V | $0.74 \pm 0.03$ | $1.06 \pm 0.01$ | $1.08 \pm 0.01$ |
|        | $j$ ($\mu\text{Acm}^{-2}$), $E_{\text{corr}} > 0.10$ V | $0.21 \pm 0.04$ | $0.11 \pm 0.01$ | $0.11 \pm 0.01$ |
| Saline solution (0.9% NaCl) | | | | |
|        | $E_{\text{corr}}$ (V) SCE | $-0.20 \pm 0.01$ | $-0.19 \pm 0.01$ | $0.22 \pm 0.01$ |
|        | $E_{\text{pit}}$ (V) | $0.62 \pm 0.04$ | $0.96 \pm 0.01$ | $0.97 \pm 0.02$ |
|        | $j$ ($\mu\text{Acm}^{-2}$), $E_{\text{corr}} > 0.05$ V | $0.82 \pm 0.05$ | $1.14 \pm 0.01$ | $1.19 \pm 0.01$ |
|        | $j$ ($\mu\text{Acm}^{-2}$), $E_{\text{corr}} > 0.10$ V | $0.28 \pm 0.15$ | $0.06 \pm 0.01$ | $0.06 \pm 0.06$ |
| SBF solution | | | | |

Table 3. Corrosion parameters obtained from the anodic polarization curves of the different austenitic stainless steel samples immersed in naturally aerated saline (pH = 8.4) and SBF (pH = 7.3) solutions at 37 °C.
breakdown potential \( (E_{\text{pit}} \cong 0.6 \text{ V}) \) than the ASTM F1586 and ASTM F2581 samples \( (E_{\text{pit}} \cong 0.9 \text{ V}, \text{ saline solution in table 3}) \). The regions of the anodic polarization curves in which current density had a low variation with the rise of potential are defined as passivation anodic regions. Knowing that passivity level increases with the increment of difference between the breakdown and corrosion potentials \( (E_{\text{pit}} - E_{\text{corr}} \cong 0.7 \text{ V}) \) than the ASTM F138 sample presented lower corrosion resistance \( (E_{\text{pit}} - E_{\text{corr}} \cong 1.0 \text{ V}, \text{ saline solution in table 3}) \). Therefore, when the ASTM F1586 and ASTM F2581 samples are immersed in saline solution, a good passivity is obtained for breakdown potentials up to around 0.9 V. From this value, there was a fast increase in current density, characterizing the transpassive anodic region. For the ASTM F138 sample, a good passivity occurred until around 0.6 V and then the current density raised quickly (figure 5). Above breakdown potential, the fast increase in current density may be indicative of the occurrence of pits formation on the passive film. The ASTM F1586 and ASTM F2581 samples exhibited the best passivity when exposed in saline solution at 37 °C, because the two samples resisted higher breakdown potentials than the ASTM F138 sample without the passive film suffer degradation by pits formation.

The anodic polarization curves were also obtained for the ASTM F138, ASTM F1586, and ASTM F2581 samples immersed in naturally aerated SBF solution with pH 7.3 and at a temperature around 37 °C, as observed in figure 6. In SBF solution, all samples were passivated spontaneously, and relatively similar \( E_{\text{corr}} \) values were observed \( (E_{\text{corr}} \cong 0.20 \text{ V}, \text{ table 3}) \). These \( E_{\text{corr}} \) values were slightly higher compared to the \( E_{\text{corr}} \) values determined for samples immersed in saline solution \( (E_{\text{corr}} \cong 0.16 \text{ V}, \text{ table 3}) \). The same behaviour was observed in the breakdown potential, once small variation in the \( E_{\text{pit}} \) values was verified among samples immersed in saline and SBF solutions (table 3). The \( (E_{\text{pit}} - E_{\text{corr}}) \) values were relatively similar between samples immersed in both solutions (table 3), showing a minor change in the corrosion behaviour of the three austenitic stainless steel. The ASTM F1586 and ASTM F2581 samples demonstrated a higher corrosion resistance than the ASTM F138 sample independent on the solutions studied. However, the onset of passivation between the ASTM F1586 and ASTM F2581 sample changed with the type of electrolyte solution, since this parameter was slightly lower for the ASTM F1586 sample immersed in saline solution (figure 5) and for the ASTM F2581 sample immersed in SBF solution (figure 6).

