

HEAT TREATMENT EFFECT ON GALVANIZED LOW CARBON STEEL

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Abstract

The objective of this study was to investigate the effect of the isothermal heat at 400°C on the microstructural evolution and corrosion resistance of galvanized low carbon steel. This heat treatment is considered as severe environment. The techniques of characterization were scanning electron microscopy, X-ray diffraction, and corrosion test. The occurrence of different sub-layers (Eta, Zeta, Delta and Gamma) on deposited zinc depended on the time of the isothermal heat treatment. Isothermal heat at 400°C did not cause a decohesion of the coating from the substrate. This heat treatment has a negative effect on the corrosion resistance of the galvanized steel, because many pores and some cracks are formed in the deposited zinc.

Keywords: Low carbon steel, galvanizing, heat treatment, microstructures, corrosion resistance

Introduction

The objective of surface engineering is to extend the life of parts and thus save time, energy, and money. Galvanizing is a surface treatment which is used to coat zinc over the iron and steel. Applying a thin coating of zinc to steel is an effective and economical way to protect it from corrosion. Galvanized steel can be successfully used in a large range of applications, because of its good resistance to environmental corrosion (Yadav *et al.*, 2007;

Amin *et al.*; 2008; Lin *et al.*, 2008; Sherif *et al.*, 2012). Among them, steel wires for bridges (Jiang *et al.*, 2009; Yang *et al.*, 2012) automotive industries (Berchem and Hocking, 2006; Berchem and Hocking, 2006), and steel structures (James, 2009) can be mentioned. Three of the most-used processes for applying zinc to iron and steel are hot-dip galvanizing, electrogalvanizing, and zinc spraying. The Most used technique is hot-dip process. It

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involves immersing steel into a bath of molten zinc at temperature close to 465°C (Dallin, 2012).

The protection obtained by zinc coating is due to barrier and galvanic double protective effect (Bajat *et al.*, 2010; Kartsonakis *et al.* 2012). The Zn protective coating structure consists of intermetallic Fe-Zn compound layers, which have been identified as Γ , δ , ζ , and η outer layers highly rich in Zn (ASM Handbook, 1992). The protective power of zinc against steel corrosion depends on numerous factors: porosity and thickness of zinc coating, its adhesion to the steel, and the nature of the oxide layer formed on the zinc surface, etc. (Legault and Pearson, 1978).

However, it has been noted that the corrosion resistance of any zinc coating can drastically change depending upon the specific corrosion environment and whether the coating is welded, contains a paint system or is deformed, and the extent to which galvanic protection is required for nearby uncoated areas (Marder, 2000). In addition to these environments, the exposure of the galvanized steel to the high temperature can be also considered as a severe environment.

In this context, there are limited research works on the effect of temperature on galvanized steel. For example, Azadeh and Toroghinejad (2009), studied the effects of annealing heat treatment for short time on the coating microstructure and formability of hit-dip galvanized sheet. They found that the heat treatment at higher temperatures and for shorter process times improves coating formability behavior. However, there is not a published work about temperature effect on corrosion resistance.

For that reason, the objective of this study is to investigate the effect of the isothermal heat at 400°C for short and long time of treatment, on the microstructural evolution and corrosion resistance of galvanized low carbon steel.

Materials and Methods

The substrate used in this study was a low carbon steel wire (SAE 1008) with a diameter $\varnothing = 4.9$ mm. The chemical composition of this steel is presented in Table 1. To eliminate any surface oxide before galvanizing process, the wire steel is cleaned, pickled and fluxed. The applied coating consisted of immersion in the molten zinc bath (99.99%), maintained at 450°C. The wire of steel is coated at speed of 20 m/min.

To investigate the effect of isothermal heat treatment on the microstructural and corrosion behavior of the galvanized steel, annealing treatments at 400°C for short time (30 min), and long time (4 h), were applied on the galvanized samples (1 cm length). Figure 1 presents the TT diagram of the annealing process applied to the galvanized steel. Cross section of the polished sample was observed by Scanning Electron Microscopy (SEM) Bruker. Phases identification of galvanized steel by the X-ray diffraction (XRD) technique using a Bruker D8 machine. XRD patterns were scanned in a range of diffraction angles from 30° to 90° of 2 θ , using Copper (Cu K α) as X-ray source with a wavelength (λ) of 1.5406 Å.

