Research Article

Corrosion Behaviour of a Highly Alloyed Austenitic Alloy UB6 in Contaminated Phosphoric Acid

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Received 8 March 2013; Revised 9 June 2013; Accepted 15 June 2013

Academic Editor: W. Ke

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The influence of temperature (20–80°C) on the electrochemical behaviour of passive films anodically formed on UB6 stainless steel in phosphoric acid solution (5.5 M H₃PO₄) has been examined by using potentiodynamic curves, electrochemical impedance spectroscopy, and Mott-Schottky analysis. UB6 stainless steel in contaminated phosphoric acid is characterised by high interfacial impedance, thereby illustrating its high corrosion resistance. The obtained results show that the films behave as n-type and p-type semiconductors in the potential range above and below the flat band potential, respectively. This behaviour is assumed to be the consequence of the semiconducting properties of the iron oxide and chromium oxide regions which compose the passive film.

1. Introduction

In the phosphoric acid industry, the main stages of the wet process phosphoric acid (WPA) manufacture involve the attack of phosphate ore by concentrated sulphuric acid (98%), filtration of the pulp, and concentration of acid [1]. Phosphoric acid in pure state is not very corrosive compared to nitric or sulphuric acids, but this process generates severe corrosion problems of the equipments made of stainless steels due to the presence of impurities such as chlorides, fluorides, and sulphides [1–4].

Depending on the nature of phosphates and the type of phosphoric acid manufacturing process used, the equipments (reactors, agitators, pumps, drain, etc.) are subjected to slower or faster deterioration [1].

The choice of materials used in this industrial process plays an important role since they must have both good chemical and mechanical resistance. These two characteristics are not always easy to obtain and a tradeoff between these properties must be reached [5]. In this sense, austenitic stainless steels are a good choice for phosphoric media. In this study, a highly alloyed austenitic stainless steel (UB6) has been used.

Stainless steels proved their good corrosion resistance in acid solutions. It was shown in the literature that chloride and fluorides ions accelerated the anodic process by altering passivity and activating the material dissolution rate [6–14].

UB6 stainless steel is used extensively in phosphoric acid industry, because of its good corrosion resistance; passive films formed on its surface have been the subject of some investigations [15].

The major disadvantage of these new alloys is their high cost compared with conventional stainless steels, due to the higher percentage of the alloying elements such as Cr, Ni, and Mo, as well as the complexity of the fabrication process [16].

The favourable effect of these alloying elements on the corrosion resistance is attributed to the formation of a protective passive surface film [17, 18]. This film is stable, invisible, adherent, and self-repairing. In order to prevent corrosion, it is of paramount importance that stainless steels
have a stable passive film with rapid passivation even in severe corrosive environments [17].

Several studies on the corrosion of various materials in phosphoric acid with addition of chemical ions [19, 20] and solid particles (abrasion effect) [21] have been carried out in our laboratory, as well as measurements in industrial phosphoric acid to study the behaviour in a real and complex medium [22].

The purpose of the present paper is to study the influence of the medium temperature (20–80°C) on the corrosion behaviour of Alloy UB6 in a phosphoric acid solution by means of electrochemical techniques.

2. Experimental Procedure

The material used in this investigation has been stainless steel Uranus B6 (UB6); the chemical composition of this alloy is listed in Table 1. For all measurements, electrodes were mechanically polished using successively thinner grade of emery papers (400–4000 grades), then washed with distilled water, and dried with blowing warm air. Electrodes were circular shaped and the area of the samples exposed to the solution was 0.60 cm². Platinum and Ag/AgCl 3 M KCl electrodes were used as counter and reference electrodes, respectively. The electrolyte used in this study has been (5.5 M) H₃PO₄ contaminated with addition of 4% of H₂SO₄ and 400 ppm of chloride ions (KCl). In this case, the solution has been called contaminated H₃PO₄ solution (pH = 0.42).

The experiments were conducted under thermostated conditions at 20°C, 40°C, 60°C, and 80°C in order to study the influence of temperature on the electrochemical behaviour and semiconducting properties of UB6 stainless steel.

Electrochemical measurements were performed by using an Autolab PGSTAT302N potentiostat. Potentiodynamic polarisation tests began at −0.6 VAg/AgCl and the potential was subsequently scanned anodically at a scan rate of 0.5 mVs⁻¹.

