



EFFECT OF CHEMICAL BATH COMPOSITION ON MICROSTRUCTURE AND CORROSION RESISTANCE OF ZINC COATINGS BY HOT DIP: A REVIEW

EFEECTO DE LA COMPOSICIÓN QUÍMICA DEL BAÑO EN LA MICROESTRUCTURA Y RESISTENCIA A LA CORROSIÓN DE LOS RECUBRIMIENTOS DE ZINC POR INMERSIÓN EN CALIENTE: UNA REVISIÓN

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Abstract

Metal coatings are widely used methods for protection of metal alloys, with the hot dip galvanizing process being one of the most industrially evolved. The objective of this work is to carry out a literature review about the influence of the addition of alloying elements in the bathroom, on the microstructure and corrosion behavior of zinc coatings obtained by the hot dipping technique. It was determined that the chemical composition of the galvanized baths influences the microstructural characteristics of the coatings and their corrosion behavior. The improvement of the corrosion resistance of zinc coatings is produced by the addition to the baths of elements generally more active than zinc, such as magnesium or aluminum that allow the formation of passive layers that delay the corrosive process.

Keywords: Zinc, Corrosion, Microstructure, Coating, Galvanized, hot dip.

Resumen

Los recubrimientos metálicos son métodos ampliamente utilizados para la protección contra la corrosión de aleaciones metálicas, siendo el proceso de cincado por inmersión en caliente uno de los que presenta mayor evolución a nivel industrial. El objetivo de este trabajo es realizar una revisión bibliográfica sobre la influencia de la adición de elementos aleantes en el baño, en la microestructura y en el comportamiento a la corrosión de recubrimientos de zinc obtenidos por la técnica de inmersión en caliente. Se estableció que la composición química de los baños galvanizados influye en las características microestructurales de los recubrimientos y en su comportamiento a la corrosión. La mejora de la resistencia a la corrosión de los recubrimientos de zinc se produce por la adición a los baños de elementos generalmente más activos que el zinc, tales como el magnesio o el aluminio que permiten la formación de capas pasivas que retardan el proceso corrosivo.

Palabras clave: zinc, corrosión, microestructura, recubrimiento, galvanizado, inmersión en caliente.

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1. Introducción

The processes for obtaining coatings through hot dip technologies, and in particular pure zinc coatings, have been used as protection against corrosion in different environments, especially urban, in which their behavior results very satisfactory in general. Nevertheless, in marine environments, in which the humidity and the concentration of sodium chloride are usually high, the resistance to corrosion of steels coated with pure zinc can significantly diminish [1].

Some alternatives proposed for overcoming this limitation include the generation of zinc-based coatings with the addition of some alloying elements, among which the most studied are aluminum, magnesium, silicon, copper, tin, nickel and other elements in a smaller proportion [1, 2].

From a technological point of view, the operational parameters to conduct the process of zinc coating on steel by the hot dip technique have remained practically invariable over time, but the new applications in the automotive and construction industries have caused that, at present, there exists a considerable number of research works about the aspects of the process and new types of zinc coatings [3, 4], which have increased the studies of the influence on the microstructure and the obtained coatings, of the addition of alloying elements to the zinc bath [3, 4].

In view of the above, the objective of this work is to conduct a literature review about the influence of adding alloying elements to the bath, on the microstructure and on the behavior against the corrosion of zinc coatings obtained through the hot dip technique.

2. Development of zinc coatings on steel

The American Galvanizers Association [5] indicates that the recorded history of galvanization dates back to the year 1742, when the French chemist Melouin, in a presentation to the Royal French Academy, described a method of iron coating through dipping in liquid zinc.

In 1836, Sorel, another French chemist, obtained a patent to manufacture a zinc coating on iron, after performing a cleaning with 9 % sulfuric acid and using a flux with ammonium chloride.

By 1850, the British galvanizing industry used yearly 10,000 tons of zinc for protection of the steel, and the first galvanizing plant in the United States was installed in 1870.

The coatings obtained through the galvanizing technique are widely used in diverse industries. Companies such as public services, chemical processes, pulp and paper, automotive and transportation, have extensively used galvanization for corrosion control, and

keep doing it nowadays. For more than 150 years, galvanization have had a proven history of commercial success as a method for protecting against corrosion in a great variety of applications worldwide.

Research studies conducted in recent years, have focused on the influence of the chemical composition of the bath on the microstructure and properties of the galvanized coatings. The changes in the chemical composition of the zinc baths search, undoubtedly, a significant improvement in the properties of the galvanized coating, either in its resistance to corrosion, in the weldability processes, and/or in its mechanical properties.

Figure 1 presents a typical coating of galvanized steel, where it can be observed three well-defined layers that are formed during the galvanized process. Each layer corresponds to the formation of intermetallic products, which according to their composition are known as Gamma, Delta and Zeta, and the top layer of pure zinc is Eta. Thru the galvanization process, the layers are naturally developed during a metallurgic reaction between the iron of the steel and the zinc of the bath [5].