The corrosion test consists of voltammeter cyclic technique by using Voltalab PGZ 402. The coated samples (1 cm length) were immersed in corrosive solution

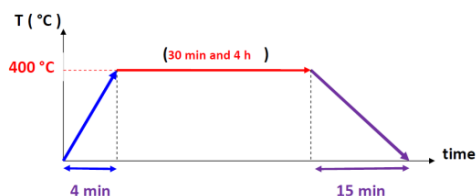


Figure 1. Annealing process applied to the galvanized steel

Table1. Chemical composition of low carbon steel

C	Si	Mg	P	S	Cr
0.090 %	0.220 %	0.370 %	0.005 %	0.009 %	0.02%

(20 ml) which contains 3.5 wt % NaCl. The range of applied potential was from -1.2 V to 1.3 V. The scan velocity is 50 mV/s, and the range of applied potential was from -1.2 V to 1.3 V.

Results and Discussion

Morphological Properties

Figure 2 shows the surface of the galvanized steel, without heat treatment (Figure 2(a)) and after isothermal heat treatment at 400°C for 30 min (Figure 2(b)), and 4 h (Figure 2(c)). The average thickness o

f the deposited layer is 20 μm . A typical morphology of the coating is observed in the non heat treated of the galvanized steel (Figure 2(a)), because the overlay layer is made up of dendrites of pure zinc eta (η) phase and appears as a polycrystalline structure (Marder, 2000). Applying isothermal heat treatment at 400°C for 30 min (Figure 2(b)), did not reveals a significant change in the morphology of the deposited zinc. However, by prolonging the time of heat treatment until 4 h, many pores are formed in the deposited zinc.

Figure 3 presents the microstructure evolution of the galvanized coating during isothermal treatment at 400°C, for 30 min, and 4 h. The microstructure of the non heat treated galvanized steel (Figure 3(a)) tends to be more compact, and reveal a good adhesion of the Zn with the substrate, because the coating and substrate inter-penetrates in the rough surface zone. The deposited zinc on substrate is formed with three sublayers: the thin outer layer Eta, followed by thick sublayer Zeta

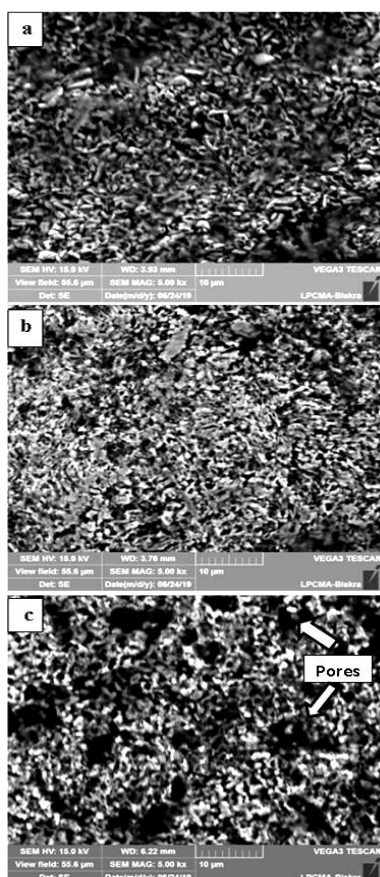


Figure 2. SEM observations of the surface of the galvanized steel; without heat treatment (a), and after isothermal heat treatment at 400°C for 30 min b) and 4 h c)

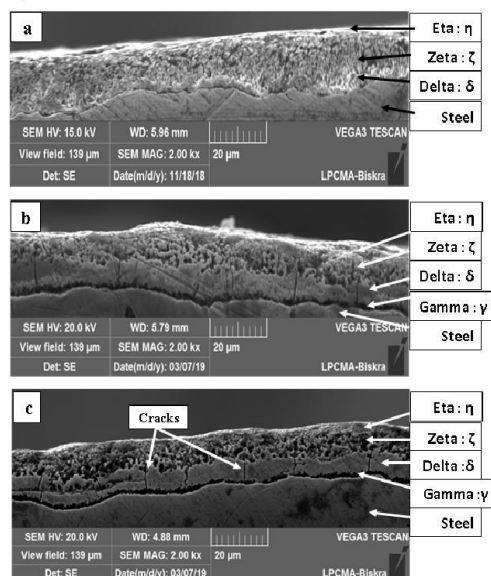


Figure 3. Cross section observations by SEM of the galvanized steel; without heat treatment a), and after isothermal heat treatment at 400°C for 30 min b), and 4 h c)

which grows in a columnar morphology, and thin and not homogeneous Delta. A columnar morphology of the sublayer Zeta is its main characteristic. This morphology was a result of a preferred growth perpendicular to the interface. It was reported that the zinc coating by the hot-dip zinc galvanized process is an interdiffusion between the zinc and carbon steel, forming several intermetallic phases (γ , δ , ζ), with the last one (η) consisting of practically pure zinc (Mainier *et al.*, 2019).