Before the potentiostatic passivation experiments, the surface of the samples was pretreated cathodically at −0.6 VAg/AgCl for 15 minutes to create reproducible initial conditions. Afterwards, the working electrode was polarised at a formation potential of 0.6 VAg/AgCl (within the passive range) for 1 hour at different temperatures to form a steady-state passive film.

EIS and capacitance measurements were performed after potentiostatic passivation tests, once a stable passive film was formed on the samples surface. EIS measurements were conducted at the formation potential (0.6 VAg/AgCl) in the frequency range of 100 kHz–10 mHz, with an amplitude signal of 10 mV. Subsequently, the capacitance of the interface was calculated at a constant frequency of 5 kHz using a 10 mV amplitude signal and scanning the potential from the formation value in the negative direction at a rate of 25 mV s⁻¹. The high scanning rate was used to avoid the electroreduction of the passive film and the change in the film thickness during the measurements. Moreover, at a sufficiently high scanning rate, the defect structure within the passive film is, “frozen-in” which avoids the defect density from being affected by potential.

3. Results and Discussion

3.1. Potentiodynamic Response. Polarisations curves of Alloy UB6 recorded in the contaminated phosphoric acid solution at different temperatures are illustrated in Figure 1.

Figure 1 shows that Alloy UB6 has a good passive behaviour with a large passive domain. This behaviour may be attributed to the chemical composition of the alloy rich on Cr, Ni, and Mo. At anodic potentials, the formation of Fe, Cr, and Ni oxides expected the following the reactions [4]:

\[
\begin{align*}
Fe + H_2O & \rightarrow FeO + 2H^+ + 2e^- & (1) \\
Ni + H_2O & \rightarrow NiO + 2H^+ + 2e^- & (2) \\
Cr + H_2O & \rightarrow CrO + 2H^+ + 2e^- & (3)
\end{align*}
\]

The formation of iron oxide took place through a dissolution-precipitation mechanism, in which the formed compound was soluble and started to deposit on the electrode surface, whereas the formation of both chromium and nickel oxides took place by direct nucleation and growth mechanism on the electrode surface. Then, the formation of higher oxidized forms of iron and chromium was expected as well as some thinning of nickel oxide,

\[
\begin{align*}
2FeO + H_2O & \rightarrow Fe_2O_3 + 2H^+ + 2e^- & (4) \\
2CrO + H_2O & \rightarrow Cr_2O_3 + 2H^+ + 2e^- & (5)
\end{align*}
\]

Some authors considered that chromium oxide (Cr₂O₃) is the main component of the passive film formed on stainless steels [23, 24]. Nickel is able to reduce the corrosion rate and passive current density, and molybdenum addition in stainless steels is known to increase the resistance to pitting corrosion [25]. Besides, the role of Ni and Mo in stainless steel at anodic potentials in phosphoric acid solution is to stabilise the passive film and to eliminate the active surface sites. In highly concentrated H₃PO₄ electrolytes, precipitation of iron phosphate can occur at the interface [26, 27], according to

\[
\begin{align*}
6H_3PO_4 + 3Fe & \rightarrow 3Fe(H_2PO_4)_2 + 3H_2 & (6) \\
3Fe(H_2PO_4)_2 & \rightarrow Fe_3(PO_4)_2 + 4H_3PO_4 & (7)
\end{align*}
\]
temperatures. The increase in temperature from 20 to 80
∘C induces a shift in the corrosion potential (Ecorr) towards more anodic values, from −172.3 to 157.1 mV, respectively. An increase in corrosion current density values from 40.9 to 80.4 μA·cm−2 can also be observed as temperature increases from 20 to 80°C.

In spite of the temperature increase, Alloy UB6 preserves a stable passivity in the range of potentials studied. The sharp increase in current density at a high potential (i Clark) indicate the onset of transpassive dissolution of the Cr-species present in the passive film formed on Alloy UB6.

Polarisation curves have been used to set the value of the film formation potential within the passive range of UB6. A film formation potential of 0.6 VAg/AgCl has been selected.

### 3.2. EIS Measurements

Electrochemical impedance spectroscopy (EIS) has been employed to investigate the steady-state properties of the passive films formed on Alloy UB6. Once the passive film was formed on the electrode surface, the EIS measurements were conducted at the formation potential (0.6 VAg/AgCl) at different temperatures (20°C, 40°C, 60°C, and 80°C).

