

# **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 steels 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 steels 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).

### **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 segurança das estruturas de concreto armado, que pode ser ainda mais severo na presença concomitante de carbonatação do concreto. A*

*fim de evitar 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 utilizada como um elemento de crescente resistência à corrosão em ambientes ácidos, a influência da adição de Mo sobre a resistência à corrosão por pite de aços inoxidáveis não é muito clara nestas condições. O entendimento do mecanismo do Mo na resistência à corrosão em meio alcalino é, portanto, de grande importância, sobretudo para as novas classes de baixo níquel e molibdênio que apresentam um bom equilíbrio entre as propriedades exigidas nestas aplicações e o custo final do material. Neste trabalho vamos mostrar o efeito da adição de Mo sobre propriedades de corrosão por pite de aços inoxidáveis austenítico, ferrítico e duplex. Uma comparação entre os aços contendo Mo (ligas: 1.4404, 1.4113 e 1.4462) e aqueles com muito baixos teores de molibdênio (ligas: 1.4301, 1.4016 e 1.4362) é feita considerando sua resistência à corrosão por pites em diferentes condições de corrosão. Os resultados são discutidos com relação à influência da adição de Mo sobre comportamentos em corrosão por pites para os aços inoxidáveis de diferentes famílias de vergalhões em diversos meios agressivos, principalmente em sintético, clorada e solução carbonatada reproduzir o ambiente real de poros do concreto (pH10 solução com íons carbonatos e cloretos)*

## **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 steels 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 are required to depassivate them (ABBOTT et al., 1997). The localized corrosion and generalized attack of 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 as 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 electrochemical behavior of Mo and its role to increase the corrosion properties of the SS, the presence of this element in the passive film and his influence on pitting corrosion mechanism is not clearly understood (HALADA et

al., 1995). However, several works with pure Mo were done in order to understanding its influence on the corrosion resistance mechanism of SS (HALADA et al., 1995; BADAWEY 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 this element presence reduces progressively the corrosion rate, increasing Critical Pitting Temperature CPT values and ennobling both  $E_{\text{pit}}$  and  $E_{\text{corr}}$  moreover these authors proposed that Mo promotes a important role on the repassivation process and consequently a decreasing of the pitting propagation by formation of Mo oxides on the pit walls. These results are in well agreement with the studies done by (LEMAITRE et al., 1993) which describe the effect of Mo additions on ferritic and austenitic SS as a improving of the resistance to local breakdown of the passive film in neutral solutions for both steels. However, in the alkaline medium, the molybdenum addition seems has no positive effect for 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 great 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 reproducing 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.

### **3. MATERIAL AND METHODS**

#### **3.1. SAMPLES CHEMICAL COMPOSITION**

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

All specimens used in this work are sampled of industrial draw wires which are 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.**

Type	Elements (wt.%)										
	C	Si	Mn	Ni	Cr	Mo	Cu	N	Ti	Co	
Ferritic	430	0.01	0.31	0.30	0.29	16.16	0.05	0.1	0.033	0.002	0.024
	434	0.03	0.39	0.39	0.45	16.17	0.92	0.115	0.048	0.002	0.027
Austen.	304	0.02	0.49	0.599	11.123	18.29	0.211	0.305	0.028	0.003	xxx
	316	0.01	0.492	0.733	11.08	16.89	2.172	0.475	0.032	0.005	0.248
Duplex	1.4362	0.02	0.414	1.097	4.022	22.3	0.277	0.303	0.151	0.004	0.129
	1.4462	0.019	0.4	1.61	05.45	22.91	2.78	0.22	0.15	0.005	0.073

### 3.2. 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<sup>2</sup>. The test media were aerated 0.025 M NaHCO<sub>3</sub> + 0.025 M Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O + 0.6 M NaCl solution at 25°C and at several pHs in the 0.6 – 12.5 range 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 hydrogen electrode.

