Cement & Concrete Composites 34 (2012) 1075–1081

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Electrochemical and analytical investigation of passive films formed on stainless steels in alkaline media

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ARTICLE INFO

Article history:
Received 21 March 2011
Received in revised form 13 March 2012
Accepted 10 June 2012
Available online 16 June 2012

Keywords:
Passive film
Cyclic voltammetry
Stainless steel
XPS

ABSTRACT

Passive films were grown in potentiodynamic mode, by cyclic voltammetry on AISI 316 and AISI 304 stainless steels. The composition of these films was investigated by X-ray photoelectron spectroscopy (XPS). The electrochemical behaviour and the chemical composition of the passive films formed by cyclic voltammetry were compared to those of films grown under natural conditions (by immersion at open circuit potential, OCP) in alkaline solutions simulating concrete. The study included the effect of pH of the electrolyte and the effect of the presence of chloride ions.

The XPS results revealed important changes in the passive film composition, which becomes enriched in chromium and depleted in magnetite as the pH decreases. On the other hand, the presence of chlorides promotes a more oxidised passive layer. The XPS results also showed relevant differences on the composition of the oxide layers for the films formed under cyclic voltammetry and/or under OCP.

1. Introduction

In recent years there was an increasing interest in applying stainless steel reinforcement in concrete structures to reduce chloride-induced corrosion problems [1] and, therefore, to increase the structures lifetime. Thus, nowadays, stainless steel is regularly used in several new or repaired projects. Since stainless steel is more expensive than carbon steel, various procedures have been adopted as for example the use of stainless steels rebars in critical areas, in closer contact with the aggressive medium and the use of carbon steel rebars in the more protected parts of the structure. This combination is economically attractive due to the improved durability conferred by the stainless steel rebars.

The higher corrosion resistance of stainless steel is due to the presence of a very thin passivating and self-renewable protective layer formed on the surface. In neutral or alkaline solutions, this film is described by a bilayer structure. The passive behaviour has been related with the formation of a complex oxide film, consisting in a rich chromium-oxide/hydroxide inner layer and an iron-oxide rich outer layer [2,3]. The composition of the outer layer depends on the potential of the film formation and may change from Fe_3O_4 and $Fe(OH)_2$, in the lower potential range, to Fe_2O_3 and FeOOH at more positive potentials. Nickel is depleted in the oxide layer but is enriched in the metal surface beneath. Molybdenum, on the other hand, is enriched in the passive oxide layer, specifically in the internal chromium rich layer [4,5].

The composition, the electrochemical and the semiconductive behaviour of the passive films on stainless steels are important factors, which control the passivity and, therefore, the corrosion resistance [6,7]. Thus, it has been widely studied in several stainless steel materials for various applications. However, combined electrochemical and analytical investigations, regarding the behaviour of stainless steels in alkaline media simulating concrete are scarce and somewhat controversial. The composition and the properties of the passive film are dependent on several variables, including the composition of the alloy and the composition of the electrolyte in which the films are grown [8]. Temperature, the presence or the absence of oxygen and pH are additional parameters to take into account in the formation and characterisation of the passive film. The relative influence of these factors is complex and it is not completely understood, especially in alkaline media, simulating concrete.

In the recent decades, a variety of experimental electrochemical techniques has been applied to study the chemical, electrochemical and the electronic properties of passive films formed on iron

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http://dx.doi.org/10.1016/j.cemconcomp.2012.06.002

[9,10], carbon steel [11,12] and stainless steel [13–15]. Nowadays, localised techniques are also used to study the process of localised pitting corrosion, typically in stainless steel alloys in the presence of chlorides [16–18].

Cyclic voltammetry has been one of the most applied d.c. techniques, being widely used to grow and to characterise passive films in alkaline media simulating concrete. The procedure became popular because it allows forming thicker films and simultaneously acquiring qualitative information on the electrochemical reactions [19–23]. In particular, it offers a rapid identification of the redox potentials of the electroactive species, and an accurate evaluation of the effect of the media on the redox processes. However, the number of cycles and the scan rate are also parameters affecting the properties of passive films generated by cyclic voltammetry [19]. A systematic study comparing the behaviour of surface films formed by cyclic voltammetry and formed at open circuit potential (OCP) is needed to point out the main differences and similarities of these films.

