Corrosion Behavior of Stainless Steel Rebars Embedded in Concrete: an Electrochemical Impedance Spectroscopy Study

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This work aims at studying the electrochemical behavior, by Electrochemical Impedance Spectroscopy (EIS), of austenitic (AISI 304 and AISI 316) and duplex (SAF 2205 and SAF 2304) stainless steels, when embedded in concrete specimens. Concrete specimens were exposed to chloride containing solutions simulating the aggressive conditions found in sweater environments. Samples were fully immersed and submitted to periodic immersion/emersion cycles. EIS and open circuit potential (OCP) were monitored in a monthly basis. Samples containing carbon steel (C-steel) rebars were also prepared for comparison of the corrosion rates between the different materials.

The results showed that the austenitic and duplex SAF 2205 stainless steels were passive for all the testing period, due to the formation of protective oxide layer, with the AISI 316 presenting the higher corrosion resistance value. The EIS results suggest an increase of more than one order of magnitude in the corrosion resistance of the duplex steels and AISI 316 comparatively to C-steel rebars.

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1. Introduction

Reinforced concrete is the most economic, versatile and successful construction material for structural purposes. It presents long lifetime and generally performs well. However, corrosion of reinforcing steel may dramatically affect the performance of the structure, causing economic and safety problems. When carbon steel (C-steel) is embedded in concrete, it becomes passive due to the formation of a thin, but protective oxide layer (about 10 nm thick). This layer is very stable in the alkaline pH ranges typical of the concrete pores (pH around 12.5). Though, the presence of aggressive species in the concrete, such as chloride ions and carbon dioxide, can induce corrosion problems in the concrete rebars. Chlorides induce localized pitting corrosion of the steel and carbonation induces a uniform depassivation of the rebars.

With the aim at minimizing the damages caused by the corrosion phenomena in reinforced concrete structures, several solutions have been suggested. The use of stainless steel (SS) rebars seems to be an interesting solution, by the economic point of view, in specific applications [1]. It has been reported [2, 3] as expected, that stainless steel presents higher corrosion resistance than ordinary C-steel. However, detailed quantification of the corrosion processes and the gain relatively to C-steel is not available. Several types of galvanized rebars was also investigated and stainless steel rebars showed the best performance [4].

Recently austeno-ferritic (duplex) stainless steels have been also studied [5–8]. Due to its content in chromium, molybdenum and nitrogen, this material presents highest pitting and crevice corrosion resistance [9]. In these studies, it was demonstrated that the duplex SS corrosion resistance in alkaline simulated concrete pore solutions is higher, depending on the composition of the studied duplex stainless steel.

Electrochemical Impedance Spectroscopy (EIS) has been used as an interesting technique for determination the corrosion rate of C-steel reinforcing bars embedded in concrete [11, 12]. In reinforced concrete/mortar samples, the electrochemical behavior of reinforcing steel can be simulated by a modified Randles circuit (Fig. 1 (a)). In this model, Re is the ohmic resistance, R1 is the charge transference resistance, ZD is the Warburg impedance and the Cdl is the double layer capacitance which was replaced by a constant phase element (CPE). This model can be used to determine quantitative aspects of the electrochemical behavior of the steel-concrete interface, thus providing information in terms of both passive and active reinforcements [10]. EIS has been used to characterize the electrochemical behavior of stainless steels, when exposed to concrete simulated pore solution [7]. In these cases, the most common equivalent circuit used to describe the austenitic and duplex stainless steel electrochemical behavior immersed in
alkaline solutions is the one presented in Fig. 1(b). In this circuit, the Re corresponds to the ohmic resistance of the solution, the CPE$_1$ and R$_1$ was ascribed to areas covered with the passive film, and the low frequency time constant was ascribed to active surface areas, i.e., film defects/pores in the absence of chlorides and active pits and film defects in the presence of chlorides, in which R$_2$ represents the charge transfer resistance and CPE$_2$ is a constant phase angle element associated with the double layer capacitance in the active areas.

However, many authors have proposed other suitable models and equivalent circuits that fit well with the experimental results. Thus, alternatively the first time constant can be attributed to the barrier properties of the surface film and the second time constant to the interfacial processes.

The aim of this work was to study the pitting corrosion induced by chlorides in stainless steel rebars embedded in concrete. Therefore austenitic (AISI 304 and AISI 316) and duplex (SAF 2205 and SAF 2304) stainless steels were studied by EIS. Simultaneously, concrete samples with carbon-steel rebars were used as reference. Concrete specimens were exposed to drying/immersion cycles in high chloride containing solutions (NaCl saturated solution) to accelerate the pitting corrosion initiation of the SS concrete structures.

