Original Article

Corrosion behaviour of Ti–Ni–Al alloys in a simulated human body solution

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\textbf{A B S T R A C T}

The effect of Al additions (5, 10, 15 and 20 at.\% ) on the corrosion behaviour of a 50 at.\% Ti-50Ni alloy in Hank solution has been investigated by using potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS), electrochemical noise (EN) and linear polarization resistance (LPR) measurements. Microstructure evolution was observed from columnar grains to equiaxed grains in samples with low and high Al additions, respectively. All the different techniques indicated that with the addition of either 5 or 10 at.\% Al not only decreases the uniform corrosion rate, but also the susceptibility to pitting corrosion. EIS technique has shown that the corrosion resistance of these alloys is due to a TiO\textsubscript{2} layer with a duplex structure. Results have been explained in terms of the difference in microstructures for the different alloys.

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1. Introduction

Ti and Ti-alloys are widely used for orthopaedic and dental applications due to their low density, high corrosion resistance, good mechanical properties and biocompatibility [1–4]. Because NiTi alloys are used in the fabrication of components for orthodontic and orthopaedic applications, mechanical considerations have to be taken into account in order to establish the best alloys performance such as hardness, toughness, compression, flexion and wear resistance (among others) in agreement to the alloy design for a specific application. It is important to consider that in the human body, each part is exposed to different stress types, in such way that the component need to be evaluated in agreement to the particular condition not only in mechanical point of view but in the fluid type that will affect the corrosion resistance and for consequence the element performance. Depending upon the environment used, these alloys spontaneously develop oxides, mainly TiO\textsubscript{2} which have an important role in determining their biocompatibility and corrosion resistance of these alloys [5–10]. Namely, the formation of a stable passive oxide film on metallic implants considerably reduces their corrosion [4]. The composition and thickness of the formed oxide determine the corrosion resistance of bi-metallic materials and release of metal ions from the implant that can affect health [11–13].

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Various oxides are reported to form on Ti alloys surface [4,14]. The passive film on Ti implants is mainly composed of TiO₂, existing in a rutile-type tetragonal structure [4].

The presence of this thermodynamically stable and adherent oxide contributes to high corrosion resistance [14]. However, the structural changes in passive films of various Ti-based implants may alter their corrosion resistance. Thus, the V₂O₅ in the passive film formed on Ti-6Al-4V alloy dissolves and results in the lower film corrosion resistance [1]. On the other hand, the concentration of metal release is remarkably reduced by the addition of niobium (Nb), zirconium (Zr) and tantalum (Ta) [1,3]. Since their oxides are less soluble than those of aluminium (Al) and vanadium (V), the passive oxide film on the implant surface is more inert consisting of a dense rutile structure, providing greater protection to the underlying implant material [15,16]. On the other hand, in alloys such as Ti-6Al-7Nb, the incorporation of formed oxides such as Al₂O₃, Nb₂O₅ or NbO₃ into the TiO₂ matrix increased this oxide corrosion resistance [17]. Consequently, new Ti alloys, containing elements such as Nb, Zr and Ta are receiving a great deal of attention [3,15].

TiNi alloys are an alloy which is widely used for orthopaedic and dental applications also due to their mechanical and corrosion resistance [18,19]. The corrosion resistance is due to the formation of a TiO₂ layer which has a duplex structure, with an inner compact layer which acts as a barrier against the ion dissolution, so that the corrosion resistance increase with its thickness. There is also an outer porous layer, which is less corrosion resistance, but the incorporation of components from the electrolyte into its pores favours osteo-integration [20,21]. However, despite of its high corrosion resistance, TiNi alloys suffer from corrosion in human body fluids, with the release of Ni²⁺ ions which can be allergic and toxic, which can be avoided by the addition of some alloying elements [22,23]. Light materials are currently being needed for structural applications mainly due to the low density and ductility properties [24], is for such reason that aluminium additions is the most popular element to enhance the applications for several type of materials. For Ti–Ni alloys, aluminium additions in low proportions, allows to obtain a low density material without change the biomaterial condition, in other words, to keep the biocompatibility property [25]. Aluminium additions in NiTi alloys can be considered as a high potential option to produce a material with low density characteristics, specifically in leg bones implants and hand prosthesis applications. Additionally, aluminium can be considered non-toxic since very little gets into the blood stream and it is poorly absorbed within the gastrointestinal tract [26]. Thus, in this study, the effect of Al addition on the corrosion behaviour of a TiNi alloy will be evaluated in the Hank solution by using electrochemical techniques.