In this work, films were formed on austenitic stainless steels (AISI 316 and AISI 304) using cyclic voltammetry. The electrochemical study was done in solutions of different pH (pH 13, 11 and 9), in the absence and in the presence of chloride ions (3% of NaCl). The films were compared to those formed under open circuit potential conditions in the same media. X-ray photoelectron spectroscopy (XPS) studies were carried out in order to compare the composition of the films formed by cyclic voltammetry and the films formed under natural open circuit conditions. A marked enrichment in oxidised Fe species and an important film thickening was found for the films formed under applied potentials. According to these results and in good agreement with Veleva et al. [19], the use of OCP conditions has the advantage that it simulates really the passivation process of materials and it is recommended for passivation and passivation breakdown studies in stainless steel in order to obtain more real results. Polarisation induces several changes in the outer layers of the surface film, which may affects conclusions related to corrosion resistance and pitting propagation.

2. Experimental

2.1. Materials

Two austenitic stainless steel rebars: AISI 316 (w/w: 18% Cr, 10% Ni, 3% Mo) and AISI 304 (w/w: 18%Cr, 10%Ni), supplied by *Goodfellow* were used. These are the most common applied stainless steels in reinforced concrete structures.

The working electrodes were embedded in cold curing epoxy resin with an exposed surface of 1.27 cm^2. The metallic surface was polished with wet SiC paper of decreasing grit size down to 4000 to eliminate the heterogeneities of the steel surface and ensure the same surface finishing. Then, they were rinsed in distiled water and dried with a stream of air just before immersion.

2.2. Electrolyte

The electrolyte was a 0.1 M NaOH + 0.1 M KOH solution (pH 13), prepared with p.a. chemicals and Millipore® water, to simulate the interstitial electrolyte of concrete pores. Solutions with pH ranging from 13 down to 9 were prepared by dilution of the 0.1 M NaOH + 0.1 M KOH solution. These pH values were selected to simulate the carbonation process: CO_2 can penetrate in the concrete structure pores and react with calcium hydroxide forming carbonates. This reaction decreases the concrete pH down to values close to 9. The pH of the solutions was checked by a Metrohm pH meter.

In order to study the effect of the chlorides, NaCl was added to the blank alkaline solutions in order to obtain a 3% NaCl containing solution.

2.3. Electrochemical measurements

The electrochemical experiments were performed at room temperature and under natural aeration in a classical electrochemical cell with three electrodes, where the working electrode was the stainless steel. The reference electrode was a saturated calomel electrode (SCE) connected to the cell via a salt bridge. All the electrode potentials are referred to the SCE. A platinum counter electrode was also used.

A potentiostat from Radiometer Analytical, model Voltalab PGZ301 was employed to perform the cyclic voltammetry; it was coupled to a computer and the experimental parameters were fitted by means of Voltamaster4 software.

The potentiodynamic plots were registered from -1.4 V to +0.6 V vs. SCE, scanning the potential from hydrogen (-1.4 V vs. SCE) to oxygen (+0.6 V vs. SCE) evolution reactions, within the entire water stability domain. In order to establish the evolution of the voltammetric curves and to generate passive films thick enough, each sample was cycled eight times at a scan rate of 10 mV s^{-1}, which allows relaxation of the redox processes that take place in the passive layer and defining the reactions taking place in the electrode surface [24].

2.4. Surface analysis

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Microlab 310 F (VG Scientific) equipped with an Mg (non-monochromated) anode and a concentric hemispherical analyser.

The XPS analysis was performed under pressures below 5×10^{-9} mbar, using an Al-radiation (non-monochromator). The spectra were taken in CAE mode = 30 eV and accelerating voltage of 15 kV. The quantification was determined after peak fitting. The peak fitting function used was a Gaussian-Lorentzian product function and the algorithm was based on the Simplex optimization as used in the Avantage® software.

3. Results and discussion

3.1. Cyclic voltammetry

Oxides films were grown by d.c. potentiodynamic polarisation (8 cycles) on the stainless steel surfaces immersed in the electrolyte with different alkaline pH values. At pH 13, the current density develops with continued cycling for these stainless steels in good agreement with the findings already reported in [19,23], in spite of the different scan rate used. Passive layer formation is rapid in this alkaline solution (0.1 M NaOH + 0.1 M KOH) and the film behaves as an effective barrier between the metal surface and the electrolyte.