2. Experimental

Prismatic concrete specimens with laboratorial dimensions were prepared using concrete with a w/c = 0.6. The concrete composition used in this study is presented in Table 1.

For electrochemical measurements 15 × 15 × 30 cm$^3$ concrete specimens were used and four different stainless steel rebars (AISI 316, AISI 304, SAF 2205 and SAF 2304—see Table 2) were embedded in symmetric position in these samples, with an exposed area of 75 cm$^2$ (Fig. 2a). Samples with C-steel rebars were also prepared.

The pull out tests were made using cubic concrete samples (15 × 15 × 15 cm$^3$) containing a flat SS rebar of 50 cm long and 12 mm diameter at the center of the specimen were also prepared with the purpose of testing the influence of corrosion products on the adherence of rebar to concrete, by means of a pull out test (Fig. 2b).

All the concrete specimens were exposed to saturated (NaCl) at room temperature. To account for the NaCl solubility variation with temperature, the immersion solution were kept in equilibrium with a layer of NaCl salt at the bottom of the container. The first fully immersion period occurred during 1 month, i.e., 7 days immersed in chloride saturated solution, followed by 7 days drying and finally 15 days immersed in aggressive solution. Afterwards, the samples were submitted to periodic 15 days drying/immersion cycles. The measurements were always performed 24 hours after removing the samples from the solution.

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**Table 1**

<table>
<thead>
<tr>
<th>Concrete composition.</th>
<th>w/c = 0.6</th>
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<tbody>
<tr>
<td>Gravel 1</td>
<td>50.3 kg</td>
</tr>
<tr>
<td>Gravel 2</td>
<td>47.3 kg</td>
</tr>
<tr>
<td>Sand</td>
<td>76.7 kg</td>
</tr>
<tr>
<td>Sand (fine)</td>
<td>13.9 kg</td>
</tr>
<tr>
<td>Ciment</td>
<td>28.0 kg</td>
</tr>
<tr>
<td>NaCl</td>
<td>12 kg</td>
</tr>
<tr>
<td>Water</td>
<td>17.3 L</td>
</tr>
</tbody>
</table>

**Table 2**

<table>
<thead>
<tr>
<th>Stainless steel alloying main components (wt %).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
</tr>
<tr>
<td>Cr</td>
</tr>
<tr>
<td>Ni</td>
</tr>
<tr>
<td>Mo</td>
</tr>
</tbody>
</table>

**Fig. 1.** Equivalent circuit used to simulate (a) the behavior of the carbon steel, reinforcing bars embedded in concrete [12] and (b) the austenitic and duplex stainless steel electrochemical behavior when exposed to concrete simulated pore solution [6].

**Fig. 2.** Concrete specimens: (a) for electrochemical measurements and (b) for pullout measurements.
Monthly, electrochemical measurements as EIS and open circuit potential (OCP) monitoring, using a graphite reference electrode, were performed.

EIS measurements were performed in situ, at OCP using a Gamry 600 potentiostat. All the EIS tests were carried out applying a r.m.s. voltage of 10 mV in a frequency range from 100 kHz down to 3.7 mHz.

The EIS measurements were made using two electrodes: the reference and counter electrodes were short-circuited and connected to a graphite bar and the working electrode connected to the stainless rebar, respectively. The impedance results were fitted using the ZView® software.

The pull out tests were performed in a Servosis ME-404/CI tensile test machine (2000 kN maximum force). To measure the relative displacement between the rebar and the concrete, an inductive transducer with a measurement range of 10 mm (LVTD HBM WI/10mm-T) was used. The tests were run through a closed-loop displacement control, by increasing slip at a 2.5 μm per second rate.

For pull out, samples were tested after 1 year and 1.5 years of exposure.

3. Results and Discussion

3.1. Electrochemical Tests

The evolution of the potential for the C-steel and the different SS embedded in concrete are presented in fig. 4.

Despite the fluctuations of the potential values, some trends can be observed and it is possible to evidence two classes of rebars; the first one containing the austenitic SS (types AISI 304, AISI 316) and duplex type SAF 2205 that present potential values in the range of -250 mV to -150 mV vs. graphite electrode. The second category of rebar, showing more negative potential values, in the range of -400 mV to -700 mV, was observed for duplex stainless steel type SAF 2304 and for the C-steel. This second category of rebar seems to present a more active surface with more intense corrosion, comparatively to the others. This fact was confirmed by visual inspection of the rebars, after 20 months of immersion. It can be observed in this fig. that AISI 316 and SAF 2205 SS did not presented evidenced signs of corrosion (figs. 5a and 5c), which is in agreement with a passive state. The C-steel rebar (fig. 5e) that presented the lowest potential values showed a uniform corrosion trend, while the SAF 2304 displayed localized corrosion. Evidence of mild corrosion in AISI 304 SS can be observed. Even this slight corrosion is in agreement with potential measurements since for AISI 304 SS the potential is less stable (range 0 to -300 mV vs graphite electrode).

