Chemical composition and electronic structure of the oxide films formed on 316L stainless steel and nickel based alloys in high temperature aqueous environments

M.F. Montemor, M.G.S. Ferreira*, N.E. Hakiki1, M. Da Cunha Belo

Department of Chemical Engineering, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

Received 23 July 1999; accepted 17 January 2000

Abstract

Auger analysis, capacitance measurements and photoelectrochemical measurements have been used in order to study the oxide films formed on 316L stainless steel, Alloy 690 and Alloy 600 in high temperature aqueous environments at pH 8 and 10. The analytical study reveals the duplex character of the films formed on 316L stainless steel and Alloy 690. For these materials it is assumed that the capacitance and the photoelectrochemical results can be related to the semiconducting properties of mixed iron-nickel oxide and chromium oxide which represent the outer and the inner parts of the film, respectively. In the case of the Alloy 600 the presence of nickel oxide controls the semiconducting properties of the film formed at pH 10, but for the film formed at pH 8 the presence of mixed iron-nickel oxide in the outer layer still controls those properties. Finally, it is demonstrated that the capacitance behaviour of the thin passive films formed at room temperatures could serve as a useful basis for interpreting the higher temperature results. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Stainless steel; Nickel; High temperature corrosion

* Corresponding author. Tel.: +351-21-841-72-34; fax: +351-21-840-45-89.
E-mail address: mgferreira@ist.utl.pt (M.G.S. Ferreira).
1 Permanent address: Institut de Physique, Laboratoire d’Optique des Couches Minces, Université d’Oran, Es-Senia, Algerie.
1. Introduction

Stainless steels and nickel based alloys type Alloy 600 generally corrode at very low rates in high temperature aqueous environments because of their tendency to form a protective oxide film. However, with their use in nuclear power systems certain corrosion problems can be observed. Unfortunately, it is not always possible to establish direct correlation between the protective quality of the films and a well defined chemical or structural factor.

Relatively recent investigations carried out with oxide films formed on 304 stainless steel exposed to lithiated water reveal a transition in the semiconductivity of the films (p-type to n-type) when the temperature of film formation increases [1].

It is highly probable that the electronic structure of the oxide films also plays a major role when their protective character is considered. However, the system formed by the oxide film, the metallic substrate and the electrolyte is rather complex. The film itself, generally, presents strong gradients of chemical composition and can be constituted of regions of different semiconductivity [2]. In the case of 316L stainless steel the films can generally be described as a duplex composed by an inner chromium oxide region and an outer mixed iron-nickel oxide region [2], which exhibit different types of semiconductivity. An equivalent duplex can also be identified in the case of the thin passive films [3–6,15].

In the present work Auger Electron Spectroscopy (AES), capacitance measurements (Mott-Schottky plots) and photoelectrochemistry were used to study the chemical composition and electronic structure of the oxide films formed on 316L stainless steel, Alloy 600 and Alloy 690 in high temperature aqueous environments.

2. Experimental

The composition of the alloys used in this study is depicted in Table 1. All of the samples were first vacuum-annealed at 1050°C for 20 min and then polished with diamond paste down to one micron. They were subsequently oxidised by exposure to aqueous solutions, which simulate possible environments created in the secondary circuit of pressurised water reactors. The test solution contained

<table>
<thead>
<tr>
<th>Alloy</th>
<th>C</th>
<th>S</th>
<th>P</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L</td>
<td>0.030</td>
<td>0.0010</td>
<td>0.021</td>
<td>0.44</td>
<td>1.84</td>
<td>12.3</td>
<td>17.54</td>
<td>65.36</td>
<td>2.470</td>
</tr>
<tr>
<td>Alloy 600</td>
<td>0.1</td>
<td>0.015</td>
<td>0.025</td>
<td>0.31</td>
<td>0.78</td>
<td>74</td>
<td>16</td>
<td>8.63</td>
<td>–</td>
</tr>
<tr>
<td>Alloy 690</td>
<td>0.019</td>
<td>0.0006</td>
<td>0.006</td>
<td>0.32</td>
<td>0.31</td>
<td>59.73</td>
<td>29.25</td>
<td>10.35</td>
<td>0.01</td>
</tr>
</tbody>
</table>
NaOH and H₂SO₄ in different concentrations in order to obtain two different pHs (pH = 8 and 10). The autoclaves used for the oxidation were made of 316 stainless steel and had a volume of 3 l. The oxidation time was 720 h for the sample tested at pH 8 and 1000 h for the samples tested at pH 10. The solution at pH 8 was held at 350°C and that of pH 10 was at 320°C. Results of passive films anodically formed at 0.6 V in a buffer solution of composition H₃BO₃ (0.05 M) + Na₂B₄O₇·10H₂O (0.075 M) and pH = 9.2 are also reported for comparison. The former type of films will be designated in the text by oxide (thick) films and the latter by passive (thin) films.