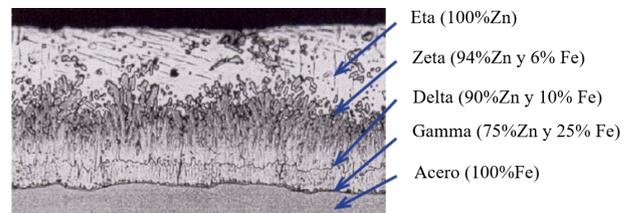


Figure 1. Microstructure of a typical Zn coating, showing the formed layers with their respective chemical composition [5].

The research studies have been oriented to studying the metallurgy of the galvanized steel from a scientific point of view, to develop relations to the practical applications. These studies involve the systematic evaluation of the hot dip process, together with the diagrams of equilibrium or of phases Fe-Zn and the kinetics of formation of the layers of the Zn coating [3].

It should be noted that the aluminum is one of the elements mostly used in the zinc bath. The commercial development of these coatings, for instance Galvalume® (Zn-55Al) in 1970 and Galfan® (Zn-5Al) during 1980, successfully demonstrated that incorporating aluminum significantly improves the resistance to corrosion of the zinc base coating. Since then, numerous research studies have been carried out about the Zn-Al coatings applied on the steel by hot dip.

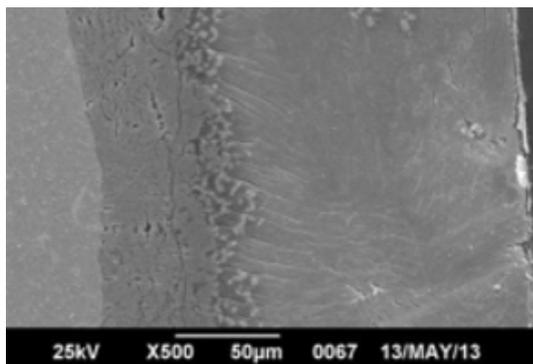
Galvalume® is a coating with approximately 55 % of aluminum, and also contains approximately 1.5 % of silicon which is added with the purpose of preventing an exothermic reaction in the coating/steel substrate interface. During the process, Fe-Zn-Al intermetallic

compounds are generated in the interface. The surface of the Galvalume® has characteristics of sequins, which consist in aluminum dendrites with a clearly measurable distance of the dendritic arm.

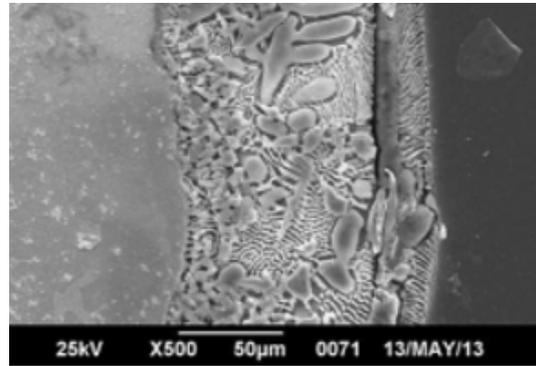
Galfan® is a zinc coating with 5 % of aluminum, which is close to the eutectic point, and has an excellent conformability and protection against corrosion. Two compositions have been reported based on the additions to the eutectic composition: small additions that contain lanthanum and cerium up to around 0.5 %, and additions of 0.5 % of magnesium. These additions are made to improve the wettability of the molten bath, without reducing the resistance of the coating to corrosion. The microstructure of the Galfan® is characterized by a two-phase structure, the eta (η) pro-eutectoid phase rich in zinc, surrounded by a eutectoid type phase constituted by beta (β) and eta (η). Nevertheless, the structure may vary depending on the cooling velocity [3].

Figure 2 shows the latter effect, where Rico and Hernandez [6] studied the influence of the cooling velocity in the morphology and distribution of the phases of the Zn-7Al coatings on steel. The microstructures of the coating cooled in water shows the eutectic mixture segregated in the coating/steel interface, and the cooled in the furnace have a monotectoid micro-constituent of dendritic morphology.

According to the ASM Handbook: Corrosion [7], there is good evidence that small quantities of alloying elements may affect the resistance against corrosion of the galvanized coatings. The mechanisms for these effects are complex and not completely understood, but the literature suggests that the alloy elements segregate to the grain boundaries, where they can accelerate or delay the intergranular attack. Considering the alloy Zn/0.1-0.2Al typically used in hot galvanizing, it was found that adding it in the magnesium and copper bath reduces the intergranular corrosion mechanism, while the presence of bismuth, cadmium, lead and tin increases the localized attack. There are also some evidences that the addition of nickel to the bath reduces the hydrogen evolution reaction, and increases the resistance against the corrosion in environments that contain chlorides [8,9].



(a)



(b)

Figure 2. Micrographs through scanning electron microscopy (SEM) of Zn-7Al coatings, with different cooling conditions. A) water. B) furnace [6].

Recently, studies about the Zn-Al-Mg coatings have attracted attention. The reason for their systematic massive study is their performance in saline environments, where better behaviors against corrosion have been obtained, specifically in the order of 10 to 20 times with respect to Zn coatings, and 2 to 5 times with respect to Zn-Al coatings. Other important properties have also been found, such as the self-healing capacity (thus the area of the incision can be closed and protected again), scratch and wear resistance and lighter coating density, among other advantages [10].

