The role of Mo in the chemical composition and semiconductive behaviour of oxide films formed on stainless steels

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Abstract

The oxide films grown in air, inside a furnace, during two hours at temperatures between 250°C and 450°C, on the surface of commercial alloys (AISI 304 and AISI 316) and on the surface of high purity alloys with and without Mo addition (Fe-17Cr, Fe-17Cr-5Mo, Fe-17Cr-25Ni and Fe-17Cr-25Ni-10Mo) were characterised by analytical (AES and XPS) and capacitance measurements (Mott-Schottky plots).

The analytical results have shown that the oxide films formed on the stainless steels are composed by an external iron oxide region and an inner chromium oxide region. Mo was not detected in the former region, whereas the later region reveals the presence of Mo. Whenever Mo is present in the alloy there is an enrichment of chromium oxide in the film. The film thickness is practically independent of the presence and content of Mo.

The raise in the temperature of film growth from 250°C to 450°C led essentially to the thickening of the external iron oxide region, whereas the thickness of the inner chromium oxide region remains unchanged. The capacitance measurements indicate that the influence of Mo on the film capacitance can be related to a decrease of the number of donors in the iron oxide layers of the film. The presence of Mo also affects the defect structure of the inner chromium oxide region. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Ferritic and austenitic stainless steels (SS) have attracted extensive interest due to their good corrosion resistance over a wide range of environments.

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The beneficial effect of Mo in the corrosion resistance of stainless steels has been attributed to several factors such as: an enrichment of Mo in the passive film [1, 2] or in the alloy layer just below the passive film [3,4]; enrichment of Cr in the oxide layer [4,5]; thickening of the passive film and stabilisation of the Cr oxides [1] by the presence of Mo\(^{6+}\). It has also been suggested that Mo retards the corrosion process by adsorption [6], by formation of Mo compounds [7], by synergistic interaction of Mo ions with other oxides of the passive film [1,8], and by elimination of the active surface sites through formation of Mo oxides or oxihydroxides [9]. A model based in solute-vacancy interaction was also developed [10, 11] where the beneficial effect of Mo is explained in terms of interaction between Mo\(^{6+}\) and cation vacancies to reduce the cation vacancy flux from the film/solution interface to the metal/film interface.

Controversy also exists when the chemical composition of the films [3,12,13] is discussed. Thus, there are some analytical results showing the presence of Mo in the oxide film [1,3,14,15], namely the presence of Mo\(^{4+}\) and Mo\(^{6+}\), whereas in other studies Mo was not found in the films [9,4]. The effect of the temperature of film formation has been mainly discussed in terms of film thickness [16,17]. However, the temperature also affects the film composition [15,16,18]. Consequently the explanation for the effect of Mo on the corrosion resistance is still a subject of discussion.

The purpose of this work is to study the role of Mo as an alloying element on the composition and semiconductive properties of oxide films formed in the air on commercial and on high purity stainless steels, at temperatures between 149°C and 349°C. A comparative study of the composition and thickness of the oxide films formed on the different alloys was made by AES analysis, whereas XPS was used to gain insight into the chemical state of the species present in the oxide. The analytical results were interpreted in conjunction with capacitance measurements. This latter technique gives information about the electronic structure of the oxide films and particularly about their conductivity.

2. Experimental method

2.1. Materials preparation

Austenitic stainless steels (AISI 304 and 316) were used as test materials—Table 1. The samples were cold worked and then vacuum annealed for 1/2 hour at 1050°C. The annealing treatment was made in order to eliminate plastic deformations.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Ni</th>
<th>C</th>
<th>N</th>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cu</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>304 SS</td>
<td>17.4</td>
<td>8.3</td>
<td>0.053</td>
<td>0.04</td>
<td>0.48</td>
<td>1.42</td>
<td>0.39</td>
<td>0.14</td>
<td>0.024</td>
</tr>
<tr>
<td>316 SS</td>
<td>16.9</td>
<td>10.9</td>
<td>0.053</td>
<td>0.025</td>
<td>0.75</td>
<td>1.24</td>
<td>2.11</td>
<td>0.20</td>
<td>0.027</td>
</tr>
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</table>
Very high purity alloys (Fe-17Cr, Fe-17Cr-5Mo, Fe-17Cr-25Ni and Fe-17Cr-25Ni-10Mo) containing the main elements found in the stainless steels were also used and were prepared by the plasma furnace technique [19]. In these alloys, the concentration of the non-metallic and metallic residual elements was very low (typically: 0.002% C, 0.001%N and lower than 0.002% for Si and Mn). These samples were vacuum annealed for 1 hour at 900°C.

