

Electrochemical, chemical and morphological characterization of galvanized steel coating

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Abstract

The intermetallic phases present in galvanneal coatings are of great importance to their final performance. In the present study the phases in a galvanneal coating on carbon steel for use in the automotive industry were electrochemically and morphologically characterized. The electrochemical techniques employed were potentiodynamic polarization, potentiostatic polarization and coulometric stripping. This last technique has been widely used for characterization of galvanneal coatings. Additionally, X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were carried out for chemical and morphological characterization of the phases in the coating. The results indicated that for the zinc richer phases the corrosion mechanism was similar, consisting of Zn selective dissolution and leading to enlargement of cracks and pores initially present in the coating. Two main morphologies were associated with the major phases in the galvannealing coating, namely an elongated rod-like phase and a flat and more compact type. Their chemical composition indicated that they were related to the zeta and delta phases, respectively. Three current density peaks were obtained in the anodic polarization curves and they were related to the zeta, delta and gamma-1 phases in the galvanneal coating. The cracks present in the coating previous to immersion in the stripping solution increasingly enlarged with exposure time to the stripping solution favoring the exposure of the various phases to the electrolyte and led to their concurrent corrosive attack. The corrosion product deposited on the galvanneal coating was mainly composed of a zinc rich product with a platelet-like morphology.

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1. Introduction

Zinc based coatings have been widely used for many years in the protection of carbon steels [1]. One of their main applications is in the automotive industry. The number of galvanized auto components obtained either through electrogalvanizing or hot-dip galvanizing process has increased significantly in last several years. The main disadvantage of electrogalvanized coatings is their high cost. In the search for less costly coatings, the galvannealing process was developed [2] which is being used for coating steel plates used in car parts with corrosion resistance similar to that of electrodeposited zinc, mainly after painted condition [2].

The galvanneal coating is obtained by annealing the steel plate after hot dip galvanizing. Four intermetallic phases of Fe–Zn are obtained in the coating, specifically, zeta, delta, gamma and gamma-1 [3]. The properties of the coating, such as, corrosion resistance, ductility, formability, weldability and paintability depend on the morphology, composition and structure of the phases in the coating [3]. The characterization of galvanneal coatings is therefore of great importance.

One of the main techniques used in the characterization of these coatings is the coulometric stripping, also known as galvanostatic stripping and electrochemical stripping [4–8]. This technique combines the use of a solution that selectively attacks the zinc rich phases and an anodic current density that leads to the acceleration of the selective stripping. The measurement of the potential (E) variation with time due to the galvanostatically applied current and the plot of E vs time leads to a curve with various potential plateaus which have been associated to the different intermetallic phases in the coating. A proper current

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density is important to permit a good definition of the various potential plateaus associated to the different phases in the coating.

Various current densities are proposed in the literature for the coulometric stripping [4–7]. Xhoffer et al. [8] optimized the current density in the range from 2 to 20 mA/cm², in order to obtain good resolution and short time of test. They concluded that the ideal current density for this purpose is 7.5 mA/cm². Zhang and Bravo [4] reported good definition of the various plateaus in the electrochemical stripping curves for tests carried out at 40 °C and at current densities lower than 25.4 mA/cm². On the other hand, current densities lower than 10 mA/cm² at room temperature have also been proposed for a good definition of the various plateaus [4,6,8].

The aim of the present work is to characterize the phases in a galvaneal coating on steel plates for application in the automotive industry and to correlate the phases with the morphology analyzed by X-ray energy dispersive spectroscopy (EDX). This was carried out by electrochemical techniques, mainly coulometric stripping, potentiodynamic and potentiostatic polarization. The morphology and composition of the phases in the galvaneal coating before and after immersion test were investigated by scanning electron microscopy (SEM) coupled with EDX.

2. Materials and methods

2.1. Hot dip galvanized and annealed (HDGA) steel

The steel used as substrate for galvanealing was an interstitial free (IF) type, whose composition is shown in Table 1. Interstitial free steels have appropriate drawability properties. Such property is of great importance in the automotive industry leading to their large use in this sector [9]. The micrograph of the steel used in this work is shown in Fig. 1(a).

Galvanealed steel plates with 100 mm × 150 mm size, used in this study, were provided by Usiminas — Brazil.

The annealing temperature and time were 490 °C and 45 s, respectively. The coating weight determined (side to side) was 57.2/51.5 g m⁻².

2.2. Samples preparation and experimental set-up for electrochemical tests

Steel samples with 20 mm × 20 mm were cut from galvanealed steel plates, cleaned with acetone in an ultrasonic bath, rinsed with deionized water, and then dried under a hot air stream. The samples were kept under controlled atmosphere until the time of use.

A flat cell (EG&G model K0235) and a potentiostat (EG&G 273A) coupled to a computer controlled software were used for the electrochemical tests. The electrode area exposed to the

Table 1
Composition of interstitial free (IF) steel substrate used in this study

IF ^a steel								
Element	Mn	P	S	Al	Nb	Ti	N	C
(mass %)	0.15	0.0142	0.0078	0.041	0.015	0.016	0.022	0.0028

^a Interstitial free.

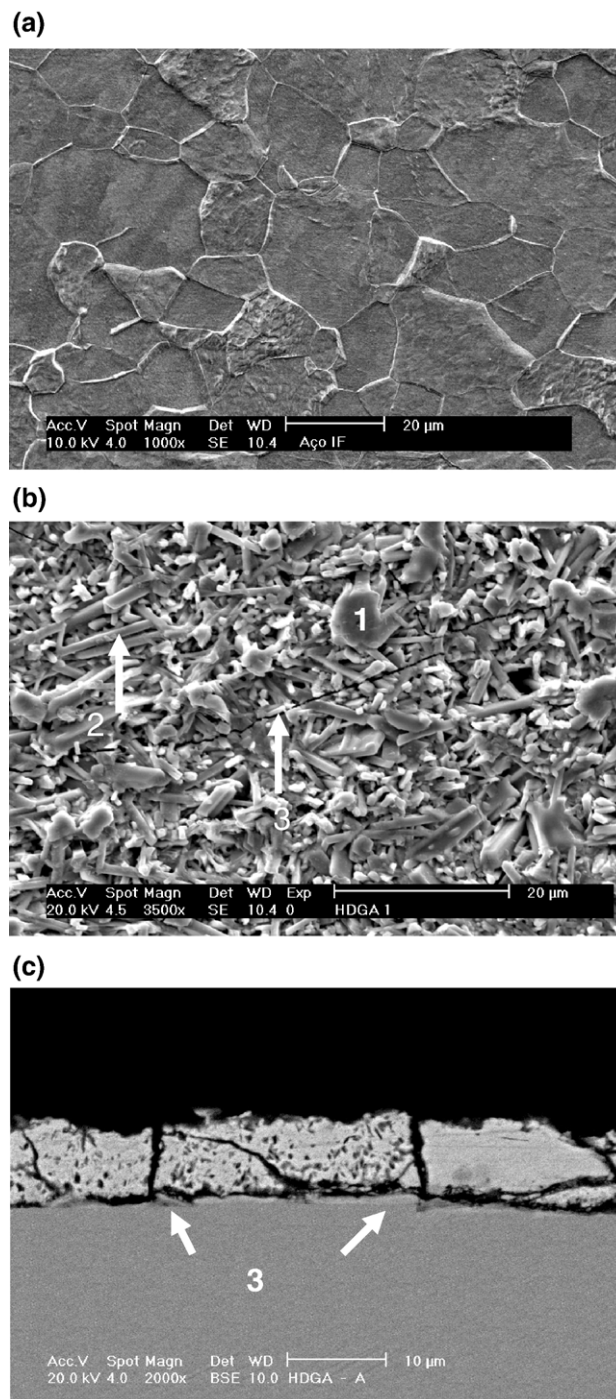


Fig. 1. Scanning electron micrographs of the (a) IF steel used and of the (b) galvaneal coating investigated; (c) cross section view showing the coating and the substrate. Arrows point to (1) areas with flat and compact morphology; (2) areas with elongated rod-like morphology; (3) cracks.