The evolution of the current densities are similar for both materials and the potentials at which the current density increases, can be assigned to the different processes that take place during the film formation as published in previous works [25].

The voltammograms present the typical features of the iron activity region observed for iron samples in alkaline media [26,27], where the magnetite formation peak takes place at -0.8 V vs. SCE, according to the reactions (1) and (2), so the data is not shown:

$$3Fe(OH)_2 + 2OH^- \rightarrow Fe_3O_4 + 4H_2O + 2e^- \quad (1)$$

$$3FeO + 2OH^- \rightarrow Fe_3O_4 + H_2O + 2e^- \qquad (2)$$

This reaction indicates the transition from the active dissolution of the stainless steel to the passivity state.

Magnetite (Fe_3O_4) is a mixed oxide composed by Fe^{2+} and Fe^{3+}. The formula for magnetite may also be written as $FeO \cdot Fe_2O_3$, showing one part wüstite (FeO) and the other part hematite (Fe_2O_3). This refers to the different oxidation states of iron in crystalline structure, not in solid solution. Fe_3O_4 has a cubic inverse spinel-structure which consists of a cubic close packed array of oxide ions where all the Fe^{2+} ions occupy half of the octahedral sites. The Fe^{3+} ions are split evenly across the remaining octahedral sites and the tetrahedral sites. Magnetite is of paramount significance in the passive layer because it plays an important role in steel corrosion protection [8].

Other compounds described in literature [28] corresponding to the partial oxidation of magnetite or the presence of the alloying elements are not clearly differentiated in this case; however, some features can be distinguished at lower pH or with the addition of chloride ions as shown later.

Fig. 1 shows the potentiodynamic curves obtained at different pH values (13, 11, and 9) in the absence of chlorides for AISI 316.

The differences between the three curves are significant and should be pointed out. The potential peaks are shifted positively, according to the pH decrease in good agreement with the behaviour expected from the Pourbaix diagrams [29].

The intensity of the peaks corresponding to the redox processes of iron tends to decrease as the pH drops. Considering Eq. (2) for the magnetite formation, this trend indicates that the lower transformation degree was due to the lower concentration of OH^- ions. Therefore, less alkaline electrolyte induces a decrease of magnetite in the oxide film, in good agreement with previous results obtained for films formed on AISI 316 and 304 at OCP in the same electrolyte [30,31].

The peak assigned to the partial oxidation of magnetite, obtaining goethite as final product according to the reaction (3) (−0.55 V and −0.45 V vs. SCE at pH 11 and 9, respectively) is now more evidenced.

This peak is overlapped with another anodic peak, described in literature [27], corresponding to the magnetite oxidation to maghemite oxide, according to Eq. (4):

$$Fe_3O_4 + OH^- + H_2O \rightarrow 3FeOOH + e^- \qquad (3)$$

$$3Fe_3O_4 \rightarrow 4\gamma - Fe_2O_3 + Fe^{2+}_{(ads)} + 2e^- \qquad (4)$$

Conversely, a progressive current density increase was detected at anodic potential values, associated with the oxidation of chromium, as the pH decreases. The voltammetric results suggested the presence of a passive film enriched in chromium and depleted in Fe_3O_4 at lower pH.

Likewise, nickel reduction was only detected at pH 13. The voltammograms show, for both stainless steels, a current density peak attributed to Ni^{2+}/Ni^{3+} process [32] at +0.4 V vs. SCE.

Both steels present two broad reduction peaks in the reverse plot between −0.6 V and −1.2 V vs. SCE. These peaks should correspond to the consecutive reduction processes of Ni_3O_4 to NiO and NiO to Ni [32], which overlap with the partial reduction of Fe_2O_3 to magnetite, and the Fe_3O_4 reduction to Fe^{2+} peaks presented at −1.1 V.

AISI 304 presented similar cyclic curves evolution and therefore, they are not shown here.