The surface of the samples was abraded with wet SiC paper of decreasing grit size (400, 600 and 1200) and was finally polished with alumina (2 μm), rinsed in distilled water, ultrasonically cleaned and dried in air.

Oxidation of the alloys was made in air, at fixed temperatures of 250, 350 and 450°C, inside a furnace, during two hours at the atmospheric pressure. After oxidation, the samples were cooled in air. Due to the small thickness of the specimens, the cooling process was very rapid. After cooling, the samples were kept in a dry atmosphere, at room temperature before the analytical and electrochemical experiments.

2.2. Analytical techniques

The analytical experiments were made using a 310 F Microlab (VG Scientific) equipped with a field emission type electron gun, a concentric hemispherical analyser and a differentially pumped ion gun. Auger spectra were taken using a 10 keV, 50 nA primary electron beam. The angle between primary beam and the surface normal was 30°. Spectra were run in constant retard rate mode (CRR = 10 eV); the energetic resolution being about 0.2%. The calibration of the analyser was made according to the following peak energies: Cu LMM at 807.51 eV; Ag MNN at 246.79 eV and Au NVV at 69.0 eV.

Ion etching was performed at a pressure of 1.10−7 mBar using high purity argon. The etching current was approximately 0.75 μA/mm². The etched area was a crater with a diameter of 0.5 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 long sputtering.

XPS experiments were performed on the samples surface, before and after ion sputtering. The sputtering was made using a ion beam with a low energy (1.5 keV) in order to minimise the effects of reduction in the oxidised metallic species. A non-monochromated Mg anode (Kα = 1253.6 eV) was used. Spectra were obtained in constant analyser energy mode (CAE = 30 eV). For this value, the energetic resolution is ≈1 eV.

The film thickness was calculated from the Auger and XPS surface spectra (without ion etching) using the QUASES software [20-22].

All the experiments were made in duplicate samples, with a good reproducibility.

2.3. Capacitance experiments

Capacitance measurements were performed on the oxides previously formed at 350°C on AISI 304 and 316 stainless steels and on the high purity alloys containing
10% of Mo. A classical cell with three electrodes was used, with a platinum counter-electrode and a saturated calomel reference electrode (SCE). All the experiments were carried out at room temperature (22°C) under continuous deaeration with high purity nitrogen in a buffer solution of composition H₃BO₃ (0.05 M) + Na₂B₄O₇·10H₂O (0.075 M) and pH = 9.2.

The capacitance measurements were performed at 3160 Hz in the potential range 1 V to −1.5 V. The polarisation was applied by successive steps of 50 mV in the cathodic direction. A potentiostat (EG&G 273) and a double phase synchronous detector (Brookdeal 4197 lock-in amplifier) with an internal oscillator working in a large frequency range (5 Hz–100 kHz) were used. The principle is to apply simultaneously a perturbing signal $\Delta U$ (10 mV rms) to the cell via the potentiostat and to the reference chain. The response is compared to $\Delta U$ dephased by $\Delta \phi$ and $\Delta \phi + \pi/2$.

3. Results

3.1. Analytical study

The main peaks used in the AES analysis were O KL₁ at 513 eV, Fe LM₄ at 647 eV, Ni LM₂ at 842 eV, Cr LM₂ at 527 eV and Mo MN₂ at 122 eV. The use of the Fe peak at 647 eV was justified because the main peak at 703 eV is partially overlapped with one of the Ni LMM peaks. Auger depth profiles were built from spectra in the direct mode, after background subtraction using the Shirley algorithm. The determination of the elements atomic percentages was made considering the peak areas normalised using the sensitivity factors supplied by the manufacturer of the spectrometer [23]. Automatic correction of the spectrometer transmission function was also made using data available on specific software [23] for the analyser. All the Auger depth profiles were determined using the same procedure in order to allow the best comparison of the results.

