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Influence of Mo alloying on pitting corrosion of stainless steels used as concrete reinforcement

Influência do Mo na corrosão por pites de aços inoxidáveis utilizados como reforço de concreto armado

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Abstract

Corrosion of reinforcement steels, induced by chloride ions penetrating into the concrete, is the main cause of early damage, loss of serviceability and safety of reinforced concrete structures, which can be even more severe in the presence of concomitant concrete carbonation. In order to prevent reinforcement steel corrosion in highly aggressive alkaline environments, the use of stainless steels is becoming increasingly popular in coastal and marine constructions. Although widely used as an increasing corrosion resistance element in acidic environments, the influence of Mo addition on pitting corrosion resistance of stainless steels is not very clear in these conditions. Understanding Mo mechanism on corrosion resistance in alkaline media is hence of major importance, particularly for new lean grades with low Nickel and Molybdenum contents which presents a good balance between the properties required in these applications and the final cost of the material. In this work we will show the effect of Mo addition on pitting corrosion properties of austenitic, ferritic and duplex SS. A comparison between Mo content steels (alloys: 1.4404, 1.4113 and 1.4462) and very low molybdenum contents steels (alloys: 1.4301, 1.4016 and 1.4362) is done considering their pitting corrosion resistance (pitting potential E_{pit}) in different corrosion conditions. The results are discussed with respect to the influence of Mo addition on pitting behaviors for the different stainless steel rebar families in several aggressive media mainly in synthetic, chlorinated and carbonated solution reproducing the real concrete pore environments (pH10 solution with carbonates and chlorides ions).

Keywords: Stainless steels, Pitting corrosion, molybdenum and reinforced concrete

Resumo

A corrosão do aço dos vergalhões, induzida por íons cloreto que penetram no concreto, é a principal causa de lesão precoce, perda de operacionalidade e de segurança das estruturas de concreto armado, fato que pode ser ainda mais severo na presença concomitante de cabonatação do concreto. Além de evitar a corrosão dos reforços de aço, em ambientes alcalinos altamente agressivos, o uso de aços inoxidáveis é cada vez mais popular em construções costeiras e marinhas. Embora *amplamente utilizado como um elemento que aumenta a resistência à corrosão, em ambientes ácidos, a influência do Mo, sobre as propriedades de corrosão por pites dos aços inoxidáveis, não é muito clara em meios alcalinos. O entendimento do mecanismo do Mo, na resistência à corrosão, nessas condições, é, portanto, de grande importância, sobretudo para a nova classe de aços inoxidáveis "lean duplex". Esses aços contêm um baixo teor de Ni e de Mo, mas apresentam um bom equilíbrio entre as propriedades exigidas, nessas aplicações, e propiciam um bom custo final do material. Nesse trabalho, mostra-se o efeito da adição de Mo sobre as propriedades de corrosão por pites de aços austeníticos, ferríticos e duplex. Os resultados serão discutidos com relação às diferentes famílias de aços inoxidáveis em diferentes meios agressivos, principalmente em uma solução sintética contendo cloretos e carbonatos. Essa solução reproduz o ambiente real de poros de concreto contaminado (pH 10, com íons carbonato e cloreto).*

Palavras-chave: *Aços inoxidáveis, corrosão por pites, molibdênio e concreto armado.*

1. Introduction

A large part of the world's transport and energy infrastructures rely on reinforced concrete. Its durability is due to the excellent chemical stability of hydrated Portland cement and the passivity of steel in the alkaline pore solution of concrete with a pH from 10 to 13.5. Corrosion of the reinforcement steels, induced by chloride ions penetrating into the concrete, is the main cause of early damage, loss of serviceability and safety of reinforced concrete structures (Addari et al., 2008). In order to prevent reinforcement steel corrosion in highly aggressive environments, the use of stainless steels (SS) is becoming increasingly popular as they exhibit much higher pitting corrosion resistance than plain carbon steel and a higher chloride content is required to depassivate them (Abbott et al., 1997). The localized corrosion and generalized attack on the steels are associated with chlorides and carbonation ions, respectively (Blanco et al., 2006). Thus, these reinforcements suffer severe corrosion problems when the reinforced concrete structure is exposed to chloride contaminated environments and when the concrete cover is carbonated.