electrolyte was 0.98 cm². A three electrode set-up was adopted in the experimental tests with a saturated calomel electrode (SCE) as the reference and a platinum mesh as the auxiliary electrode. All potentials are referred to the SCE reference electrode.

The electrolyte solution was composed of 3.42 mol L⁻¹ NaCl and 0.35 mol L⁻¹ ZnSO₄·7H₂O. This solution selectively dissolves zinc or zinc rich phases and has been known as “stripping” solution [4,5].

The electrolyte was quiescent, naturally aerated and its temperature was maintained at (20 ± 2) °C during all electrochemical tests. The pH of the electrolyte was 4.7 ± 0.2 . All the chemicals used were of analytical grade.

Open circuit potential (E) measurements were carried out as a function of immersion time in the stripping solution for periods sufficient to the occurrence of the various plateaus associated in the literature to the various Zn–Fe intermetallic phases in galvanneal coatings. Initially the E was monitored for 160 h to allow the identification of the various potential plateaus and their respective duration. After the 160 h period, the E measured was typical of the steel substrate indicating the complete removal of the coating. The aim of the immersion tests at E was to investigate the effect of the stripping solution on the galvanneal coating without external current input.

Coulometric stripping tests were also carried out applying a current density of 7.5 mA cm^{-2} . Six samples were used to evaluate the results repeatability. To investigate the effect of very low current densities on the definition of the stripping curve, coulometric stripping test at 0.5 mA cm^{-2} was also accomplished. After identification of the various potential “plateaus” related to the various intermetallic phases of the coating, from the coulometric stripping curve, five samples were polarized until potentials corresponding to that of the “plateaus” in the coulometric stripping curves. The polarization was interrupted when the potential of the “plateau” was reached.

Potentiodynamic polarization curves were obtained in the stripping solution (voltammetric stripping) in the potential range from -990 mV to -600 mV with scanning rate of 0.02 mV/s . Current peaks related to the potential of the intermetallic phases were determined and potentiodynamic polarization curves were also obtained from -990 mV until these peaks when the polarization was interrupted. At the end of both experiments, coulometric stripping and voltammetric stripping, the samples were removed from the electrolyte, washed with deionized water, dried under hot air stream and kept under controlled atmosphere until observation by SEM/EDX.

The effect of stripping on the composition and morphology of the galvanneal coating was investigated by scanning electron microscopy (SEM) and X-ray dispersive energy spectroscopy (EDX).

After removal from the stripping solution, a black film was found on the samples surface. The samples were rinsed with deionized water and the black film was manually rubbed off. The total or partial removal of this film was dependent on its adhesion to the surface. Subsequently, the samples were cleaned with acetone, rinsed with deionized water and dried under hot air stream. The samples were stored until being analyzed by SEM/EDX.

3. Results and discussion

3.1. Characterization of the galvanneal coating previous to immersion in the stripping electrolyte

Fig. 1(b), (c) and (d) show the external surface and the cross sectional micrographs of the galvanneal coating prior to immersion in the stripping solution. The coating shows cracks,

pores and phases with different morphologies. Two main morphologies were identified in the coating, one appearing as flat and compact structures and the other with an elongated rod-like morphology [10]. The presence of cracks in this type of coating has been mentioned by many authors [6,8,11,12] and have been attributed to stresses generated during the annealing stage of galvannealing [8]. According to Marder [11], the cracks form along the basal plane in the delta phase, but can also extend to the zeta and gamma phases.

The micrographs of Fig. 1 show that the intermetallic Fe–Zn phases in the galvanneal coating investigated are not separated in sequential layers, but are intertwined. The cross section of the sample also shows that the cracks penetrate deep into the coating and eventually can reach the substrate. Consequently, various intermetallic phases might be exposed to the electrolyte at the same time and this may allow their simultaneous dissolution.

The coating thickness estimated by SEM was in the range of 9 to $12 \mu\text{m}$. EDX analyses carried out on the areas near to the coating external surface and along the coating thickness in the cross sectioned sample showed that the iron concentration from the outer coating surface until approximately half of its thickness was in the range from 10 to 13%, that is, typical of delta phase, indicating that nearly 50% of the coating thickness corresponded to delta phase. The iron concentration in the coating at the vicinity of the substrate was approximately 20 to 22%, that is, characteristic of the gamma phase. It must however be pointed out that EDX analysis on the cross section areas corresponding to the outer surface of the coating was very difficult due to irregularities of the external surface, as can be seen in Fig. 1(c).

Cook and Grant [13] also analyzed commercial galvanneal coatings and concluded that the delta phase corresponds to 40% of the thickness of the coating, similarly to the results obtained in the present study.

According to literature [13], the iron composition in the delta phase that has been considered the predominant phase in the galvanneal coating, is in the range 7–12%, whereas in the gamma phase the iron concentration varies from 21 to 28%.

X-ray diffraction analysis of three of the galvannealed steel samples was carried out and the results (Fig. 2) acknowledged only the zeta and delta phases, with the predominance of zeta phase. On the other hand, EDX analysis did not indicate any region with the composition typical of the zeta phase, which is in the range of 5 to 6 wt.%, although, as mentioned above, the EDX analysis on the outer surface of the coating was very difficult. However, its clear detection by X-ray diffraction shows that it is present in the tested coating. The X-ray diffraction results therefore contradicted the EDX ones evidencing a large contribution of the most external layer (zeta phase) in the galvanneal coating, and suggesting that it must be present in significant amounts in the investigated coating. The gamma phase was not identified by XRD although this technique has been largely used for analysis of galvanneal coatings [10,14].