In qualitative terms, all the depth profiles showed a similar evolution for the elements present in the oxide film. Fig. 1 shows the AES depth profiles obtained from the high purity and commercial stainless steels, oxidised at 350°C. The film thickness was determined using the software referred in the experimental procedure. Thus, the thickness calculated from the analysis of the AES and XPS spectra was then correlated with the sputtering time necessary for the oxygen to drop to half of its initial value. This procedure allowed the conversion of the etching time to thickness, assuming a constant etching rate with time and within the oxide. Comparison of the results depicted in Fig. 1 show that the film thickness is practically independent of the alloy composition, namely the Mo content, being in the range 20 to 25 nm.

The oxygen and the alloying elements contents depicted in Fig. 1, do not correspond to definite stoichiometries of the respective oxides. In fact, the oxygen content is lower than that requested by the stoichiometries. This result may be due to the use of sensitivity factors from the literature that can induce systematic errors in the calculation of the atomic concentrations of the elements. Other factors can also have influence, as for example in the case of iron, the use of a peak different of the main
Fig. 1. Auger depth profiles obtained on the high purity alloys and on the commercial alloys, oxidised at 350°C.
peak (FeLM2 at 703 eV) that is usually recommended. In this case the proximity of other less intense peaks may induce quantification errors. However, it is necessary to stress that all the depth profiles were built using the same peaks and the same procedure, allowing the qualitative comparison of the results. Thus, the AES depth profiles reveal that the oxide film is composed by two distinct layers: the outer layer is Fe rich, without any Cr or Mo; the inner layer is Cr rich, with Mo and Ni. For the high purity alloy with a higher Ni content (Fe-17Cr-25Ni with and without Mo) some Ni was also found in the outer layers.

For the alloys oxidised at 350 °C as the etching proceeds the Cr, Mo and Ni signals become stronger. The Cr profile presents a maximum near the oxide/alloy interface. Thus, it could be said that the oxide has a region of about 10 atomic layers enriched in chromium relatively to the substrate. Fig. 2 shows that the presence of Mo affects the Cr oxide content of the film. The amount of this oxide becomes higher in the presence of Mo. This result was observed both for the commercial and for the high purity alloys.

XPS analysis was also performed on the samples oxidised at 350 °C, as introduced in the UHV chamber and after sputtering. Although the analytical apparatus does not allow a good determination of XPS depth concentration profiles, the determination of spectra with different degrees of sputtering gives interesting information on the evolution of the various chemical species inside the film. The interpretation of the XPS spectra was made after background subtraction using the Shirley algorithm and deconvolution into the contribution of the different species of the same element.

Fig. 3 depicts the evolution of the O1s, Fe2p3/2, Cr2p3/2, Ni2p3/2, Mo3d5/2 and Mo3d3/2 peaks for the alloy Fe-17Cr-25Ni (oxidised at 350 °C) with the etching time. Fig. 4 shows the deconvolution procedure used for the peaks depicted in Fig. 3 that correspond to 4 min of etching (line c).

The O1s spectra obtained at the surface (before etching)—line 1—is composed of two peaks. The peak centred at 530.3 eV is characteristic of the oxide species (O–M bond), whereas the peak centred at approximately 532.4 eV is typical of OH ions and bound water in the surface of the oxide. After etching—lines 2 and 3—only the peak at lower binding energies is present (Fig. 4) revealing the presence of hydrated species limited to the external layers.

Fig. 3 shows that the Fe2p3/2 peak obtained at the surface is centred at 711.5 eV. This energy can be attributed to a mixture of FeOOH and Fe2O3 species, which is in accordance with the O1s spectra. After etching, the Fe2p3/2 peak appears shifted to lower binding energies, revealing the presence of Fe3+ and Fe2+ oxides [4]—Fig. 4. There was no evidence of chromium at the surface—Fig. 3 (line a), but after etching, it was possible to identify Cr2O3 (576.5 eV)-lines b and c.