Figure 2 shows the Nyquist plots for UB6 stainless steel in the contaminated 5.5 M H3PO4 solution. These complex plane plots have all the same semicircular shape which may correspond to a large diameter charge-transfer dominated region with some diffusion control, as found in other corrosion systems [29]. This form of impedance is consistent with the occurrence of a charge transfer reaction in a porous film of finite thickness [30], although oxygen evolution occurring within a thick porous outer layer may exhibit such behaviour [31]. It can be observed that an increase in temperature reduces the amplitude of the semicircle, indicating a decrease of the total impedance of the system and a loss in the protective properties of the passive film. This evolution with temperature suggests an evolution of the charge exchange between the material and the solution occurring at the surface [32].

The functionality with respect to frequency is seen more clearly in the Bode-phase representation shown in Figure 3. The phase angle plots are sensitive to system parameters and, therefore, provide a good means of comparing the model to the experiment. It can be seen from these plots that an increase in temperature decreases the phase angle values at low frequencies, indicating worse protective properties of the passive film formed on the UB6 surface.

### 3.3. Equivalent Circuit and Interpretation

The superior corrosion resistance of austenitic stainless steels, such as Alloy UB6, is closely related to the passive film formed on their surface [33–39]. The compact inner layer, known as barrier layer, is composed principally of chromium oxides and is the major contribution. The porous outer layer is composed principally of iron oxides and hydroxides.

Figure 4 shows the equivalent circuit (EC) that has been usually used to interpret EIS spectra of passive films having a two-layer structure [37, 40–42]. This circuit has two hierarchically distributed time constants and it has been used to simulate the electrochemical behaviour of the present system Alloy UB6/contaminated 5.5 M H3PO4 solution. In this model, R1, CPE1, R2, and CPE2 correspond to the resistance and capacitance of the outer porous layer and inner layer, respectively. In this sense, the passive film consists of two layers: the inner barrier layer and the outer layer.

### Table 1: Chemical composition of Alloy UB6.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB6</td>
<td>25.09</td>
<td>20.77</td>
<td>43.97</td>
<td>4.39</td>
<td>0.0013</td>
<td>1.84</td>
<td>1.45</td>
<td>0.007</td>
<td>0.0029</td>
<td>2.36CU</td>
</tr>
</tbody>
</table>

### Table 2: Electrical parameters obtained by polarization curves for the alloy in the UB6 H3PO4 polluted solution at different temperatures.

<table>
<thead>
<tr>
<th>Potential (VAg/AgCl)</th>
<th>20°C</th>
<th>40°C</th>
<th>60°C</th>
<th>80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>i Clark(μA·cm−2)</td>
<td>40.9</td>
<td>57.3</td>
<td>74.6</td>
<td>80.4</td>
</tr>
<tr>
<td>Ecorr(mV/Ag/AgCl)</td>
<td>−172.3</td>
<td>136.8</td>
<td>154.8</td>
<td>157.1</td>
</tr>
<tr>
<td>i p(μA·cm−2)</td>
<td>37.1</td>
<td>44.3</td>
<td>46.3</td>
<td>57.0</td>
</tr>
<tr>
<td>E cr(mV/AgCl/Ag)</td>
<td>−10.6</td>
<td>453</td>
<td>603</td>
<td>614</td>
</tr>
</tbody>
</table>

**Figure 2:** Nyquist plots for the UB6 in contaminated 5.5 M phosphoric acid at +0.6 VAg/AgCl at the temperatures of 20°C, 40°C, 60°C, and 80°C.
A constant-phase element (CPE) representing a shift from ideal capacitor was used instead of the capacitance itself. CPEs are used to model frequency dispersion behaviour corresponding to different physical phenomena such as surface heterogeneity which results from surface roughness, impurities, dislocations, and formation of porous layers [36, 41, 43, 44]. The impedance of a constant-phase element is defined as

\[ Q = Z_{\text{CPE}} = \left[ C \, (j\omega)^{\alpha} \right]^{-1}, \]

where \( \alpha \) is defined as a CPE power, in an adjustable parameter that lies between –1 and 1. For \( \alpha = 1 \), the CPE describes an ideal capacitor, and for \( \alpha = 0 \), the CPE is an ideal resistor. When \( \alpha = 0.5 \), the CPE represents a Warburg impedance with diffusional character, and for \( 0.5 < \alpha < 1 \), the CPE describes a frequency dispersion of time constants due to local heterogeneities in the dielectric material. A pure inductance yields \( \alpha = -1 \).