Cyclic voltammetry curves have also been recorded in 3% NaCl containing-alkaline solutions in Fig. 2. The curves show an extended passive range, the intensity of the current increases with the number of cycles and the same peaks can be identified and assigned to the same redox processes previously described in the absence of chlorides. No pitting corrosion occurs when AISI 316 or AISI 304 were exposed to pH 13 solutions containing NaCl up to 3% under potential cycling between −1.4 V and +0.6 V vs. SCE. The current density remains stable in the passive domain for both stainless steels, being more reduced for AISI 316. Moreover, the reverse curve shows lower current densities than those observed for the forward scan; this behaviour is typical of passive film thickening during the forward scan [33].

As well as in free of chloride solutions, AISI 304 shows higher charge associated to the magnetite peak formation (≈−0.8 V vs. SCE) in presence of chloride anions in comparison with AISI 316, indicating the formation of a thicker passive film and a higher oxidation degree. These higher current densities obtained for AISI 304 were probably related with an easier adsorption of chloride ions on the oxide surface layer, affecting, therefore, the corrosion protective properties.

Chlorides presence promotes for AISI 304 a change in the film composition to a more oxidised structure, with a larger presence of Fe^{3+}. According with Abreu et al. [34] the action of chlorides remains at surface level and no Cl^- incorporation into the passive film was detected in XPS analysis.

The passivity domain is extended for AISI 316. This behaviour seems to be connected to the oxide film conductivity. The small

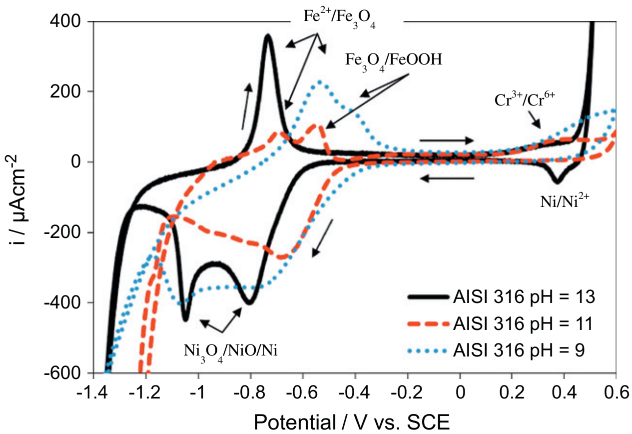

Fig. 1. Comparison of eighth cyclic voltammograms obtained for AISI 316 in NaOH + KOH solution at different pH values, from −1.4 V to +0.6 V vs. SCE at 10 mV s^{-1} scan rate.

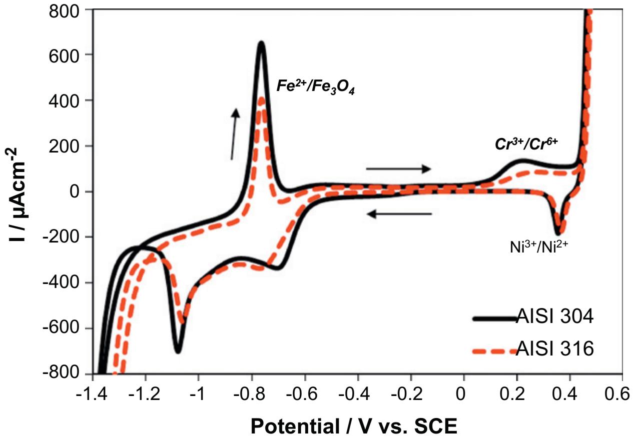

Fig. 2. Comparison of eighth cyclic voltammograms obtained for AISI 304 and AISI 316 in NaOH + KOH + 3% NaCl solution (pH 13), from −1.4 V to +0.6 V vs. SCE at 10 mV s^{-1} scan rate.

anodic potential displacement could be consequence of an induced surface modification activating the kinetic of the O_2 evolution process. This could be interpreted as a result of a less conducting oxide layer formed on the steel; this different conductivity could be attributed to two factors:

- Despite both steels present the same nickel content, it is possible that a different distribution of nickel in the passive film induces changes in the dielectric properties [34].
- Another possibility is probably linked to the existence of molybdenum in the passive film, which is only present in AISI 316, and could induce modifications in the passive film structure and also in the dielectric properties [35].

For these pH ranges, the addition of 3% of NaCl seems to be not enough to breakdown the passive layer, at least up to 8 cycles. Nevertheless, the presence of chlorides affected the chemistry and the kinetics of the redox reactions of the film, although does not induce its breakdown.

