Corrosion behavior of Zinc or 55%Al-Zn hot-dip coated steel in 0.5 m NaCl solution

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ABSTRACT

A comparative study on the anticorrosive behaviour of 55%Aluminum-Zinc-alloy and Zinc hot-dip coated carbon steel immersed in 0.5 mol/L NaCl solution was performed using DC (polarization curves) and AC (electrochemical impedance spectroscopy) techniques. Also, the corrosion products formed under these testing conditions were characterized using XRD, SEM and EDS. The experimental results showed that the corrosion resistance of the 55%Al-Zn alloy coating showed a synergistic effect being more satisfactory than the each metal used separately and the Zn tested coating. This was attributed to the effectiveness of two forms of protection: the cathodic protection and the barrier effect (afforded by a basic zinc-aluminum carbonate layer) acting together. The morphological characteristics of their corrosion products also differed.

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INTRODUCTION

Coatings based on zinc alone or some of its alloys are one of the most common ways to protect steel from corrosion in various environments. Exposed to specific aggressive media, the steel stability depends upon the chemical composition, conductivity, adherence, solubility, hygroscopicity and morphological characteristics of the film formed on its surface because all of them determine the capacity of such a film to work like a controlling barrier of the corrosion type and/or rate[1]. In this sense, the galvanic protection of steel by means of zinc is a common example not only due to the fact that being the Zn electrochemically more active than the steel that corrodes preferentially, but also to the barrier effect of the corrosion products precipitated on the metallic surface[2-4]. Particularly, Zn-based coatings are widely used in order to protect steel structures against atmospheric corrosion[5], because of the protective properties afforded by an insoluble film of basic zinc carbonate. However, under certain exposure conditions such as depletion of air, high humidity or else a medium containing strongly aggressive species like chloride or sulphate ions, the Zn dissolves forming soluble, less dense and scarcely protective corrosion products, which sometimes lead to the localized corrosion phenomenon[5-7]. This condition can be reached during the storage, transportation and/or when galvanized steel sheets are exposed to marine and/or industrial environments.

On the other hand, aluminum coatings have overcome these two factors. Nevertheless, as they cannot provide cathodic protection to exposed steel in most environments, early rusting occur at coating defects and cut edges; besides, these coatings are also subjected to crevice corrosion in marine environments[8].

For many years, attempts have been made to improve the corrosion resistance of zinc and aluminum coatings through alloying. Although the protective effect of combinations of these two elements was known, they were not used until the discovery that silicon inhibits the rapid alloying reaction with steel[9]; thus, the alloy whose composition is 55% Al, 1.6% Si, the rest Zn, was selected from a systematic study, providing an excellent combination of galvanic protection and low corrosion rate. Once such a development was commercially available, the steel sheet coated with this alloy has gained an important portion of the market to the galvanized steel, mainly in the building, electrodomestic, energy transport and automotive industries.

In order to be used under specific service conditions, the choice of the best coating should be done taking into account that the longest useful life obtained at the lowest cost is the paramount market parameter. Due to the reactive nature of these coatings, the corrosion products play an important role in the protection mechanism, making the selection procedure even more complicated. Therefore, as part of a wider[10-33] study to characterize the corrosion performance of Zn alone or 55%Al-Zn alloy hot dip coated steel, the aim of the present paper is providing results which, in this case, were obtained using polarization curves as well as free corrosion conditions in Cl⁻ containing solutions. Corrosion progress was monitored through periodic visual inspections. The corrosion products were character-

ized using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Energy Dispersive Spectroscopy (EDS) at different immersion times to give a tentative explanation of the protection mechanism in each steel/metallic coating system.

EXPERIMENTAL DETAILS

Surface characterisation

The studies were carried out on commercially available AISI 1010 steel sheets (15 cm x 8 cm x 0.1 cm) coated with Zn or 55%Al-Zn alloy by the continuous process. TABLE 1 gives the chemical composition of the coatings, while their thickness, microhardness and average roughness measured with standard equipment are summarized in TABLE 2. All the samples were degreased with alkaline detergent and toluene; they were then kept in desiccators until further used

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Salt spray cabinet (SSC) and humidity cabinet (HC) tests

The salt spray and humidity cabinet tests were performed under the criteria established by ASTM B-117/07a and ASTM D-2247/11 standards, respectively. During the tests, the specimens' position within the cabinet was changed after each inspection to neglect the possibility that the position might affect the results.

Corrosion progress was monitored through periodic visual inspections. The corrosion products morphology and coating degradation were further studied by Scanning Electron Microscopy (SEM) using a Philip model SEM 505 with ADDAII system, while its composition was determined using Energy Dispersive Spectroscopy (EDS) with a Si detector and 20 keV energy. The X-Ray Diffraction (XRD) directly applied on the tested samples or the powders was carried out using a

TABLE 1 : Chemical composition of the tested coatings (wt%)

	Zn	Al	Si	Sb	Cd	Pb	Fe
Galvanized	99.72	0.10	----	0.09	0.004	0.05	0.03
55%Al-Zn alloy	43.33	55	1.6	----	----	0.03	0.04

TABLE 2 : Coatings thickness, microhardness and roughness

	Thickness (*) (μm)	Microhardness (**) (HV)	Roughness (***) (μm)
Galvanized	15.2	157.12	0.31
55%Al-Zn alloy	22.5	221.14	0.80

(*) Elcometer mod 300; (**) Microhardmeter Shimadzu type M.I.; (***) Hommel Tester mod T 1000

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Philips diffractometer with a copper tube anode (1.54 Å) operated at 50 kV/30mA. Samples were step-scanned between 5 and 80º with a step size of 0.02º and a time step of 1 s.