The analytical experiments were made using a 310F Microlab (VG Scientific), equipped with a field emission type electron gun and a concentric hemispheric analyser. Auger spectra were taken at 10 keV, with a 50 nA primary electron beam. Ion etching was performed at a pressure of 10⁻⁷ mbar using high purity argon. The etching current was approximately 0.75 μA/mm². In these conditions the etching rate was assumed to be ~40 nm/min. Due to surface roughness and topography, as well as preferential sputtering this value can not be considered as an exact value, however comparative results are valid. The etched area was a crater with a diameter of 1 mm, whereas the electron beam had a spatial resolution of ~100 nm. The electron beam was aligned with the centre of the sputtered region. Although the roughness of the surface increases with the sputtered depth, the very high spatial resolution of the electron beam limits the deleterious effects of a long sputtering time. All the experiments were made in duplicate samples, with good reproducibility.

The main peaks used for the determination of the atomic percent in the depth profiles were: OKL₁ at 513 eV, Fe LM₄ at 647 eV, Ni LM₂ at 842 eV and Cr LM₂ at 527 eV. The atomic percentages were calculated considering the peak areas from the AES spectra in direct mode, after background subtraction using the Shirley algorithm.

The capacitance and photoelectrochemical studies were performed in a buffer solution of composition H₃BO₃ (0.05 M) + Na₂B₄O₇·10H₂O (0.075 M) and pH 9.2. A three electrode electrochemical cell was used with a saturated calomel reference electrode and a platinum counter electrode. The experiments were performed at ambient temperature (22°C) with continuous N₂ bubbling. The capacitance measurements were performed at 3160 Hz. The polarisation was applied in successive steps of 50 mV in the cathodic direction from the film formation potential (0.8 V). A potentiostat (273 EGG/PAR) and a double phase synchronous detector (lock-in Brookdeal 5208) with an internal oscillator working over a wide frequency range (5 Hz to 100 kHz) were used. The principle is to apply simultaneously a perturbing signal ΔU (10 mV rms) to the cell via the potentiostat and to the reference chain. The response is compared to ΔU dephased by Δφ (phase shift) and Δφ + π/2. Photoelectrochemical measurements were performed by using a 150 W Xenon lamp and a 1200/mm grating monochromator (H25 Jobin Yvon). The photocurrents were generated by focusing the light with a fused silica lens through the quartz window of the electrochemical cell onto the working electrode. In all experiments the lock-in technique was applied, allowing
the separation of the photocurrent from the passive current by chopping the light at a constant frequency (19 Hz) and feeding the signal, as well as the current output of the potentiostat to a lock-in amplifier. The photocurrent spectra as a function of the energy of the incident light were obtained by scanning the wavelength of the light in steps of 50 nm from 750 to 250 nm.

3. Results

3.1. Auger electron spectroscopy (AES)

Fig. 1 shows the AES depth profiles obtained for the oxide films formed on the different materials at pH 8. For the films formed on 316L stainless steel and Alloy 690, the profiles reveal an important enrichment in chromium in their internal layers. Thus, in the case of 316L stainless steel and Alloy 690 the Cr profile starts to increase at ~50 nm and it passes through a maximum of its atomic percentage at around 40% before it reaches the bulk composition. This enrichment is not so pronounced for the films formed on Alloy 600, where the maximum Cr content is about one half of that determined for 316L stainless steel and Alloy 690. For the stainless steel the external layers of the film are mainly composed of iron oxides, whereas for Alloy 600 and Alloy 690, nickel oxide replaces part of the iron oxide in the composition of these layers.

The Auger depth profiles obtained after oxidation at pH 10 during 1000 h (Fig. 2) show important changes relatively to the profiles obtained at pH 8. Thus, for the films formed on 316L stainless steel, the analytical study reveals that the Cr content in the internal layers is below 20% and that no maximum (peak) of concentration exists. The external layers of the film are essentially composed of iron oxides. The Ni content in these films is similar to that observed for the oxidation at pH 8, being about 10–15%. For the Alloy 600, the Cr content in the film is even lower (<10%). In the case of this alloy, the film is mainly composed of Ni oxides. The Fe content is constant at ~10%. The film formed on Alloy 690 reveals a distinctly different composition. In fact, the Cr content strongly increases with depth and reaches a maximum with values around 50%. The external layers of the film are composed by an equivalent amount of iron and nickel oxides.