In general, it could be stated that both stainless steels present good corrosion resistance in the presence of chlorides at pH 13, so, the risk of pitting attack in 3% of NaCl will be low under alkaline conditions.

Fig. 3 shows the polarisation behaviour of AISI 316 and AISI 304 in more aggressive conditions: pH 9 and 3% NaCl. In this case, after only one cycle it is possible to induce localised corrosion on the metal surface. The hysteresis grade of the reverse scan, with higher current values than the forward plot, suggests the formation of an important number of pits which grow and spread quickly on the metal surface.

The corrosion rate is similar for both stainless steels since comparable current density values (around $10^4\ \mu A\ cm^{-2}$) were reached, which indicate a high metal dissolution; however, the pitting potential ($E_{pit} = +0.4$ V vs. SCE) is more anodic for AISI 316. This E_{pit} was determined from the potendiodynamic polarisation curves at the point where a stable increase in current density takes place. The pitting corrosion started for AISI 304 at +0.2 V vs. SCE, so the transition to the active state takes place before, and the repassivation process is more difficult ($E_{rep304} = -0.5$ V, $E_{rep316} = -0.2$ V vs. SCE). The repassivation potential can be related to the occlusion effects in the pits, so the more cathodic values associated to AISI 304 may be connected with a larger extension of the pitting process [36]. These values reveal the lower protection characteristics at pH 9 for AISI 304. Although both stainless steels have ability to regenerate the passive film in the case of unstable pits, the repassivation will be easier for AISI 316.

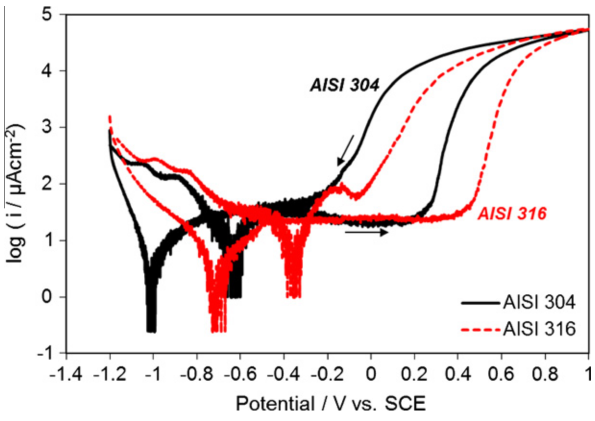

Fig. 3. Comparison of first cyclic voltammograms obtained for AISI 304 and AISI 316 in 0.1 M NaOH + 0.1 M KOH + 3% NaCl solution (pH 9), from −1.2 V to +1.0 V vs. SCE at 10 mV s^{-1} scan rate.

According to these results, AISI 316 is more stable and presents increased corrosion resistance in alkaline media contaminated with chlorides. This can be explained by the presence of molybdenum which beneficial effects in corrosion behaviour were already reported [5].

3.2. XPS analysis

The chemical composition of the passive film formed at OCP in solutions of different pH was compared with that of the films grown by cyclic potentiodynamic polarisation during eight cycles for both stainless steels.

The results show that the passive films on AISI 316 and AISI 304 are mainly composed of iron, chromium and nickel, regardless the method of growth.

According to the literature, the thickness of the passive layer is one of the most important difference detected in the composition of films formed under OCP conditions compared to those formed under potential application [19,20]. The passive layer generated by cyclic voltammetry is thicker, and it could be increased with the scan rate, the immersion time and/or the number of cycles [34]. Most of studies on steels reported in the literature have been performed on passive films formed anodically [11,13,37] since the natural formed ones are extremely thin and more complex to be evaluated by using surface analytical techniques due to the effects of the metallic substrate on the analytical data. Thus, most of the analytical results dealing with film composition under alkaline media have been obtained on anodic formed films and the results extrapolated for the general behaviour of these stainless steels in alkaline media.