Concerning the microstructural evolution of the galvanized coating at 400°C compared to non heat treated sample (Figure 3(a)), the fourth sublayer Gamma occurred between Delta and substrate (steel) (Figure 3(b)). This transformation is due to the continuity of the interdiffusion reaction between the zinc and carbon steel at 400°C. It has been found that, when the coating is heat treated at higher temperatures, δ phase by diffusion mechanism grows towards the surface of the coating consuming δ layer Fe-Zn/steel diffusion couple, allowing for the continued growth of Γ phase at the expense of the δ layer (Marder, 2000). The prolonging of the annealing time (4 h) leads to the formation of coarsened pores in the sublayer Zeta (Figure 3(c)) than annealed sample for short time 30 min (Figure 3(b)). The pore size increases twice compared to previous treatment (from 1 to 2 μm approximately).

In addition, some cracks were observed in sub-layer Delta (Figures 3(b) and (c)). The occurrence of this kind of defect in this sub-layer is due to its mechanical characteristic. Azadeh and Toroghinejad (2009), studied the effect of heat treatment on formability of hot-dip galvanized low carbon steel sheet. They observed cracks in coating layers for samples heat treated at 520°C for 135 s. According to Sharifi (2014), Zinc coating is formed by the heterogeneous assembly of the Γ , Γ_1 , δ , ζ and η phases whose mechanical properties greatly differ from each other. Thermal strains resulting from large differences between thermal expansion coefficients are partially relaxed by the formation of a crack network. Janik *et al.* (2015) observed cracks in the coating of Zn deposited on 22MnB5 steels

after annealing at 600°C for a short time (600 s). These cracks do not penetrate into the substrate. The mechanism of cracking in Zn coated steel is result of different coefficient of thermal expansion of the coating and the substrate. As confirmed by Sharifi (2014), due to the differences in the thermal expansion coefficients of the coating and the substrate, complex re-residual thermal stresses were developed in the coating.

However, the main positive feature of the deposited zinc is there was not decohesion of the coating from the substrate after applying this heat treatment.

X-Rays Diffraction Analysis

Figure 4 presents the diffractograms of X-ray diffraction of the galvanized steel and after isothermal heat treatment at 400°C, during 30 min, and 4 h. The diffractogram of the non heat treated galvanized steel reveals the following phases in deposited zinc: Eta (η : Zn), Zeta (ζ : FeZn₁₃), and Delta (δ : FeZn₇), (Figure 4(a)). However, the peak of Gamma

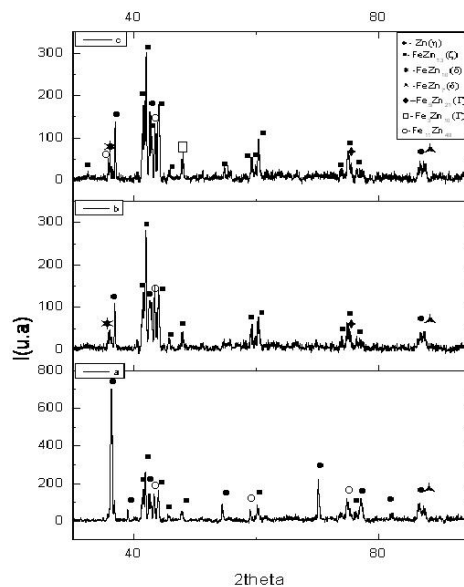


Figure 4. XRD diffractograms of the galvanized steel; without heat treatment a), and after isothermal heat treatment at 400°C for 30 min b) and 4 h c)

(Γ - $\text{Fe}_3\text{Zn}_{10}$) phase corresponding to the sublayer Gamma is revealed in diffractogram of the annealed galvanized steel at 400°C for 30 min. The prolonging of the annealing time reveals more additional peaks with the variation in intensity of some peaks (Figures 4(b) and 4(c)). These phases are; Eta (η : Zn), Zeta (ζ : FeZn_{13}), Delta (δ : FeZn_7), Gamma (Γ - $\text{Fe}_3\text{Zn}_{10}$), FeZn_{10} , $\text{Fe}_5\text{Zn}_{21}$, and $\text{Fe}_{11}\text{Zn}_{40}$.