3.2. Capacitance results (Mott-Schottky approach)

It is well established that the capacitance behaviour of a passive film–electrolyte interface is similar to that of a semiconductor–electrolyte interface [7]. Thus, the effect of the applied potential, \( U \), on capacitance values is described by the Mott-Schottky equation:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 q N_q} \left( U - U_{fb} - \frac{kT}{q} \right)
\]  

(1)
Fig. 1. Auger depth profiles of the oxide films formed on 316L stainless steel, Alloy 600 and Alloy 690 in the aqueous environment at pH 8. (Exposure time: 720 h).
where $N_q$ is the carrier concentration (donor or acceptor), $\varepsilon$ the dielectric constant of the passive film, $\varepsilon_0$ the vacuum permittivity, $q$ the elementary charge ($-e$ for electrons and $+e$ for holes), $k$ the Boltzmann constant, $T$ the temperature and $U_{fb}$ the flatband potential.

Fig. 3 shows the capacitance behaviour of the oxide films formed at pH 8 on 316L stainless steel, Alloy 690 and Alloy 600. In the case of the stainless steel, the Mott-Schottky plots acquired at 3160 Hz reveal n-type semiconducting behaviour.

Fig. 2: Auger depth profiles of the oxide films formed on 316L stainless steel, Alloy 600 and Alloy 690 in the aqueous environment at pH 10. (Exposure time: 1000 h).
(positive slope) in the region above $-0.5 \text{ V}$ and p-type semiconducting behaviour below this potential.

It is interesting to note that the capacitance results for the oxide film formed on 316L stainless steel are in good agreement with the analytical results presented in Fig. 1, that revealed an internal chromium oxide rich layer and an external iron

![Graph 1](image1.png)

![Graph 2](image2.png)

![Graph 3](image3.png)

Fig. 3. Plots of $1/C^2$ vs. applied potential, $U$, for the oxide films formed at pH 8.
oxide rich layer which are p-type and n-type semiconductors, respectively. The study of the oxide film formed on Alloy 690 also reveals n and p semiconductivity. However, the p-type semiconductivity is not so marked. This in spite of a relatively high chromium concentration in the oxide film. The oxide film formed on Alloy 600 manifests only n-type semiconductivity. The capacitance

![Graphs showing plots of 1/C^2 vs. applied potential, U, for the oxide films formed at pH 10.](image-url)

Fig. 4. Plots of 1/C^2 vs. applied potential, U, for the oxide films formed at pH 10.
values of this film are much lower than those of the films formed on the other two alloys.

Fig. 4 shows the capacitance behaviour of the oxide films formed on the different materials at pH 10. The semiconducting properties of the oxide films formed on 316L stainless steel and Alloy 690 also reveal n and p semiconductivity as the oxide films formed at pH 8. However, in the case of the stainless steel, the p-type semiconductivity is not so marked as in the case of the oxide film formed at pH 8. This agrees with the fact that the chromium concentration is lower at pH 10. The capacitance results obtained with the oxide film formed on Alloy 600 are entirely different. Thus, the film behaves as a capacitor or more probably as a low doped semiconductor in the potential region where the films formed on the other two alloys manifest p- or n-type semiconducting behaviour. The comparison between composition and capacitance will be referred to in more detail in the discussion.

3.3. Photoelectrochemical results

The photoelectrochemical behaviour of the oxide film is examined by determining the photocurrent generated under illumination, as a function of the incident light energy. Taking into account the GÄrtnert model [8] and introducing some simplifications, the quantum efficiency \( \eta \), defined as the ratio between the photocurrent and the incident photon flux, \( \Phi_0 \), is given by the following relationship:

\[
\eta = \frac{I_{ph}}{\Phi_0} = qAw \left( \frac{hv - E_g}{1} \right)^n
\]

where \( A \) is a constant, \( q \) the elementary charge, \( w \) the space charge layer thickness, \( E_g \) the bandgap energy and \( hv \) the photon energy. The value of \( n \) in Eq. (2) depends on the type of transition between the valence band and the conduction band. The best fitting values are obtained for \( n = 2 \). This value, which corresponds to indirect transitions in the crystalline band structure model, has been used in different investigations on passive films. The value of the bandgap energy obtained from the intercept of the straight line with the photon energy axis is \( 2.4 \) eV for the oxide films formed on the different alloys at pH 8 (Fig. 5(a)). At pH 10 (Fig. 5(b)), the bandgap energy of the oxide film formed on the 316L SS and Alloy 690 is identical to that of the films formed at pH 8. Only the oxide film formed on Alloy 600 has a different gap. Its value is about 2.9 eV, which approaches of the bandgap value of the nickel oxide, emphasising the importance of this oxide in the semiconducting properties of the film.
Fig. 5. Plots of $(\eta hv)^{0.5}$ vs. the incident light energy, $hv$, for the oxide films formed in the aqueous environment: (a) at pH 8; (b) at pH 10.