In Fig. 4 corresponding to the Fe2p3 ionisation spectra of films formed on AISI 316, the increase of the film thickness at pH 13 is reflected by the suppression of the peak corresponding to the metallic iron (at 707.0 eV) and to Fe^{2+} at 709.0–709.5 eV in the case

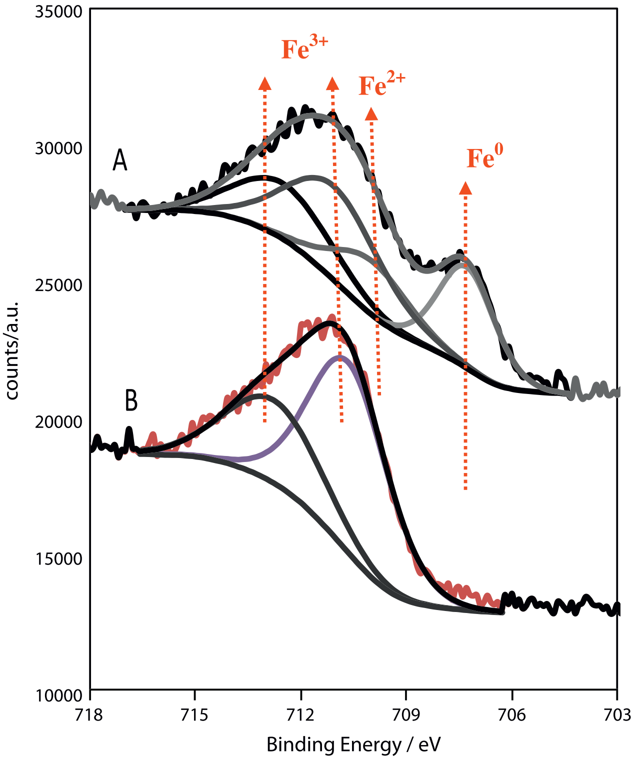

Fig. 4. Fe2p3 ionisation for the films formed on AISI 316 at pH 13, in the absence of chlorides, for 24 h in OCP conditions (A) and by cyclic voltammetry (B).

of voltammetric films (Fig. 4B). Only the peak energies corresponding to Fe_2O_3 and $Fe(OH)_3$ and/or FeOOH can be clearly observed. Thus, the surface of films formed by cyclic voltammetry (Fig. 4B) is essentially composed of Fe^{3+} species and reveals significant differences comparatively to the films formed at OCP (Fig. 4A), in which both Fe^{2+} and Fe^{3+} species are detected in much thinner layers. The total absence of the metallic iron peak and of the peak assigned to Fe^{2+} was also noticed for all the films formed on the stainless steel type 304 at pH 13 (not shown). The absence of the peaks assigned to metallic nickel and chromium for AISI 316 at pH 13 and for AISI 304 at all pH values, reveals an important thickness increase of the outermost Fe (III) rich layers.

Only the films formed on AISI 316 at pH 11 and pH 9 revealed the presence of the peaks assigned to metallic iron and Fe^{2+}. Nevertheless, the amounts of metallic iron and of Fe^{2+} are much lower than those determined for the films formed at OCP for pH 13. This trend suggests that the Fe^{3+} outer rich layers formed at pH 11 and 9 are thinner or more defective comparatively to the ones formed at pH 13. The ratio Fe^{2+}/Fe^{3+} gives an indication of the amount of the magnetite present in the film. As it can be observed from Fig. 5 [30], for films formed on AISI 316 at pH 11 and 9 by cyclic voltammetry, this ratio is about 3 times lower than that observed for the films formed under OCP conditions (>0.4). For pH 13 it was not possible to estimate the amount of Fe^{2+} since it could not be detected. This trend indicates, again, that the Fe^{3+} species predominate in the outer layers of the film as found in previous works [23,38]. Other important differences are related to the contents of Cr^{3+} in the films. The amounts of detected oxidised chromium are lower for the films formed by cyclic voltammetry. However, the amount of oxidised chromium always increases as pH decreases in accordance with the electrochemical results and the previous work [30]. Assuming that Cr species are restricted to the inner layers of the film, the thickening of the outermost Fe rich oxides hinders the photoelectron signal of Cr.

The presence of oxidised Ni in AISI 316 could not be detected at pH 13 and the values determined at pH 11 and 9 for films formed by cyclic voltammetry are lower than those determined in the OCP formed films. The XPS measurements did not reveal the presence of Mo in the different surface films formed for AISI 316.

