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Corrosion behaviour of innovative stainless steels in mortar

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Abstract

The main problem of the building sector is the limited durability of reinforcing concrete structures under highly aggressive environments due to the corrosion of reinforcements. In order to demonstrate that stainless steels are the adequate solution to avoid corrosion of reinforced concrete structures by contained chlorides, the corrosion behaviour of AISI 304 and AISI 316L stainless steels in mortar with two chloride doses is compared with the corrosion behaviour of three new stainless steels of low Ni content and reduced cost, and with the traditional carbon steel. The lowest chloride contamination (2% Cl^-) has been used in this research to provoke corrosion in an active state of reinforcing carbon steel, whereas the highest one (5% Cl^-) exceeds all expected levels found in the natural environment, including sea water. The new stainless steels remain in the passive state in mortar specimens with both chloride contents.

Keywords: Corrosion C; Electrochemical properties C; Chloride D; Mortar E; Reinforced stainless steels

1. Introduction

Steel embedded in concrete is usually in a passive state. However, there are aggressive environmental conditions that induce corrosion of steel in reinforced concrete structures (RCS), thereby severely reducing their durability [1,2]. The technical, economical and social importance of the building sector make the degradation of reinforced concrete structures the main concern of civil engineering in the industrialised world, with corrosion of the reinforcements being the main cause of premature failure in these type of structures [3].

A wide variety of protection methods have been used to prevent corrosion in RCS under highly aggressive environments, such as cathodic protection [4,5], the incorporation of inhibitors in the concrete mixing step [6–8], the use of direct coatings on the reinforced structures such as with epoxy coatings [9–11], rebar galvanisation [12,13] or waterproofing the concrete [14,15], and lately inert reinforcements like glass or carbon fibres and stainless steels [16–23] embedded in the concrete. One of the emerging prevention methods is the substitution of reinforcing carbon steel by stainless steel, which ensures a passive state in highly aggressive media. The austenitic and austeno-ferritic stainless steel types seem to offer an adequate combination of corrosion and mechanical resistance, cost and availability to consider their use in reinforced concrete structures [23]. However, the success of this application will depend on the corrosion behaviour of the stainless steel reinforcements under the most adverse service conditions and of course their cost. For this reason, new stainless steels [24], in which the Ni content has been lowered by substitution by other elements [25], are being evaluated in the literature as possible alternatives to conventional carbon steel.

In this work, the corrosion behaviour of three low-cost and low Ni-content stainless steels embedded in mortar contaminated with chloride ions is studied in order to analyse the possibilities of using these materials as concrete reinforcing steels. Two different chloride levels have been added to the mortar: the lowest one (2%) is high enough to initiate corrosion in carbon steel, and the highest one (5%) exceeds the natural level of chloride ions in the environment, including sea water.

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Table 1
Chemical composition (weight percentage) of steel and stainless steels tested

	AISI 304	AISI 316	HSS1	HSS2	HSS3	Carbon steel
C	0.06	0.03	0.06	0.04	0.03	0.25
Mn	1.14	1.64	8.0	8.5	11.3	0.69
Si	0.35	0.36	0.2	0.2	0.4	0.20
P	0.02	0.02	0.02	0.01	0.01	0.012
S	0.01	≤0.01	0.002	0.001	0.01	0.05
Cr	17.4	16.7	16.3	16.5	16.6	0.21
Ni	8.3	10.4	0.22	1.5	2.3	0.22
Mo	0.12	1.9	–	2.0	0.12	0.05
Cu	0.4	0.6	2.0	0.25	2.5	0.43
N	–	–	0.23	0.25	0.16	0.012
Fe	Balance	Balance	Balance	Balance	Balance	Balance

Those steels remaining in the passive state for the highest chloride concentrations can be considered, from the point of view of corrosion resistance, as being suitable for use as reinforcements. The corrosion behaviour of the innovative stainless steels is compared with that of austenitic AISI 304 and AISI 316 stainless steels and traditional carbon steel.

2. Materials and methods

Table 1 shows the chemical compositions of the six different types of steels tested.

Small mortar specimens of size 2 × 5.5 × 8 cm were prepared (Fig. 1), with a cement/sand/water ratio of 1/3/0.5 and chloride additions of 2 and 5%, relative to cement weight. These specimens were successively exposed in a very wet atmosphere, with a relative humidity of about 95%, then in dry laboratory environment with a relative humidity of approximately 40%, and again in the very wet environment with a relative humidity of approximately 95%. With this humidity cycle, it was intended to study whether the ennoblement of the corrosion potential, E_{corr}, occurring when the mortar dries could reach the breakdown potential of the passivating layers, and thus facilitate corrosion on returning to the humid environment.