The resistance against pitting corrosion was influenced by the use of austenitic stainless steels with different chemical compositions. The ASTM F1586 and ASTM F2581 samples, that displayed the highest corrosion resistance, had higher nitrogen (N) contents compared to the ASTM F138 sample (table 2). The ASTM F1586 and ASTM F2581 samples exhibited higher molybdenum (Mo) and manganese (Mn) quantities and lower nickel (Ni) amount than the ASTM F138 sample. In this case, the addition of higher Mo and Mn contents enhances the N solubility, resulting in a beneficial effect of the formation of passive films in austenitic stainless steels [10]. The Mo element increases the corrosion resistance through the Fe\(^{3+}\) ions stabilization into the passive film, as well as leads to Fe\(_2\)(MoO\(_4\))\(_3\) insoluble films formation.

In nitrogen high austenitic stainless steels, the pitting corrosion resistance is bound to the re-passivation, improving passive film and the pH augmentation due to NH\(_4^+\) ions formation into the active sites [15, 33, 38, 39].
The pitting corrosion resistance mechanism may be described as follows [15]: (i) N dissolves into pit site to forms \( \text{NH}_4^+ \) ions, which limits the pit growing; (ii) an N–richer layer is formed by nitrogen segregation to the metal surface, which results in an inactive surface for the Cl\(^{-}\) ions during pitting corrosion; (iii) a protective oxynitride layer is formed by the N incorporation into the passive film, that increases the film stability against any breakdown potential; and (iv) dissolved N from steel can form nitrides or nitrates, acting as corrosion inhibitors agents at the pit site. Furthermore, the addition of high nitrogen amounts leads to the formation of a stable Cl\(^{-}\) containing passive film, that results in high corrosion resistance, since few defects and high pitting potential are provided [40]. These beneficial effects of nitrogen were activated during the polarization assays of the ASTM F1586 and ASTM F2581 samples, once the two samples exhibited larger passivation anodic regions than the ASTM F138 sample apart from the used solutions [5, 35, 46].

The effect of the alloying elements on the localized corrosion in stainless steels may be empirically quantified by the pitting resistance equivalent number (PREN). For austenitic stainless steels, PREN describes the effect of Cr, Mo, and N on the pitting corrosion and is defined as follows [22, 25, 41, 42]:

\[
PREN = \text{Cr[%wt.]} + 3.3\text{Mo[%wt.]} + \beta\text{N[%wt.]} \tag{2}
\]

where \( \beta \) is a number ranging from 16 to 30. Higher PREN values are attributed to materials with a lower tendency to suffer pitting corrosion. For example, PREN values bellow 26 are recommended to avoid pitting corrosion in body fluids in vivo, whereas PREN of 40 is typically recommended for stagnant seawater [16].

The PREN values were determined by using \( \beta = 16 \) and \( \beta = 30 \) for the ASTM F138, ASTM F1586, and ASTM F2581 samples (table 4). Higher PREN values were observed in the ASTM F1586 and ASTM F2581 samples, showing that both samples had better pitting corrosion resistance than the ASTM F138 sample, agreeing to results of the anodic polarization curves obtained in saline (figure 5) and SBF (figure 6) solutions at a temperature around 37 °C.