The results above show that EDX or X-ray diffraction analysis should not be used independently for the characterization of the phases in galvanneal coatings. This is mainly due to

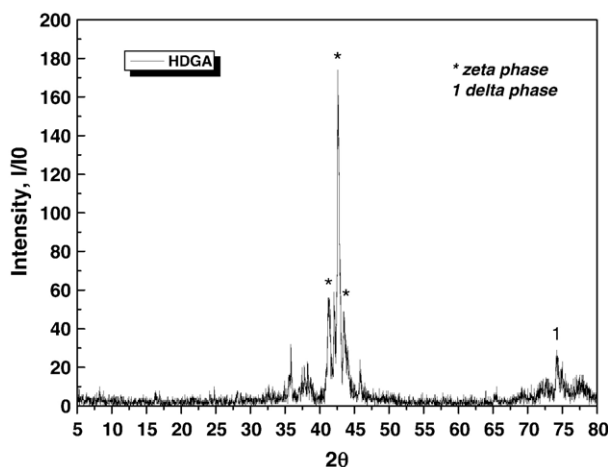


Fig. 2. X-ray diffraction spectrum of galvanized coating showing the peaks of zeta phase (peaks marked with *) and a lower contribution of delta phase (peak marked with 1).

the close proximity of the various phases in the coating leading to the interference of the other phases in the analysis. The literature [13] reports that the zeta phase is a thin and rough phase, and its low thickness might have led to the interference of the other nearby phases on its analysis by EDX.

3.2. Stripping at the open circuit potential for the characterization of the galvanized coating

The first immersion tests of the galvanized steel samples in the stripping solution were carried out at the open circuit potential to evaluate the effect of the test solution on the coating without external current input. A typical curve of electrode potential variation with time of immersion (E_{ocp} vs time) is shown in Fig. 3. The potential increased for approximately 12 h and then stabilized, indicating the first plateau (A) with a duration of approximately 50 h when the potential slowly increased with time. Three other potential “plateaus”, marked as B, C and D, were indicated in Fig. 3.

Some samples that had been previously immersed in the stripping solution at E_{ocp} for different times were analyzed by SEM and EDX to investigate the effect of the exposure time to the stripping solution on the morphology and composition of the intermetallic phases. The periods of immersion investigated were 18, 24 and 43 h. The duration of the plateau A at open circuit potential was superior to 43 h; consequently, the results all corresponded to the plateau A. The EDX analysis was carried out on the phases with different morphologies. The zinc and iron contents of the main phases in the coating are shown in Table 2.

The results in Table 2 show a very slight decrease in the Zn content and increase in Fe content on the main phases with different morphologies in the galvanized coating with time. Despite of the small variation in Zn and Fe contents, lower than 3%, that could be due to experimental errors, there is a continuous trend in the variation, mainly for larger intervals (between 24 and 43 h), suggesting that selective zinc dissolution occurred in both main phases present in the coating. Larger

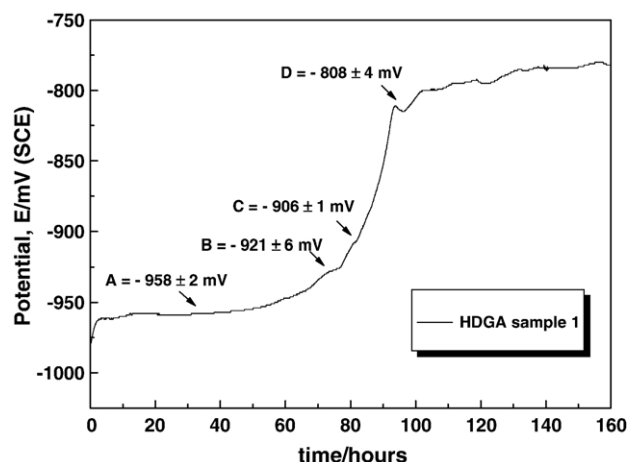


Fig. 3. Potential vs time of immersion in $3.42 \text{ mol L}^{-1} \text{ NaCl}$ and $0.35 \text{ mol L}^{-1} \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$, without external current.

amounts of zinc were however preferentially dissolved from the elongated rod-like morphology phase during the 43 h immersion [10], comparatively to the compact phase. After that period, the iron and zinc composition in both phases, determined by EDX, were very similar. The selective zinc dissolution was more evident in the results corresponding to coulometric stripping comparatively to those at the open circuit potential, due to the faster kinetics of selective dissolution, as it will be shown ahead.

Fig. 4 shows the potential variation with time and their surfaces, prior to and after increasing periods of immersion (18, 24 and 43 h). The micrographs indicate the increase in the compact phase ratio with time, mainly for 43 h, suggesting the preferential attack of the elongated phase. Based on the results of X-ray diffraction and EDX analysis, the phase which was preferentially attacked is the zeta phase. The attack of this last phase leads to the increasing preponderance of the delta phase with flat and compact morphology. The selective zinc dissolution that occurred in the compact phase resulted in a porous spongy like phase. The cracks width also increased with time, as shown in Fig. 4. Besseyrias et al. [7] investigated homogeneous Fe–Zn intermetallics and also reported porosity increase of the delta phase with time in the stripping solution. The mean potential of the samples measured by the time of removal from solution was approximately -958 mV . According to Besseyrias

Table 2

Fe and Zn concentrations in the main phases of the galvanized coating after various periods of immersion in the stripping electrolyte at the open circuit potential

Element content (wt.%)	Compact phase	Elongated rod-like phase	Time of immersion (h)
Fe	10.54	8.64	18
Zn	89.46	91.36	
Fe	10.67	8.75	24
Zn	89.33	91.25	
Fe	11.78	11.53	43
Zn	88.22	88.47	