For AISI 304 (Fig. 6) there is an important increase of the content of Fe^{3+} species and a marked decrease of the nickel content for films formed by cyclic voltammetry comparatively to the films formed at OCP. In fact, for AISI 304, in the former case the films are essentially composed of Fe^{3+} oxides, much lower concentrations of chromium and just traces of nickel. Again, this trend suggests thicker films, in which the iron oxidised layers were preferentially grown.

The contents of oxidised chromium always increase with the pH drop, revealing the increased stability of these species at less alkaline pH. Conversely, the amount of oxidised iron increases for the more alkaline values as consequence of the increased stability of Fe oxides, including the Fe^{2+} rich spinels at higher pH. According to the literature, more alkaline pH media promote the formation of magnetite on carbon steels [39]. Thus, the highest Fe^{2+}/Fe^{3+} ratio in the surface films formed at OCP at pH 13 suggests that a significant part of the iron oxides are most probably in the form of magnetite. When the surface film is exposed to solutions of lower pH, magnetite decomposes, leading to the formation of Fe^{3+} oxides/hydroxides and thus, a decrease of the Fe^{2+}/Fe^{3+} ratio as it can be observed for the OCP formed films.

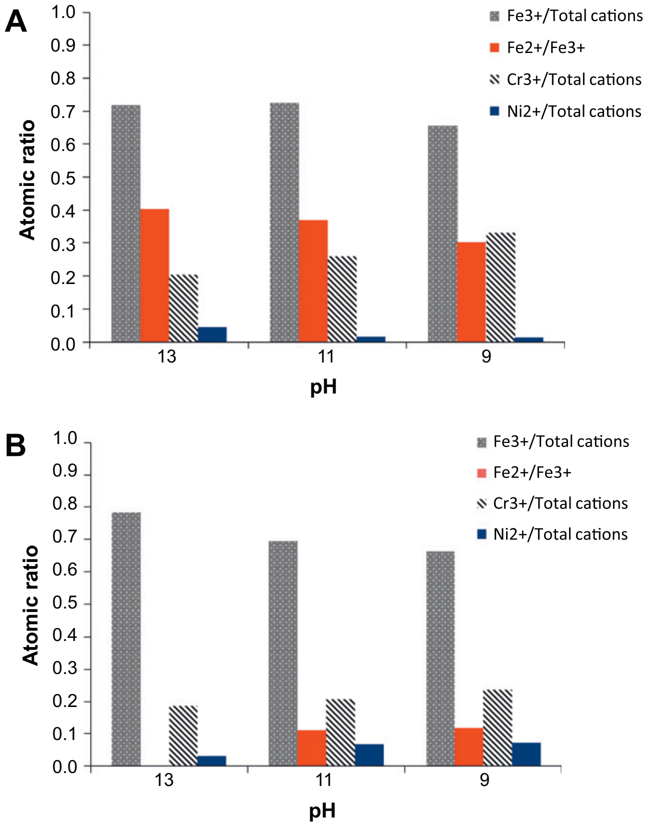

Fig. 5. Evolution of the ratios: Fe^{3+}/total of oxidised cations; Fe^{2+}/Fe^{3+}; Cr^{3+}/total oxidised cations and Ni^{2+}/total oxidised cations presented in the film formed on AISI 316 calculated from the XPS spectra at different pH values. (A) Film formed at OCP conditions during 24 h of immersion [30]. (B) Film formed by cyclic voltammetry.