Electrochemical tests

(a) Polarization curves

On each plate, and separated by a distance of 1-1.5 cm, two cylindrical tubes of transparent acrylic were fixed by means of an epoxy adhesive in order to get good adhesion to the metallic substrate. In the typical electrochemical cell with three electrodes, the working electrode (WE) was the coated steel sheet, leaving exposed to the electrolyte a geometrical area of 15.9 cm², the counter-electrode a Pt-Rh mesh of high surface area oriented parallel to the WE, and the reference a Saturated Calomel Electrode (SCE). Each cell was filled to a depth of 9 cm with 0.5 mol/L NaCl solution (pH 8.2, κ = 42.10 mS/cm) at room temperature, i.e. 20±2 ºC. The anodic polarization curves were performed in a potentiostatic mode with a PAR 273A potentiostat controlled by the Softcorr® program. The potential rate swept was 0.166 mV/s (sufficiently low to guarantee an almost steady state). All the measurements were carried out in a Faraday cage in order to minimize external interference on the system.

(b) Cathodic protection level

The ability of Zn, 55% Al-Zn alloy or Al hot-dip coatings to cathodically protect steel was also evaluated. The tested electrodes (15 cm x 3 cm x 0.1 cm) were prepared from steel sheets partially hot-dip coated with Zn or 55% Al-Zn alloy. An insulated copper wire was spot-welded to a corner of each sample. The wire was encapsulated and isolated from the electrolyte solution by using an epoxy resin. The area ratio of zinc coating to steel was 4/1 in all sets of measurements. The partly coated steel strips immersed in the electrolyte were horizontally positioned, Figure 1. Supported by a rigid frame, six Lugging probe tips with their respective SCE placed above the steel strip (WE) were submerged in the electrolyte. The first probe strip was either directly over or at the level of the coating and the rest was placed along the WE at distances of 2; 4.1; 6.1; 8.1 and 11.4 cm measured from the edge of the coating. The gap between the steel strip and the Lug-

ging probe tip was set at 2 mm. The experimental arrangement is in agreement with that reported by Baldwin et al. elsewhere[34]. Immersion tests were also accomplished using similar samples but arranged with an inclination angle of 30º from the vertical in a glass vessel filled out with the aqueous electrolyte and kept at the laboratory environment.

The steel strip and each reference electrode were connected to a voltmeter with high (> 10^7 &Ω) input impedance. The potential at each position along the WE was measured as a function of the immersion time. The experiments were halted when the potential along the entire length of the WE reached the open circuit potential of the bare steel.

In all the tests, the electrolyte was an open to the lab atmosphere and quiescent 0.5 mol/L NaCl solution, pH 8.2, κ = 42.10 mS/cm.
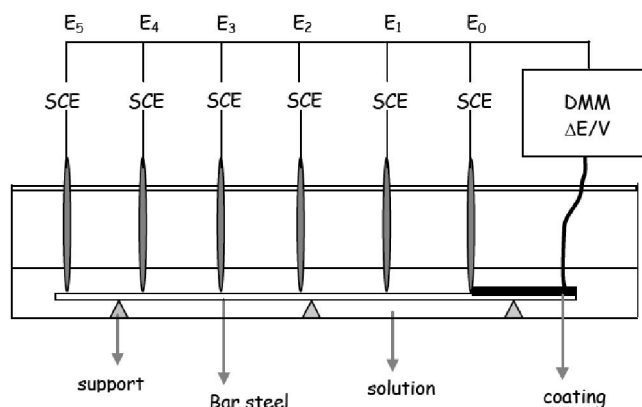

Figure 1 : Scheme of the cell used to measure the potential distribution in partially coated steel sheets.