Japanese, European and South African companies have already developed Zn-Al-Mg coatings, such as the Nisshin Steel Co., which has patented the ZAM® brand. Nevertheless, detailed information is still lacking in the open literature about the anticorrosive mechanism of the Zn-Mg-Al coating, and also little is specifically known about its electrochemical performance. On the other hand, the operating conditions of the hot dip process have not been optimized in order to obtain a smooth surface of such coating, and this is a challenge in this field [10].

Li *et al.* [2] evaluated the coating Zn-5Al-0.5Mg-0.08Si on alloy steel, which was compared with the coating Zn-5Al. They found that the resistance against corrosion of the Zn-5Al is not very high, compared to the resistance provided by magnesium and silicon.

Figure 3 shows the morphology of the surface of the coating Zn-5Al, and the results corresponding to the chemical composition at points A and B. The coating consists in thick β (Zn) and binary eutectic phases of Zn-Al.

Due to the difference of potential between the two phases (Figure 3), when the coating is placed in the corrosive environment the phase with more electronegative potential will accelerate the corrosion process, while the phase with less electronegative potential will be protected from being corroded.

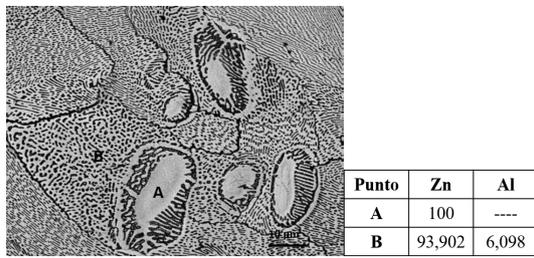


Figure 3. Micrograph through scanning electron microscopy (SEM) of a Zn-5Al coating and chemical composition in percentage of weight by energy dispersive Xray spectroscopy (EDS) at points A and B [2].

Figure 4 shows the image through scanning electron microscopy (SEM) of a Zn-5Al-0.5Mg-0.08Si coating. It can be seen that the separation of the dendritic arm of Zn-5Al of the coating significantly reduces from $\sim 10 \mu m$ to $2-5 \mu m$, after adding the alloying elements Mg and Si. The phases β (Zn) (A), another rich in Al (B) and a tertiary eutectic MgZn₂-Zn-Al (C) are formed [2]. The magnesium is only distributed in the grain boundaries, and this can cause that such grains become finer, thus preventing the intergranular corrosion.

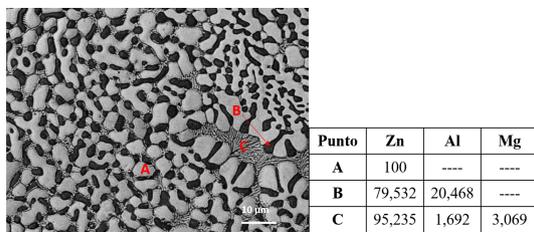


Figure 4. Micrograph through scanning electron microscopy (SEM) of a Zn-5Al-0.5Mg-0.08Si coating and chemical composition in percentage of weight by energy dispersive Xray spectroscopy (EDS) at points A and B [2].

In this same sense, Schuerz *et al.* [11] carried out a study on steel sheets conventionally coated by hot dip of Zn (Z) and of Zn-Al-Mg (ZM) alloy, with the chemical composition indicated in Table 1.

Table 1. Chemical composition, in percentage of weight, of the coatings evaluated [11]

Coating	Zn	Al	Mg
Z	99,8	0,2	—
ZM	96	2	2

The microstructure of the conventional coatings of zinc (Z) and zinc-aluminum-magnesium (ZM) differ considerably, as illustrated in Figure 5.

The Z coating consists of a layer of homogeneous material of pure zinc. The aluminum is enriched in the steel/coating interface in the form of a very thin layer of the intermetallic compound Al-Fe, which ensures a correct adherence of the coating on the steel surface.

On the other hand, the ZM coating consists of different phases: a zinc phase, which also includes small quantities of aluminum, an aluminum phase and the phase of MgZn₂. The latter and the zinc also appear in the form of a binary eutectic (marked with a rectangle), as well as a tertiary eutectic of zinc, aluminum and the phase MgZn₂ (marked with an oval). The metallic coating ZM becomes a stable and adherent material, and a layer of oxide rich in aluminum that protects the steel substrate in corrosive environments. This layer is the main reason of the improved resistance against corrosion of the ZM coating in an environment that contains sodium chloride.