In these contexts, improving of the corrosion characteristics of SS is the major priority, so that the molybdenum used as an alloy element is a valve metal to play this role. It has long been known that Mo additions on SS improve their corrosion resistance and also favor an easier repassivation (Pardo et al., 2008; Halada et al., 1995). Although there are several studies about the electrochemical behavior of Mo and its role to increase the corrosion resistance properties of the SS, the presence of this element in the passive film and its influence on the pitting corrosion mechanism is not clearly understood (Halada et al., 1995). However, several works with pure Mo were done in order to understand its influence on the corrosion resistance mechanism of SS (Halada et al., 1995; Badawy et al., 1998; Yang et al., 1984; Ürgen et al., 1990; Lu et al., 1989).

The studies of (Ilevbare et al., 2001) explain the action of Mo, principally on nucleation and metastable pitting corrosion of austenitic SS. As these steps of pitting corrosion constitute the embryonic stage of a pit growing, the probability associated with the successful generation of these events will affect the onset of stable pitting. According to (Pardo et al., 2008), the Mo addition enhances the pitting corrosion resistance of austenitic SS studied in 3.5 wt.% NaCl, because the presence of this element progressively reduces the corrosion rate, increasing Critical Pitting Temperature CPT values and ennobling both E_{pit} and E_{corr}. Moreover, these authors proposed that Mo plays and important role in the repassivation process and consequently, there is a decrease in the pit propagation when Mo oxides form on the pit walls. These results are in good agreement with the studies done by (Lemaitre et al., 1993), which describe the effect of Mo additions on ferritic and austenitic SS as improving the resistance to local breakdown of the passive film in neutral solutions for both steels. However, in the alkaline medium, the molybdenum addition seems to have no positive effect for the austenitic ones (Chauveau et al.).

In summary, the explanation for the effect of Mo on the pitting corrosion resistance of stainless steels is, at the moment, a subject of discussion for the greater part of the scientific community in neutral, acidic and mainly in alkaline media which present a lack of scientific knowledge. On this basis, the present paper attempts to provide a further understanding of the effect of Mo addition on pitting corrosion and repassivation behavior of three different types of commercial stainless steels (ferritic, austenitic and duplex) in several chloride solutions, mainly in the synthetic chlorinated and carbonated solution that reproduce the real concrete pore environments. Furthermore, the effect of molybdenum addition on the pit morphology of Duplex SS has been studied by Scanning Electron Microscopy SEM, which presents a higher susceptibility of the austenitic phase in the presence of Mo.

2. Material and methods

Samples chemical composition

Three different types of commercial stainless steels were investigated: two ferrites (AISI 430 and 434), two austenites (AISI 304L and 316L) and two duplex (1.4362 and 1.4462). The chemical compositions of these materials are given in Table 1.

All specimens used in this work are samples of industrial draw wires which were provided by Ugitech Company. Prior to general corrosion tests, specimens were grounded till P1200 grade, followed by rinsing with ethanol and dried with hot air.

Table 1
Chemical composition of stainless steels provided by UGITECH. *Sppm

Industrial Material		Elements (wt. %)										
		C	Si	Mn	Ni	Cr	Mo	Cu	N	Co	S *	PREn
Austenitic	304L	0.02	0.49	0.60	11.12	18.29	0.21	0.31	0.03	0.00	9	19.46
	316L	0.01	0.49	0.73	11.08	16.89	2.17	0.48	0.03	0.25	10	24.53
Ferritic	430	0.01	0.31	0.30	0.29	16.16	0.05	0.10	0.03	0.02	5	16.80
	434	0.03	0.39	0.39	0.45	16.17	0.92	0.12	0.05	0.03	23	20.01
Duplex	1.4362	0.02	0.41	1.09	4.02	22.30	0.28	0.30	0.15	0.13	4	25.62
	1.4462	0.02	0.4	1.61	5.45	22.91	2.78	0.22	0.15	0.07	3	34.48

Electrochemical measurements

DC electrochemical measurements were performed with a potentiostat/galvanostat SOLARTRON, Schlumberger model SI 1287 Electrochemical Interface Potentiostat. The working surface was 2.5 cm^2. The test media were aerated with a 0.025 M $NaHCO_3$ + 0.025 M $Na_2CO_3.10H_2O$ + 0.6 M NaCl solution at 25°C and at several pHs in the 0.6 – 12.5 range and adjusted with HCl or NaOH. A three-electrode cell was used, where the working electrode was the test material, whereas the counter and reference electrodes were platinum and saturated calomel electrode (SCE), respectively. This reference electrode presents a potential of -241V with respect to the hydrogen electrode.

The anodic polarization curves were performed after 1 hour of immersion in the electrolyte at a 1 $mV.s^{-1}$ scan rate from 30 mV below the open circuit potential up to 100$\mu A.cm^{-2}$ current density.