Table 2
Doping density ($N_d$) of the oxide films formed at pH 8

<table>
<thead>
<tr>
<th>316L</th>
<th>Alloy 690</th>
<th>Alloy 600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.9 \times 10^{20}$ cm$^{-3}$</td>
<td>$0.6 \times 10^{20}$ cm$^{-3}$</td>
<td>$0.02 \times 10^{20}$ cm$^{-3}$</td>
</tr>
</tbody>
</table>

*The doping density of passive films is in the range $5 \times 10^{20}$ to $9 \times 10^{20}$.}
4. Discussion

4.1. Comparison of the capacitive behaviour of oxide films and passive films

The capacitive behaviour of the relatively thick oxide films formed on stainless steel in high temperature aqueous environments is qualitatively similar to that of thin passive films formed on the same materials in aqueous solutions at room temperature. This, in spite of the fact that the capacitance values and donor density values are different (Table 2) [3,4]. Fig. 6 shows that both thick and thin films, formed on 316L stainless steel, present equivalent flatband potentials and manifest p-type and n-type semiconductivity in the same potential ranges. The existence of negative and positive slopes in the $C^{-2}$ vs. $U$ curves has been interpreted as representative of the capacitance behaviour of a system, which has a duplex character, with an inner p-type semiconducting region formed by chromium oxide and an outer n-type semiconducting region formed by iron oxide [3,4]. Further, the change in the slope of the $1/C^2$ vs. $U$ plots at about 0 V/SCE is also observed for the two kinds of films. This change must be considered as an important feature of the Mott-Schottky plots. Indeed, according to published data [9–11], this change of capacitance behaviour can be related to the existence of a second donor level formed by the Fe$^{2+}$ ions placed in the octahedral sites of the unit cell of the spinel. This means that the outer layers of the relatively thick and very thin films have equivalent spinel structures.

The study of the passive films formed on nickel based alloys also helps to interpret the capacitance behaviour of the oxide films formed in high temperature aqueous environments. Fig. 7 shows that the passive films formed on Alloy 600 and Alloy 690 in a borate buffer solution, behave as a n-type semiconductor at potentials higher than the flatband potential and as a p-type semiconductor at

![Fig. 6. Plots of $1/C^2$ vs. $U$ for an oxide film formed at high temperature in aqueous environment (thick film) and for a passive film formed at 0.6 V (vs. SCE) in borate buffer solution (thin film) on stainless steel.](image)
potentials lower than this potential. It also appears that the capacitance values of these alloys in the potential region close to the flatband potential are equivalent to those of the passive film formed on nickel and are lower than those obtained for passive films formed on stainless steels. Such a behaviour was explained for Alloy 600 [5], and could be extended to Alloy 690, by the fact that the film formed in that alloy depicts in this potential region a capacitance response essentially controlled by the nickel oxide. The passive films formed on stainless steels and nickel-base alloys although contain Ni and Fe in both cases, have a much larger Ni/Fe ratio in the case of nickel-base alloys [12,13].

The main difference between the semiconducting properties of the passive films and of the thick oxide films can be related to different carrier concentrations (Table 2). This is particularly the case when the films formed on 316L stainless steel and Alloy 690 are considered. For Alloy 600 at pH 8 the semiconductivity properties of the external layers of the passive films and thick oxide films are in both cases strongly influenced by iron oxide, but at pH 10 in the case of thick oxide films, the nickel oxide dominates the capacitance response.

4.2. Correlation between the chemical composition and the capacitance results

Fig. 8 shows the influence of pH on both AES depth composition profiles and capacitance behaviour of the oxide films formed in high temperature water. The following complementary remarks can be made.

In the case of the films formed on 316L stainless steel, the decrease of chromium in the oxide film with increasing pH, explain the evolution of the capacitance values in the regions of p-type semiconductivity. There is a direct relationship between the chemical composition and the capacitance behaviour of

![Graph](image_url)
the films as a consequence of their strong duplex character i.e. n-type and p-type behaviour. The larger amount of chromium oxide for pH 8 strengthens the p-type behaviour at potentials lower than the flatband potential (−0.5 V).