At the surface the Ni2p3/2 peak position (856 eV) was characteristic of that for NiO3 and/or NiOOH or Ni(OH)2. It is difficult to identify the oxidation state of the Ni because the peak positions for NiOOH, Ni2O3 and Ni(OH)2 are very close (~856 eV). However, Ni(OH)2 is not a likely compound, because the samples were always kept in dry atmosphere. As the etching proceeds, the Ni2p3/2 peak started to shift to lower binding energies, characteristic of NiO (854.5 eV) and metallic Ni (853 eV)—Fig. 4. For the 304 and 316 stainless steels, with a lower Ni content, there was no evidence
Fig. 2. Evolution of the Cr at. % obtained from the Auger depth profiles for the high purity alloys and for the commercial alloys oxidised at 350°C.
Fig. 2. XPS spectra obtained on the Fe-10Cr-14Ni-9Mo high purity alloy oxidised at 249°C: 1-surface; 2-after 1 min. of etching; 3-after 3 min. of etching.

Fig. 3. XPS spectra obtained on the Fe-17Cr-25Ni-10Mo high purity alloy oxidised at 350°C. 1-surface; 2-after 2 min. of etching; 3-after 4 min. of etching.
Fig. 4. Fitting of the XPS spectra obtained on the Fe-17Cr-25Ni-10Mo high purity alloy oxidised at 350°C after 4 min of etching.
of Ni at the surface. However, after etching, a peak for metallic Ni was detected. This result suggests that metallic Ni seems to accumulate in the oxide, probably near the oxide/alloy interface. However, the presence of a peak for the metallic Ni can also be the result of preferential reduction of Ni oxides during the sputtering process.

Fig. 3 also shows the Mo$_{4d}$ doublet. At the surface—line 1—it is not possible to identify the presence of Mo. However after etching, the Mo$_{4d}$ doublet becomes evident. The structure of this doublet is complex, because both the Mo$_{4d_{3/2}}$ and Mo$_{4d_{5/2}}$ ionisation and the different oxidation states are strongly overlapped. The Mo$_{4d}$ spectrum is composed by three shoulders—Fig. 4. The shoulder at 235.6 eV (corresponding to Mo$_{4d_{5/2}}$) reveals the presence of Mo$^{6+}$ whose intensity decreases after etching—line 3. At lower binding energies, the Mo$_{4d_{3/2}}$ peak at 228.4 eV allows the identification of metallic Mo, with an intensity that increased with the etching time-line 3. In the intermediate energy range, the shoulder corresponds to the overlapped peaks for Mo$^{4+}$ (Mo$_{4d_{3/2}}$ at 229.6 eV and Mo$_{4d_{5/2}}$ at 232.4 eV), for metallic Mo (Mo$_{3d_{3/2}}$ at 231.2 eV) and for Mo$^{3+}$ (Mo$_{3d_{5/2}}$ at 232.8 eV). For the alloys containing a lower Mo content, the shoulder at higher binding energies was much less sharp than in the above case, meaning a very low concentration of Mo$^{3+}$.

The effect of temperature on the composition and thickness of the oxide was studied on the Fe-0.6Cr-14Ni-0.9Mo alloy and on the 304 stainless steel. Fig. 5 shows the Auger depth profiles obtained on films formed at 250°C and 450°C. The evolution of the profiles is similar to that observed for films formed at 350°C—Fig. 1. The oxide film is also composed by an external iron oxide region and an internal chromium rich region, where molybdenum is accumulated. For both alloys, the film thickness increases from ≈14 nm to 24-27 nm, when the temperature changes from 250 to 450°C—Fig. 6. The largest change was felt essentially in the outer Fe rich layer whose thickness is raised by a factor of two. The Cr rich layer, in contrast, remains practically unaffected by the increase of the oxidation temperature. Thus, results obtained from the oxides formed at three different temperatures revealed that the chemical composition of the oxide remains qualitatively unchanged, but the thickness of the oxide is strongly affected, especially the thickness of the outer Fe rich layers.

Fig. 7 depicts the Fe$_{3p_{3/2}}$, Cr$_{3p_{3/2}}$, Ni$_{3p_{3/2}}$ and Mo$_{3d_{5/2}}$ and Mo$_{3d_{3/2}}$ spectra for the Fe-17Cr-25Ni-10Mo alloy oxidised at 250°C and at 450°C.