Microstructure and morphology of corrosion attack (SEM)

A scanning electron microscope SEM equipped with EDS microanalysis hardware was used in order to examine both the microstructure and morphology of the corrosion attack produced on the duplex structure.

Prior to general microscopy tests, the duplex SS were ground till P2400 grade followed by polishing with diamond compounds (6, 3 and 1 µm) and then rinsed using ethanol and dried with hot air. The anodic polarization was carried out in order to start the pitting corrosion on the material's surfaces.

3. Results and discussion

Effect of Mo adition on pitting potential of stainless steels in function of pH

Figure 1 A, B and C shows typical polarization curves obtained for 304 and 316 SS at pH 0.6, 10 and 12, respectively. Figure 1A illustrates the huge positive effect of Mo on the corrosion resistance of austenitic grades in chloride acidic environments (pH 0.6), as the 304 steel shows no passive behavior and already corrodes at open circuit potential whilst 316 shows a passivation range and a pit potential (E_{pit}) of about 200 mV_{sce}. In the alkaline domain, however, the Mo-free austenitic SS 304 becomes more resistant than the 316, as seen in Fig. 1B and C (E_{pit} for 316 < E_{pit} for 304).

It seems that, for these austenitic grades, there is a monotonic loss of the Mo effect as the pH increases, and an absence of the Mo positive role in alkaline media as already pointed out in a previous study (Chauveau et al.). Indeed, the E_{pit} difference between the 316 and 304, monotonically decreased with the pH increase from +450 (pH 0.6) to –160 mV (pH 12.5); negative values indicating that the Mo-free alloy became more resistant than the Mo-containing 316, as seen in Fig. 1B and C.

Figure 2 and 3 show the typical cyclic polarization curves of ferritic and duplex alloys in different *pH* media, respectively. The beneficial effect of Mo addition on pitting corrosion resistance

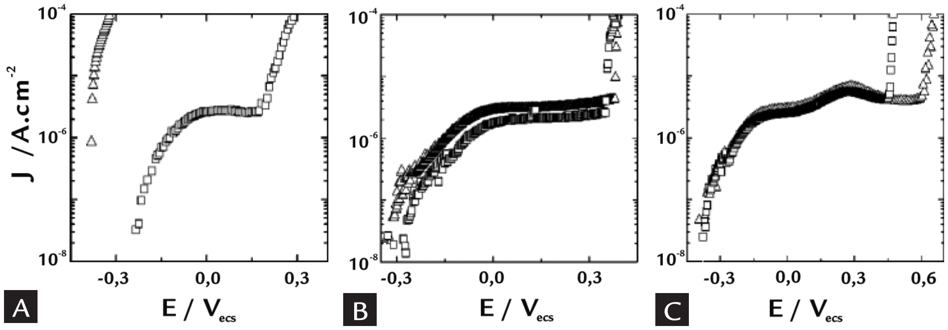

Figure 1
Polarization curves obtained for 304 (△) and 316 (☐) austenitic SS in different pHs of chloride solution (A: pH 0.6; B: pH 10 and C: pH 12.5) at 25°C.

(determined by the E_{pit}) of ferritic and duplex steels can be clearly observed. For a similar pH solution (example pH 7), additions of Mo shifted E_{pit} values for more noble values, from 0.073 to 0.152V_{sce} for ferritic SS (Figure 2B) and from 0.415 to more than 0.900V_{sce} for duplex ones (Figure 3B). All anodic polarization graphs in Fig. 2 and 3 are just typical examples of a quite reproducible behavior: on the average, the presence of Mo increased the pit potential about 50 mV for the ferritic and more than 150 mV for the duplex grades.

Unlike for austenitic grade, it clearly appears that Mo has a positive effect in their corrosion resistance in alkaline environments (Figs. 1B and 1C). On the other hand, these results seem to indicate that Mo does have a protective role in alkaline media, but mostly related to the improvement of the ferrite pitting corrosion resistance (Figures 2 and 3).