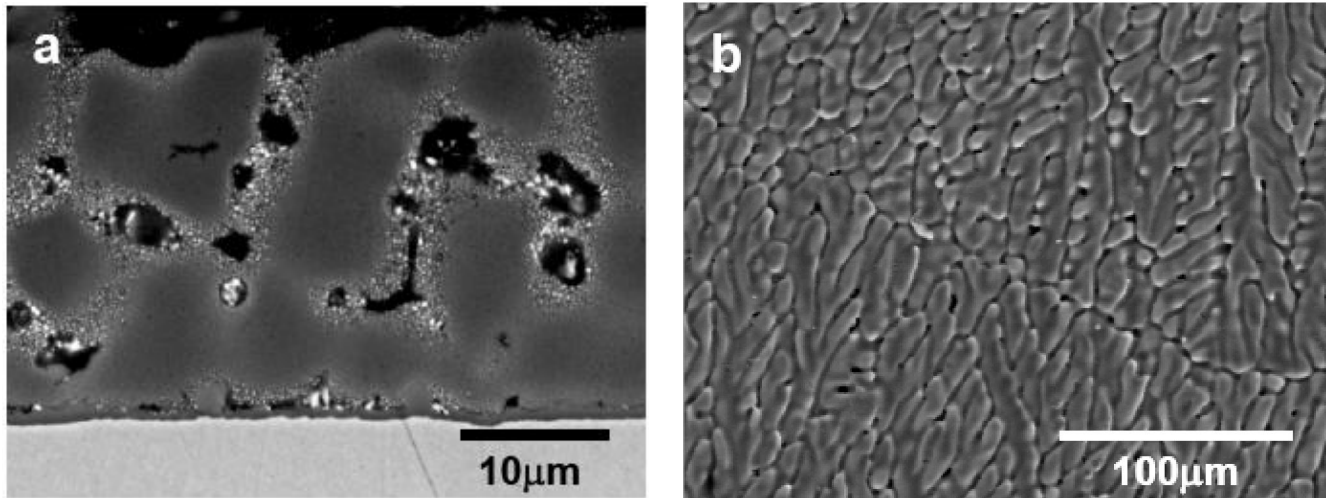**Figure 2 : Surface aspect of the hot-dip galvanized steel**

Figure 3 : Microstructure of the 55%Al-Zn hot-dip coated steel. a) coating' cross section; and b) surface view

RESULTS AND DISCUSSION

Surface characterization

Figure 2 exhibits the characteristics "flowers" of the Zn, while Figure 3a-b shows the two-phase structure of the 55%Al-Zn alloy coatings, respectively[35].

The latter was formed by an Al rich phase occupying dendritic places and another one, rich in Zn, filling the interdendritic ones. It is important to remark that these results were confirmed by EDS studies and are in accordance with publications by other authors[8,35-37].

Salt spray cabinet

Figure 4 displays the surface state of both coated steel panels 264 h after exposure in SSC. After 5 h exposure, hexagonal plane crystals called platelets having preferential facing (normal to the substrate plane) could be observed on the galvanized steel samples. These crystals grew forming islands which spread over all the surface as the exposure time increased; many of them nucleate heterogeneously on the surface defects but the majority do it on NaCl crystals that, in turn, precipitate on the metallic surface[38]. XRD analysis indicated that $Zn_6(OH)_8Cl_2.H_2O$ (Simonkolleite) was the major component of the corrosion products, whilst EDS results confirmed that chlorine, zinc and oxygen were the main elements present in the hexagonal crystals. It can be assumed, therefore, that in agreement with the proposal of other authors[38,39], the hexagonal crystals observed by means of SEM are of Simonkolleite. Traces
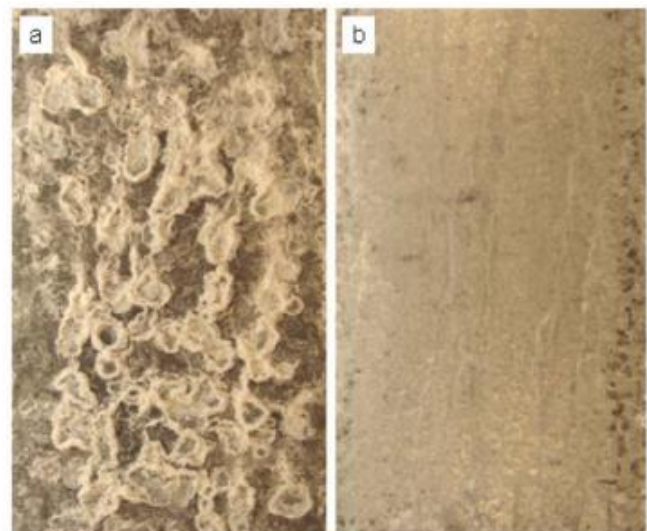

Figure 4 : Surface state after 264 h exposure in SSC. a) Zn; and b) 55%Al-Zn.

of zinc oxide (ZnO) and zinc hydroxycarbonate (Hydrozincite) $[Zn_5(CO_3)_2(OH)_6]$ were also detected.

After 24 h exposure, the two-phase structure of the 55%Al-Zn coating displayed no evidence of attack; however, when the same zone was seen with 1500X, the formation of small acicular crystals could be observed into the interdendritic places (Zn rich phase). These acicular crystals, mainly of Hydrozincite, would demonstrate a preferential interdendritic dissolution of the zinc rich phase as the first step of the coating corrosion with a lower kinetics than in the galvanized steel. After 360 h, the XRD analysis identified the basic zinc aluminum carbonate $[Zn_6Al_2(OH)_{16}CO_3.4H_2O]$ as the main corrosion product. This compound has also been

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found in Galfan (5%Al, Zn the rest) in marine environments accompanied, in smaller amount, by $Al(OH)_3$[37,39,40].