The CPE elements, \( Q \), have been converted into a pure capacitance (\( C \)) by means of the following equation [45–47]:

\[ C = \frac{(Q \cdot R_1)^{1/\alpha}}{R}, \]

where \( Q = Z_{\text{CPE}} \) (see (8)).

The conversion shown in (8) has been done in order to relate pure capacitance values (\( C \)) to the thickness of passive film layers, according to the following equation [48, 49]:

\[ C = \frac{\epsilon \cdot \epsilon_0}{d}, \]

where \( \epsilon \) denotes the relative dielectric constant of the layer, \( \epsilon_0 \) is the permittivity of vacuum \((8.85 \times 10^{-14} \text{Fcm}^{-1})\), and \( d \) is the layer thickness. A value of 15.6 has been assumed for \( \epsilon \), as in the literature for austenitic stainless steels [27, 50]. This value is reasonable, since the dielectric constants of the bulk oxides formed on stainless steels (CrO\(_3\), FeO, Fe\(_3\)O\(_4\), and Fe\(_6\)O\(_5\)) are about 10–20 [50, 51]. It is complicated to obtain an accurate thickness value of the passive film when the dielectric constant is not well established and when the surface roughness varies substantially during the oxidation process [41, 47, 48, 52]. Moreover, because of the open porous structure, it is difficult to calculate the thickness of the outer layer from the \( C_1 \) values [37]. Nevertheless, neglecting some variations in the surface roughness and the dielectric constant, the capacitive response under different conditions can give an indication of how the passive film thickness changes with the changing system conditions.

Parameters obtained by adjusting the experimental data, as well as the thickness of both porous and barrier layers obtained from (9), are given in Table 3. It can be seen that \( R_1 \) and \( R_2 \) values are far higher than \( R_3 \) values for all tests. Thus, \( R_1 \) and \( R_2 \) can be related to the passive film. Moreover, the resistance of the inner oxide layer \((R_1)\) is larger than the values associated with the outer porous layer \((R_{1s})\), which is consistent with the chosen physical model. It can be said that \( R_1 \) is associated with the resistance of charge transfer processes in the defects of the outer layer of the passive film, while \( R_2 \) is assigned to the areas covered with the protective inner layer of the passive film (barrier layer) [53]. These results indicate that the protection provided by the passive film was predominantly due to the barrier layer. Similar results were obtained by other authors [36, 54–56].

\( R_1 \) slightly decreases as temperature increases, which suggests that temperature favours the formation of a more porous film and this behaviour could be related to the fact that at lower temperatures the outer porous layer is more stable. On the other hand, the parameter \( R_2 \) associated with the inner oxide film is more sharply affected by temperature. \( R_2 \) clearly decreases when temperature increases, which suggests a loss of the protective properties of the inner layer of the passive film.

Concerning the capacitance values, it can be observed that \( C_1 < C_2 \), which suggests that the outer layer of the passive film is thicker than the inner layer, although its resistance is lower. These results evidence that the passive film thickness is not directly related to its protective properties.

The high values of the exponent \( \alpha_1 \) reveal that CPEs correspond to a nearly capacitive response and support the physical validity of the proposed equivalent circuit, showing that a better agreement between theoretical and experimental data is obtained. The exponent has values close to 0.9, which indicates that the interpretation of the CPE\(_1\) element as a capacitance should be acceptable, whereas the values of \( \alpha_2 \)
were between 0.5 and 0.8. The values of $\alpha_1$ and $\alpha_2$ decrease as temperature increases, indicating that the electrode surface becomes more rough and heterogeneous with temperature.

The estimated values of $d_T = d_1 + d_2$ calculated with (9) show that the layers formed on Alloy UB6 are typically on the order of nm in thickness, within the typical range for passive films formed on stainless steel (1–3 nm) [57].

3.4. M-S Analysis. The Mott-Schottky (M-S) analysis has been employed to determine the electronic properties of the passive films formed on UB6 stainless steel in the contaminated 5.5 M H$_3$PO$_4$ solution.