### Table 4. PREN values for the ASTM F138, ASTM F1586, and ASTM F2581 samples.

| Sample        | Cr   | Mo   | N    | PREN \( \beta = 16 \) | PREN \( \beta = 30 \) |
|---------------|------|------|------|------------------------|------------------------|
| ASTM F138     | 17.490 | 2.640 | 0.077 | 27.434                 | 28.512                 |
| ASTM F1586    | 20.280 | 2.360 | 0.345 | 33.688                 | 38.518                 |
| ASTM F2581    | 16.710 | 3.020 | 0.490 | 34.516                 | 41.376                 |

3.3. Electrochemical impedance spectroscopy in saline and SBF solutions

The Nyquist diagrams of the ASTM F138, ASTM F1586, and ASTM F2581 samples immersed in naturally aerated saline solution with pH 8.4 and 37 °C are shown in figure 7(a). The three samples exhibited Nyquist diagrams with a capacitive arc-shaped, where the diameters of these semicircles were depressed as a function of the chemical composition of the austenitic stainless steels. Relatively similar values of semicircle diameter were observed for samples ASTM F1586 and ASTM F2581, with a lower value seen in sample ASTM F138 (figure 7(a)). This semicircle diameter extrapolated in the Nyquist diagram represents the charge transfer resistance equivalent to the polarization resistance (Rp). Rp increases with a rise in the semicircle diameter, meaning a lower corrosion rate. For the austenitic stainless steels, the semicircle diameter reduction indicates a diminution of the passive film resistance [43, 44]. The ASTM F1586 and ASTM F2581 samples immersed in saline solution had more resistant passive films compared to the ASTM F138 sample, showing same corrosion behaviour foreseen in the anodic polarization curves measured in saline solution (figure 5).

The figure 7(b) shows the Bode diagram (\( |Z'| \) impedance modulus and phase angle) for the ASTM F138, ASTM F1586, and ASTM F2581 samples immersed in naturally aerated saline solution with pH 8.4 and 37 °C. In these conditions, the log \( |Z'| \) curves were relatively similar for all samples (figure 7(b)), showing that the corrosion behaviour was little influenced by the difference in the chemical composition of the austenitic stainless steels. In the high-frequency range, the log \( |Z'| \) values remained practically constant and the phase angles almost reached zero degrees (figure 7(b)), indicating the resistive nature of the austenitic stainless steels’ surfaces. Moreover, the phase angle curves of the ASTM F1586 and ASTM F2581 samples were characterized by a well-defined maximum phase angle for a broad frequency range (0.1 to 100 Hz, figure 7(b)). These maximum phase angles achieved around −80°, getting close to an ideal capacitive behaviour (phase angle = 90°). This capacitive behaviour is seen in passive materials and indicates the formation of a very stable surface film [33, 45]. As result, the ASTM F1586 and ASTM F2581 samples showed good passivation characteristics under this condition, also seen by other authors [5, 35, 46]. Although all samples immersed in saline solution displayed similar log \( |Z'| \) curves (figure 7(b)), the ASTM F138 sample had a lower maximum phase angle than the ASTM F1586 and ASTM F2581 samples for a wide frequency range (0.1 to 100 Hz), suggesting a slight penetration of the passive...
layer during the corrosion test. This failure may be attributed to surface roughness, local inhomogeneity on the dielectric layer, porosity, mass transport and relaxation effects [32, 45].

The Nyquist and Bode diagrams of the ASTM F138, ASTM F1586, and ASTM F2581 samples immersed in naturally aerated SBF solution with pH 7.3 and at a temperature around 37 °C are shown in figure 8. In these conditions, the ASTM F2581 sample presented a lower semicircle diameter than the ASTM F1586 samples (figure 8(a)), evidencing a high corrosion rate for the ASTM F2581 sample. These results were different from those obtained for the same samples immersed in saline solution (figure 7(a)), once the highest corrosion rate was attributed to the ASTM F138 sample. The lowest capacitive performance of the ASTM F2581 sample immersed in SBF solution may be associated with the presence of defects in its passive layer.

Similar Bode diagrams were obtained for the three samples immersed in SBF solution (figure 8(b)), showing the occurrence of small variation in the corrosion behaviour of these austenitic stainless steels. Again, all samples immersed in SBF solution exhibited a resistive nature in the high-frequency range (log |Z| constant and phase angle close to 0°, figure 8(b)), as well as a typical capacitive behaviour between 0.1 and 100 Hz (maximum phase angle around −80°, figure 8(b)). Concerning to samples immersed in saline solution (figure 7(b)), the ASTM F138 sample achieved a lower phase angle maximum than the ASTM F1586 and ASTM F2581 sample between 0.1 and 100 Hz, disagreeing from results obtained for the samples immersed in SBF solution (figure 8(b)). The corrosion behaviour improved when the ASTM F138 sample was exposed to the SBF solution. In contrast, there was a worsening in the corrosion behaviour of the ASTM F2581 sample when the electrolytes solutions were changed from saline to SBF.