8 mm diameter rebars of each kind of steel were used as working electrodes. Some of the specimens were prepared using welded rebars as working electrodes to compare their corrosion behaviour. As counter electrode, an external disc of 7 cm diameter stainless steel with a central hole of 1 cm diameter was used, in which the reference electrode, a saturated calomel electrode, was introduced. For the corrosion tests, the counter electrode was placed on the prism surface covered with a wet sponge to facilitate the electrical conduction during the electrochemical measurements.

Corrosion characterisation was carried out by periodic evaluation of the corrosion potential, E_{corr}, and the corrosion current density, i_{corr}, obtained from the determination of the polarisation resistance, R_p. Polarisation curves were not performed until the end of the two-year testing period, in order to avoid affecting the electrodes with the large potentials that need to be applied. The potential scanning rate was 0.6 V/h applied from the corrosion potential to the breakdown potential, after this point the sense of scanning was reversed until the corrosion potential was reached again. Repassivation of the pits generated on the samples after the anodic polarisation curves was assessed by the comparison of the polarisation resistance data obtained before and after the anodic polarisation curves.

3. Results

3.1. Corrosion current density, i_{corr}, determinations

Fig. 2 shows the evolution with time (about 3 years), of i_{corr} values for the carbon steel electrodes and the HSS1 and HSS2 innovative steels embedded in mortar with 2% Cl^-. From the start of testing up to point A, the specimens were maintained at a

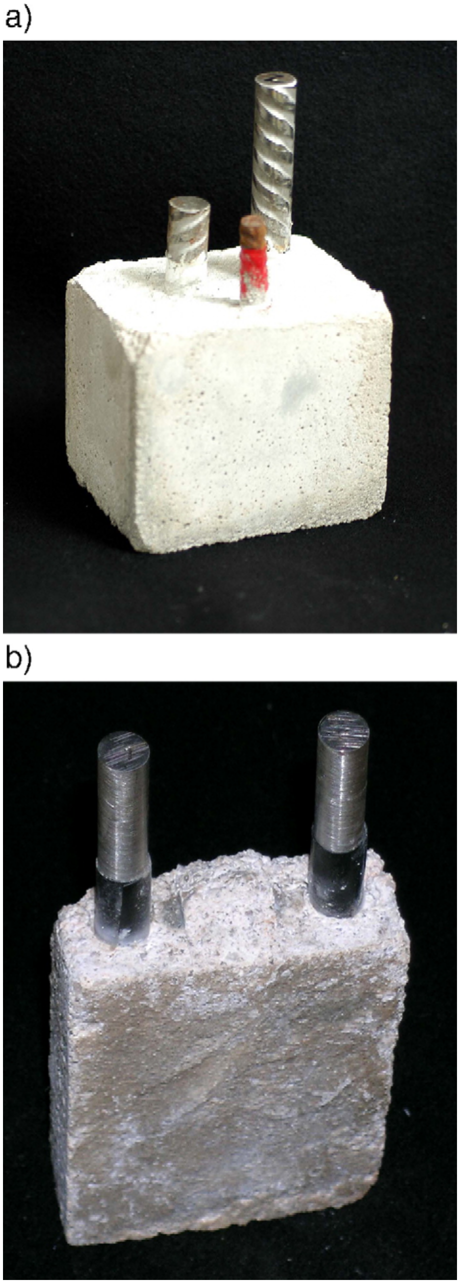

Fig. 1. Photograph of a small mortar specimen used to test ribbed rebars of: a) carbon steel and welded and non-welded HSS3 stainless steel; b) AISI 304, AISI 316, HSS1 and HSS2.