Humidity cabinet

Figure 5 shows the surface state of both coated steel panels after 624 h of exposure to HC. XRD studies carried out on the galvanized steel samples showed that basic zinc carbonate was the only constituent of the corrosion products. On the other hand, the XRD results corresponding to the steel/55%Al-Zn alloy samples (together with the SEM ones) indicated that there was neither corrosion products on the coating surface nor changes in its structure.
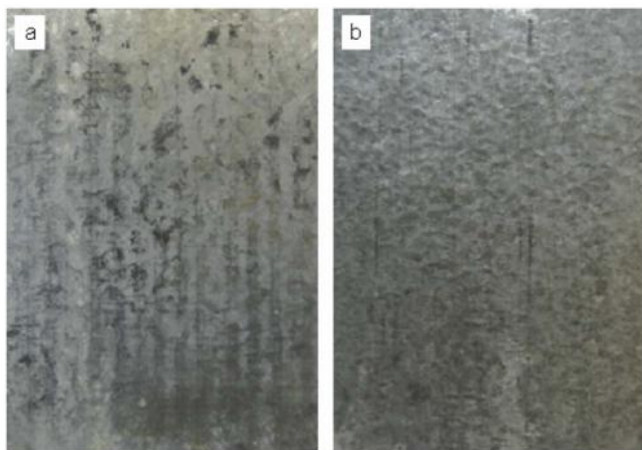

Figure 5 : Surface state after 624 h of exposure in HC. a) Zn; and b) 55%Al-Zn

Polarization curves

Figure 6 shows the anodic polarization curves obtained for the Zn or 55%Al-Zn coated steel samples. None of the samples showed meaningful differences in their anodic behavior; all the samples dissolved at a similar rate and no passivation effect was observed. As the anodic polarization progressed the electrolyte became opalescent due to corrosion product suspension; thus, after polarizing 0.5 V the dissolution current gradually decreased in the Zn or 55%Al-Zn alloy coatings, because of the barrier protection provided by a layer of such products that completely covered the surface. In addition, on the 55%Al-Zn alloy coating a gas bubble evolution was noted. As at the reached potential level neither hydrogen nor oxygen can evolve electrolitically, the bubbles would probably be a consequence of the water hydrolysis in presence of active aluminum.
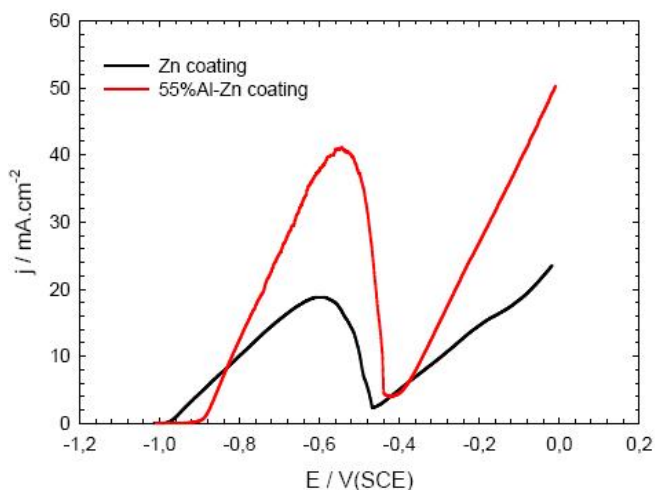

Figure 6 : Polarization curves of Zn, or 55%Al-Zn coated steel samples in 0.5 mol/L NaCl solution, pH = 8.

Moreover, considering that the corrosion potential of bare steel exposed to 0.5 mol/L NaCl solution is about -0.7 V/(SCE), and the measured values for the Zn/steel and 55%Al-Zn/steel couples were -1.02 and -0.98 V/SCE, respectively, it was inferred that both coatings may provide effective cathodic protection to the underlying steel.

Cathodic protection level

Figure 7 shows the surface potential distribution over a zinc/steel or 55%Al-Zn/steel couples as a function of the distance during immersion in quiescent 0.5 mol/L NaCl solution. In general, as the distance from the coating/steel boundary was increased, the steel potential moved towards more positive values, however, due to the high electrolyte conductivity, the potential drift was no more than 0.020 V. A potential dependence with the immersion time was also found; thus, as the time elapsed the shape of the curves did not change but the open circuit potential shifted to more positive values, reducing the cathodic protection level.

At the beginning of the tests, the partially galvanized steel samples had the most active potential value, -1.020 V/(SCE).