2. Experimental procedure.

2.1. Testing material

Material tested in this study was a 50 at.% Ti–50Ni base alloy with the addition of 5, 10, 15 and 20 at.% Al. During the alloying, Ti contents remained constant, with a value of 50 at.%, with Al replacing Ni. Alloys with nominal high purity Ti–Ni–Al elements (99.98%) were fabricated by induction melting technique. In order to obtain lower amount of impurities a quartz crucible was used for melting the alloys inside of a chamber under vacuum atmosphere (10⁻³ Torr). After reaching the liquid state, alloys were cooled down in the same crucible. After this, specimens were annealed at 700 °C during 60 min in order to relieve any obtained stress and to get a more homogenous microstructure.

2.2. Corrosion tests

As corrosive agent, the Hank solution with a chemical composition given in Table 1 was used at 36.5 °C. This solution simulates the physiological media of the human body. To perform the corrosion tests, specimens of 5 × 5 × 3 mm were machined, encapsulated in epoxy resin and then ground with 600 grade emery paper. Electrochemical experiments were performed using an ACM-Instruments potentiostat controlled by a personal computer. Potentiodynamic polarization curves were obtained by varying the applied potential from −1500 mV with respect to the free corrosion potential, Ecorr, up to +1000 mV at a scan rate of 1 mV/s. Before the experiments, the Ecorr value was measured for approximately 30 min, until it was stable. All the potentials were measured using a saturated calomel electrode (SCE) as reference electrode. The counter electrode was a graphite rod. Corrosion rates were calculated in terms of the linear polarization resistance curves, LPR, which were obtained by polarizing the specimen from +10 to −10 mV, respect to Ecorr, at a scan rate of 1 mV/s, a standard scanning rate for this kind of experiments, to get the polarization resistance, Rₚ. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the Ecorr value by applying a signal with an amplitude of 10 mV in a frequency interval of 100 mHz–100 kHz. A model PC4 300 Gamry potentiostat was used for this. The susceptibility to pitting corrosion, was evaluated by using electrochemical noise (ECN) readings in both current and potential. For the ECN measurements, a zero resistance ammeter (ZRA) from ACM Instruments was used, controlled using a desktop computer. Time records consisted of blocks of 1024 readings, taken at 1 s intervals, using two identical working electrodes and a SCE arrangement. All the tests were carried out at 37 °C. Finally, the noise resistance value, Rn, was calculated as the ratio of potential noise standard deviation, σₚ, over current noise standard deviation, σi. Corroded specimens were observed in the scanning electronic microscope (SEM).

3. Results and discussion

3.1. Microstructures

Microstructures of the different TiNiAl alloys are shown in Fig. 1a–e. For alloys containing 0, 5 and 10 at.% Al, Fig. 1a–c, samples present grains with columnar type structure, and a grain size of 5, 10 and 15 μm for 0, 5 and 10 at.% Al, respectively. Some second phases in low proportion can be observed in the surface sample which was a consequence of the aluminium oversaturation. For samples with 15 and 20 at.% Al, Fig. 1d–e,
grains with an equiaxed structure and an average size of 10 μm could be observed, as well as the presence of a much higher amount of second phases than that found for lower Al concentrations. For samples with 0, 5, 10, 15 and 20 at.% Al addition, an average area fraction of 3, 5, 8, 13 and 18 percent was obtained respectively of the Al2NiTi secondary phase, being NiTi the predominant primary phase (B2 structure with Al in solid solution).