It is not so easy to relate the capacitance behaviour of the oxide formed on Alloy 690 to its chemical composition. The duplex character of the film is also observed but the Cr/Fe, Fe/Ni and Cr/Ni ratios are very different. Only the evolution of the iron depth profile reveals a very important modification of the chemical composition, which is reflected in the fact that the donor concentration is lower for the higher pH. The decrease in the donor density corresponds to a diminution of film defects, which is expected for films richer in iron oxide [14].

Finally, for films formed on Alloy 600 the pH plays a very important role. The

Fig. 8. Auger results and capacitance behaviour obtained with the oxide films (comparative study).
increase in nickel observed with increasing pH, is accompanied by a transition from a n-type semiconductor to probably a low doped p-type semiconductor.

4.3. Electronic structure of the films

The study by photoelectrochemistry shows that at pH 8 the bandgaps of the different oxide films have the same value. This can be explained by the fact that all the films examined have an equivalent structure (a spinel structure) with practically the same lattice parameter. Only in the case of the film formed at pH 10 on Alloy 600, the gap energy corresponds to a relatively pure nickel oxide. Thus, based on capacitance and photoelectrochemical studies it can be assumed that the electronic structure of the films formed on 316L stainless steel in high temperature water can be compared to that of a p–n heterojunction constituted by a p-type chromium oxide layer on the metal side and an n-type layer on the electrolyte side. The flatband potential is determined by the flatband potential of the iron oxide situated at about −0.5 V/SCE. The schematic band structure model

Fig. 9. Schematic representation of the band structure model of the different films under polarisation: (a) oxide film formed on 316L; (b) oxide film formed on Alloy 600. $U_{fb1}$ = flatband potential of iron oxide (~−0.5 V vs. SCE); $U_{fb2}$ = flatband potential of nickel oxide (~+0.5 V vs. SCE).
in Fig. 9(a) shows that in the potential region below the flatband potential the internal chromium oxide layer acts as a Schottky barrier and reveals p-type semiconductivity. At potentials higher than the flatband potential it is the external layer that is in a condition of depletion showing n-type semiconductivity. The internal layer is in a condition of accumulation (ohmic contact) at potentials higher than the flatband potential while the external layer is in condition of accumulation at potentials below the flatband potential. It is important to remark that in case of the oxide films formed on Alloy 690 their electronic structure can also be compared to a p–n heterojunction.

The influence of the nickel appears more clearly when the oxide films formed on the high nickel content alloy (Alloy 600) are considered. Although the presence of iron oxide still dominates the capacitance response at potentials higher than the flatband potential in films formed at pH 8, for films formed at pH 10 it is the nickel oxide that dominates the response in the range of potentials studied (Fig. 9(b)). The film formed at pH 8 reveals only n-type semiconductivity with lower doping level than in the case of 316L stainless steel and Alloy 690. At pH 10 the capacitance response is similar to that of a pure nickel oxide and reveals a blocking character of this oxide in the potential region near the flatband potential, where the iron and chromium oxides are conductors.

5. Conclusions

The results obtained in this study allow to describe the complex relationship existing between the chemical composition and the semiconducting properties of the oxide films formed on 316 stainless steel, Alloy 600 and Alloy 690 in high temperature aqueous environments.

The study demonstrates that iron as an alloying element has a very great influence on the electronic structure of the oxide films formed on Alloy 600 and Alloy 690. It also appears that the study of the oxide films formed on both stainless steel and nickel based alloys reveal semiconducting properties qualitatively similar to those of the thin passive films formed at room temperatures.

The basic electronic structure model in the case of the films formed on 316L stainless steel reflects the development of a p–n heterojunction. The pH of the environment does not change the duplex character of the film but affects the proportion of chromium oxide and of iron oxide in the film, essentially in the internal region.

The existence of the p–n heterojunction is also an important feature of the electronic structure of the films formed on Alloy 690. However, the slopes of the straight lines of the Mott-Schottky plots, reflect the influence of the nickel in the oxidation processes. It also appears that the iron concentration in the film increases when the pH of the environment increases.

The duplex character of the oxide films is hidden for the films formed on Alloy 600. Depending on the pH, the films formed on this alloy behave either as a n-
type semiconductor (because they are mixed nickel–iron oxides) or as a p-type semiconductor with relatively low doping density.

Acknowledgements

The authors are indebted to Electricité de France (EDF-GDL) for carrying out the oxidation treatments in autoclave.

References