In general, the cathodic protection level provided by the Zn or the 55% Al-Zn coatings to the stripped steel decreased monotonically with the distance from the point 0, defined as the position of the bare steel/coating interface. The falling value of the protection potential is directly dependent on the electrochemical reactivity of the coating and the electrolyte conductiv-
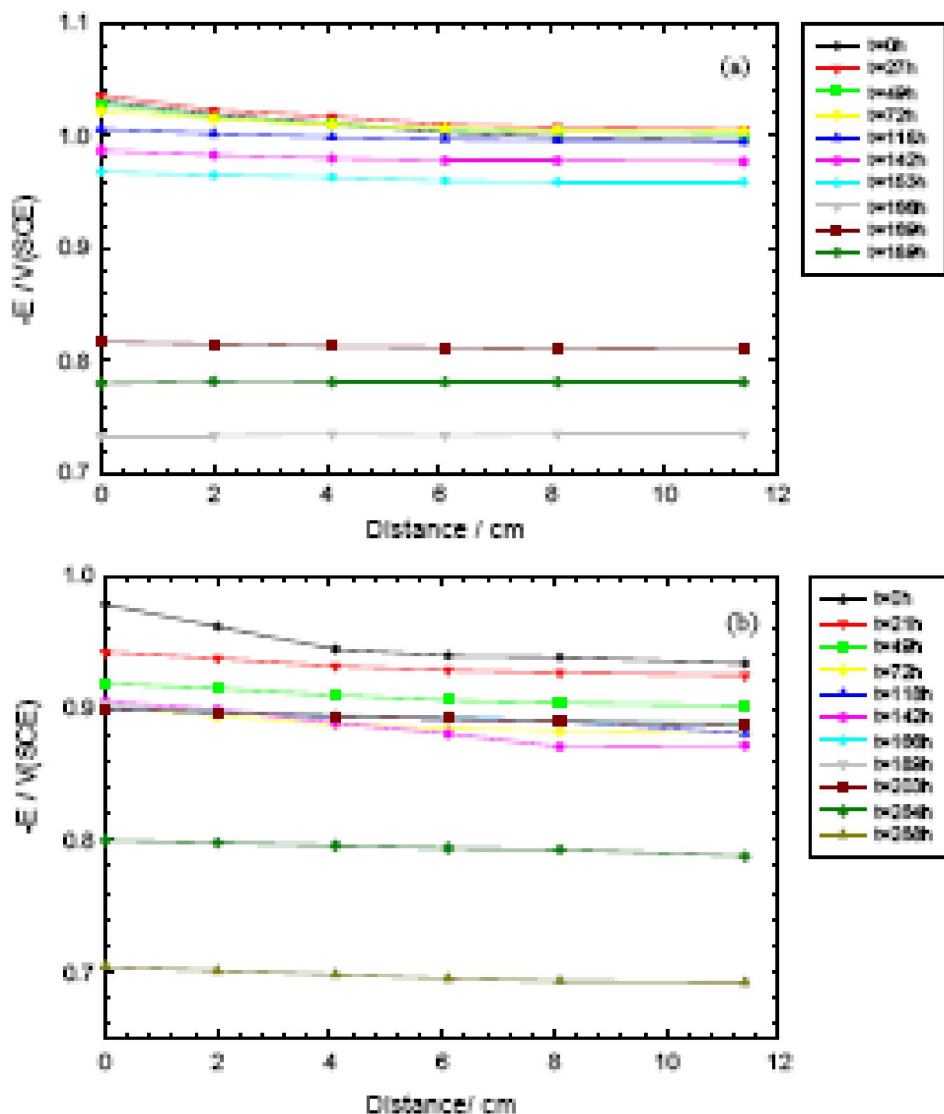
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Figure 7 : Open circuit potential distribution vs. distance from the edge of the partly coated steel area, using the exposure time as parameter.
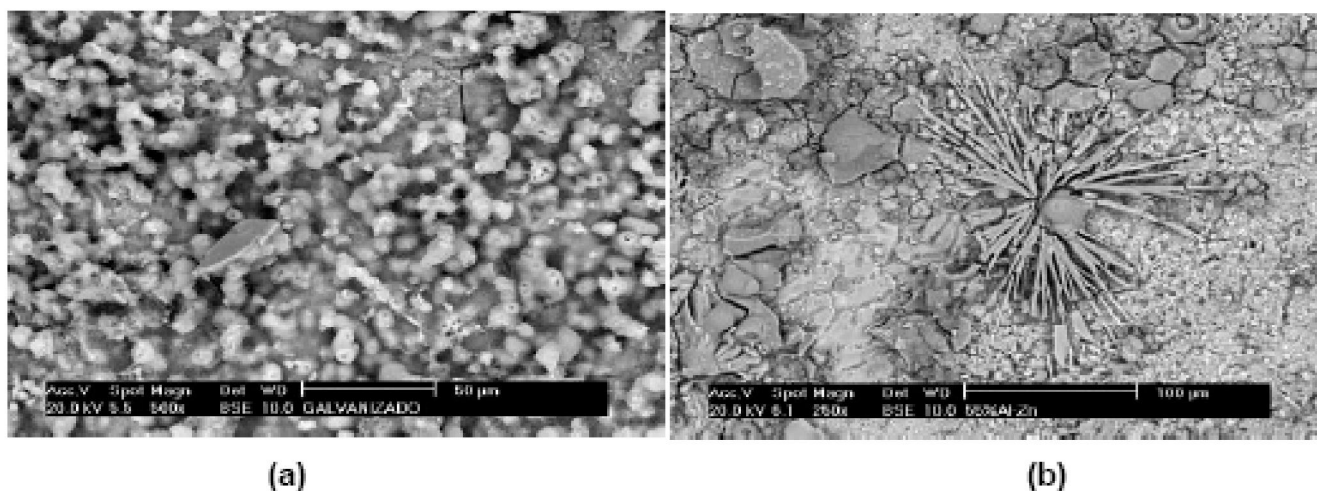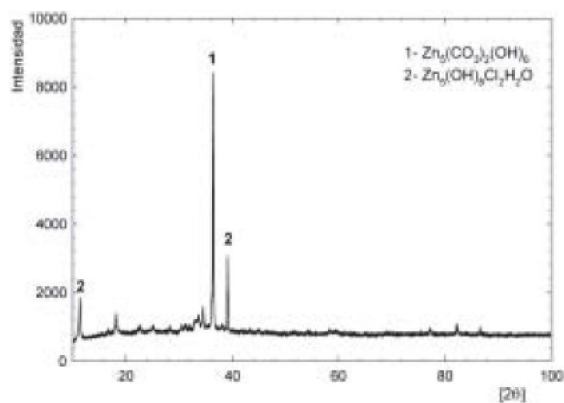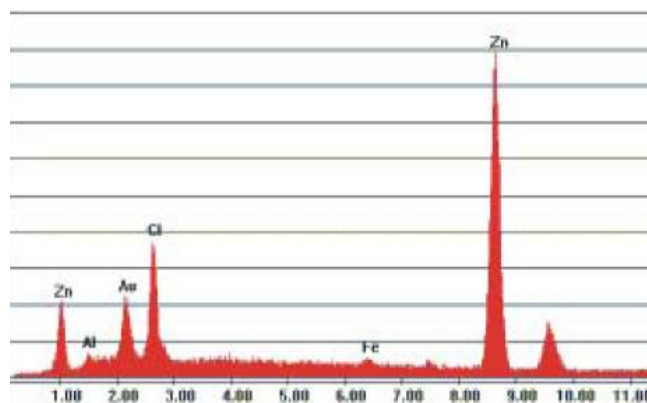