3.2. Polarization curves

The effect of Al concentration in the polarization curves for the 50Ti–50Ni alloy in the Hank solution is shown in Fig. 2. It can be seen that unalloyed, base 50Ti–50Ni alloy displays an active-passive behaviour, with an Ecorr value of −850 mV and a corrosion current density value close to 1.9E−5 A/cm². Similar results have reported by other authors [18,19]. A wide passive zone can be observed from −850 mV up to −160, where a pitting potential, Epit is observed, reaching a passive current density mean value of 1.0E−4 A/cm². This passive zone has been attributed to the formation of a TiO2 layer, maybe with some other Ti-oxides such as TiO and Ti2O3 [18,19] which has a duplex structure, with an inner compact layer, which acts as a barrier against the ion dissolution, and an outer porous layer, which, according to literature, is less corrosion resistance [27–29]. As soon as Al was added to the 50Ti–50Ni base alloy, the Ecorr value shifted towards nobler values, whereas the Icorr value decreased, maybe due to the incorporation of

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Table 1 – Chemical composition of the Hank solution (g/L).

<table>
<thead>
<tr>
<th></th>
<th>NaCl</th>
<th>CaCl₂</th>
<th>KCl</th>
<th>Glucose</th>
<th>NaHCO₃</th>
<th>MgCl₂·6H₂O</th>
<th>Na₂HPO₄·2H₂O</th>
<th>KH₂PO₄</th>
<th>MgSO₄·7H₂O</th>
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<tbody>
<tr>
<td></td>
<td>8</td>
<td>0.14</td>
<td>0.4</td>
<td>1</td>
<td>0.35</td>
<td>1</td>
<td>0.06</td>
<td>0.06</td>
<td>0.06</td>
</tr>
</tbody>
</table>

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Fig. 1 – SEM micrographs showing the microstructures of the as-received (a) 50Ti–50Ni, (b) 50Ti–45Ni+5Al, (c) 50Ti–40Ni+10Al, (d) 50Ti–35Ni+15Al, and (e) 50Ti–30Ni+20Al alloys.
the Al₂O₃ oxide into the TiO₂ film reinforcing it [17,18]. For instance, Okazaki et al. [30] found that, when Al is added to Ti and tested in physiological environments, the passive layer of the Ti alloy is reinforced by Al₂O₃ either in the interstitial or substitutional sites in the TiO₂ matrix. The passive formed layer acts as a barrier layer against the ion dissolution. The \(E_{\text{corr}}\) value reached its noblest value with the addition of 10% Al, as shown in Table 2, whereas the lowest corrosion current density value was obtained with this Al contents also.

With a further increase in the Al contents up to 15 or 20 at.%, the \(E_{\text{corr}}\) shifted in the opposite direction, and the corrosion current density increased. The \(I_{\text{corr}}\) value for the alloy containing 20 at.% Al was very similar to that for the base, unalloyed 50Ti–50Ni alloy. Corrosion current density values, \(I_{\text{corr}}\), can be used to calculate the penetration rate by using Faraday’s law [31]:

\[
\frac{d}{t} = \frac{3.2706M_{\text{corr}}}{z\rho}
\]

where \(d\) is the thickness of the removed metal, \(t\) the time, \(M\) the molecular mass, \(z\) the number of electrons involved in the corrosion reaction and \(\rho\) the metal density. The corrosion current density to get a penetration rate of 1 mm y⁻¹ for Ti, Ni and Al are 86.25 × 10⁻⁶, 92.07 × 10⁻⁶ and 91.81 × 10⁻⁶ A/cm² respectively. Calculated penetration rates are listed in Table 2.