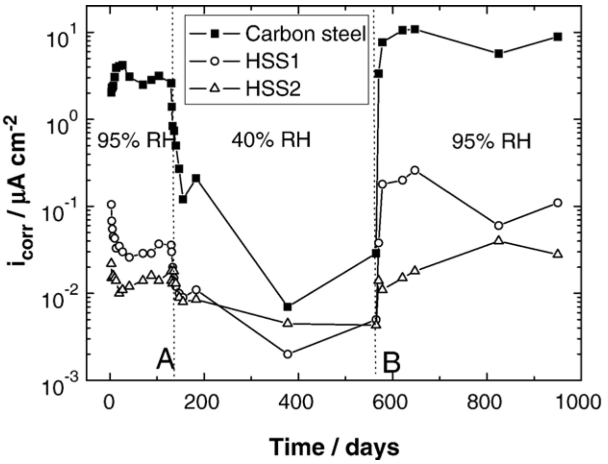

Fig. 2. Comparison of i_{corr} values of carbon steel and HSS1 and HSS2 stainless steels embedded in mortar with 2% Cl$^-$, exposed to a dried atmosphere (relative humidity of about 40%) between points A and B and the remaining time exposed to a wet atmosphere (relative humidity of about 95%).

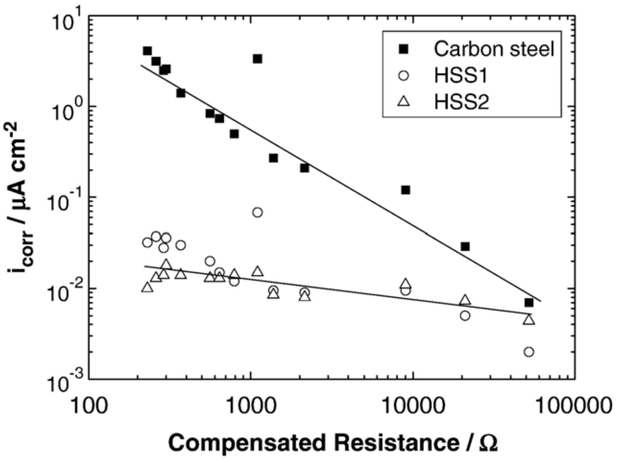

Fig. 4. Correlation between i_{corr} of steels embedded in mortar with 2% Cl$^-$ and compensated resistance between the working and reference electrodes.

very high relative humidity, of approximately 95%; between points A and B they were maintained in the laboratory atmosphere with a low relative humidity, around 40%; and after point B they were returned to the initial humid atmosphere with a relative humidity of about 95%. In this figure, it is clear that the carbon steel electrodes corrode about 100 times more than the stainless steels in humid environments of 95%. However, a progressive drop in i_{corr} values when the specimens are moved to dry environments is observed (point A), that is much higher for carbon steel than for stainless steel specimens. From point A to point B carbon steel and stainless steel specimens show similar i_{corr} values. Finally, the reactivation of corrosion in the carbon steel is observed when the mortar is newly wetted, returning to the initial i_{corr} values or even greater values. There is also a significant increase in the i_{corr} values of the HSS1 stainless steel when the mortar is rewetted, which may suggest the appearance of some pitting during the wetting–drying–wetting cycle.

Fig. 3 shows identical information, i_{corr} versus time, for the carbon steel, AISI 304 and 316 and innovative stainless steels, in mortar with 5% Cl$^-$. Again, it is possible to appreciate a drop in the i_{corr} of carbon steel with the continuous decrease in mortar wetness, that is not appreciable in the corrosion behaviour of the passive stainless steel electrodes HSS1, HSS2 and AISI 304 and 316. When the wetness is increased, the corrosion current density, i_{corr}, of carbon steel also increases. A considerable increase is also seen in the i_{corr} values of HSS1 steel, although these are much lower than for carbon steel, which suggests the appearance of pitting corrosion for this stainless steel.

Figs. 4 and 5 show i_{corr} values estimated for the various steels in the mortars with 2 and 5% Cl$^-$, respectively, versus the ohmic resistance compensated (IR) by the potentiostat (proportional to the resistivity of the mortar). The results reveal an inverse relationship between the corrosion rate of the active carbon steel rebars and the resistivity of the mortar. The effect of

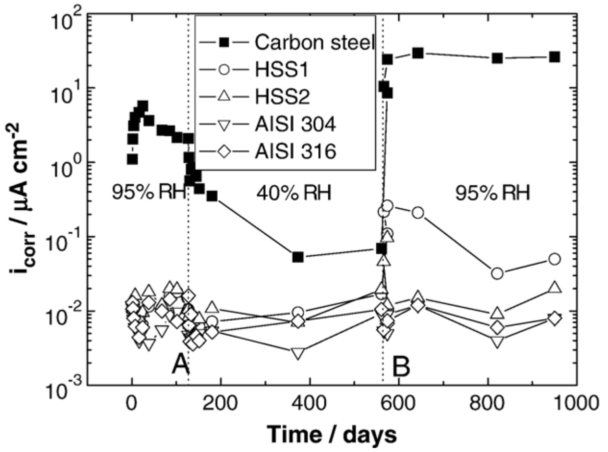

Fig. 3. Comparison of i_{corr} values of carbon steel and HSS1, HSS2, AISI 304 and AISI 316 stainless steels embedded in mortar with 5% Cl$^-$, exposed to an atmosphere of relative humidity of about 95%; except between points A and B, during which time they were maintained in a much drier environment (relative humidity of about 40%).