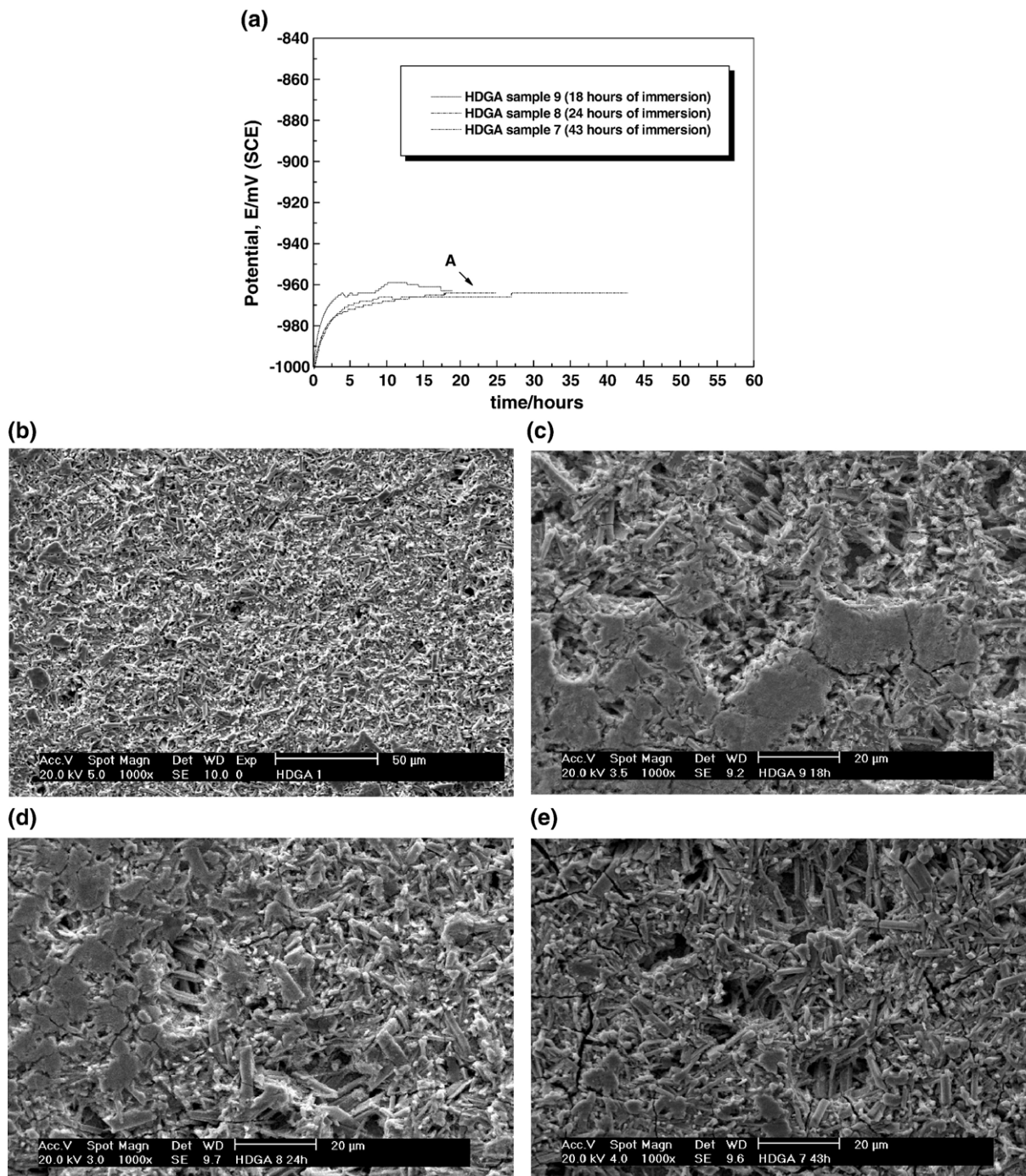


Fig. 4. (a) Potential variation of galvanneal coating with time of immersion in the stripping electrolyte for samples maintained in the solution during 18, 24 and 43 h. Scanning electron micrographs of (b) surface prior to immersion; showing the cracks and pores in the coating; (c) surface after 18 h, (d) after 24 h and (e) after 43 h of immersion.

[7] potentials of this order are related to the zeta phase. The results obtained by the techniques used in this study also indicated that the plateau A, here associated to the elongated rod-like phase, corresponded to the zeta phase.

A black film due to corrosion products formed during stripping of the zeta and delta phases [7] was found on the samples surface after their removal from solution. Although the black film was formed at short periods of immersion its adherence to the substrate decreased with stripping time.

The precipitation of a black film on the surface of galvanneal coating during stripping has been largely reported in the literature [4,7,8], being mainly related to the selective attack of the delta phase that becomes increasingly porous with time [7]. The composition of this film has been associated to Fe and Zn oxides and hydroxides and also to metallic Zn.

Zhang and Bravo [4] investigated the stripping of hot dip galvanized plates and found that the black film does not form on

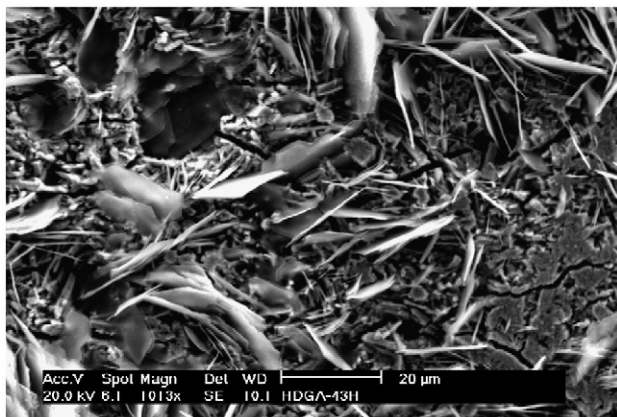


Fig. 5. SEM micrograph of galvanized steel after 43 h of immersion in the stripping electrolyte at the open circuit potential. Corrosion products on the sample were not stripped off previous to surface analysis. Zinc rich platelets are shown.

the eta phase (99.97% Zn). According to those authors [4] its formation starts on the zeta phase suggesting that it depends on the iron presence in the coating. Similar results were also reported by Xhoffer et al. [8].

In the present study the presence of zinc rich platelets on the specimens which were exposed for 43 h to the stripping solution was also found, as shown in Fig. 5.

Perkins [15] also detected these platelets on zinc electrodes immersed in seawater and associated them to a dissolution–precipitation mechanism of zinc on the electrodes. It is possible that the same mechanism might occur during the selective dissolution of the zinc richer phases in galvanneal coatings. A phase with a compact morphology was seen underneath the zinc rich platelets.

The corrosion products on the sample surface shown in Fig. 5 were not scrapped previous to SEM/EDX analysis explaining the larger amounts of platelets observed on this sample comparatively to the other ones. The platelets were analyzed by EDX and it was found that they correspond to zinc rich corrosion products. All other samples had their surface brushed previous to SEM/EDX analysis, once it was found that the platelets composition interfered with the analysis of the intermetallic phases.

From the results obtained in this study it can be inferred that the phase with an elongated rod-like morphology corresponds to the zeta phase, that is preferentially attacked in the stripping solution, whereas the flat and compact phase to the delta phase.

Angeli et al. [10], investigating the morphology of galvanneal coatings also related the delta phase to compact crystallites and the zeta phase to a rod-like morphology. Their results are supported by the results of the present study. The EDX results also support this hypothesis, since the iron content in the compact phase was always superior to that of the zeta phase, whereas the iron content in the compact phase corresponded to that of the delta phase as reported in the literature [10].

The results of stripping at the open circuit potential (E) show that long periods are necessary to its completion (over 90 h) and this is a too long period for use in commercial processes.

Consequently, coulometric stripping with current densities of 0.5 and 7.5 mA cm⁻² were carried out.