Corrosion Test

The polarization curve gives important information on the kinetics of anodic and cathodic reactions. The polarization curves of steel and galvanized steel immersed in 3.5 wt % NaCl solution and heat treated at 400°C for 30 min and 4 h are presented in Figure 5. The polarization curves relating to the galvanized low carbon steel before and heat treatment at 400°C show a significant displacement of the corrosion potential towards the more negative values. This is related to the presence of Zinc

on the surface, i.e., this coating reduces the corrosion rate of steel in chloride solutions. The zinc gives galvanic protection to steel, playing the role of anode in the zinc-iron (steel) pair, as its electrochemical potential is more negative than the potential of iron (Angel *et al.*, 2015). The protection obtained by zinc coating is attributed to barrier and galvanic double protective effect (Sun *et al.*, 2013). It has been reported that the Zn protective coating structure consists of intermetallic Fe-Zn compound layers, which have been identified as Γ , δ , ζ , and η outer layers highly rich in Zn (ASM Handbook, 1992).

However, the corrosion potential of the heat treated galvanized steel shifted slightly towards the positive values, i.e., from -1.03V to -0.86V (Table 2). This corrosion behavior is due to the dissolution of zinc in the corrosive environment. This dissolution can be attributed to the microstructural and morphological change of the deposited zinc during isothermal treatment at 400°C , such as the occurrence of pores and cracks. For heat treated at $t = 4\text{h}$ of the galvanized steel, the value of the corrosion potential increases to -0.86 V which corresponds to a potential short circuit $E_{\text{Zn/Fe}}$ intermediate between that of zinc and steel. However, this value is very close to that of the zinc than the steel. The heat treated galvanized steel is still protected.

In addition, the low corrosion current is measured in galvanized steel without heat treatment ($7.62 \mu\text{A}/\text{cm}^2$) (Table 2), which more higher than measured in steel sample. However, by applying a heat treatment on the galvanized steel, the current corrosion increases which indicate the dissolution of zinc in the corrosive environment. The dissolution reaction of the zinc leads to the appearance of small iron surfaces, which consequently shifts the

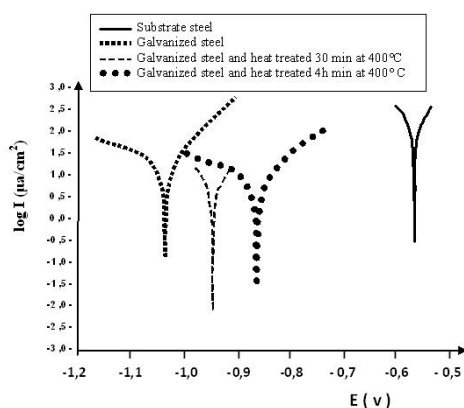


Figure 5. Polarization curves of low carbon steel (substrate), galvanized steel, and galvanized steel and heat treated at 400°C for 30 min and 4 h

Table 2. Values of corrosion current and corrosion potential after corrosion tests on substrate, galvanized steel

Material	$I_c(\mu\text{A}/\text{cm}^2)$	$E_c(\text{V})$
Substrate (Steel)	63.91	-0.56
Galvanized steel	7.62	-1.03
Galvanized steel and heat treated at 400°C for 30 min	16.42	-0.94
Galvanized steel and heat treated at 400°C for 4 h	12.51	-0.86

potential of zinc to an $E_{Zn/Fe}$ short circuit potential. Based on the microstructural observation, the pores (Figure 2(c)), and cracks (Figures 3(b) and 3(c)) are preferential sites for the penetration of the corrosive solution which accelerate the oxydation of the deposited zinc. It has been found that a porous zinc oxide superficial layer forms on the surface by a mechanism of dissolution/precipitation, leading to preferential corrosion pathways across the high porosity areas, which accounts for the linear corrosion rate (Goodwin, 1990).

Conclusions

The effect of heat treatment at 400°C on microstructural evolution and corrosion resistance of galvanized low carbon steel was studied. The non heat treated galvanized steel has a compact and a good adhesion of the deposited Zn with the substrate, because the coating and substrate inter-penetrated in the rough surface zone, which increased its corrosion resistance. The X-ray diffraction technique detected some non observable phases in the deposited zinc. The main sub-layers (Eta, Zeta, Delta and Gamma) were observed in heat treated deposited zinc, with the occurrence of some cracks and pores which contribute to the decreases of the corrosion resistance of the galvanized steel. The pore size increases twice compared to previous treatment. The main positive feature of the deposited zinc is there was not decohesion of the coating from the substrate after applying this heat treatment. For any industrial application, the exposure of the galvanized steel to such severe environment gives an idea about its corrosion resistance.

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