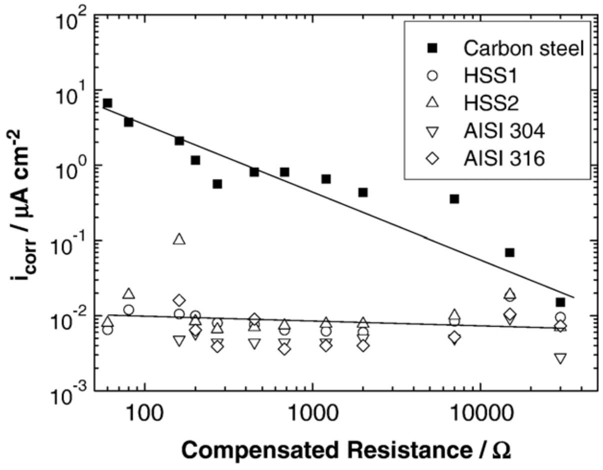

Fig. 5. Correlation between i_{corr} of steels embedded in mortar with 5% Cl$^-$ and compensated resistance between the working and reference electrodes.

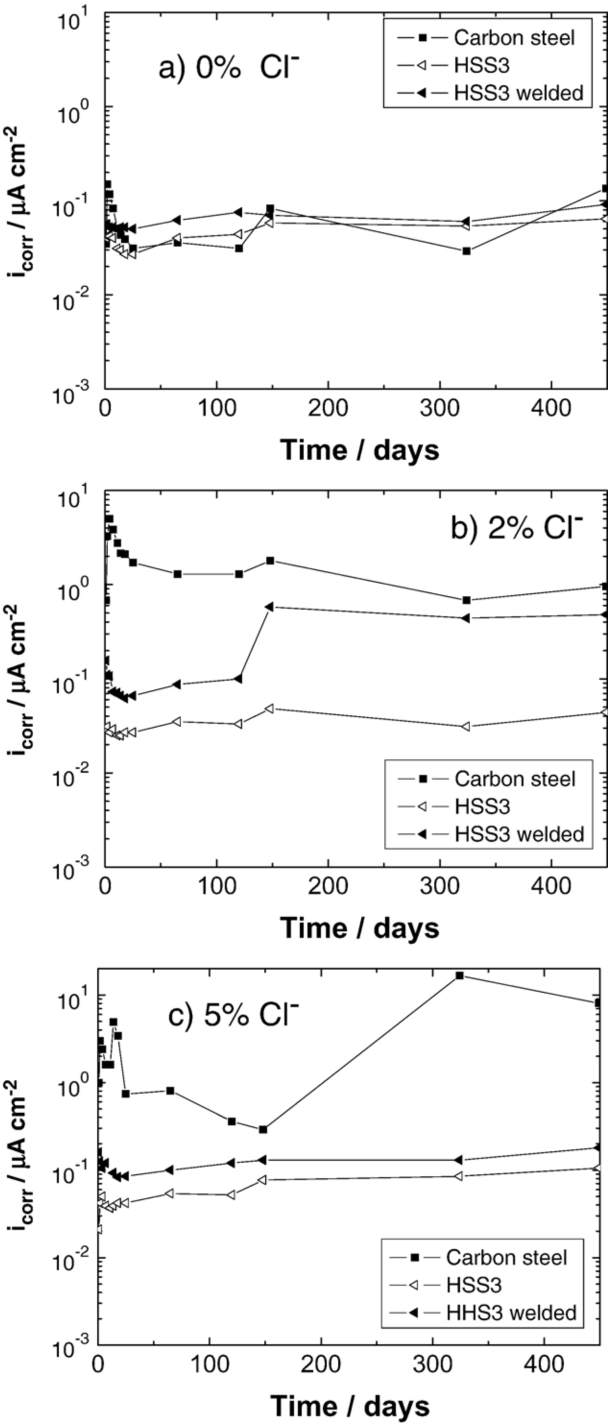

Fig. 6. Evolution versus time of i_{corr} of carbon steel and HSS3 stainless steel electrodes, the latter in welded and non-welded condition, exposed to mortars with different chloride additions: a) without chloride additions; b) with 2% Cl$^-$; and c) with 5% Cl$^-$.

resistivity is much weaker on i_{corr} of the rebars that are maintained in the passive state (HSS1, HSS2, AISI 304 and AISI 316). So if inspections are carried out on very dry concrete, it is difficult to distinguish between the passive or active state of the reinforcement.