Impedance spectra obtained for the different steels after 12 and 20 months of immersion are depicted in fig. 6. The lowest corrosion resistance was observed in the C-steel rebar, as expected. In the case of SS reinforcements, AISI 316 and SAF 2205 definitely reveals a marked capacitive behavior with lower phase angles even in the low frequency domain comparatively to the others. These results could be explained taking in consideration the molybdenum (Mo)
content of the different SS studied [Table 2]. As already stated in the introduction, the Mo content increase resistance to pitting corrosion [9]. This fact was confirmed in this study as the austenitic (AISI 316) and duplex (SAF 2205) SS with Mo content show the highest impedance values and no apparent corrosion (Fig. 5).

This fact is more evident if comparison of $|Z|_{f=3.7\, \text{mHz}}$ were made (Fig. 7). AISI 316 SS presents higher impedance values ($1.8 \times 10^6 \, \Omega \, \text{cm}^2$) while the C-steel presents the lowest impedance ones, around $7.3 \times 10^4 \, \Omega \, \text{cm}^2$. Indeed, the values for AISI 316 SS were even higher than those measured for SAF 2205 samples. Results from literature obtained in solutions simulating the concrete pore electrolyte, contaminated with chloride ions show that SAF 2205 presents higher performance comparatively to the austenitic AISI 304 SS [5,6], which is accordance with the obtained results. However, such type of studies containing AISI 316 SS are uncommon; G. Blanco et al. [7] studied the charge transfer resistance in simulated concrete pore solutions, containing chloride ions and showed that all the austenitic rebar included the AISI 316 SS, presented lower values, which is a result in opposition to the results obtained in this work. Though, these results may not be comparable with the ones presented in this article since G. Blanco et al. [7] showed also that AISI 316 SS presents a lower charge transfer resistance than the AISI 304 SS.

To better understand the electrochemical phenomena, equivalent circuits were used to simulate the electrochemical behavior of a SS rebar embedded in concrete samples.

To describe the electrochemical behavior of the different rebars embedded in concrete specimens, three different equivalent circuits were used as presented in Fig. 8. These circuits were based on the one presented in the literature [10,12] for C-steel rebars embedded in concrete and for stainless steel samples immersed in alkaline solutions, simulating the concrete pore environments, as already discussed. For the samples studied in this work, $\Re$ can only be associated with the ohmic resistance of the concrete pores, presenting values in the range of $5 \times 10^4 \, \Omega \, \text{cm}^2$ to $1 \times 10^5 \, \Omega \, \text{cm}^2$. Concerning the other parameters, $\text{CPE}_1$, $\Re_1$ can be ascribed to areas covered with the passive film and the $\text{CPE}_2$ to the response associated with the double layer capacitance in the active areas.

Fig. 9 shows the evolution of the equivalent circuit used to fit the EIS spectra obtained for the different tested rebar. The fitting results for all types of tested rebar, after 20 months of exposure

![Fig. 6. Impedance spectra for reinforced concrete specimens with w/c = 0.6 ratio after, 12 and 20 months of exposure.](image)

![Fig. 7. Lowest frequency impedance values (3.7 mHz) with time for the samples, exposed to the drying/immersion cycles.](image)

![Fig. 9. Evolution of the equivalent circuit used with exposure time for different rebars.](image)

![Fig. 8. Equivalent circuits used to fit the EIS data.](image)
time are presented in fig. 10, while the obtained parameters values are shown in Table 3.

As it can be observed, the electrochemical behavior of the more resistive stainless steels, i.e., the SAF 2205 and AISI 316, can be simulated, for all exposure time with model 1. Regarding the SAF 2304, after ten months of exposure to the drying/immersion cycles, it was necessary to add a resistance in parallel to the CPE (model 2) in order to simulate its electrochemical behavior. For the AISI 304, and at the beginning of exposure, the model 2 was used and after four months of exposure, a second CPE in series was added to the previous circuit (model 3). For the C-steel rebar, it was only possible to simulate its electrochemical behavior with model 3.