As discussed above, the existent passive film in all samples immersed in saline and SBF solutions deviated from ideal capacitive behaviour (phase angle = 90°). The experimental data were fitted for several equivalent circuit models constituted by discrete electronic components comparable to the different parameters measured by electrochemical impedance spectroscopy. The experimental data of the samples immersed in saline and SBF were better adjusted for the equivalent circuit illustrated in figure 9. In this study, the R1/CPE1 components

![Figure 8](image_url)
were associated to the electrochemical behaviour in the interface between the passive film and the electrolytic solution (figure 9), whereas the R2/CPE2 components were linked to interface between the passive film and the metallic substrate. The electronic components of the equivalent circuit can be described as follows: Rs is the solution resistance; CPE1 is a constant phase element (CPE), which represents the capacitive behaviour of the

Figure 8. Nyquist (a) and Bode (b) diagrams of the different austenitic stainless steel samples immersed in naturally aerated SBF solution with pH 8.4 and a temperature of 37 °C.

Figure 9. The equivalent circuit used for experiment data fitting of the samples immersed in the saline (pH = 8.4) and SBF (pH = 7.3) solutions at 37 °C. The experimental data corresponded to the measurements obtained by the electrochemical impedance spectroscopy.
passive film; R1 represents the resistance of the passive oxide layer; CPE2 and R2 represent the capacitive behaviour and resistance in the interface between the passive film and the metallic substrate, respectively.

Table 5. Determined electrical parameters from the equivalent circuit (figure 9) fitting for the experimental data of the three austenitic stainless steel samples submitted to electrochemical impedance spectroscopy.

| Sample       | Parameter | ASTM F138 | ASTM F1586 | ASTM F2581 |
|--------------|-----------|-----------|------------|------------|
| Saline solution (0.9% NaCl) | Rs (Ωcm²) | 16.600    | 17.000     | 20.100     |
|              | CPE1 (μFcm⁻²) | 76.700    | 45.800     | 43.100     |
|              | R1 (kΩcm²) | 100.000   | 120.000    | 164.000    |
|              | n₁        | 0.894     | 0.887      | 0.888      |
|              | CPE2 (μFcm⁻²) | 42.000    | 40.000     | 40.000     |
|              | R2 (kΩcm²) | 60.000    | 126.000    | 173.000    |
|              | n₂        | 0.976     | 0.800      | 0.700      |
|              | Rp = R1 + R2 (kΩcm²) | 160.000   | 246.000    | 337.000    |
| SBF solution | χ²        | 7.4 × 10⁻³ | 13.5 × 10⁻³ | 12.3 × 10⁻³ |

| Sample       | Parameter | ASTM F138 | ASTM F1586 | ASTM F2581 |
|--------------|-----------|-----------|------------|------------|
| Saline solution (0.9% NaCl) | Rs (Ωcm²) | 15.700    | 14.000     | 14.800     |
|              | CPE1 (μFcm⁻²) | 77.300    | 59.000     | 70.000     |
|              | R1 (kΩcm²) | 39.200    | 91.000     | 30.000     |
|              | n₁        | 0.945     | 0.900      | 0.900      |
|              | CPE2 (μFcm⁻²) | 0.380     | 4.000      | 20.000     |
|              | R2 (kΩcm²) | 186.000   | 200.000    | 120.000    |
|              | n₂        | 0.830     | 0.786      | 0.820      |
|              | R = R1 + R2 (kΩcm²) | 225.200   | 291.000    | 150.000    |
| SBF solution | χ²        | 2.3 × 10⁻² | 6.0 × 10⁻³ | 5.0 × 10⁻² |

where A represents the pseudo-capacitance, i is an imaginary number (i = −1^{1/2}), ω is the angular frequency, and n is defined as a CPE exponent and a variable parameter (0.5 < n < 1.0). CPE describes an ideal capacitor for n = 1.0 and represents a Warburg impedance with the diffusional character for n = 0.5; for the 0.5 < n < 1.0 range, CPE describes a distribution of dielectric relation times in the frequency space.