Fig. 6a, b and c compare the corrosion behaviour of welded and non-welded corrugated HSS3 stainless steel bars with that of carbon steel in mortar with 0%, 2% and 5% Cl$^-$, respectively. The i_{corr} of carbon steel are similar to those of HSS3 steel, welded or not, in the mortar without chlorides, but are 10 times higher in the mortar with 2% or 5% Cl$^-$ additions. The i_{corr} of the electrodes that are welded are systematically higher than those of the non-welded electrodes, being approximately double. The comparison of Figs. 2, 3 and 6a, b, c, shows that i_{corr} of HSS3 are very similar to those of HSS1 and HSS2 steels.

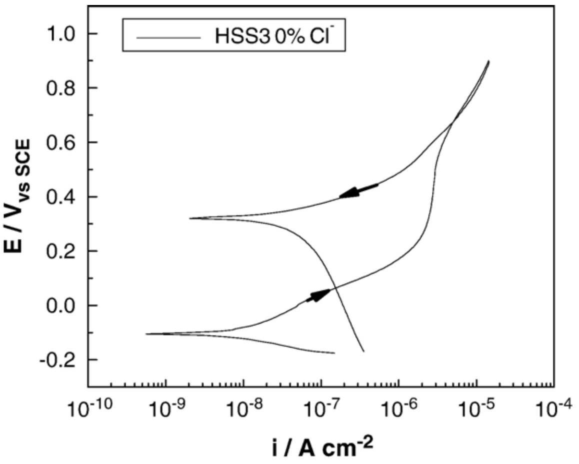

Fig. 7. Polarisation curve of HSS3 stainless steel in mortar without chloride additions.

3.2. Polarisation curves. Possibility of repassivation

Two essentially different types of behaviour may be seen when high polarisations are applied to the electrodes after approximately two years of exposure, as seen in the anodic polarisation curves (APC) of the Figs. 7 and 8:

(a) In the absence of chlorides, at about 100 mV of anodic polarisation, a region with a much gentler slope appears, demonstrating the passive state (Fig. 7). This continues until after 500 mV where oxygen starts to be produced,

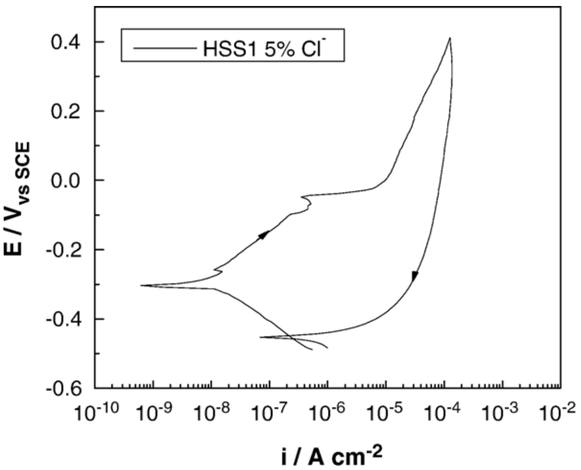

Fig. 8. Polarisation curve of HSS1 stainless steel in mortar with 5% Cl$^-$.

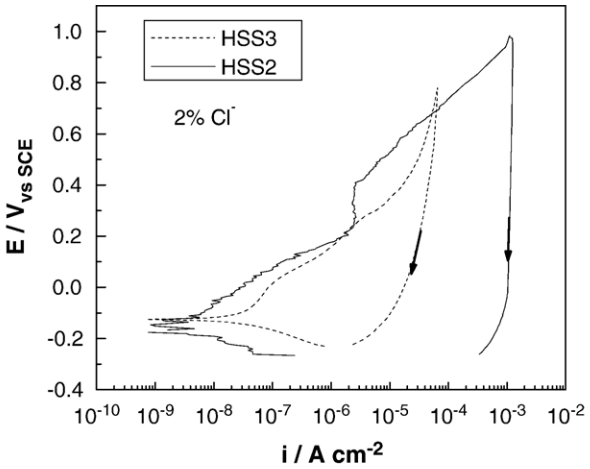

Fig. 9. Polarisation curves of HSS2 stainless steel and welded HSS3 stainless steel in mortar with 2% Cl$^-$.

which gives rise to a progressive increase of the current density. In this case the reverse curve returns at lower current densities than the curve in the anodic direction.