The Fe$_{3p_{3/2}}$ spectrum shows a peak for Fe$^{3+}$ species (711.5 eV) suggesting a mixture of Fe$_2$O$_3$ and FeOOH. The spectrum obtained at 250°C also reveals a peak at 709 eV arising from Fe$^{2+}$ species, probably in the inner layers of the oxide as observed at 350°C. For the oxides formed at 450°C there is no evidence of Cr at the surface. However, for the oxides formed at 250°C, the Cr$_{3p_{3/2}}$ spectrum reveals a weak signal from Cr$_2$O$_3$. The Ni$_{3p_{3/2}}$ peak obtained at 250°C is composed by two peaks: the peak at 856 eV is characteristic of Ni$^{2+}$ oxides, whereas the peak at 853 eV reveals the presence of metallic Ni. The oxide formed at 450°C only reveals a peak for the Ni$^{3+}$ species. Comparison of the Fe, Cr and Ni spectra obtained for the oxides formed at 250°C reveals that the contribution from the metallic species is negligible in the Fe and Cr spectra, but significant in the Ni spectra. This result suggests the presence of some metallic Ni within the oxide, probably situated deep in the oxide.
Fig. 5. Auger depth profiles for the 304 SS commercial alloy and for the Fe-17Cr-25Ni-10Mo high purity alloy oxidised at 250°C and 450°C.

Fig. 6. Evolution of the film thickness with the temperature of film formation.
Fig. 7. XPS spectra obtained on the surface of the Fe-17Cr-25Ni-10Mo high purity alloy oxidised at 250°C and at 450°C.

The Mo$_{2d}$ spectra obtained on the surface of the alloy oxidised at 250°C reveals the presence of some Mo$^{5+}$, Mo$^{4+}$ and metallic Mo. For the oxides formed at 450°C there is no evidence of Mo at the surface. The effect of Mo addition on the composition of the oxides formed at 250°C was described above.

The XPS results obtained for films formed at 250°C are not necessarily in disagreement with those of the Auger profiles. Whereas in the AES analysis neither chromium nor molybdenum were detected at the surface, the XPS analysis revealed the presence of some molybdenum and chromium. This discrepancy, however, was only observed for the thinner oxides (formed at 250°C) and can be consequence of some surface roughness, as explained by other authors [24,25]. As XPS has a poor spatial resolution (2 × 3 mm) than AES (100 nm), some thinner areas of the oxide can be analysed. In these thinner areas, the contribution from species situated a little deeper in the oxide may also contribute to the overall spectra, leading to the presence of Cr and Mo in the XPS spectra.

A comparison of the depth concentration profile, as obtained by AES, for chromium
in the films formed on Fe-17Cr-25Ni-10Mo and 304 SS alloys at the various oxidation temperatures is presented in Fig. 8. It is apparent that in the Mo containing alloy the chromium content is always higher for all the temperatures tested. It is true that in this study the amount of nickel in the alloys also increased from \( \sim 11\% \) to 25%, but based on the results of Fig. 2 we believe that the mentioned effect is due to the presence of molybdenum.

3.2. Capacitance measurements

Important information about the semiconducting properties of the oxide film can be obtained by capacitance measurements, which reflect the charge distribution when a semiconductive oxide film is exposed to an electrolyte. The great interest of this study is undoubtedly its contribution for the determination of the electronic structure of the film, which comes from the knowledge of the doping level, the flatband potential and the bandgap. In fact, the measured capacitance corresponds to the space charge region developed in the oxide near the film/electrolyte interface. The relation between this capacitance, called differential capacitance, and the applied potential is given by the well known Mott-Schottky equation:

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

where \( N_d \) represents 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 Boltzman constant, \( T \) the absolute temperature and \( U_{FB} \) the flatband potential.

It is clear that plotting \( 1/C^2 \) vs. \( U \), a straight line should result. The slope of this line gives the doping value and the intersection (at \( 1/C^2 = 0 \)) gives the flatband potential.