Considering the evolution observed in the equivalent circuit used for each specimen (fig. 10) and the values for impedance and fitting parameters (fig. 6 and Table 3), it can be assumed that:

(i) Model 1: corresponds to capacitive spectra in which CPE1 values are ascribed to the passive layer plus the influence of a rich Fe oxide region [9] near the rebar;

(ii) Model 2: corresponds to spectra in which the protection made by the oxide layer (CPE1) becomes less efficient and other process can be detected. When this progression occurs, it seems that there is a resistive behavior control at low frequencies. That can be due to some corrosion activity or more probably due to passive layer permeation;

(iii) Model 3: This equivalent circuit only appears for less corrosion resistant specimens where a capacitive behavior (CPE2) appears at low frequencies that can be ascribed to a diffusion controlled process or surface film formed due to corrosion processes.

3.2. Pull out tests

Fig. 11 depicts the pull out test results for some samples after 12 and 18 months of exposure. In every situation the carbon-steel rebar presented a much higher adhesion than the stainless steel ones. The force necessary to pull out the carbon-steel rebar is at least three times higher than the other samples. These results may be related with a higher level of corrosion at the rebar surface (see fig. 5e), which lead to higher pressure near the metal surface,

| Table 3 |
| Best fitting results for the impedance spectra obtained after 12 and 20 months of exposure to the drying/immersion cycles. |
|----------------|-----------------|--------------|----------|---------|---------|---------|-----------------|
| Sample         | Equivalent circuit | Exposure time | $R_0$ (Ω·cm²) | $Y_{0,1}$ (S.cm²) | $\alpha_1$ | $R_1$ (Ω·cm²) | $Y_{0,2}$ (S.cm²) | $\alpha_2$ | $\chi^2$ |
| AISI 316       | Model 1          | 12 months     | 9180         | $1.77 \times 10^{-5}$ | 0.91 | –           | –               | –         | 0.00045   |
| (similar for SAF 2205) | –               | –             | –             | –               | –         | –           | –               | –         | –         |
| AISI 304       | Model 2          | 12 months     | 11235        | $1.61 \times 10^{-5}$ | 0.90 | –           | –               | –         | 0.00052   |
|                 | 20 months        | 8355          | $3.26 \times 10^{-5}$ | 0.85 | 1.15 $\times 10^7$ | –               | –         | 0.00016   |
| AISI 2304      | Model 3          | 12 months     | 10597        | $2.86 \times 10^{-5}$ | 0.85 | $2.4 \times 10^7$ | $5.18 \times 10^{-5}$ | 0.66 | 0.00014   |
|                 | 20 months        | 6900          | $2.40 \times 10^{-5}$ | 0.86 | $2.4 \times 10^7$ | $5.18 \times 10^{-5}$ | 0.67 | 0.000075  |
| C-Steel        | Model 3          | 12 months     | 7867         | $2.90 \times 10^{-5}$ | 0.85 | $1.0 \times 10^7$ | $1.06 \times 10^{-4}$ | 0.91 | 0.00088   |
|                 | 20 months        | 9922          | $1.30 \times 10^{-4}$ | 0.89 | 6483 | $1.5 \times 10^{-4}$ | 0.91 | 0.00193   |

Fig. 10. Fitting results for AISI 316 using circuit 1. (Similar results obtained for SAF, 2205), AISI 304 using circuit 2, AISI 2304 and C-steel using circuit 3 after 20 months, of exposure.
either because the corrosion products occupy a higher volume or because these products improve the adhesion by a chemical interaction mechanism and also by a mechanical effect, since there is a decrease in the surface smoothness. In spite of this apparent good effect, the level of corrosion accumulated in carbon-steel rebar, in a very narrow time frame, allows to foresee the cracking and spalling of the concrete near the rebar. However, much longer experiment must be carried out to observe this effect.

This interpretation can be verified when pull out and EIS measurements are compared. In Fig. 12 the comparison between the pull out tests and $Z_{f\rightarrow3.7}$ mHz can be observed.

The comparison between all the others stainless steels showed that the adhesion level is quite similar between them. However, SAF 2304 SS seems to present a slightly different tendency, which is particularly visible with immersion time.

4. Conclusions

The use of stainless steel rebar provides a strong increase of the corrosion resistance when concrete samples contaminated with chlorides are submitted to continuous immersion/drying cycles.

The rebar showing the highest performance are the austenitic AISI 316 and the duplex SAF2205 SS.

The duplex steels show good performance, however SAF 2304 is less resistant to corrosion attack and revealed the poorest performance.

There is a good correlation between OCP and the EIS measurements.

The interpretation of the EIS results demands the use of various models, allowing to extract the several parameters that characterize the electrochemical behavior of the rebar.

The pull out tests reveal that the adhesion of stainless steel rebar is lower comparatively to C-steel at least for the periods tested. Moreover, the results evidence a good correlation between EIS and pull out tests.

Acknowledgements

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References