3.3. Coulometric stripping

The results of coulometric stripping of six galvannealed steel samples at current densities corresponding to 7.5 mA/cm² are shown in Fig. 6(a). The six curves show good repeatability and in all of them five regions, acknowledged as A to E, were identified. There are some points worth mentioning on the characteristics of the stripping curve, such as, whereas a plateau A was well defined, the three regions identified as B, C and D rather correspond to significant changes in the slope of the stripping (E vs time) curve. These last regions were also here called “plateaus”. The duration of “plateau” C is too short, approximately half of “plateau B” and consequently, it is hardly noticeable in some curves. At potentials around -450 mV a final and large plateau, E, occurred, due to substrate exposure to the electrolyte, after coating stripping. In the first minutes of stripping, a potential drop is clearly seen, followed by potential stabilization. The reason for the potential decrease, according to Zhang and Bravo [4] is that the surface area increases with stripping time and selective dissolution of zinc, due to the

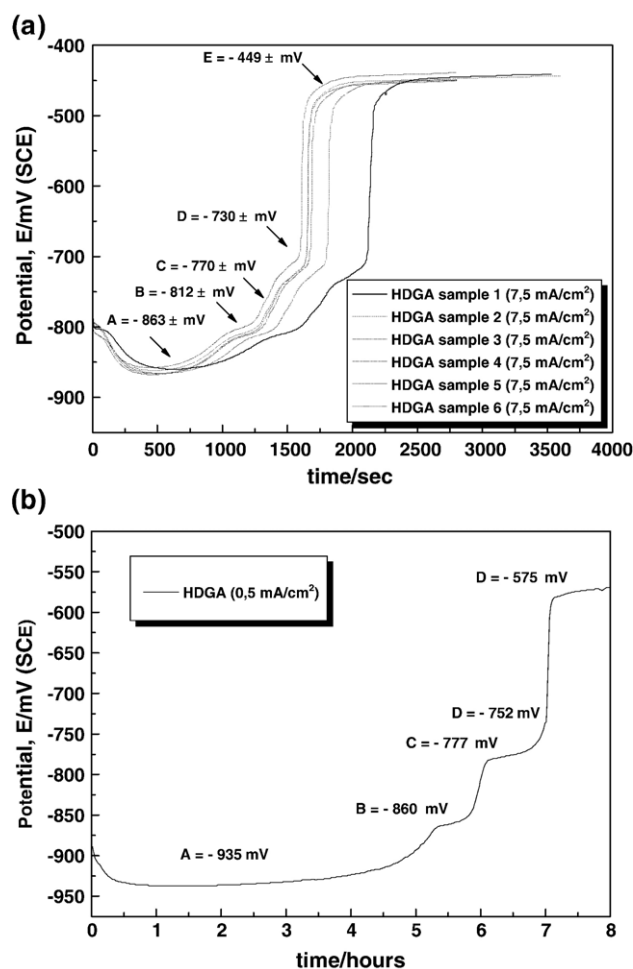


Fig. 6. Coulometric stripping curves obtained for the galvanized steel using a current density of (a) 7.5 mA/cm², (b) 0.5 mA/cm².

increasing pores and cracks in the coating. The current applied in the coulometric stripping is constant, consequently, if the surface area increases, the current density (i) decreases. Once the potential for metal dissolution is dependent on the current, the reduction in i causes a potential drop. As the surface area and composition become more stable, the process is stabilized and also the electrode potential.

The potentials corresponding to the five “plateaus” obtained from the curves were also indicated in Fig. 6(a) and these were

compared with results from literature [6]. Very similar results were obtained with that of Besseyrias [6] although larger differences were found between the ones of this work and those of Zhang and Bravo [4]. The differences between the potential values of this work and those obtained by Zhang and Bravo [4], always with lower potential values associated to the last authors, might be related to the different current densities used in the two works, 7.5 mA/cm^2 and 6.3 mA/cm^2 , respectively. More anodic potentials are associated to higher current densities. The better

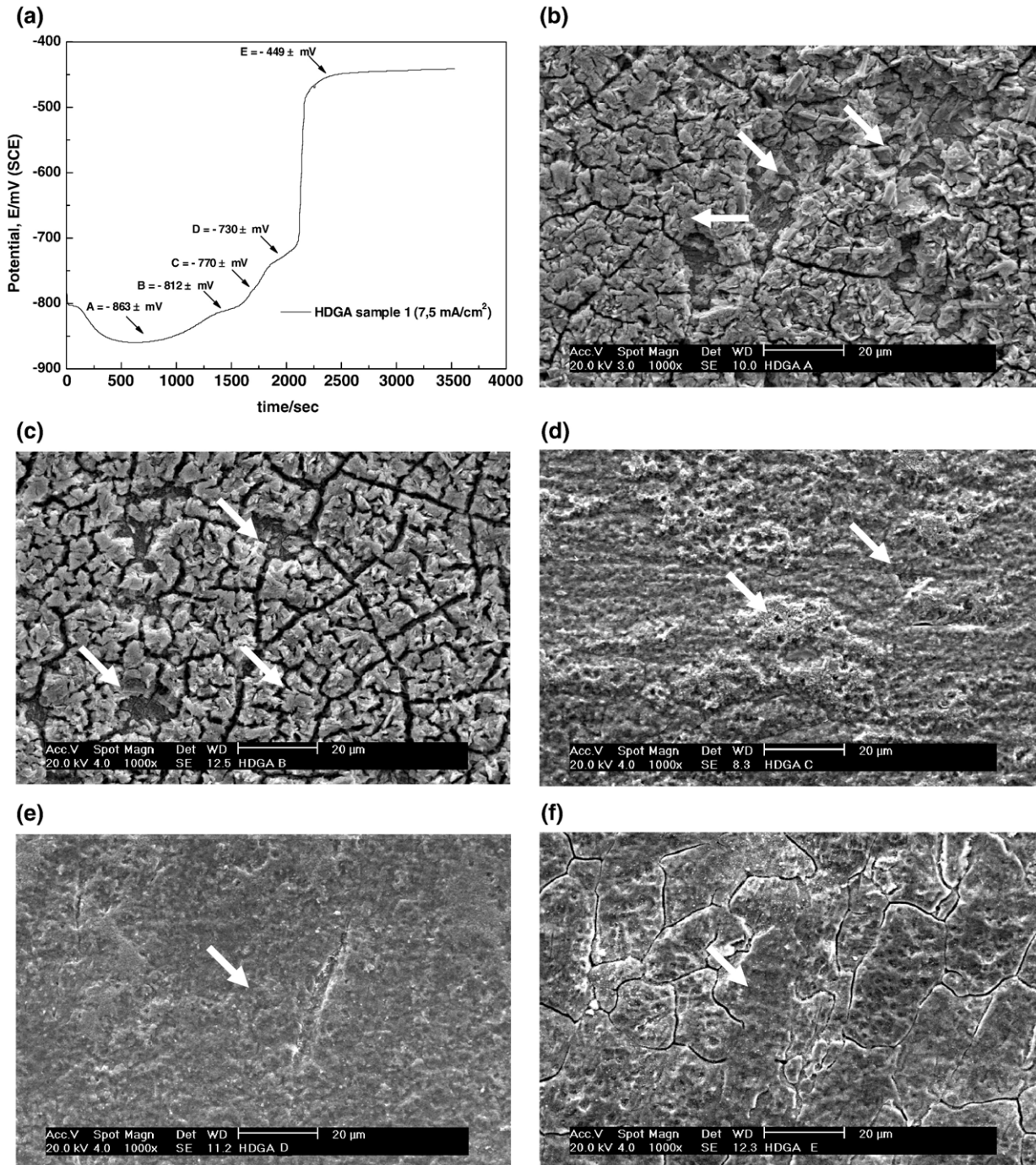


Fig. 7. (a) Potential variation with time during coulometric stripping at 7.5 mA/cm^2 . Scanning electron micrographs showing surface morphology at: (b) plateau A; (c) “plateau B”; (d) “plateau C”; (e) “plateau D” and (f) of substrate. Arrows point to area analysed by EDX.

correlation between the results of the present work with that of Besseyrias are likely due to the closer i values used in both works, 7.50 and 7.35 mA/cm², respectively.