Fig. 9 depicts the Mott-Schottky plots for oxides, formed on the commercial alloys and on the high purity alloy containing 10% of Mo previously oxidised at 350°C. The existence of a straight line with positive slope for potentials higher than \( -0.5 \) V reveals n-type semiconductivity, as observed in previous works [26,27]. For potentials lower than \( -0.5 \) V a straight line with a negative slope can be observed, meaning that the oxide behaves as a p-type semiconductor in this potential region. Such behaviour has recently been reported for passive films formed on stainless steels immersed in borate buffer solution [26,27] and was explained assuming that the capacitance response is controlled by the film structure and composition—an inner Cr oxide rich layer and an outer Fe oxide rich layer. Another feature of the Mott-Schottky plots depicted in Fig. 9, is the existence of a break at \( \approx 0 \) V. This break has been associated with the participation of a second ionisation process [26,27]. The Mott-Schottky plots for the three alloys shows that there are no significant differences in the capacitance behaviour of the oxides formed on 304 and 316 SS. However, for the alloy with 10% of Mo a decrease in the capacitance was observed, particularly for potentials higher than \( -0.5 \) V, which leads to larger slopes of the two straight lines in this region. An
Fig. 8. Evolution of the Cr at. % obtained from the Auger depth profiles for the Fe-17Cr-25Ni-10Mo high purity alloy and for the commercial alloy (304) oxidised at 250 °C, 350 °C and 450 °C.
identical effect of the Mo was found for passive films formed on stainless steels in borate buffer solution [26,27]. In one of these works [27] it was showed that the influence of nickel oxide on the capacitance behaviour in the potential range under study can be compared to that of a capacitor and it has no influence on the slopes of the Mott-Schottky plots obtained. Thus, although the amount of nickel present in the alloys varies between the commercial alloys and the high Mo containing alloy, the observed effect in the slopes should be ascribed to the Mo. Using eq. (1) with a value of 12 for the dielectric constant of the iron oxide the density of donors was estimated to be in the range $10^{19}$–$10^{20}\text{cm}^{-2}$. The lower values were calculated for the oxides formed on the alloys with a higher Mo content. The value of the flatband potential ($-0.5\text{V}$) is identical in all the cases.

4. Discussion

The analytical results gave helpful information about the oxide composition and thickness. Thus, the Auger depth profiles have shown that the oxide films formed at temperatures between 250°C and 450°C have a typical duplex structure. They are composed by an external Fe oxide rich layer and an internal Cr oxide rich layer. Mo was only detected in the inner part of the oxide, being accumulated in the Cr oxide region. According to the Auger profiles, the presence of Mo has no significant effect on the oxide thickness. However, the presence of Mo as an alloying element affects the composition of the inner Cr oxide layers. The amount of Cr in this region is higher in the Mo-containing alloys. These results have also been observed in other works [4, 5] and have been used to explain the beneficial effect of Mo in the corrosion resistance of stainless steels.

The XPS spectra obtained for the Fe-17Cr-25Ni-10Mo high purity stainless steel
oxidised at 350°C, revealed the presence of Mo$^{4+}$, Mo$^{6+}$ and metallic Mo in the inner Cr oxide layers. The presence of metallic Mo in the inner regions of the film suggests an accumulation of metal near the film/alloy interface. The presence of metallic Mo just under the surface film has been observed by other authors [4, 28, 29] and it was explained, by postulating that Mo oxidises less easily than iron or chromium [28]. The presence of metallic Mo is not surprising, since Mo is not considered an oxide phase forming element. Mathieu et al. [28] have suggested that the Mo present in the metal/oxide interface can decrease the activity of the metallic iron or act as a diffusion barrier for the Fe and Cr ions in the oxide. From the results obtained in this work, it is also plausible to envisage that the presence of metallic Mo in the interface, where it may lead by both the above effects to a raise of the chromium oxide/iron oxide ratio in the film. This would explain the enrichment in chromium observed in the film. In the inner regions of the oxide, the Cr appears only as Cr$_2$O$_3$, whereas Fe appears as a mixture of Fe$^{3+}$ and Fe$^{2+}$. This is compatible with a spinel-type structure that has been postulated for the oxides formed on iron [30] and stainless steels [31].