The passive corrosion current density value also decreased with the addition of Al whereas the \(E_{\text{pit}}\) value increased only with the addition of either 5 or 10 at.% Al. With the addition of either 15 or 20 at.% Al, the \(I_{\text{pas}}\) value increased, whereas the \(E_{\text{pit}}\) value decreased, perhaps due to galvanic effect due to the presence of second phases into the alloy. Thus, the beneficial effect of the Al addition to the 50Ti–50Ni alloy is only with the addition of either 5 or 10 at.% Al. A further increase in the Al contents brings a detrimental effect on the corrosion resistance of the 50Ti–50Ni alloy in the Hank solution.

3.3. Linear polarization resistance measurements

In order to have a better insight of the Al effect on the corrosion behaviour on the 50Ti–50Ni alloy in the Hank solution, some 24 h LPR tests were carried out, and the results are shown in

<table>
<thead>
<tr>
<th>Table 2 – Electrochemical parameters obtained from the polarization curves for Ti–Ni–Al alloys immersed in Hank solution.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy</strong></td>
</tr>
<tr>
<td>50Ni–50Ti</td>
</tr>
<tr>
<td>45Ti–50Ni+5Al</td>
</tr>
<tr>
<td>50Ti–40Ni+10Al</td>
</tr>
<tr>
<td>50Ti–35Ni+15Al</td>
</tr>
<tr>
<td>50Ti–30Ni+20Al</td>
</tr>
</tbody>
</table>

3.4. EN readings

The susceptibility towards localized type of corrosion such as pitting was evaluated in terms of noise in current and potential measurements. The main use of this technique is that it can tell us mainly if a metal or alloy is susceptible to a localized type of corrosion such as pitting, crevice, etc. but it can also tell us if the metal is susceptible to uniform or mixed type of corrosion, and, very important, by calculating the ratio of the potential noise standard deviation, $\sigma_p$, over the current noise standard deviation, $\sigma_i$, a parameter equivalent to the polarization resistance, in this case it is called noise resistance, $R_n$, it can be used to calculate the metal corrosion rate. Fig. 4 shows the time series for the noise in both current and in potential for the 50Ti–50Ni base alloy in the Hank solution, where the presence of anodic transients in the current time series simultaneously with some cathodic transients in the potential time series can be observed. The current transients intensity was around 0.1 $\mu$A/cm$^2$, whereas the potential transients intensity was lower than 1 mV. This type of transients is due to the rupture of the passive layer and its repassivation, and, thus, to the nucleation of localized type of corrosion such as pits [32]. The noise in current time series for the Ti–Ni alloys with different Al contents is shown in Fig. 5. The alloy containing 5 at.% Al, Fig. 5a, shows anodic current transients with lower inten-

Fig. 5 – Noise in current for (a) 50Ti–45Ni+5Al, (b) 50Ti–40Ni+10Al, (c) 50Ti–35Ni+15Al, and (d) 50Ti–30Ni+20Al alloys during the first day of exposure to the Hank solution.

Fig. 3. It can be seen that the 50Ti–50Ni base alloy has an $R_p$ value of 4000 $\Omega$ cm$^2$ during most of the testing time, indicating the stability of the passive TiO$_2$ film. When either 5 or 10 at.% Al were added to the 50Ti–50Ni alloy, the $R_p$ value increased, reaching values of 9E4 and 1E5 $\Omega$ cm$^2$ respectively. These values did not remain constant as time elapsed, instead they showed a decrease in a certain period of testing time indicating that the film became less protective as time elapsed. However, they remained higher than the $R_p$ values for unalloyed 50Ti–50Ni alloy. On the other hand, the $R_p$ value for the alloy containing 15 at.% Al was lower than that for the alloy containing 10 at.% Al, and it reached its lowest value with a further increase in the Al contents up to 20%, increasing, thus, the corrosion rate of the 50Ti–50Ni alloy. Maybe this fact is due to the microstructure of the different alloys. Alloys with contents of Al lower than 15 at.%, microstructures contain very few second phases, but for Al contents than 15 at.%, the number of second phases increases tremendously as shown in Fig. 1, inducing galvanic pairs. The number of second phases is greatest for the alloy containing 20 at.%, increasing the number of galvanic cells, and thus, the corrosion rate. Thus, the beneficial effect of the Al contents on the corrosion resistance only up to 10 at.% and the detrimental effect of adding either 15 or 20 at.% Al was confirmed with these experiments.