Figure 8 : Corrosion products of (a) Zn; or (b) 55%Al-Zn hot-dip coated steel in 0.5 mol/L NaCl solution.
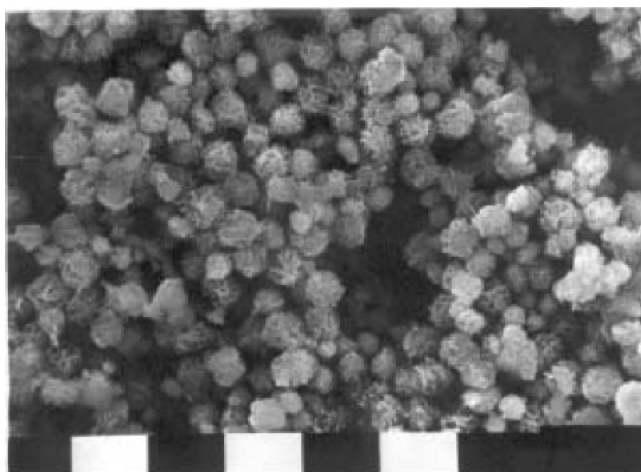
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XRD

EDS - Corrosion Products

SEM Image (1500 X)

Figure 9 : Characterization of the Zn coating corrosion products in 0.5 mol/L NaCl solution.

ity. For the Zn/steel couple, the higher potential drop along the uncovered steel area, i.e. E_0 - E_5 = E_{max}, was around 0.005 V (Figure 5), while the protection potential remained in the order of -1 V/SCE for about 120 h. After 153 h of testing, a sharp drop (about 0.2 V) was observed at the protection level, and the visual observation allowed determining almost total consumption of the Zn coating. This brought about the corrosion of the underlying steel and led to subsequent shielding of the substrate by the formed corrosion products. This layer caused the corrosion potential decreases to about -0.82 V at 169 h and then to -0.78 V at 189 h, time at which the test was ended.

The initially slow potential displacement can be explained by taking into account the existence of air formed oxide on galvanized coating. When galvanized coating with air formed oxide film corrodes in a chloride medium, dissolution of the air formed oxide layer precedes that of the zinc; subsequently, once this layer is consumed, the higher electrochemi-cal activity of the bare zinc particles accelerates their dissolution with the above-mentioned consequences[3,41].

The 55%Al-Zn coating performance was better than the previous one. The $\Delta E_{máx}$ for the alloy/steel couple was 0.03 V, while a satisfactory protection level (-0.9 V/SCE) was maintained for 200 h.

After 260 h, this potential fell 0.1 V, and the visual inspection allowed certifying a depletion of the zinc-rich phase, the main factor of the cathodic protection provided by this type of coating. The total loss occurred 268 h after the experiment, when the potential distribution was around -0.7 V/(SCE).

For the inclined arrangement, the potential vs. distance curve (not shown here) was of the same order of magnitude than in the horizontal case. An acceptable cathodic protection level (H" -0.9 V/(SCE)) was kept up to 50 h and 104 h by the Zn and 55%Al-Zn coatings, respectively; however, at 146 h and 172 h such a