The XPS spectra showed a peak for the metallic Ni, whereas for the Cr and Fe there was no significant contribution of the metal signal. This effect is not caused by differences in the mean free path of the electrons, because the values of this parameter for metallic Fe, Cr and Ni are very close. Furthermore, according to the literature [32] the escape depth for Ni electrons is even lower than that for Fe and Cr. The accumulation of metallic Ni near the oxide/alloy interface has been previously observed [3,13,33,34]. A possible explanation for the presence of metallic Ni can be obtained based on thermodynamic considerations. The formation of the oxide film on Fe-Cr alloys involves successive formation of Cr$_2$O$_3$, duplex Cr$_2$O$_3$/Fe$_2$O$_3$ and a more complex Cr$_2$O$_3$/Fe$_2$O$_3$/Fe$_3$O$_4$ structure, which is in fact a spinel structure with different Cr and Fe concentrations. Because the self-diffusion coefficient of Cr in Cr$_2$O$_3$ is very weak, it can be assumed that the development of the oxide film is controlled by the diffusion of the Fe ions through the inner Cr oxide layers. The diffusion coefficient of Ni is even lower than that of iron. Thus, in stainless steels with high Ni contents the dissolution of nickel oxides in the iron oxides can lead to reduction of nickel oxide with consequent formation of metallic Ni [35]. The presence of a peak for metallic Ni in the XPS spectra may be the result of this process within the oxide spinel.

XPS results have also shown the presence of hydrated species in the films limited to the external layers of the Fe rich region. In fact, FeOOH and NiOOH were observed in the spectra obtained at 350°C for the Fe-17Cr-25Ni-10Mo alloy, only before etching. The presence of hydrated species in the surface of the oxide films may result from further oxidation of the external layers, between the process of film formation and analytical analysis. However, these species are only limited to the more external layers, being removed after ion etching.

In previous works [26,27], on passive films formed on stainless steels in a borate buffer solution the existence of a break in the plots, at approximately 0 V has been interpreted by the ionisation of a second donor level, situated deep in the bandgap of the oxide. The existence of two donor levels has been suggested for passive films formed on iron [36] and on stainless steels [37]; the deep and shallow levels being
respectively ascribed to the Fe$^{2+}$ ions in octahedral and tetrahedral positions in the unit cell of a spinel structure. The number of Fe$^{2+}$ ions, in each of these positions is affected by the presence of other ions (possibly Cr and/or Mo) in the oxide lattice.

The capacitance results obtained in this work revealed that the oxide capacitance is affected by the presence of Mo. Thus, the presence of Mo results in the decrease of the number of donors, in both donor levels of the iron oxide layer. This is in agreement with the suggestion that the presence of MoO$_3$ in the outer part of the film, even in very low concentration, neutralises the positive donors and hence decreases the conductivity [37]. Although the presence of Mo$^{6+}$ in the outer layers of the oxide was not evident from the XPS analysis, it does not exclude its presence from these layers. Small amounts of these ions are enough to cause the above effect and these can be lower than the detection limit of the technique. The XPS experiments revealed the presence of molybdenum ions (Mo$^{4+}$ and Mo$^{6+}$) in the inner Cr$_2$O$_3$ rich layer, where they can affect the defect structure of this layer, as suggested previously by Olefjord et al. [38]. These authors, based on an XPS study of stainless steels passivated in chloride solutions suggested that the defects created by Fe$^{2+}$ in the Cr oxide layer are cancelled by those created by Mo$^{4+}$ and Mo$^{6+}$.

It is important to remark that pure Cr$_2$O$_3$ is a p-type semiconductor, becoming a n-type semiconductor [39] when doped with Fe$^{2+}$. This means that the electronic current is carried not only by holes, but also by electrons. This modifies the nature of the electric barrier at the oxide/alloy interface. Furthermore, because Mo addition decreases the doping density of the outer layers of the film, the space charge developed at the oxide/solution interface is also modified. This modification also influences the electrochemical potential of the stainless steel, which is an important feature in the corrosion behaviour of stainless steels.

5. Conclusions

The analytical experiments have shown a duplex structure for the oxides grown in stainless steels at temperatures between 250 and 450°C. The oxides are composed by an external Fe oxide region and an internal oxide rich region. The oxide thickness seems to be independent of the alloy composition, but increases, as expected, with the temperature of oxide formation.

Auger and XPS experiments have shown the presence of Mo in the internal Cr rich layers. Molybdenum is also present at the Cr oxide/metal interface, in metallic state. The presence of Mo in this region results in an enrichment of chromium in the internal region of the film.

Although molybdenum is not a phase forming element (and this is the reason for the presence of metallic Mo just under the surface film), Mo as an alloying element modifies the properties of the oxide film because it introduces changes in its defect structure. More precisely, Mo decreases the number of acceptors of the p-type Cr oxide layers and decreases the number of donors in the deep and shallow donor levels of the outer Fe rich oxide layers that have a n-type semiconductivity.
References