Fig. 6 – Change in the $R_n$ values with time for Ti–Ni–Al alloys immersed in the Hank solution.
sity to that for unalloyed 50Ti–50Ni alloy but with a higher frequency, indicating that the protective formed film in this alloy has a lower susceptibility to be disrupted, and thus, to pitting corrosion. When the Al contents increases to 10 at.%, Fig. 5b, the current transients intensity decreased markedly for up to two orders of magnitude as compared to that for unalloyed 50Ti–50Ni alloy, indicating that the susceptibility to pitting type of corrosion is significantly reduced. For alloys containing either 15 or 20 at.% Al, Fig. 5c and d, the intensity of the noise transients increases once again, reaching, however, values lower or similar to those found for unalloyed 50Ti–50Ni base alloy, indicating a decreased susceptibility towards pitting type of corrosion with these alloys. Thus, in general terms, by adding Al, the susceptibility of the Ti–Ni alloy to a localized type of corrosion is greatly decreased except with the addition of 20 at.% Al which does not affect it.

The combination of standard deviation in current, \( \sigma_i \), and standard deviation in potential, \( \sigma_v \), allow us to calculate the noise resistance, \( R_n \), by dividing \( \sigma_v \) over \( \sigma_i \) and thus, calculate the overall corrosion rate since \( R_n \) is inversely proportional to \( i_{corr} \). The change in the \( R_n \) values with time for the different inhibitor concentrations are shown in Fig. 6, where it can be seen that addition of either 5 or 10 at.% Al to the base 50Ti–50Ni alloy increases its \( R_n \) value, increasing its corrosion resistance, whereas the additions of either 15 or 20 at.% Al decreases the \( R_n \) value, increasing its corrosion resistance. A very similar behaviour was observed with the \( R_p \) value, Fig. 3, which is very encouraging, since different techniques give similar results. However, since \( R_n \) is related to localized events, and thus, to localized type of corrosion. Therefore, the addition of contents lower than 10 at.% Al not only increase the resistance towards uniform type of corrosion, but also towards localized type of corrosion, whereas additions of Al contents higher than 10 at.% increases both the uniform corrosion rate and the susceptibility to pitting corrosion.

3.5. EIS measurements

EIS measurements in both Nyquist and Bode formats for the different Ti–Ni–Al alloys are shown in Fig. 7. Nyquist plots, Fig. 7a, indicate that for unalloyed, base 50Ti–50Ni and alloy containing 20 at.% Al data display a capacitive loop at high frequency values followed by a straight line at about 45°, indicating a diffusion controlled process. Alloys containing 5, 10 and 15 at.% Al display, at all frequency values, a single, capacitive-like, depressed loop, which means a corrosion process controlled by charge transfer. The semicircle diameter increases with increasing the Al contents, reaching its highest value for the alloy containing 10 at.% Al, decreasing with a further increase in the Al contents. Bode plots, Fig. 7b, indicates a near capacitive behaviour with a phase angle close to −80° for alloy containing 15 at.% Al over a wide frequency range, indicating a passive film acting as an insulator, suggesting that a highly stable film is formed on tested alloy in the electrolyte used. In this case, phase angles during the first day of exposure is around −75°. Alloy containing 5 at.% Al showed a very similar behaviour to this alloy, but the phase angle was −70° and did not remain as constant with the frequency as that for the alloy containing 10 at.% Al did, indicating a passive film less stable. Alloy containing 10 at.% Al exhibited two time constants illustrated by two phase angles at −81 and −79°, whereas for alloy containing 20 at.% Al the two time constants were at −52 and −38°. According to the literature [8–12]. The high corrosion resistance of these alloys is due to a dense porous layer of TiO2 which has a duplex structure, with an external porous outer layer and an inner compact layer which acts as a barrier against the ion dissolution; thus, the two time constants correspond to these two layers. The corrosion resistance is attributed to the inner compact layer. Normally, a highly capacitive behaviour, typical of passive materials, is indicated from medium to low frequencies by phase angles approaching −90°, close to the phase angles shown by the alloys containing 10 or 15 at.% Al. Unalloyed, base 50Ti–50Ni alloy also displayed two time constants at −50 and −38°.