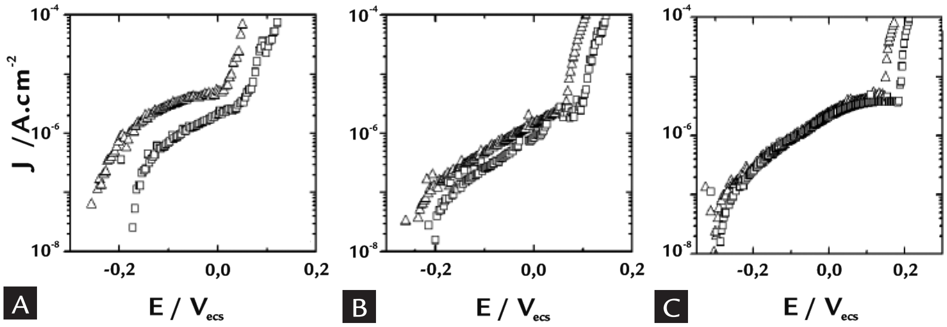

Figure 2
Polarization curves obtained for 430 (△) and 434 (☐) ferritic SS in different pHs of chloride solution (A: pH 4; B: pH 7 and C: pH 10) at 25°C.

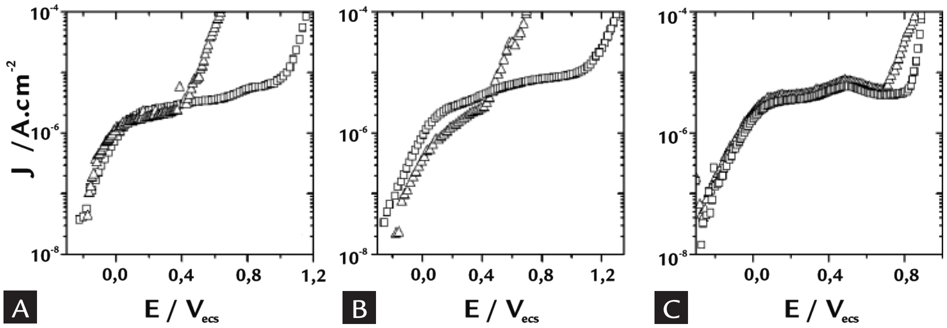

Figure 3
Polarization curves obtained for 1.4362 (△) and 1.4462 (☐) duplex SS in different pHs (A: pH 4; B: pH 7 and C: pH 10) at 25°C. The current increases upwards for the 1.4462 grade are due to oxygen evolution and not pitting corrosion.

Influence of Mo adition on pitting potential of stainless steels in function of temperature

The SS were tested in a pH 10 chloride solution at three different temperatures using anodic polarization measurements as well as n several different pH media as mentioned above. The histograms, illustrated in Figure 4, show the Mo effect on the E_{pit} for ferritic, austenitic and duplex alloys in function of temperature. Thus, the beneficial influence of molybdenum on the corrosion resistance of ferritic and duplex SS in alkaline environments were confirmed, even at high temperatures because the E_{pit} was elevated about 40 mV for ferritic SS and more than 150 mV for duplex SS, thanks to the Mo addition.

On other hand, for the austenitic ones, the absence of the Mo effect was verified for all studied temperatures. According to literature (Pardo et al., 2008), these unlikely results were previously detected when 316 SS has a greater amount of manganese than 304. In these cases, the SS usually exhibits an uncompleted dissolution of this element in the austenite phase, resulting in the formation of manganese-rich sulphide inclusions, which are not thermodynamically stable at the passivity region potentials. As a result, these inclusions tend to dissolve, starting a localized attack at the inclusion/austenitic matrix interfaces and consequently hide the protective Mo effect. However, our austenitic alloys have almost the same Mn content (0.733wt.% Mn and 0,599wt.% Mn for AISI 316 and AISI 304, respectively) which eliminates the possibility of a bigger MnS inclusion content for 316 and then an undesirable E_{pit} reduction for this material.

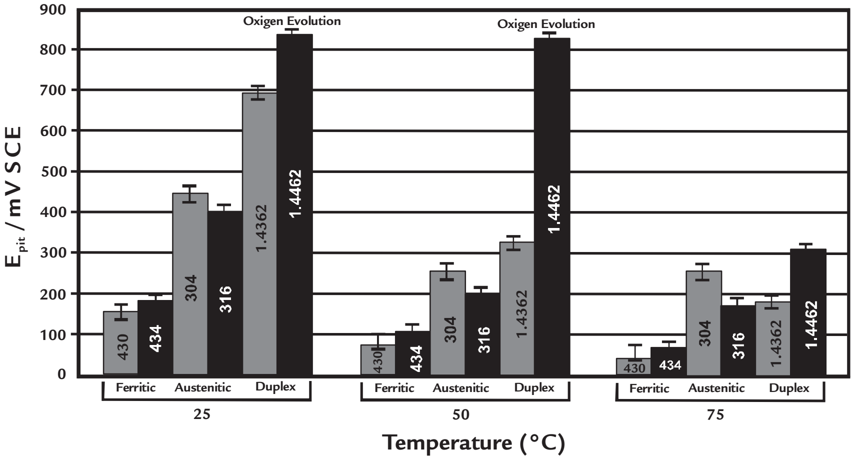

Figure 4
Pit Potential for ferritic, austenitic and duplex SS in chloride alkaline solution (pH 10) at 25, 50 and 75°C. The grey and black histograms correspond to Free Mo SS and Mo content SS, respectively.