XRD

EDS - Corrosion Products
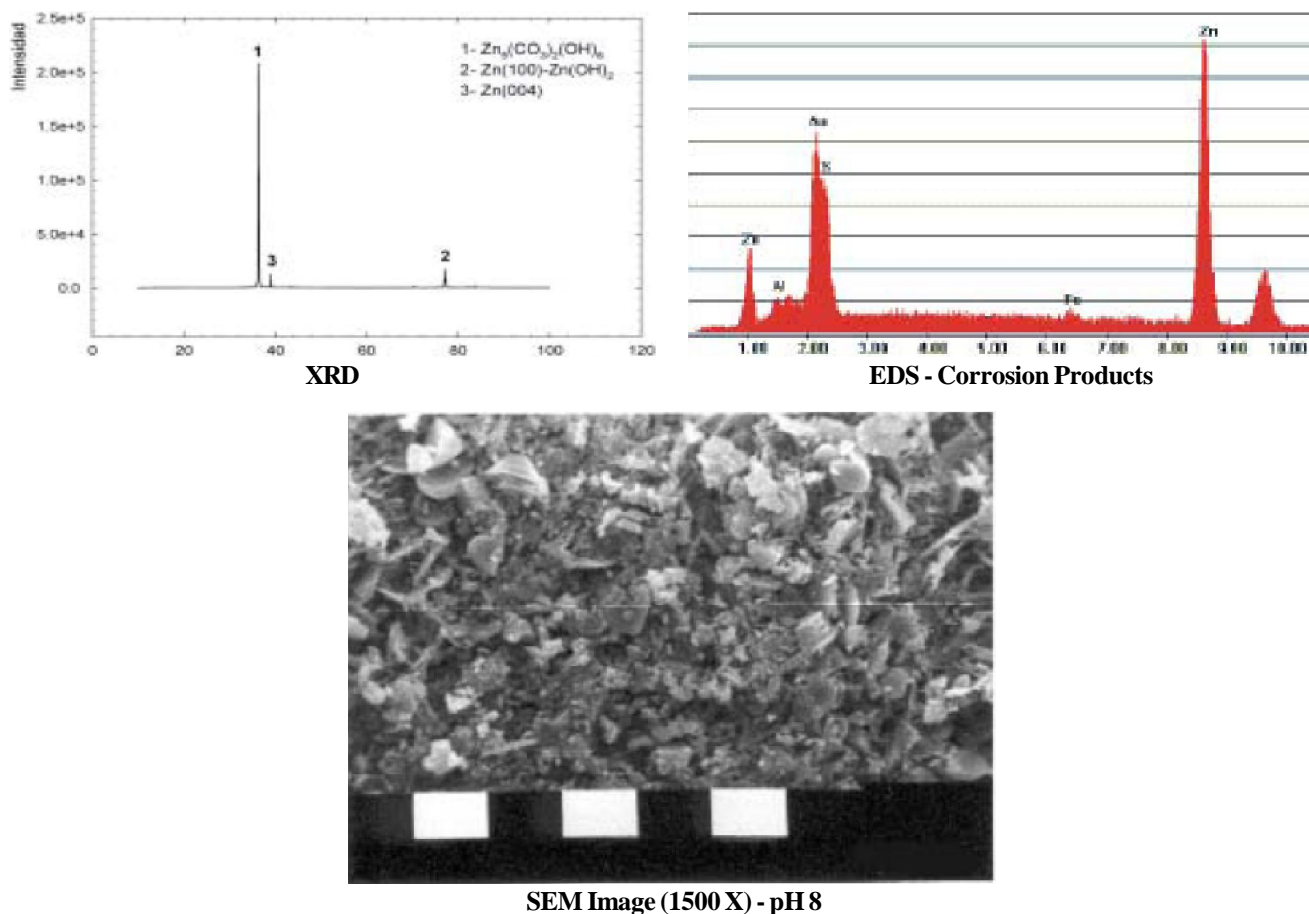

SEM Image (1500 X) - pH 8

Figure 10 : Characterization of the 55%Al-Zn coating corrosion products in 0.5 mol/L NaCl solution

protection had completely been lost.

For both arrangements, the solution became opalescent because of the great amount of white corrosion products formed. In general, the horizontal arrangement gave the longest cathodic protection period, probably due to the barrier protection afforded by the corrosion products deposited on the surface of the whole strip.

The results of surface potential measurements were supported by the visual inspection of the galvanically protected steel sheets. Such inspections accomplished throughout the experiments showed that galvanized coating dissolution was total and uniform, whilst the morphology of the corroding 55%Al-Zn coating surfaces indicated a selective interdendritic dissolution of the Zn-rich phase, in accordance with reports by other authors[33].

Figure 8a-b shows the different morphology presented by the corrosion products formed from the (a) Zn and (b) 55%Al-Zn coatings dissolution in naturally aerated 0.5 mol/L NaCl solution.

The XRD spectra of the Zn corrosion products (Figure 9) indicated that $Zn_6(OH)_8Cl_2.H_2O$ (Simonkolleite) was the major component, whilst EDS results confirmed that chlorine, zinc and oxygen were the main elements present in the hexagonal crystals. Traces of zinc oxide (ZnO) and zinc hydroxycarbonate (Hydrozincite) $[Zn_5(CO_3)_2(OH)_6]$ were also detected.

Figure 10. shows the same study carried out on the 55%Al-Zn alloy corrosion products identified the basic zinc aluminum carbonate $[Zn_6Al_2(OH)_{16}CO_3.4H_2O]$ as the main corrosion product, and traces of zinc hydroxide This compound has also been found in Galfan (5%Al, Zn the rest) in marine environments accompanied, in smaller amounts, by $Al(OH)_3$[8,33,34].