The anodic polarization curves were performed after 1 hour of immersion in the electrolyte at 1 mV.s<sup>-1</sup> scan rate from 30 mV below open circuit potential up to 100µA.cm<sup>-2</sup> current density.

### 3.3. MICROSTRUCTURE AND MORPHOLOGY OF CORROSION ATTACK (SEM)

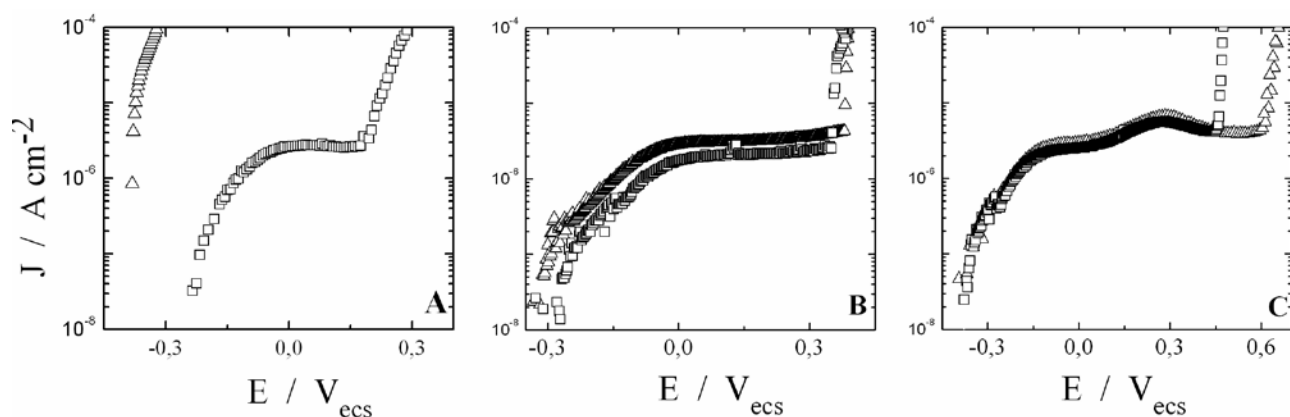
A scanning electron microscope SEM equipped with EDS microanalysis hardware was used in order to examine both microstructure and morphology of the corrosion attack produced on duplex structure.

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 these material's surfaces.

## 4. RESULTS AND DISCUSSION

### 4.1. EFFECT OF Mo ADDITION 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. The 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 corrodes already at open circuit potential whilst 316 shows a passivation range and a pit potential ( $E_{pit}$ ) about of 200 mV<sub>sce</sub>. 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).