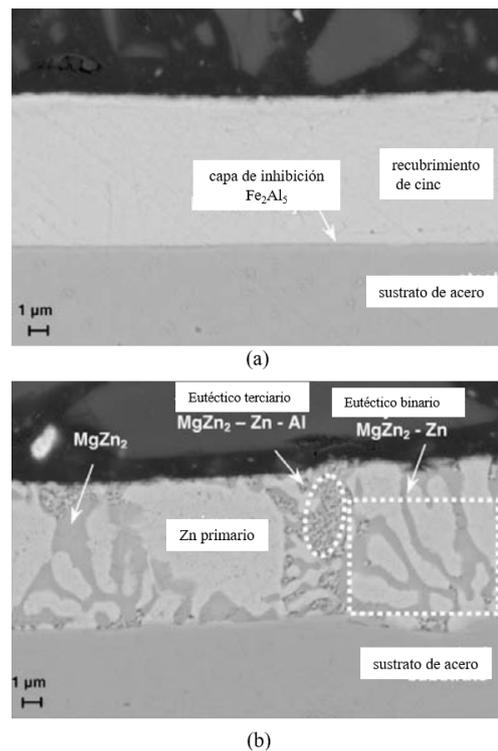


Figure 5. Micrograph through scanning electron microscopy (SEM) of (a) a conventional coating Z of Zn, and of (b) an alloy coating ZM of Zn-Al-Mg [11].

Other developments that have emerged as innovation to the processes of galvanizing by hot dip are the double dip processes, which were raised based on the operational problems during the hot dip of the Zn-Al coatings, since they do not have a good compatibility with the typical flux systems, and using others do not make it practical in the galvanization industry. Besides, the quantity of aluminum that gets in the coating layer represents an additional problem in the composition of the bath, since the concentration of aluminum is considerably reduced; this generates a continuous monitoring [4].

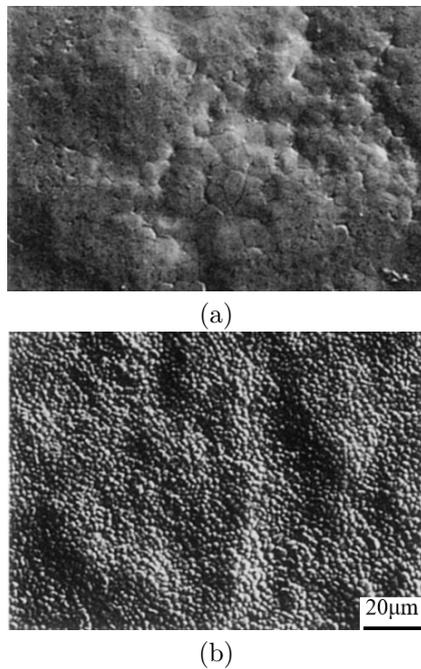


Figure 6. Superficial morphology by SEM of the coatings formed on steels of low carbon, by hot dip in two stages (a) Z6A and (b) Z6AMS [12].

In this sense, Tanaka *et al.* [12] evaluated coatings on steel with low carbon content by hot dip in two stages (double dip), mainly in a bath of Zn and then in a bath of Zn-6Al (Z6A), with or without the addition of 0.5 % in weight of Mg and 0.1 % in weight of Si (Z6AMS). Figure 6 shows the morphology of the surface of the coatings formed by the hot dip of two stages with secondary baths of (a) Z6A and (b) Z6AMS. The surface of the coating formed in the Z6AMS showed very fine grains and few defects in comparison with the Z6A.

The layers of coating consisted in a duplex structure; an external layer and an internal alloy layer (Figure 7). They identified that the alloy layer was mainly constituted by an intermetallic phase of $\text{Fe}_4\text{Al}_{13}\text{-Zn}$. They observed that the crystals of this phase are randomly distributed in the Z6A coating, while the Z6AMS coating has a columnar structure with growth perpendicular to the steel substrate.

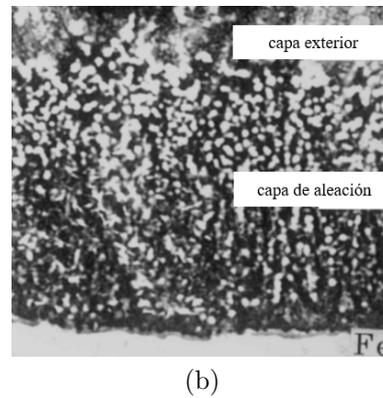
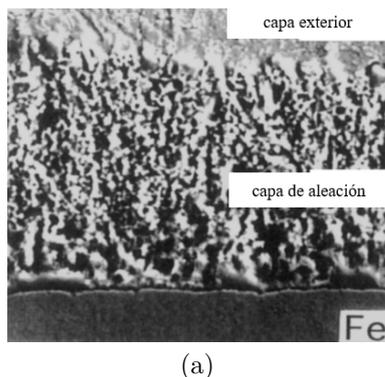


Figure 7. Microstructures of the cross sections of the coatings (a) Z6A and (b) Z6AMS [12].

Figures 8(a) and 8(b) show the external layer for the Z6A and Z6AMS coatings, respectively. The dark area is mainly a phase $\alpha\text{-Al}$ and the clear area is the structure of a eutectic of Zn (Al) and $\alpha\text{-Al}$. It was found that the $\alpha\text{-Al}$ in the Z6A coating in Figure 8(a) is much thicker than the one of the Z6AMS coating in Figure 8(b). The coating Z6AMS corroded slowly and in a homogeneous manner, while the coating of Z6A locally degrades due to a preferential corrosion along defects. The coating Z6AMS possesses Mg and Si in the external layer, and Si in the internal alloy layer, which makes it more anticorrosive.