Table 5 shows the electrical parameters determined by the fitting procedure from the equivalent circuit observed in figure 9. Disregarding the ASTM F2581 sample immersed in saline solution, all samples immersed in saline and SBF solutions had relatively close values of Rs (14–17 Ωcm², table 5). Rs varied slightly with a change in the chemical composition of the austenitic stainless steels independent on the electrolytic solution type used (table 5). For both the electrolytic solutions, the n values were close to 1 (n = 0.7–0.9, table 5), indicating that the n elements exhibited a capacitive behaviour extremely close to an ideal capacitor. These results agree to the Bode diagrams (maximum phase angles around ~80°, figures 7 and 8). In saline solution, similar values of CPE1 were determined for the ASTM F1586 and ASTM F2581 samples (~44 μFcm⁻², table 5), however, the highest value was observed for the ASTM F138 sample (~77 μFcm⁻²). Low values of CPE1 are indicative of a more reactive interface between the passive layer and the electrolytic solution [5]. High values of R1 were measured for the ASTM F1586 and ASTM F2581 sample (saline solution, table 5), indicating that both samples restrain more the ionic transporting through the passive layer compared to ASTM F138 sample. The ionic transfer paths were formed by the existence of pores into the passive layer. Pores were filled by the electrolytic solution, which resulted in the resistance decrease of the passive film on the austenitic stainless steel. In saline solution, the ASTM F138 sample displayed a lower maximum phase angle than the ASTM F1586 and ASTM F2581 samples (figure 7), where the dropping phase angle has been linked to several defects’ types into the passive layer [32, 45]. Relatively similar values of CPE2 were determined for the three samples (table 5), indicating that variation in the chemical composition of steels caused a slight influence on the corrosion behaviour in the inner interface between the passive film and the metallic substrate. As observed in R1, the ASTM F1586 and ASTM F2581 samples presented higher values than in R2 (table 5), indicating that both samples restricted charge transferring on the double layer compared to the ASTM F138 sample. As mentioned above, the corrosive rate reduces with the increase of Rp. Thus, the ASTM F2581 sample showed better corrosion resistance (Rp = 337.0 kΩcm²).
Table 5, being followed by the ASTM F1586 ($R_p = 246.0 \, \Omega \cdot cm^2$) and ASTM F138 ($160.0 \, \Omega \cdot cm^2$) samples, respectively. These results agree with the Nyquist diagram (Figure 5), where it was found the best capacitive properties for the ASTM F1586 and ASTM F2581 samples.

4. Conclusions

The purpose of this research was to evaluate austenitic stainless steel for biomedical applications. The approach used to investigate was perform microstructural and electrochemical experiments. As result of this work, the following main findings concerning to the nature of corrosion were:

- The chemical composition presented a low variation in alloying elements, excepting nickel and nitrogen, indicating that the corrosion rate of the ASTM F2581 sample immersed in SBF solution decreased by the almost full remotion of the nickel amount.
- The use of high contents of nitrogen and nickel improves the corrosion behaviour of the austenitic stainless steels immersed in SBF solution, once the ASTM F1586 sample displayed an excellent corrosion resistance compared with the ASTM F138 and ASTM F2581 samples.
- The use of high contents of nitrogen and nickel improves the corrosion behaviour of the austenitic stainless steels immersed in SBF solution, once the ASTM F1586 sample displayed an excellent corrosion resistance compared with the ASTM F138 and ASTM F2581 samples.
- A change in the electrolyte solution, from saline to SBF, implies a better corrosion performance of the ASTM F138 and ASTM F1586 samples. However, ASTM F2581 steel presented the passive film with better protective capacity in the saline solution while ASTM F1586 had better performance in the SBF.

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