Analysis of the corrosion process

The zinc corrosion products play an important role in determining the galvanic ability of zinc alone or its alloys to steel. After a relatively short immersion pe-

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riod, the galvanized steel samples exhibited an intense zinc dissolution process extended to the most part of the surface and traces of the steel corrosion process. Conversely, after an induction period, the 55%Al-Zn coating provided not only cathodic protection but also barrier protection to the steel substrate, the latter due to the alloy coating further enhanced by the formation of a layer of the coating corrosion products precipitated on the surface active sites. This synergistic effect may help to account for its improved performance against corrosion, when it is compared with the Zn coating under the current experimental conditions.

These results suggest that the first step in galvanized steel surface degradation may be zinc oxidation followed by hydration and fast carbonation, mechanism also outlined by several other authors[38-40,42,43], being the last step the formation of Simonkolleite because of the NaCl crystallization on some surface points[10]. Under these conditions, a localized concentration of Cl- ions in combination with the electrolyte at the metal/solution interface may promote the coated substrate corrosion by substitution of the carbonate ions of the dense, slightly soluble, thin and partially insulating Hydrozincite layer, thereby weakening its protective capacity[10,38]. Furthermore, being slightly dense and highly soluble, the Simonkolleite could provide a low barrier effect when it diffuses towards the bulk of the solution, leaving bare zinc exposed. Thus, a dynamic and quick Zn consumer process leads to poor results after short exposure periods, at least, from the anticorrosive point of view.

In the 55%Al-Zn coating the first stage of the corrosion process would be the formation of aluminum hydroxide from the reaction between Al^{3+} ions with H_2O[44] within the dendrites (Al rich phase), which creates a thin film adhered to the metallic surface[45]. After exposure, there was a layer on the 55%Al-Zn coating surface with the basic zinc-aluminum carbonate, formed presumably from the reaction between aluminum hydroxide and Hydrozincite as the main component[10]. Although being cracked, this layer covers homogeneously all the surface and it is denser and more ordered than the film deposited on the zinc coating, which is highly voluminous and grows forming islands. In addition, the absence of Cl- ions in the layer of 55%Al-Zn

corrosion products turns it slightly soluble and, therefore, provider of barrier protection limiting both the exposed area and the corrosion rate; however, as the steel is not completely isolated from the medium, the coating also works as a sacrificial anode supplying cathodic protection to the substrate.

It is emphasized that to better understand the complex processes involved in all the above-mentioned environments new studies are in progress: However, a first approach to explain changes observed in the behavior of coatings exposed to different testing conditions assumes that differences in the oxygen availability may be a variable to take into account. This may be confirmed from the fact that: 1) the attack intensity decreased as the submerged part of the coated steel moved away from the air/solution interface; and 2) the different state showed by the two faces of the tested panels after being submerged (inclined 30º from the vertical) in the NaCl solution. Such a difference, the upper face much less attacked than the down one, was attributed to the better protective properties afforded by the thicker corrosion products layer deposited on the upper face.

CONCLUSIONS

The following conclusions can be drawn from the present study on the corrosion behavior of the zinc/steel and 55%Al-Zn/steel couples exposed to 0.5 mol/L NaCl solution:

- All the coatings were electrochemically more active than steel and none of them showed passivation under the current experimental conditions. Therefore, although with a variable level along the immersion time, the Zn or 55%Al-Zn coatings provided cathodic protection to the underlying steel.

- Due to the high crystalline degree of the corrosion products formed from the Zn or 55%Al-Zn coatings dissolution, the XRD and EDS resulted to be very useful techniques for their characterization. The nature and composition of such products allowed explaining some differences found in the performance of the tested samples. So, in the galvanized steel samples the $Zn_6(OH)_8Cl_2.H_2O$ (Simonkolleite) was the main component of the corrosion products, while zinc, chlorine and oxygen were the main elements present in the hexagonal crystals. Traces of ZnO and $Zn_5(CO_3)_2(OH)_6$

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(Hydrozincite) were also detected. On the other hand, in the 55%Al-Zn coated steel panels, the main component of the corrosion products was initially $Zn_5(CO_3)_2(OH)_6$ but after 360 h of exposure the $Zn_6Al_2(OH)_{16}CO_3.4H_2O$ (basic zinc aluminum carbonate) was the main corrosion product. Traces of $Zn(OH)_2$ were also detected.

- After a relatively short exposure time the galvanized steel samples exhibited an intensive zinc dissolution process extended to the most part of the surface and traces of steel corrosion. On the contrary, after an induction period, the 55%Al-Zn coating provided not only cathodic but also barrier protection to the steel substrate for a longer time. The latter was attributed to the alloy coating protection was further enhanced by the presence of a layer of the coating corrosion products precipitated on the electrochemically surface active sites. This synergistic effect may help to account for its improved performance against corrosion, when it is compared with the Zn coating used alone under the current experimental conditions.

- Although the experimental evidence showed that the corrosion behavior of the 55%Al-Zn coating was always better than the Zn one, an electrochemical investigation is in progress. Its main purpose is to obtain more information concerning the protection mechanisms of these coated low carbon steel sheets, which led to optimize their paintability as well as to develop new anticorrosive organic coatings capable of resisting highly aggressive environments.

ACKNOWLEDGEMENTS

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