(b) In the presence of chlorides, it is usual to reach a breakdown potential after which the current density increases much more quickly, as can be seen in Fig. 8, which reproduces the polarisation curve of HSS1 steel in mortar with 5% Cl$^-$. The reverse curve returns at much higher current densities than the curve in the anodic direction, evidence of the start of pitting corrosion.

The value of the breakdown potential is often not identified so clearly, as in the Fig. 8, and the change in slope is much less abrupt, as can be seen in the curves in Fig. 9, corresponding to HSS2 and HSS3 steels in the mortar with 2% Cl$^-$. However, the reverse curve shows much higher current densities than the curve in the anodic direction for the same potentials, suggesting local destruction of the passivating layers.

In the case of the carbon steel rebars, the difference in the corrosion behaviour between the absence and the presence of 5% Cl$^-$ is very marked, as may be expected between passive electrodes and electrodes where a generalised corrosion process is developed, as seen in Fig. 10.

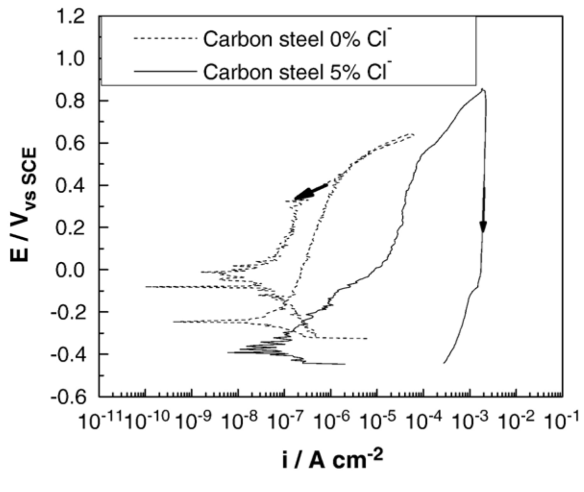

Fig. 10. Polarisation curves of carbon steel in mortar without chloride additions and with 5% Cl$^-$.

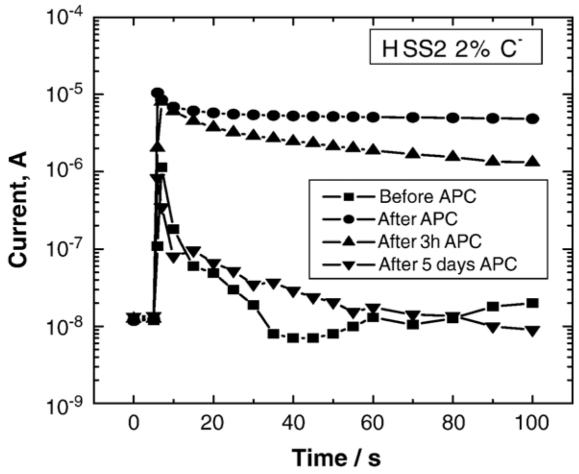

Fig. 11. Current responses of HSS2 stainless steel in mortar with 2% Cl$^-$ to 20 mV steps.

As can be seen from the results of Fig. 11, that show the current responses to potential steps of 20 mV applied to HSS2 steel in the mortar with 2% Cl$^-$, once pitting has been induced during the anodic polarisation, the passivating films naturally restore themselves. The current responses after the anodic polarisation curves, i.e., after the formation of pitting, or even 3 h later, are around two orders of magnitude higher than before the curve is obtained. However, 5 days later, the value is again indistinguishable from the initial one, an evident sign that repassivation has occurred. This is not always observed, and sometimes the current response does not return to the initial value even after 5 days, as may be seen in Fig. 12, which reproduces the results obtained with HSS1 steel in the mortar with 2% Cl$^-$.