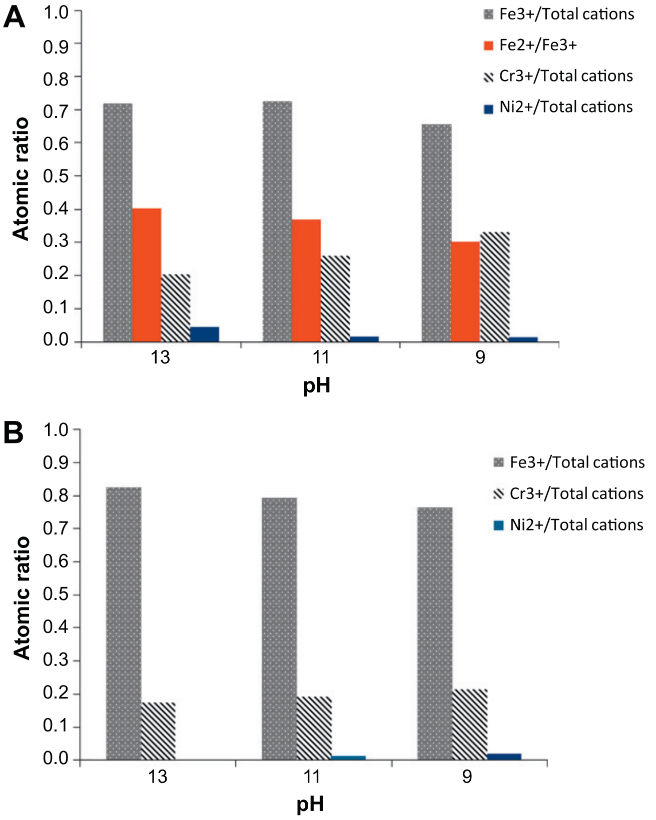

Fig. 6. Evolution of the ratios: Fe^{3+}/total of oxidised cations; Fe^{2+}/Fe^{3+}; Cr^{3+}/total oxidised cations and Ni^{2+}/total oxidised cations presented in the film formed on AISI 304 calculated from the XPS spectra at different pH values. (A) Film formed at 111 OCP conditions during 24 h of immersion. (B) Film formed by cyclic voltammetry.

For the films formed by cyclic voltammetry (Figs. 5B and 6B) the low content or the absence of Fe^{2+}, suggests that the films present outermost layer enriched in Fe^{3+} species, which seems to be the outer growing part of the film. Moreover, for the films formed on AISI 316 by cyclic voltammetry the evolution of the Fe^{2+}/Fe^{3+} ratio with pH show an opposite trend. At pH 13, Fe^{2+} could not be detected and the ratio Fe^{2+}/Fe^{3+} increased with the pH drop, being slightly higher at pH 9. This trend has two possible explanations: (i) the films formed at pH 13 are thicker, and, therefore the outer Fe^{3+} rich layers completely hinder the more internal ones, richer in magnetite and (ii) as the pH drops, Fe^{3+} species become unstable, the outer Fe^{3+} rich layers do not grow and the film becomes thinner and/or more porous.

Summarising, the main difference lies on the formation of a thicker and more oxidised Fe layer when formed by cyclic polarisation. Assuming a bilayer structure, the oxide films are composed of external Fe rich layers and inner Cr-rich layers. The Cr content is always lower in the films formed by voltammetry but the Cr signal was easily detected. However, in some conditions, the absence of Fe^{2+} species, which should exist nearby the Cr oxides, can be related to the depletion of these species during the cycling process. If so, the pitting susceptibility can be reduced, since magnetite plays an important role in preventing pitting onset and pitting propagation. This effect is more marked for the films formed on AISI 304, which may increase its susceptibility to chloride attach under these conditions.

4. Conclusions

The oxide films were successfully generated and characterised by cyclic voltammetry on AISI 316 and AISI 304 stainless steels. The film with a higher Fe^{3+} content was obtained for AISI 304.

For the films formed under OCP conditions, as the pH drops, the presence of magnetite decreases due to the difficulty of redox transformation because of the decrease in OH^-. On the contrary, the film is enriched on chromium oxides.

The amount of chromium species present in the surface film always increase as the pH drops from 13 to 9 and this trend is independent of the process of film growth.

The films formed on AISI 316 under d.c. potentiodynamic polarisation are thicker, since the metallic contribution was hardly or even could not be detected. Moreover, the outer layers of the cycled films are extremely rich in Fe^{3+} oxides and depleted in Fe^{2+}, chromium oxides and nickel oxides.

The process of formation of Fe^{3+} rich layers is more evident on the films formed on AISI 304 for all the pH ranges tested. In this steel the presence of magnetite was completely suppressed.

According to the voltammograms, the presence of 3% of chloride ions has little influence in the stainless steel behaviour since thicker layers were obtained after the eight cycles for both steels at pH 13. In conditions of pH 9, AISI 316 presents a decreased pitting susceptibility and a faster repassivation process, thus it could be a good strategy to increase the life –cycle of the reinforced concrete structures.

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