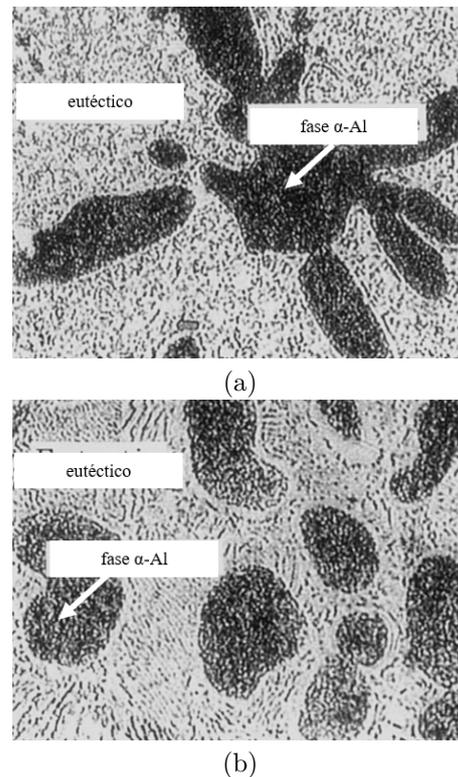


Figure 8. Microstructures of the external layer of the coatings (a) Z6A and (b) Z6AMS [12].

Among the double dip processes it is also high-

lighted the study conducted by Tachibana *et al.* [13], who evaluated a new coating by hot dip of Zn₇Al on structural steel, which was applied through a double layer Zn-Zn₇Al to prevent severe corrosion in coastal zones. The double coating was significantly effective in the prevention of the corrosion, particularly in the seaside. It was estimated that in the seaside, the life of the Zn-Zn₇Al coating on the steel was four times the life of the steel coated with Zn. It was revealed that the excellent adhesiveness of the double coating Zn-Zn₇Al on steel was due to the formation of the interface region that consists of a fine heterogeneous phase of a mixture of zinc, aluminum and iron.

Likewise, Rico and Carrasquero [8] carried out a microstructural characterization of zinc coatings on steel by the double dip method. The temperature of the dip bath was 550 °C, and the coatings were made using different immersion times. All the coatings showed three defined zones. The first zone, which corresponds to the steel/coating interface, presents properties which are typical of a traditional galvanization process at high temperatures. In zone II it was observed a very heterogeneous microstructure, while zone III showed a matrix of Zn-Fe with particles of compounds of Fe₂Al₅Zn_{0,4}, as observed in Figure 9. The microstructural properties of the coatings were similar during the three immersion times. They determined the presence of Fe and Al along all the coating, due to the diffusion of the iron from the base metal and the aluminum provided by the second dip bath.

In such a way, the development of zinc coatings by hot dip has been based in modifying the chemical composition of the bath, which implies microstructural changes that improve the properties for a specific application. Aluminum [3, 6, 13–17], magnesium [2, 10–12, 16–19] and silicon [2] have been the alloying elements which have been more studied, with the purpose of establishing their influence in the general properties of these coatings. Other elements that have been studied in smaller proportion are copper [1, 20], titanium and nickel [21, 22].

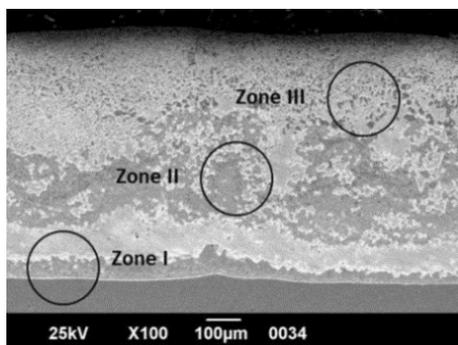


Figure 9. Micrograph through SEM of the Zn/Zn-5Al coating with a total immersion time of 120 s, in which the three zones of the coating are shown [8].

3. Behavior against corrosion of the zinc coatings

The zinc coatings add resistance against corrosion in various ways; one as a barrier layer, since the continuous coating separates the steel from the corrosive environment; other by galvanic protection, since the zinc acts as a sacrificial anode that protects the steel in areas adjacent to the holes, scratches and edges of the coating. The behavior of the zinc can be seen in a galvanic series where zinc is less noble than steel in the majority of the media at ambient temperature [3].

A porous superficial layer of zinc oxide is formed in the surface due to a mechanism of dissolution/re-precipitation, which leads to preferential corrosion routes in the high porosity area or discontinuities; this explains the linear corrosion rate. Besides, after the dissolution of the metallic zinc, the zinc hydroxide may precipitate to the cathodic areas of the exposed steel, forming a secondary barrier layer. As a consequence, the zinc coating will corrode at a slower velocity than the steel substrate, even though the zinc corrosion rate will vary depending on the exposition environment [3].

In the case of Zn-Al coatings such as Galfan®, the corrosion in non-marine environments occurs in two stages: temporary protection due to the formation of passive layer of aluminum oxide, and the galvanic action of the zinc where the zinc sulfate is formed on the oxide layer. The kinetics is controlled by the second stage due to the diffusing need through the oxide layer, which explains the decrease of the corrosion velocity of the Galfan® with respect to conventional zinc coatings. It has been also demonstrated that the phase rich in zinc (η - *eta*) is preferentially corroded respect to the pro-eutectic and eutectic. The additions of Mg (up to 0.8 % in weight) increase the quantity of pro-eutectic of phase Al, which improves the resistance against corrosion. The Galfan® corrodes in a parabolic manner, while conventional coatings corrode in a linear manner [3].