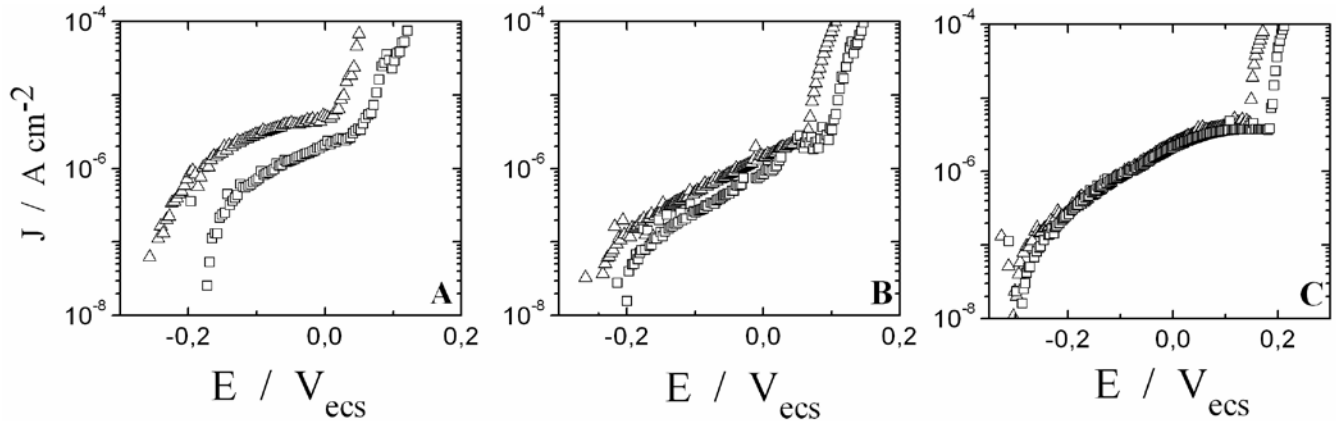


**Figure 1** – Polarization curves obtained for 304 ( $\triangle$ ) and 316 ( $\square$ ) austenitic SS in different pHs of chloride solution (A: pH 0.6; B: pH 10 and C: pH 12.5) at 25°C.

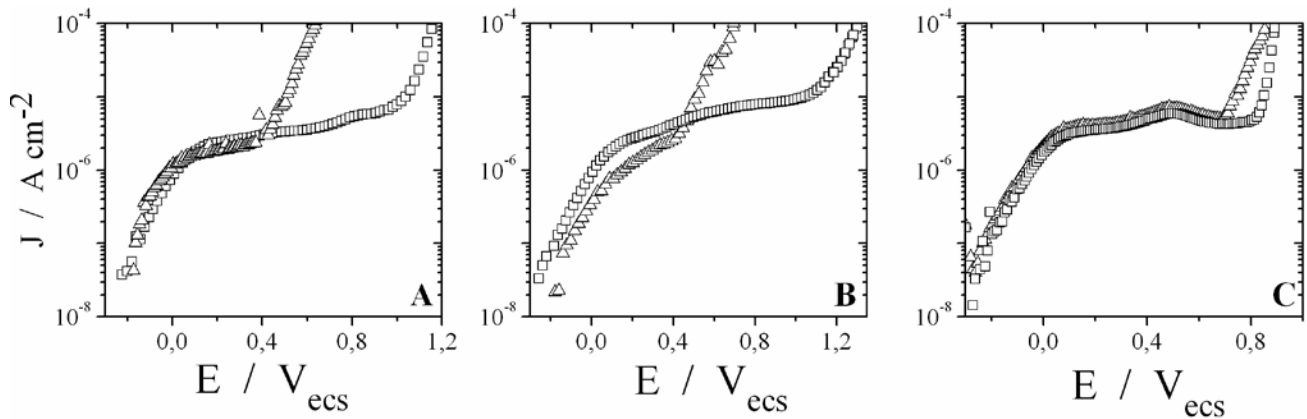
It seems that, for these austenitic grades, there is a monotonic loss of Mo effect as the pH increases and an absence of Mo positive role in alkaline media as already pointed out in previous study (CHAUVEAU et al.) [12]. Indeed, the  $E_{pit}$  difference between the 316 and 304, monotonically decreased 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. 1 b) and c).

Figure 2 and 3 show the typical cyclic polarization curves of ferritic and duplex alloys in different pHs media, respectively. The beneficial effect of Mo addition on pitting corrosion resistance (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<sub>sce</sub> for ferritic SS (Figure 2b)) and from 0.415 to more than 0.900V<sub>sce</sub> for duplex ones (Figure 3b)). All anodic polarization graphs in Fig. 2 and 3 are just typical examples of a quite reproducible behavior: in

average the presence of Mo increased the pit potential about 50 mV for the ferritic and more than 150 mV for the duplex grades.