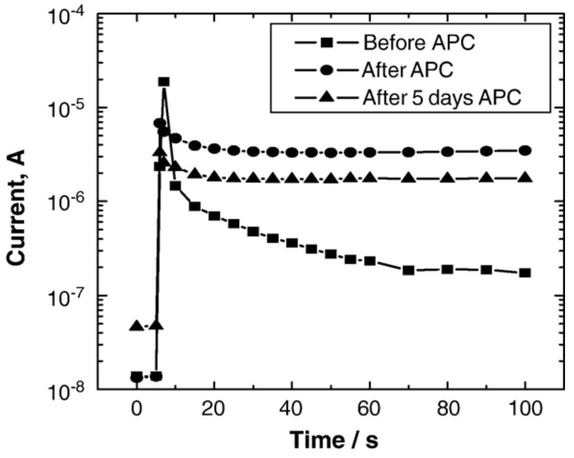

Fig. 12. Current responses of HSS1 stainless steel in mortar with 2%Cl$^-$ to 20 mV steps.

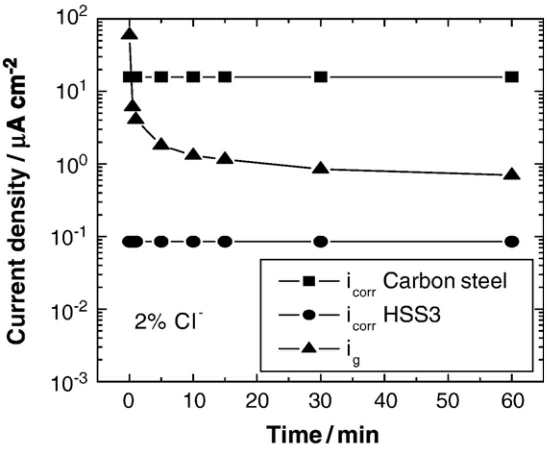

Fig. 13. Comparison between i$_g$ of the carbon steels/HSS3 stainless steel macrocouple in mortar with 2% Cl$^-$ and i_{corr} values of the two components independently.

The stainless steels HSS2, AISI 304 and AISI 316 are able to repassivate in mortars with 2% or 5% Cl$^-$, but not the HSS1 steel and the welded HSS3 electrodes.

Finally, Fig. 13 shows the galvanic macrocouple current, i_g, of the HSS3 stainless steel–carbon steel electrodes, obtained by short-circuiting both materials in the mortar with 2% Cl$^-$, compared with i_{corr} estimated from R$_p$ measurements for the separate electrodes. It can be seen that the i_{corr}, corresponding to the microcouples in the active state, are much greater than the i$_g$ values between the active and passive states.

4. Discussion

The technical, economical and social importance of the building sector, one of the most important contributors to the standard of living of a country, is widely known. Unfortunately, the durability limitations of reinforced concrete structures caused by corrosion in aggressive environments lead to severe problems, giving rise to high costs associated with the maintenance of the existent structures [26]. Considering that the number of structures undergoing repairs compared with those under construction is steadily rising [27], the situation requires the use of new materials more resistant to corrosion. Actually, the high price of stainless steels (4–9 times higher than for carbon steel [16,18,22]) is counterbalanced by the considerably extended service life of the structures and reduced accumulative maintenance costs (by 50%) [23].

According to the results, the stainless steels embedded in mortar with Cl$^-$ additions of 2% and 5%, Figs. 2 and 3, show i_{corr} values 2–3 orders of magnitude lower than for carbon steel, i.e., they would require times of 2 or 3 orders of magnitude greater than carbon steel to produce a similar degree of deterioration: as such corrosion would cease to be a problem throughout the service life of the structures. These results prove that the use of stainless steels reinforcements increases substantially the service life of reinforced concrete structures.

In the absence of chlorides, both carbon steel and stainless steels remain in a passive state and their corrosion behaviour is very similar, as Fig. 6a shows for HSS3 steel. In the presence of 2% or 5% Cl$^-$ (Fig. 6b and c) the HSS3 preserves its passivity but the carbon steel is active, and it corrodes at high corrosion rates. In the case of welded HSS3 samples, the corrosion rates are 2–3 times higher than those exhibited by the non-welded material. This means that surface irregularities and oxidation products on the welded zones generate conditions that promote local depassivation of the material.