The atmospheric corrosion of the Galvalume® coating occurs in the inter-dendritic regions rich in zinc, which enables a galvanic protection. Then, the products of corrosion remain trapped in those spaces, and act as a barrier against corrosion. The corrosive process is of parabolic type [3].

In view of the importance of systematically evaluating the behavior against corrosion of these coatings in different environments, multiple researchers have embarked in conducting accelerated corrosion tests, the traditional that involve exposition at atmospheric conditions, by dip and in saline mist chamber, to determine the velocity of corrosion, as well as the electrochemical techniques that allow to obtain more information about the mechanism and kinetics of the corrosion. These studies are normally carried out as a comparison of different coatings, in order to estab-

lish analogies and differences that allow industry to decide about the applicability of each of the coatings evaluated.

Table 2 shows a summary of the utilized techniques and the environments in which the different zinc base coatings are evaluated.

On the other hand, the study of the behavior against corrosion of the zinc coatings depends on many factors, but the most common orientation of the research studies is to relate the microstructural changes of the coatings with their resistance to corrosion; the addition of alloying elements to traditional zinc baths allow to obtain these changes. Also, in these research studies becomes important to establish the mechanisms that govern the corrosive processes, based on techniques that enable the characterization of the products of corrosion, to relate them with the species present in the environment and the elements that constitute the material [9, 15, 18, 19, 23, 24].

In this sense, Hosking *et al.* [25] studied the behavior against corrosion of Zn-Mg coatings, in comparison with traditional zinc coatings. Specifically, they followed an experimental program that included conducting corrosion tests in an acidified solution of NaCl, characterizing the products of the corrosion and proposing a mechanism of the corrosive process. Results revealed that the resistance against corrosion of the Zn-Mg coatings was three times the resistance of conventional

zinc coatings, and that this improvement was caused by the precipitation on the corrosive surface of insoluble Simonkolleite ($\text{Zn}_5\text{Cl}_2(\text{OH})_8\cdot\text{H}_2\text{O}$) possibly modified with absorbed magnesium, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and a specie of hydroxycarbonate, thus delaying the corrosion reactions.

Similarly, Yao *et al.* [10] comparatively evaluated the behavior against corrosion of three types of zinc coatings with different combinations of Zn, Al, Mg and Cu (Zn-0.1 Cu (G), Zn-5Al-0.1Cu (ZA) and Zn-5Al-1Mg-0.1Cu (ZAM)). They conducted saline mist chamber and electrochemical tests in an aqueous solution of 5 and 3.5 %, respectively, of NaCl, to study the behavior against corrosion of the coatings.

Figures 10(a) and 10(b) show the polarization curves of the coatings, superficially prepared and after five days of tests in the saline mist chamber, respectively. Some changes in the parameters of the corrosion process were observed. There is a region in the polarization curve of the ZAM coating, in the range from -1.5 V to -1.2 V (Figure 9(b)), in which the current density is kept relatively constant independently of the variation of the potential; this indicates that the cathodic reaction of the ZAM coating was inhibited in this range of potential, due to the precipitation of corrosion products in the cathodic area that act as inhibitors, thus increasing the impedance of the surface of the coating.

Table 2. Techniques and environments to evaluate the behavior against corrosion of the zinc coatings

Type of coating	Corrosive environment	Evaluation technique	Ref.
Zn Zn-4,9Al	5 % NaCl in laboratory 3 % NaCl in laboratory	Saline mist chamber Potentiodynamic polarization	[26]
Zn-5Al Zn-55Al	Real Seawater (78 % NaCl) Synthetic Seawater (68 % NaCl)	Measurement of potentials	[27]
Zn Zn-5Al	3 % NaCl in laboratory	Saline mist chamber Potentiodynamic polarization	[28]
Zn-0,2Al Zn-2Al-2Mg	5 % NaCl in laboratory	Saline mist chamber	[11]
Zn Zn-5Al Zn-55Al	Atmospheric in field	Field tests	[29]
Zn Zn-55Al	Atmospheric in field Saline mist chamber and of SO ₂ in the laboratory	Electrochemical impedance spectroscopy	[30]
Zn-55Al	0.5 M NaCl 0,5 M Na ₂ SO ₄ 0.5 M NaClO ₄	Electrochemical impedance spectroscopy	[31]
Zn Zn-5Al	5 % ammoniacal solution	Test of cyclic corrosion	[32]
Zn/Zn-6Al Zn/Zn-6Al-0,5Mg-0,1Si	5 % NaCl in laboratory	Dip	[12]
Zn Zn/Zn-7A	Real Seawater	Dip	[13]

Figures 11(a) and 11(b) show the EIS spectra for the coatings G, ZA and ZAM. The shapes of the (a) Nyquist diagrams and of the (b) phase angle Bode diagrams for the three coatings are similar. The Nyquist diagrams consist of a semicircle at high frequency and a circle at low frequency. The phase angle Bode diagrams exhibit two crests of wave, which indicates that the three coatings may have similar corrosion mechanisms. While the ZA coating has a larger impedance than the other two coatings in the high frequency range (10 Hz ~ 100000 Hz), the G coating has a relatively larger impedance than the ZA and ZM coatings at low frequency (0.01 Hz ~ 10 Hz).