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

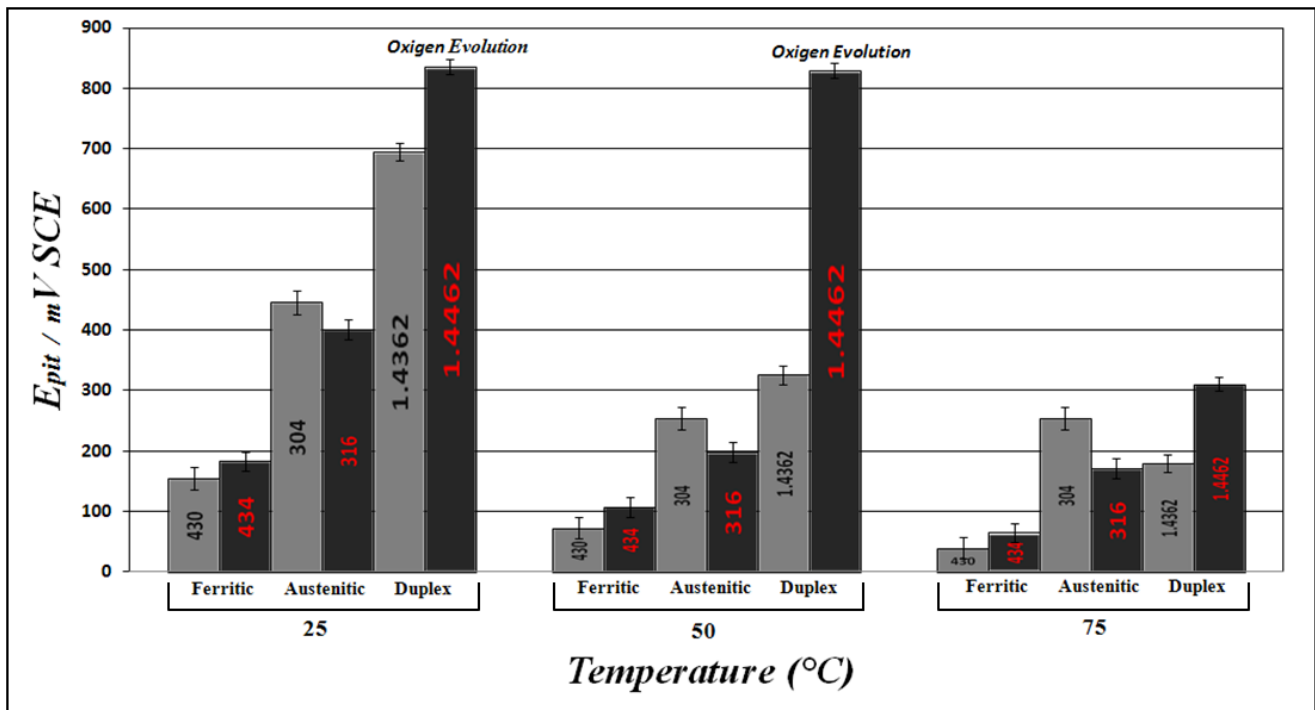


**Figure 3** – Polarization curves obtained for 1.4362 ( $\triangle$ ) and 1.4462 ( $\square$ ) duplex SS in different pHs (A: pH 4; B: pH 7 and C: pH 10) at 25°C. The current increases up for the 1.4462 grade are due to oxygen evolution and not pitting corrosion.

Unlike for austenitic grade, it clearly appears that Mo has a positive effect in their corrosion resistance in alkaline environments (Figs. 1b) and 1c)). In 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 (Figs. 2 and 3).

## 4.2. INFLUENCE OF Mo ADDITION ON PITTING POTENTIAL OF STAINLESS STEELS IN FUNCTION OF TEMPERATURE

The SS were experimented at pH 10 chloride solution in three different temperatures using anodic polarization measurements as well as were done in several different pHs media 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 corrosion resistance of ferritic and duplex SS on alkaline environments were confirmed even in high temperatures because the  $E_{pit}$  was elevated about 40 mV for ferritic SS and more than 150 mV for duplex SS thanks of Mo addition.