The Mott-Schottky approach assumes that the capacitance response is controlled by the band bending and can be described by the variation of the space charge capacitance under depletion conditions. When the passive or oxide films are in contact with an electrolyte, the space charge region developed in the passive film and the Helmholtz layer can be considered as two capacitors in series. Thus, the measured capacitance of the film-electrolyte interface can be described by the following relation [58, 59]:

$$\frac{1}{C} = \frac{1}{C_{SC}} + \frac{1}{C_H}, \quad (11)$$

where $C_{SC}$ and $C_H$ are the space charge layer capacitance and the Helmholtz layer capacitance, respectively. Presented as the Mott-Schottky relation, the expression becomes

$$\frac{1}{C^2} = \frac{1}{C_{SC}^2} + \frac{1}{C_{SC}^2} + \frac{2}{C_{SC}C_H}. \quad (12)$$

In the case of the classical semiconductors (type: Si, Ge, ...) characterized by a doping density around $10^{18}$ cm$^{-3}$, the space charge capacitance is very small compared to that of the Helmholtz layer. In these conditions, the contribution of the second and third terms can be neglected. When the heavily doped ($10^{19}$–$10^{20}$ cm$^{-3}$) passive films are considered, the capacitance of the space charge region becomes important (but is still smaller than that of the Helmholtz layer). In this case, the passive film-electrolyte interface can be described by the following Mott-Schottky relation [60]:

$$\frac{1}{C^2} = \frac{1}{C_{H}^2} + \frac{2}{\varepsilon_0 e N_D \varepsilon_0} (E - E_{FB}) - \frac{kT}{e} \quad \text{n-type, (13)}$$

$$\frac{1}{C^2} = \frac{1}{C_{H}^2} - \frac{2}{\varepsilon_0 e N_A \varepsilon_0} (E - E_{FB}) - \frac{kT}{e} \quad \text{p-type, (14)}$$

where $N_D/N_A$ are the donor/acceptor density in the passive film, $\varepsilon$ is the dielectric constant of the oxide, $\varepsilon_0$ is the vacuum permittivity constant, $e$ is the electron charge, $k$ is the Boltzmann constant ($1.38 \times 10^{-23}$ J·K$^{-1}$), $T$ is the absolute temperature, and $E_{FB}$ is the flatband potential. For a p-type semiconductor, $1/C^2$ versus $E$ should be linear with a negative slope that is inversely proportional to the acceptor density. On the other hand, an n-type semiconductor yields a positive slope which is inversely proportional to the donor density.

Figure 5 presents Mott-Schottky curves for the passive films formed in the contaminated phosphoric acid solution at 20°C, 40°C, 60°C, and 80°C at the formation potential of 0.6 V$_{Ag/AgCl}$. These curves exhibit two linear regions, above and below the flat band potential, $E_{FB}$, which is located between 0 and 0.1 V$_{Ag/AgCl}$. Inside the potential region above $E_{FB}$, the measured capacitance corresponds to the outer layer of the film, which is composed mainly of iron (III) oxide, and there is also the effect of phosphates [26] as well as the presence of other compounds [58, 61, 62]. The positive slope of this linear region clearly shows that the outer layer of the passive film formed on UB6 is an n-type semiconductor. On the contrary, inside the potential region below $E_{FB}$, the slope of the straight line is negative, so the capacitance measured corresponds to a p-type semiconductor that may be attributed to an inner Cr enriched oxide layer of the passive film formed on the alloy surface [26, 63–65]. These results have also been observed in other works [66, 67].

According to Mott-Schottky theory [68], the capacitance of the film/electrolyte interface for p- and n-type semiconductors is given by (13) and (14). Donor density, $N_D$, and acceptor density, $N_A$, can be determined from the slope of the experimental $C^{-2}$ versus $E$ plots.

Table 4 summarises the values of $N_D$ and $N_A$ corresponding to Alloy UB6. The density of defects is in the range between $10^{20}$ and $10^{21}$ cm$^{-3}$, which are of the same order of magnitude as those reported for austenitic stainless steels in several papers [35, 69–72]. These defects act as dopants, that is, oxygen vacancies and cation interstitials imparting n-type properties and cation vacancies yielding p-type character [70, 71].