A greater value of impedance normally indicates a lower corrosion velocity of the material. The impedance

of the ZAM coating is lower than other at this stage, which may be due to the addition of less noble Mg; this will make it react first when the ZAM coating is in a NaCl solution, contributing to a high density of current of corrosion at the initial stage.

The protective nature of the ZAM coating can be attributed to the initial corrosion of the phases rich in Mg. The corrosion products of Zn, Al and Mg are agglomerated in the cathodic area and act as inhibitors, blocking the corrosion routes (the micro-routes for the diffusion of O₂ and H₂O) along the grain boundaries of the Zn crystals and increasing the impedance of the coating, thus the general corrosion process of the ZAM coating is delayed.

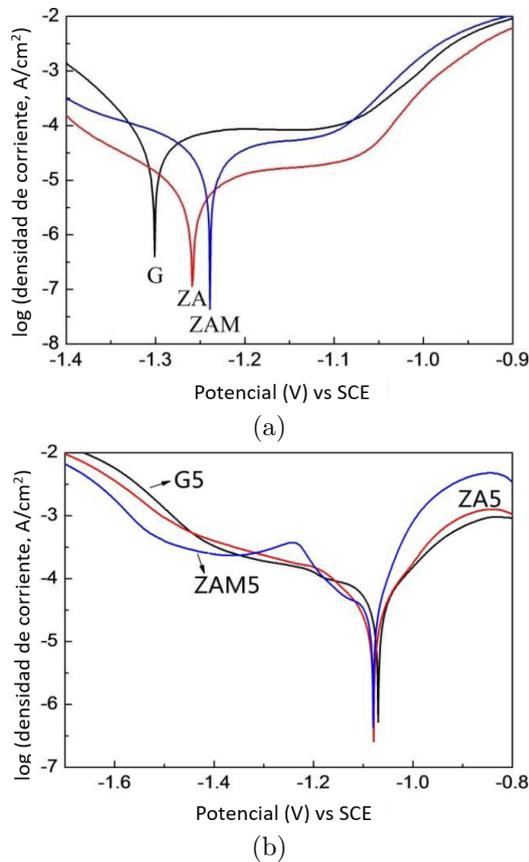


Figure 10. Potentiodynamic polarization curves for the zinc coatings; (a) superficially prepared, (b) after 5 days of saline mist chamber test [10].

As was previously indicated, the behavior against corrosion depends on many factors, and among the most studied are the referred to the operating parameters of the hot dip process. For instance, Elvins *et al.* [14] studied the effect of the cooling velocity on the microstructure and the resistance against corrosion of the Galfan® (Zn-4,5Al) coating on the steel. They applied three different cooling velocities.

The increase in the cooling velocity did not significantly alter the volume of the fraction of primary zinc; nevertheless, the size and number of primary dendrites of zinc were altered. The specimens cooled quickly contained small but numerous dendrites, and on the ones of slow cooling there were less dendrites of bigger size.

The quantity of zinc dendrites influence the corrosion process since it is the phase that is preferentially corroded, thus resulting in a larger anodic area and consequently a larger corrosion velocity as the cooling velocity increases. Figure 12 shows the preferential corrosion of the zinc dendrites with respect to the eutectic.

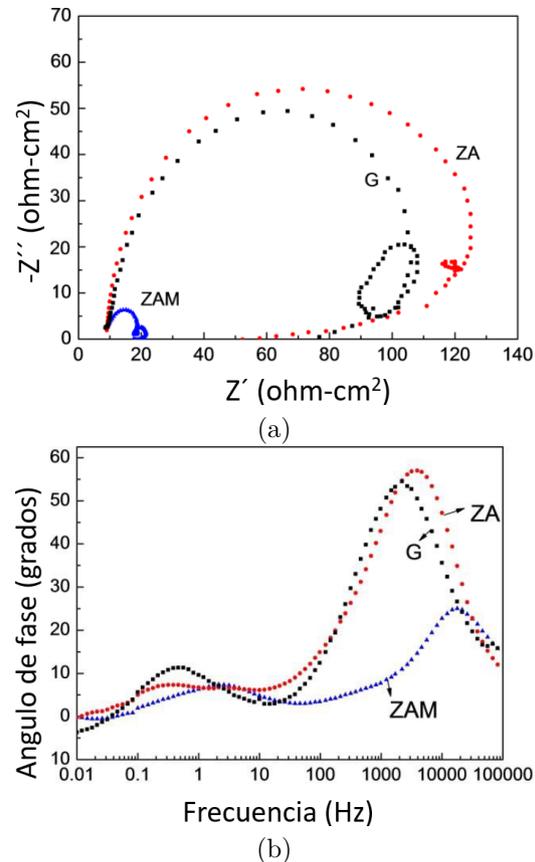


Figure 11. Electrochemical impedance spectroscopy of the zinc coatings (a) Nyquist diagram, (b) Bode diagram [10].