On the other hand, the abrupt drop of more than 2 orders of magnitude in the i_{corr} values of carbon steel in mortar contaminated with chlorides during the dry period indicates that its corrosion rate is strongly dependent on the resistivity of the concrete, as seen in Figs. 4 and 5, in agreement with the literature [28,29]. However, the influence of the degree of wetness of the mortar is much smaller in the passive state, so the responses of the active and passive reinforced structures can be indistinguishable during long dry periods. For this reason inspections of structures must be performed after periods of rain or of high relative humidity in order to assess the corrosion risk correctly and the i_{corr} corresponding to unfavourable conditions.

When other parameters, such as breakdown potentials or the critical chloride level needed to begin the pitting corrosion are examined, the conclusion is the same: the reinforcing stainless steels are able to preserve the passive state in the most adverse conditions. In Figs. 7–10, large differences, several hundreds of mV, between corrosion potential and breakdown potential, $E_b - E_{corr}$, are observed. This indicates that it will be very unlikely that natural corrosion cells are able to generate such differences in potential in the absence of external polarisations, and to cause the corrosion in active state of the reinforcing stainless steels. In addition, in mortar with additions of 2% and 5% Cl$^-$, the AISI 304 and 316 and innovative steels exhibit i_{corr} values lower than 0.1 µA/cm^2 (Figs. 2, 3 and 6). The critical chloride levels needed to cause pitting corrosion of austenitic stainless steels is commonly reported to be 10 times higher than in the reinforcing carbon steel, of about 0.4% [30].

In most cases (for the AISI 304 and AISI 316, HSS2 and HSS3 steels) the passive films are restored even if they are accidentally broken, as it is evidenced by the results in Fig. 11 for HSS2 steel in mortar with 2% Cl$^-$. In this figure, the intensities return to previous ones after several days. Only for the HSS1 steel (Fig. 12) and the welded HSS3 steels is this not seen, probably due to the differences in composition and surface heterogeneities in the welding zone that avoid repassivation.

4.1. Galvanic risk

The great difference of the galvanic current, i_g, of the HSS3 stainless steel–carbon steel macrocouple compared with the i_{corr} values corresponding to the carbon steel electrodes (Fig. 13) on its own confirm that the additional corrosion, attributable to galvanic macrocouples, was negligible compared with the i_{corr} values of microcells formed in active areas of the reinforcements in the active state [31]. Other authors have obtained this result and noted the absence of any significant additional risk due to the galvanic couple. This is explained by the fact that the cathodic oxygen reduction current is greater in the carbon steel than in easily polarised stainless steels [18,32], and thus a very small current leads the two components of the galvanic couple to adopt a common potential. The risk would therefore be greater between the pits that are initiated in the reinforcing carbon steel and the passive areas that surround them, with a similar potential to that of the stainless steels and lower cathodic activity [16,19].

What really limits the durability of reinforced concrete structures, however, is the amount of corrosion (generalised corrosion) from the point of view of the expansive character of the corrosion products and the low tensile strength of concrete. These are often responsible for cracking the concrete at very low corrosion penetrations, ≤ 100 μm [33,34], that can be reached in just a few years after the critical chloride level has been exceeded.

5. Conclusions

- None of the tested stainless steels presents sudden changes in i_{corr} values that indicate the initiation of pitting corrosion in the mortar specimens with 2 or 5% Cl^- maintained in high relative humidity environments.
- The results prove that the critical chloride levels needed to cause pitting corrosion in austenitic and duplex stainless steels are at least 10 times higher than those of the carbon steel reinforcements.
- The difference between breakdown potential and corrosion potential tends to be several hundred mV, in AISI 304 and 316 and innovative stainless steels, and so the natural formation of corrosion cells that can produce these potential differences and trigger pitting corrosion is unlikely.
- When the breakdown potential is exceeded, e.g. when obtaining polarisation curves, all stainless steels with the exception of HSS1 and welded HSS3 steels are repassivated after a few hours or days.
- Differences of corrosion behaviour between welded and non-welded HSS3 steel seem to indicate that corrosion behaviour depends strongly on the surface state; an aspect that would merit careful research.
- The carbon steel i_{corr} values are similar to those of the AISI 316, HSS1, HSS2 and HSS3 stainless steels in mortar without chloride additions, and at least 10 times higher in the presence of 2% or 5% Cl^-. As a consequence, it is highly improbable that corrosion will limit service life when stainless steels are used as reinforcements in concrete structures.
- The i_g value of the stainless steel–carbon steel macrocouple is much lower than the i_{corr} value of the carbon steel in the presence of 2% or 5% Cl^-, demonstrating that the coupling of the two materials does not introduce any significant additional risk of corrosion.

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