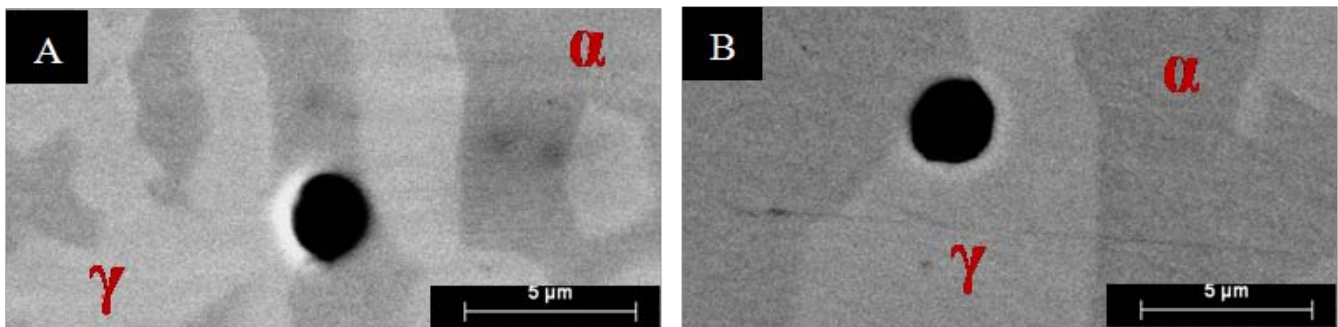
**Figure 4** – Pit Potential for ferritic, austenitic and duplex SS on chloride alkaline solution (pH 10) at 25, 50 and 75 °C. The grey and black histograms correspond to Free Mo SS and Mo content SS, respectively.

In other hand, for the austenitic ones, the absence of Mo effect was verified in all studied temperatures. According to the literature (PARDO et al., 2008), these unlike results were previously detected when 316 SS has an higher amount of manganese than 304. In these cases, the SS usually exhibit 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 protect Mo effect. However, our austenitic alloys have almost the same Mn contents (0,733wt.% Mn and 0,599wt.% Mn for AISI 316

and AISI 304, respectively) which eliminate the possibility of a bigger MnS inclusion contents on 316 and then an undesirable  $E_{pit}$  reduction for this material.

### 4.3. INFLUENCE OF Mo ADDITION ON PIT NUCLETION IN THE DUPLEX STRUCTURE

Figure 5 a) 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 pits was more occluded with a dimension of  $\approx 2\mu\text{m}$ , which is consistent with the results found by (DENG et al., 2008). For the Free Mo duplex SS (Fig. 5 a)), the lower pitting resistance of ferrite ( $\alpha$  phase) was responsible for the fact that pitting preferentially occurred in this phase. For the Mo content duplex SS (Fig. 5 b)), 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 enhanced ferrite phase corrosion resistance by addition of Mo on the bulk alloy can of course drastically change in the presence of sigma phase ( $\delta$ ) precipitates, as this precipitation is located at ferrite and impoverishes its Cr and Mo contents (BASTOS et al., 2007).



**Figure 5** – Back-scattered electron pictures of **A**: Free Mo duplex SS (1.4362) and **B**: Mo containing duplex SS indicating the preferential pitting attack on the ferrite and austenite, respectively. Both samples were observed after anodic polarization til  $40\mu\text{A}/\text{cm}^2$  at pH 10 solution and  $75^\circ\text{C}$ .

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).

## 5. CONCLUSION

The role of molybdenum in the pitting corrosion resistance is quite positive for duplex and ferritic SS in all experimental conditions even if only 0.8 wt% Mo was added in the ferritic one. In other words, the Mo addition increase the  $E_{pit}$  of both ferritic and duplex SS even in synthetic, chlorinated and carbonated solution 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 at alkaline solutions although this scenario was inversed in acidic and neutral media. These unlike results were only reported in the case which the 316 has a higher Mn inclusions 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 on ferrite than austenite phase. Furthermore, this indirect evidence of the higher Mo effect on ferrite phase was confirmed by the SEM analyses of duplex SS.

## 6. ACKNOWLEDGMENTS

The authors wish to thank UGITECH Company and also International Molybdenum Association - IMOIA for the technical and financial supports in this project realization.

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