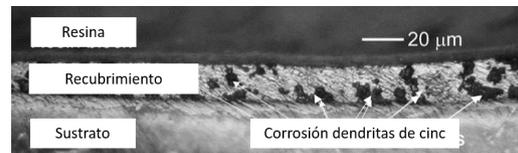


Figure 12. Microstructure of the Zn-4,5Al coating, where it can be observed the preferential attack of the zinc dendrites [25].

Another way to study mechanisms and understand in a better manner the behavior against corrosion of the zinc coatings, is utilizing techniques of analysis of the corrosion products to propose process mechanisms, such as the work by Carbuicchio *et al.* [33], who studied the corrosion products formed in galvanized steel pipes exposed to hot water for two years, through metallographic techniques of X ray diffraction, as well as the Mössbauer and Raman spectroscopic techniques. The results obtained allowed to establish that the corrosive process was caused by an excess in the service temperature, occurring an inversion of the electrochemical polarity between the zinc and the iron, growing tubers of corrosion products in the dezincified zones of the pipe walls until perforation. The compounds present in the corrosion products allowed to suggest a mechanism of the process.

On the other hand, it is also important to mention that the corrosive processes are affected by some mechanical stresses, or some specific element such as hydrogen that contributes to enhance the corrosive process. As a consequence, there are also research works that evaluate synergic behaviors of the corrosion with other types of wear or mechanical stresses. In this sense, Reumont *et al.* [34], studied the influence of the microstructure in the susceptibility to assisted stress corrosion cracking (SCC) of a galvanized steel in an aqueous solution of sodium chloride. Deformation tests were carried out in an aqueous solution of NaCl at 3 %. The general behavior of the galvanized steel is ductile. There is a transition from ductile to fragile for a particular velocity of deformation in this environment. Little mechanical resistance of the coating and the hydrolysis reaction of the zinc is necessary to lead to the fragility, which may be associated with a fragility process by hydrogen. The formation of intermetallic components may produce a coating with microstructure resistant to the SCC.

A similar work was carried out by Sacco *et al.* [31], who evaluated the behavior of steel sheets with conventional zinc coatings and with Zn-55Al coatings uniaxially tractioned and exposed to solutions 0.5 M NaCl, 0.5 M Na₂SO₄, and 0.5 M NaClO₄. The specimens were deformed until reaching elongations of 1.3, 3.75, 6.25, 7.5 and 12.5 %. These and other specimens without deformation were subjected to electrochemical tests and measures of electrochemical impedance. The results obtained allowed to infer that there are notable differences in the kinetics of the corrosion reactions that take place on the surface of both types of coatings, and that for both steel/metallic coating systems such kinetics is a function not only of the degree of applied deformation, but also of the composition of the aggressive medium under consideration.

Rico and Carrasquero [4] carried out a revision where it is established that the chemical composition of the galvanized baths, strongly influence the microstructural characteristics of the coatings and their mechanical behavior. This assertion together with the studies reported in this work, establish that the behavior against corrosion is also affected by the addition of elements to the zinc bath; besides, this is supported by other works that studied the synergic effects of the corrosion with the mechanical behavior [31, 34–38].

As was mentioned in the first section of this paper, other research works highlight because of their purpose of improving the properties against corrosion of zinc coatings by carrying out double dip processes, which consist of consecutively immersing the steel in two liquid baths with different chemical compositions; the first immersion is in a conventional galvanizing bath, and the second in a bath of a zinc base alloy with other elements, such as aluminum, magnesium and silicon. In this sense, Tanaka *et al.* [12] demonstrated that the

double dip has advantages such as good adherence of the coating and the viability of better controlling the thickness and the microstructure of the coating, thus also improving its resistance to corrosion. Standardized laboratory tests were carried out to establish the improvement in the behavior against corrosion.

Tachibana *et al.* [13], applying a double dip process as well, determined that the coatings obtained by this method exhibit a better performance against corrosion than the one manufactured by conventional methods. These results were obtained in tests carried out in a real saline environment.

It is important to remark that although some research works have been conducted about the application of double dip processes, there is no accurate information about the mechanisms that enable to establish the improvement in the resistance to corrosion of these processes compared with other conventional methods; nevertheless, it is estimated that the addition to the baths of elements generally more active than zinc, such as magnesium and aluminum, promote the formation of passive layers that delay the corrosive process.

4. Conclusions

The chemical composition of the galvanized baths influence the microstructural characteristics of the coatings.

The increase in the resistance against corrosion of the zinc coatings by hot dip is oriented to change the chemical composition of the baths, with the purpose of expanding the applicability of these coatings on more aggressive environments such as those that contain chlorides.

The improvement in the resistance against corrosion of the zinc coatings is caused by the addition to the baths of elements generally more active than zinc, such as magnesium or aluminum, that allow the formation of passive layers that delay the corrosive process.

The studies of the Zn-Al-Mg coatings have reported behaviors against corrosion of the order of 10 to 20 times with respect to the Zn coating, and of 2 to 5 times with respect to the Zn-Al coating.

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