Considerably different stripping curves were obtained at 0.5 mA/cm² comparatively to at 7.5 mA/cm². A typical stripping curve for applied current density of 0.5 mA/cm² is shown in Fig. 6(b). For these last type of curves, better defined potential “plateaus” were associated to the B and C regions comparatively to that of the curve for 7.5 mA/cm². Also, the potentials corresponding to “plateaus” A, B and D were very different from the ones obtained at 7.5 mA/cm², with values significantly lower for the curves at 0.5 mA/cm² than at 7.5 mA/cm². The potentials at “plateau” C were similar for both stripping curves, but the duration of “plateau” C significantly increased, being superior to that of “plateau” B for the curves obtained at lower applied current density. In both curves, “plateau” D was slightly indicated by only a minor slope variation of very short duration. A comparison of the stripping curves obtained at the two current densities tested shows that for a better definition of the various potential plateaus corresponding to the various phases in the galvanneal coating, very low current densities, such as the one tested in this study (0.5 mA/cm²) should be used. Obviously a compromise between a reasonable time of characterization of coating for practical purposes must be taken into consideration. For this last current density, a period of approximately 8 h is necessary to completion of the coating stripping.

Most of the published literature on galvanneal coatings characterization by coulometric stripping report results obtained at current densities significantly higher than 0.5 mA/cm². However, the results of the present study shows that the very short duration of some of the presumed potential plateaus associated to stripping at high current densities impedes a proper characterization of each phase in the coating.

The repeatability of the coulometric stripping curves were always superior to that obtained from stripping at open circuit potentials (Figs. 4 and 6), indicating that besides accelerating the stripping process the applied current density increases repeatability. This is likely due to a lower influence of the heterogeneities in the alloy when more aggressive conditions are used.

Coulometric stripping of samples at 7.5 mA/cm² until potentials corresponding to the five “plateaus” was also carried out and the samples surface exposed to the solution were analyzed by SEM and EDX to investigate their morphology and composition. The results are shown in Fig. 7.

The micrographs of Fig. 7 show the cracks enlargement and the development of new cracks during stripping. Besseyrias et al. [6] studying coulometric dissolution of galvannealed steel suggested that the cracks are originated during stripping. Xhoffer et al. [8], on the other hand, demonstrated that the cracks are present in the coating previous to stripping, as it was also confirmed by the results of the present work. According to Xhoffer et al. [8] the cracks are formed during the galvannealing process due to thermal tension generated during the annealing treatment. The cracks act as paths through which the electrolyte penetrates. The results of the present work also showed cracks enlargement during electrochemical stripping.

Fig. 7(d) and (e) indicate that most of the galvanneal coating was attacked at the end of “plateau” D with the substrate being easily recognized on the micrograph of Fig. 7(f), despite of the presence of cracks on the surface, suggesting that part of the coating was still present.

Taking into consideration the presence of cracks in the coating previous to stripping it is presumed that the surface area in contact with the electrolyte is not known, consequently, thickness estimation by Faraday’s law is not possible. Besides, hydrogen evolution occurred during stripping leading to further uncertainties in the determination of the dissolved material at each “plateau”. These assumptions are supported by Zhang and Bravo [4] who proposed that cracks enlargement occurs due to preferential dissolution of the zinc richer phases corresponding to “plateaus” A and B, until the gamma phase starts dissolving. According to them, the dissolution of the gamma phase occurs more uniformly and it only starts after the dissolution of zeta and delta phases.

The cracks enlargement and pores development observed in this study suggest that the “plateaus” A and B are associated to the zeta and delta phases attack, and confirmed that the attack of these phases occur by selective zinc dissolution (Table 3). In fact, the results of surface analysis by EDX of samples removed at the end of each “plateau” of the stripping curve, shown in Table 3, suggest that most of the coating was removed during coulometric stripping at potentials corresponding to “plateau” B.

The decrease in the black film adherence occurred at potentials corresponding to “plateau” C, suggesting that this is related to dissolution of the gamma phase. Xhoffer et al. [8] mentioned that the black film is only easily removed after dissolution of gamma phase starts. Besseyrias [7] studied a homogeneous alloy of similar composition to the gamma phase and concluded that it is uniformly dissolved. In the same work [7], Besseyrias concluded that the zeta and delta phases present similar dissolution mechanism and proposed that both phases have two dissolution stages, leading to two potential plateaus in the stripping curve. The first plateau was related to the selective dissolution of zinc in the zeta and delta phases, and the second one, to the uniform co-dissolution of components, zinc and iron, and the appearance of ferrous ions in the electrolyte.

During the coulometric stripping the phase of compact morphology, here associated to the delta phase, became

Table 3

Fe and Zn contents in the surface of samples analysed by EDX after coulometric stripping at 7.5 mA/cm² being interrupted at potentials of the various plateaus

Content (mass %)	Elongated rod-like phase	Spongy layer (formerly compact layer)	Substrate	Plateau
Fe	12.90	18.00	82.70	A
Zn	87.10	82.00	17.30	
Fe	27.07	48.02	94.73	B
Zn	72.93	51.98	5.27	
Fe	–	–	96.62	C
Zn	–	–	3.38	
Fe	–	–	96.53	D
Zn	–	–	3.47	
Fe	–	–	100	E
Zn	–	–		

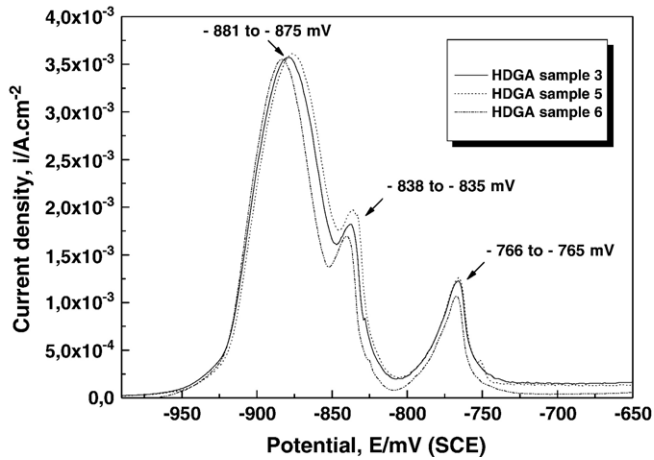


Fig. 8. Anodic polarization curves of galvanized steel in $3.42 \text{ mol L}^{-1} \text{ NaCl}$ and $0.35 \text{ mol L}^{-1} \text{ ZnSO}_4 \cdot 7\text{H}_2\text{O}$ electrolyte. (Scan rate 0.02 mV/s).

porous (spongy layer). Table 3 shows that the iron content of the phase with elongated rod-like morphology and of the spongy layer (previously compact layer), after stripping at potentials corresponding to plateau A, are close to that of the delta phase, mainly for the elongated rod-like phase. It is worth mentioning that even if some zeta phase still remains on the surface after stripping at plateau A, the interference of the

predominant delta phase will not allow its identification by EDX analysis. It can also be noted that there are areas on the surface where the substrate was apparently exposed, with high iron contents being detected by EDX analysis. The significant reduction of zinc content both phases, zeta and delta, from “plateaus” A to B indicated that selective zinc dissolution occurs in both phases.