EIS data were simulated by the equivalent electric circuits shown in Fig. 8. For alloys containing 5, 10 or 15 at.% Al, which exhibited a charge transfer controlled corrosion process, electric circuit contains two time constants, Fig. 8a, whereas for 50Ti–50Ni base alloy and for alloy containing 20 at.% Al, electric circuits contain the diffusion Warburg impedance, W, Fig. 8b. In these circuits, \( R_p \) is the solution resistance, \( R_b \) and \( C_p \) are the outer porous layer resistance and capacitance respectively, and \( R_m \) and \( C_m \) the inner compact layer resistance and
Fig. 8 – Electric circuits to simulate EIS data for (a) 50Ti–50Ni and 50Ti–30Ni+20 Al alloys and (b) 50Ti–45Ni+5Al, 50Ti–40Ni+10Al and 50Ti–35 Ni+15Al alloys.

Table 3 – Electrochemical parameters used to simulate EIS data for 50Ni–50Ti and 50Ti–30Ni+20Al alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( R_s ) (Ω cm²)</th>
<th>( Y_s ) (Ω⁻¹ s⁻¹)</th>
<th>( n_s )</th>
<th>( R_o ) (Ω cm²)</th>
<th>( \Delta Y ) (Ω⁻¹ s⁻¹)</th>
<th>( n_o )</th>
<th>( R_in ) (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50Ti–50Ni</td>
<td>19</td>
<td>2.3E–4</td>
<td>0.66</td>
<td>2.0E+2</td>
<td>4.8E+3</td>
<td>0.63</td>
<td>3.40E–4</td>
</tr>
<tr>
<td>50Ti–30Ni+20Al</td>
<td>26</td>
<td>1.74E–5</td>
<td>0.81</td>
<td>0.6E+2</td>
<td>1.48E+2</td>
<td>0.25</td>
<td>9.10E–4</td>
</tr>
</tbody>
</table>

Table 4 – Electrochemical parameters used to simulate EIS data for 50Ti–45Ni+5Al, 50Ti–40Ni+10Al and 50Ti–35Ni+20Al alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>( R_s ) (Ω cm²)</th>
<th>( Y_s ) (Ω⁻¹ s⁻¹)</th>
<th>( n_s )</th>
<th>( R_o ) (Ω cm²)</th>
<th>( \Delta Y ) (Ω⁻¹ s⁻¹)</th>
<th>( n_o )</th>
<th>( R_in ) (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50Ti–45Ni+5Al</td>
<td>21</td>
<td>4.33E–5</td>
<td>0.80</td>
<td>8.6E+4</td>
<td>1.23E–5</td>
<td>0.82</td>
<td>8.6E+5</td>
</tr>
<tr>
<td>50Ti–40Ni+10Al</td>
<td>33</td>
<td>8.4E–6</td>
<td>0.90</td>
<td>6.7E+4</td>
<td>1.4E–6</td>
<td>0.91</td>
<td>5.5E+7</td>
</tr>
<tr>
<td>50Ti–35Ni+15Al</td>
<td>41</td>
<td>1.40E–5</td>
<td>0.87</td>
<td>295.3</td>
<td>7.5E–6</td>
<td>0.87</td>
<td>4.33E+6</td>
</tr>
</tbody>
</table>