Influence of Mo addition on pit nucleation in the duplex structure

Figure 5A and B show the pits formed on the etched surface of DIN 1.4362 and DIN 1.4462 after polarization experiments in pH 10 solution, respectively. This kind of pit was more occluded with a dimension of ≈ 2µm, which is consistent with the results found by (Deng et al., 2008). For the Free Mo duplex SS (Fig. 5A), the lower pitting resistance of ferrite (α phase) was responsible for the fact that pitting preferentially occurred in this phase. For the Mo content duplex SS (Fig. 5B), however, the Mo addition substantially increased the ferrite corrosion resistance and in this case the pits were almost exclusively nucleated at austenite, especially near the grain boundary. This scenario of the enhanced ferrite phase corrosion resistance by addition of Mo to the bulk alloy can of course drastically change in the presence of sigma phase (δ) precipitates, as this precipitation is located at ferrite and impoverishes its Cr and Mo contents (Bastos et al., 2007).

This indirect evidence of the higher role of Mo in ferrite was confirmed by a quantitative EDS analysis. The chemical composition of each phase for the 1.4462 steel confirmed that Mo is preferentially dissolved into the ferrite phase (3.32%) compared to austenite which contains less Mo (1.95%); consequently both the ferrite and the bulk material have their corrosion resistance improved. Nevertheless, this better ferrite behavior cannot be associated to different Cr contents between 1.4362 and 1.4462 steel since their Cr contents were roughly the same (precisely for ferrite 24.35 and 24.6 and for austenite 21.1 and 20.3, for 1.4362 and 1.4462, respectively).

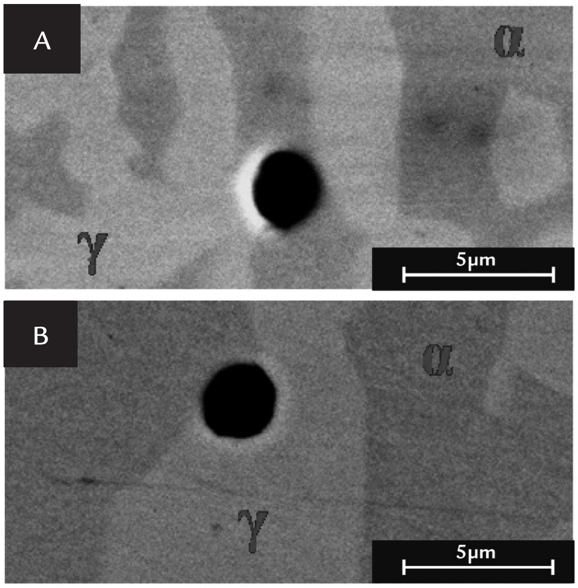

Figure 5
Back-scattered electron pictures of A: Free Mo duplex SS (1.4362) and B: Mo countainig duplex SS indicating the preferencial pitting attack on the ferrite and austenite, respectively. Both samples were observed after anodic polarization til 40µA/cm² at pH 10 solution and 75°C.

4. Conclusion

The role of molybdenum in the pitting corrosion resistance was quite positive for duplex and ferritic SS under all experimental conditions, even if only 0.8 wt% Mo was added to the ferritic one. In other words, the Mo addition increases the E_{pit} of both ferritic and duplex SS even in synthetic, chlorinated and carbonated solutions, reproducing the real concrete pore environments at high temperatures. However, the influence of Mo was not consistent for austenitic SS in different environments. Surprisingly, the AISI304 has shown a higher resistance than AISI316 for alkaline solutions, although this scenario was inversed in acidic and neutral media. These unlikely results were only reported in the case where the 316 has a higher Mn inclusion amount than 304 (Pardo et al., 2008).

The comparative studies of the pitting corrosion potential of duplex, austenitic and ferritic stainless steels suggest a higher positive influence of Molybdenum addition at the ferrite rather than austenite phase. Furthermore, this indirect evidence of the higher Mo effect at the ferrite phase was confirmed by the SEM analyses of duplex SS.

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