Fig. 7(d) and (e) indicated that the galvanneal coating was practically all removed during stripping at “plateaus” C and D. The results of Table 3 support this indication showing that the iron content for the samples removed at potentials corresponding to these “plateaus” were nearly 100%.

Most of the published works [4,6] on galvanized steels only identifies the potential plateaus in the stripping curve. In order to associate the potential “plateau” with a phase in the galvanneal coating, the X-ray diffraction and energy dispersive spectroscopy (EDX) results have to be taken into consideration. The combination of the results from the various techniques indicated that zeta, delta and gamma phases were present in the coating. Consequently, potential “plateaus” corresponding to each of these phases are expected in the stripping curve. All the coulometric stripping curves obtained in this study showed 5 “plateaus”. The four first “plateaus” were sequentially associated to the dissolution from the outer phases (zinc richer phases) to the inner phases, and the fifth one to the substrate.

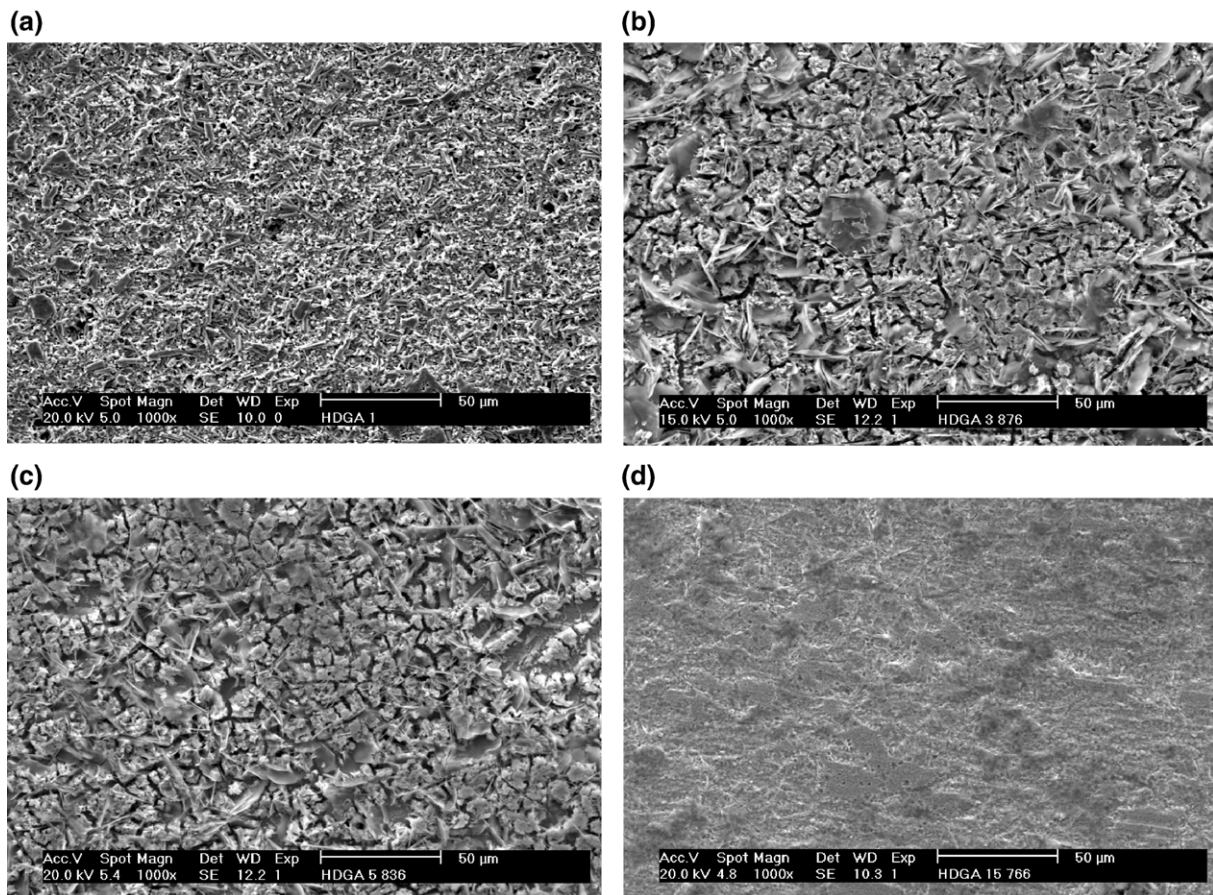


Fig. 9. Scanning electron micrographs showing evolution of galvanneal coating morphology due to polarization up to various potentials corresponding to peaks in the coulometric stripping. Sample (a) as received; (b) polarized up to -876 mV ; (c) polarized up to -836 mV and (d) polarized up to -766 mV .

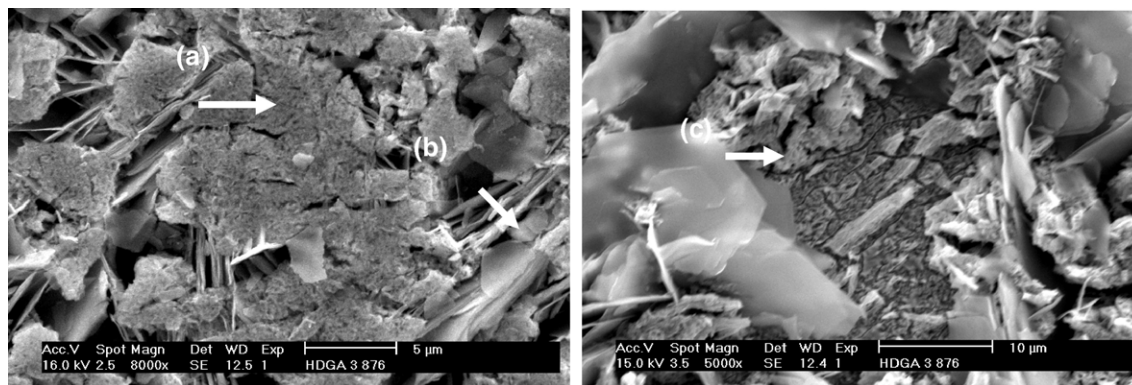


Fig. 10. Scanning electron micrographs of galvanized steel surface after anodic polarization up to -876 mV. Arrows indicate the areas analysed by EDX: (a) spongy phase; (b) platelets and (c) substrate.

3.4. Potentiodynamic anodic polarization curves

Potentiodynamic anodic polarization technique or anodic voltammetric stripping has also been used in the characterization of the phases in galvanneal coatings [5,6]. This method was also used in the present work with the electrolyte corresponding to the stripping solution (3.42 mol L^{-1} NaCl and 0.35 mol L^{-1} $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) at a scan rate of 0.02 mV/s . Fig. 8 shows the polarization curves of three galvanized steel samples with three anodic peaks easily seen in these curves. The potentials corresponding to the three peaks are indicated in Fig. 8.