Table 5 – Thickness values of scales formed on corroded Ti–Ni–Al alloys immersed in Hank solution during 30 days.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Scale thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50Ni–50Ti</td>
<td>21</td>
</tr>
<tr>
<td>45Ti–50Ni+5Al</td>
<td>10</td>
</tr>
<tr>
<td>50Ti–40Ni+10Al</td>
<td>7</td>
</tr>
<tr>
<td>50Ti–35Ni+15Al</td>
<td>11</td>
</tr>
<tr>
<td>50Ti–30Ni+20Al</td>
<td>16</td>
</tr>
</tbody>
</table>

capacitance respectively. Capacitance values can be calculated with following equation [9,24]:

\[
C = (YR^{(n–1)})^{1/n}
\]  

(2)

where \( Y \) is the admittance. Parameters used to simulate EIS data for the different alloys are given in Tables 3 and 4. In Table 3, \( R_d \) is the resistance of the diffusion layer. From Tables 3 and 4, it can be seen that the outer, porous layer resistance values, \( R_o \), are lower than the inner, compact layer resistance, \( R_in \), supporting the idea that the corrosion resistance of the TiO₂ layer is given by the internal, compact layer [8–12]. The highest \( R_in \) value, thus, the lowest corrosion rate, was for the alloy containing 10 at.% Al, whereas the lowest values were for the 50Ti–50Ni base alloy as well as for the alloy containing 20 at.% Al. Very similar trends in these values were given by the \( R_p \) and \( R_R \) values (Figs. 3 and 6). The thickness of the scales found on corroded specimens after 30 days of exposure are given in Table 5, where it can be seen that the thickest scale, and thus the specimen with the highest corrosion rate, is for base 50Ti–50Ni alloy, whereas the thinnest scale was for alloy containing 10 at.% Al, as predicted by polarization data in Table 2. Nominally, the thickness of an oxide layer, \( \delta \), can be calculated by using following expression:

\[
\delta = \frac{\varepsilon \varepsilon_0 A}{C}
\]  

(3)

where \( \varepsilon \) and \( \varepsilon_0 \) are the dielectric constants for the oxide and vacuum (8.85E–12 F/m) and \( A \) the effective surface area [9]. By using Eq. (3) and the admittance values given in Tables 3 and 4, it can be seen that the inner layers were thicker and more compact than the outer porous layer, which may be due to the formation of aluminium oxides and their incorporation in to the TiO₂ passive layer [17,18,30], which gives more protection against the diffusion of the electrolyte. The base 50Ti–50Ni alloy and the alloy containing 20 at.% Al had the highest \( Y_in \) values, and, thus, the thinnest inner layer, therefore the lowest corrosion resistance. Due to a thicker and porous outer layer in these alloys, slower diffusion processes appear, which is the rate controlling step. The \( n_in \) values were in all cases either similar or lower than those for \( n_o \), indicating a less capacitive behaviour of the inner layer, suggesting that the mass diffusion through the inner layer is the rate controlling step [22,25]. Only the alloy containing 10 at.% Al had an \( n \) value close to 1.0 (0.91) for the inner layer, indicating a nearly ideal capacitive behaviour, resulting in a highly corrosion resistant alloy. For this alloy, the porous layer was thicker than the inner layer, probably due to the incorporation of the electrolyte components into the pores of the outer porous layer, resulting in an increased corrosion resistant of this oxide layer.
4. Conclusions

The effect of adding Al (5–20 at.%) to a 50 at.% Ti–50Ni base alloy in its corrosion resistance in a Hank solution has been evaluated by electrochemical techniques. All different techniques have shown that the best corrosion resistance properties were achieved with the addition of either 10 or 15 at.% Al. Also, the pitting resistance increased for Al contents lower than 15 at.%. Finally, EIS data indicated that corrosion mechanism is under diffusion control for 0 and 20 at.% Al, and under charge transfer control for the rest of the alloys. Modelling the EIS data are consistent with a duplex structure of the passive TiO$_2$ layer, consisting of an inner, and an outer, porous layer.

Conflicts of interest

The authors declare no conflicts of interest.

REFERENCES