Based on the values of Table 4, it can be concluded that the passive film formed on UB6 steel is disordered, which becomes more visible at higher temperatures. The decrease in the slope when the temperature increases indicates that the concentration of donor and acceptor species in the passive film increases with temperature [69]. Higher donor and
Table 4: Donor and acceptor density of the oxide films formed on UB6 stainless steel at different temperatures between 20 and 80°C.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$N_A \times 10^{20} \text{cm}^{-3}$</th>
<th>$N_D \times 10^{20} \text{cm}^{-3}$</th>
<th>$C_{\text{1sc (outer)}} \times 10^4 \text{Fcm}^{-2}$</th>
<th>$C_{\text{2sc (inner)}} \times 10^4 \text{Fcm}^{-2}$</th>
<th>$d_{1 \text{(outer)}} \text{nm}$</th>
<th>$d_{2 \text{(inner)}} \text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>5.54</td>
<td>2.03</td>
<td>24.66</td>
<td>20.89</td>
<td>0.67</td>
<td>0.66</td>
</tr>
<tr>
<td>40°C</td>
<td>9.33</td>
<td>3.95</td>
<td>20.61</td>
<td>29.55</td>
<td>0.66</td>
<td>0.46</td>
</tr>
<tr>
<td>60°C</td>
<td>10.3</td>
<td>4.71</td>
<td>18.6</td>
<td>36.52</td>
<td>0.60</td>
<td>0.37</td>
</tr>
<tr>
<td>80°C</td>
<td>24.3</td>
<td>5.60</td>
<td>17.0</td>
<td>75.2</td>
<td>0.57</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Figure 5: Mott-Schottky curves for the passive films formed in contaminated 5.5 M phosphoric acid at 20°C, 40°C, 60°C, and 80°C at the formation potential of 0.6 VAg/AgCl.

acceptor density values at elevated temperatures means that the passive films formed on UB6 steel exhibit a more defective structure and worse protective properties, as observed in the EIS measurements.

According to the results obtained in the Mott-Schottky analysis, two space-charge regions appear at the metal/inner layer and outer layer/electrolyte interfaces. The capacitance of these two space-charge layers can be estimated from the capacitance values measured at those two-potentials, where $1/C^2$ reaches a maximum in the Mott-Schottky plots, that is, at the formation potential (thickness of the outer layer) and at the most negative potential (thickness of the inner layer). The contribution of the Helmholtz layer capacitance ($C_{\text{H}}$) to the total capacitance has not been neglected, and its value has been taken as the capacitance at the flat-band potential, for each temperature. Arranging (11) is as follows:

$$C_{\text{SC}} = \frac{C \cdot C_{\text{H}}}{C_{\text{H}} - C}. \quad (15)$$

Thereafter, the thickness of the outer and inner layers of the film can be calculated using (10). Values of $C_{\text{SC}}$ and thicknesses ($d$) are presented in Table 4.

It can be observed that the inner layer exhibits higher capacitance ($C_{\text{SC}}$) than the outer layer ($C_{\text{H}}$), especially at high temperatures, which means that the inner layer is thinner than the outer layer. These findings agree with the previous results obtained by EIS, validating the equivalent circuit chosen to interpret the experimental results.

4. Conclusions

The electrochemical behaviour of the passive film formed on Alloy UB6 in contaminated phosphoric acid (5.5 M) was investigated using potentiodynamic polarisation, EIS, and M-S analysis, and the following conclusions were drawn.

1. The potentiodynamic polarisation curves were characterised by a very wide passive range indicating good protection efficiency. The passive current density increased and the transpassive potential decreased as temperature increased in the studied solution, indicating a decrease in corrosion resistance with temperature.

2. The impedance has been found to be dependent on the temperature of the electrolyte, indicating the occurrence of a charge transfer reaction in a porous film. EIS measurements showed that the protection provided by the passive film was predominantly due to the inner oxide film. The resistance of the outer porous layer $R_1$ decreased slightly as the temperature increased, which suggests that the temperature favoured the formation of a more porous film. Capacitance values increased in general with temperature, indicating a decrease in the passive layers thickness and worse behaviour of UB6 against corrosion.

3. The Mott-Schottky plots have shown both p-type and n-type semiconducting behaviours. Calculated acceptor/donor densities of UB6 in the contaminated phosphoric acid revealed an increase of the acceptor/donor densities with temperature, whose values are of the order of $10^{20}$ cm$^{-3}$. According to the obtained results, it can be concluded that the passive film formed on UB6 steel has a disordered structure and becomes more defective at higher temperatures.

References