Besseyrias et al. [6] also obtained three current peaks and associated the proximity of the first two peaks to the hard separation between the two outer Fe–Zn intermetallic phases in the coating. The potential corresponding to the first peak obtained by Besseyrias was close to that of the present work. However, larger differences between the present results and Besseyrias' were obtained for the two following peaks, always 25 to 30 mV nobler in comparison to the ones of this work.

Nogueira et al. [5] also carried out anodic voltammetric stripping and associated the potential peaks to the potential plateaus obtained by coulometric stripping. A comparison was also carried out in this work and the results showed that there is good correlation between the potential of the first peak potential and the first plateau potential in the coulometric stripping curve that has been related to the zeta phase. The third peak obtained from potentiodynamic anodic polarization curve showed good correlation with the potential of "plateau" C in the coulometric stripping curve previously associated to the gamma phase. The potential of the second peak, however, did not show good correlation to any "plateau" of the stripping curve. This peak might either be due to the dissolution of the delta phase, or, perhaps to the first step of the delta phase dissolution that could occur in two steps, the first in the range of -900 mV to -870 mV, and the second one at -770 mV, according to literature [7], although the last potential might also be related to gamma or gamma-1 phase dissolution.

According to Landriault [16] the first two peaks could also be related to the delta-p and delta-c phases, whereas the third

peak would be associated to the gamma phase. However, the potential values obtained by Landriault were much lower than most of other literature results, even though the author used a current density of 5 mA/cm^2 , comparatively lower than most of the other reported values.

Some samples were anodically polarized from the open circuit potential until potentials corresponding to the three current peaks in the polarization curves, when the polarization was interrupted and the samples were observed by SEM and analysed by EDX. Previous to the analysis, loose corrosion products were removed from the surface by rubbing followed by rinsing with deionized water. Fig. 9 shows the SEM micrographs of these samples. Polarization resulted in increasingly cracks enlargement, Fig. 9(b) and (c), with polarization potential from -876 mV (ECS) to -836 mV (ECS), comparatively to the non-polarized samples (Fig. 9(a)). Similar effects were obtained by coulometric stripping. It is proposed that similar mechanisms are occurring during both types of stripping, coulometric or anodic polarization, which is selective dissolution of zinc in the zeta and delta phases, leading to cracks and pores growth.

Black corrosion products were observed on the samples surface after anodic polarization and their adhesion to the

Table 4

Fe and Zn contents corresponding to the areas of different morphologies on the samples after polarization from the open circuit potential up to potentials corresponding to the peaks obtained from the anodic polarization curve (potential at the end of test)

Composition (wt.%)	Spongy layer	Platelets	Substrate	Potential at the end of test, mV (SCE)
Fe	52.78	21.88	85.45	-876
Zn	47.22	78.12	14.55	
Fe	55.80	19.38	92.78	-836
Zn	44.20	80.62	7.21	
Fe	51.54	15.99	98.58	-766
Zn	48.46	84.01	1.42	
Fe	69.94 ^a	44.58 ^b	98.74	-600
Zn	30.06 ^a	55.42 ^b	1.26	

^a Analysis in the areas where spongy layer was still found.

^b Analysis in the areas with platelets remaining.

substrate decreased at potentials corresponding to the second peak. For potentials corresponding to the third peak, the black film was easily removed from surface only by rinsing with water. As mentioned previously the loss of adhesion is an indication of gamma phase dissolution [8]. Based on these evidences, it is proposed that the third peak in the anodic polarization curve is due to the gamma phase. For samples polarized up to -766 mV, the coating was practically removed, as Fig. 9(d) suggests.

EDX analysis of various areas on a sample polarized up to -876 mV, indicated by arrows and identified as spongy phase, platelets and substrate in Fig. 10), was carried out and the results are presented in Table 4.

Similar iron and zinc compositions were associated to the areas corresponding to the spongy phase for samples polarized up to -766 mV. The platelets are mainly composed of zinc. Platelets are the result from selective zinc dissolution followed by deposition of zinc rich precipitates on the surface, and are associated to the black film also observed by many authors [4,7,8,15,16]. The spongy layer, on the other hand, is due to the selective dissolution of the initially compact delta phase.

The platelets iron concentration decreased and that of zinc increased with the anodic potential up to -766 mV. For the samples polarized up to -766 mV, the coating was removed from large areas, exposing the substrate, Fig. 9(d). This was confirmed by EDX analysis. These results indicated iron contents around 99% for both samples, either polarized up to -766 mV or -600 mV. High iron contents, suggesting the exposure of the steel substrate were also associated to the samples polarized up to -876 mV or -836 mV, at some areas. This result indicates that the stripping solution penetrates most of the coating through the cracks and or pores present in it previous to immersion tests. The simultaneous exposure of various phases to the solution stripping must result in galvanic effects between the various phases in the coating, as suggested by Besseyrias [6], with the preferential dissolution of the more active phases. Zhang and Bravo [4] proposed similar processes for electrochemical stripping of galvanneal coatings and brass dezincification.

4. Conclusions

Cracks were present in the galvanneal coating previous to immersion in the stripping solution showing that these were originated during the coating process. The zeta and delta phase were identified by X-ray diffraction analysis. However, the zeta phase was not indicated by EDX analysis. Although the EDX results indicated the predominance of the delta phase in the galvanneal coating the XRD suggested that the zeta was the main phase in the coating. The gamma phase was not identified by this last analysis.

A correlation between the phase morphology identified by SEM and the phase composition analyzed by EDX was established. The elongated rod-like phase was related to the zeta phase whereas the phase with a flat and compact morphology was associated to the delta phase. Selective zinc dissolution occurred

in the zeta and delta phases, during stripping. After stripping tests the flat and compact phase showed a porous morphology, here called spongy phase.

The coulometric stripping curves showed five potential “plateaus” associated to the zeta, delta and gamma phases in the galvanneal coating, and the last one associated to the substrate. The occurrence of the gamma 1 phases is not clearly evidenced in the results. It is worth mentioning that this phase is only detected by transmission electron microscopy that was not used in this study. The potential “plateau” corresponding of each phase showed high repeatability. For good definition of the various potential “plateaus” corresponding to the various phases in the galvanneal coating, very low current densities must be used in the characterization of this type of coating by coulometric stripping.

Similar mechanisms were associated to the outer zinc richer phases (zeta and delta), specifically, selective zinc dissolution, which were indicated by EDX results. This led to cracks and pores growth during the stripping tests. The cracks and pores in the coating favored the exposure of the various intermetallic phases to the electrolyte, and might have led to their concurrent corrosive attack.

A black film with a platelet-like morphology was found on the galvannealed steel samples after stripping. The adherence of this film decreased with the polarization potential, dropping significantly at potentials above that corresponding to the delta phase stripping.

Three current density peaks were obtained in the anodic polarization curves and they were also related to the zeta, delta and gamma phases in the galvanneal coating.

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