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Effect of the delta phase in crack initiation in the deposited zinc

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Abstract

This work reports on the results of a study of dynamic stresses on hot dip galvanizing steel substrates. Galvanizing was performed using molten zinc containing 0.43% Pb, 0.25% Al and 0.03% Fe. Dynamic bend-fatigue tests involved deformation 1.8 mm at a cyclic frequency of 25 Hz. The crack in deposited zinc started after 2000 cycles. The propagation of cracks seemed to depend on the morphology and the kinetics growth of zinc coating during the galvanizing process. Cracks appeared to initiate at the grain boundaries. The brittle characteristics of the grain boundaries may be due to the chemical segregation of impurities.

1. Introduction

The use of zinc coated steels for automotive, construction and appliance applications has increased continually at a greater rate than the overall growth in steel industry during the last decade of the twentieth century [1-2]. In hot dip galvanizing, a zinc coating is applied to the fabricated iron or steel material by immersing it in a bath consisting primarily of molten zinc. During hot dip galvanizing, even a very short time contact between steel and liquid zinc leads to the formation of Fe-Zn intermetallics at the coating-substrate interface [1]. Though these intermetallics provide a high degree of bonding between the substrate steel and the zinc outer coating, they are hard and brittle. Formation of various intermetallics during galvanizing depends on several process parameters, including temperature, dipping time, withdrawal speed, steel grade, and composition of the bath [1-4]. Understanding the effect of these process parameters on the physical and chemical nature of the coating layer formed is important to develop the correct alloy layers on the strip surface. In several applications, the galvanized steel is not only exposed to corrosive atmospheres but must also tolerate vibrations and cyclical stresses that can limit its useful life [5-7]. Unfortunately, Galvanized coatings under applied loads are susceptible to crack propagation and interfacial delamination [8-14]. Tzimas et al. [9] demonstrated that micro cracks are formed in the δ layer by tensile residual stress, and they act as nucleation sites for cracks that advance normally to the coating interface. Ploypech et al. [10] showed that similar fracture behaviour is observed for steels galvanized at 450°C where, under bending, cracks in the galvanized layers gradually advance from the δ layer to the ξ layer. Carlos Camurri P. et al. [7] reported the results of a study of the effect of static and dynamic stresses on hot dip galvanized coatings on SAE 1020 steel substrates. Galvanizing was performed using baths maintained at 450°C, and the coating alloy mixed as follows: 0.16% Ti and 0.02% Fe and with Al and Ni in the ranges 0-0.2% and 0-0.3%. Static three – point bend tests were conducted with applied stresses in the range of 428 to 90 MPa. Dynamic bend – fatigue tests involved stresses in the range of 228 to 78 MPa at a cyclic frequency of 0.25 Hz for up to 700 cycles. The total crack density in the coatings was measured before and after the test. The crack density increased as the applied stress increased and crack propagation was promoted perpendicular to the substrate. The best bath composition for preventing fatigue crack propagation was one that minimized the formation of thinner brittle layers in the galvanized coatings [7]. Examples of such situations included the galvanized support beams used in wharves and, bus structures in public transport. The paper aims to study the cyclic stresses were applied by means of three-point bend tests. The galvanized coatings were characterized after testing, the focus being on the initiation and the orientation of crack.

2. Experimental details

The galvanizing tests were conducted into a furnace operating with Special High Grade (SHG) 99.99% of zinc. The molten zinc was contained in a low carbon steel kettle heated by an electric resistance. The control of the temperature was monitored by a K-type thermocouple and a digital temperature regulator. The immersion of the sample in the bath was guaranteed by a pneumatic jack which controls both the duration of immersion and the withdrawal speed (figure 1).

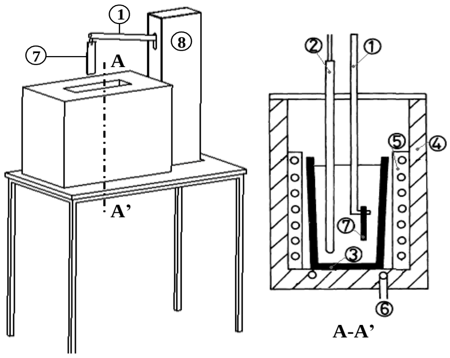


Figure 1: Experimental apparatus, 1 sample support, 2 K type thermocouple, 3 kettle, 4 refractory brick, 5 electric resistances, 6 current supply, 7 sample, 8 pneumatic jack.

The experiments were carried out using steel samples prepared by cutting thin rectangular slices (20 x 100 mm) of about 2 mm in thickness. The composition of the steel is given in table 1.

Table 1: Chemical composition of the steel (wt. %).

C	Si	P	Mn	S	W	Cr	Fe
0.120	0.019	0.004	0.376	0.010	0.011	0.006	Bal.

The composition of molten zinc is given in table 2. Prior to galvanizing, the steel samples were initially prepared in the appropriate solutions.

Table 2: Chemical composition of the zinc bath (wt.%).

Pb	Al	Fe	Zn
0.430	0.250	0.030	Bal.

The samples were degreased with a 15% NaOH solution, rinsed with water and then pickled for 30 min with a 16 % HCl solution containing 3 g/l of hexamethylenetetramine ($C_6H_{12}N_4$) as inhibitor. They were pre-fluxed at room temperature in a solution containing 550 g/l of $ZnCl_2 \cdot 2NH_4Cl$, then dried in an oven at 120 °C for 15 min. Finally, they were dipped into the galvanizing bath, and then quenched immediately in water upon removal from the bath in order to preserve the structure existing at the end of the galvanizing reaction.

The experimental setup developed for testing fatigue performance of materials is presented in figure 2. The machine is available at the laboratory of the electromechanical systems (LASEM), the unit of physical mechanical materials (UPMM), in the National Engineering School of Sfax Tunisia (ENIS). It consists of an engine shaft, an eccentric, a connecting rod slide, a strength sensor, Adjustable jaws, a panne, internal supports, a plateau, and an adjustable plateau. The specimen is secured against lateral movement by the panne. Due to this design, one oscillation per revolution is applied to the panne and consequently forced onto the specimen. The oscillation frequency is 25 Hz. The maximum applied force depends on the specimen's materials bending stiffness. A software was developed to control the cycle number, the applied strain and the deformation. The yield stress of the examined galvanized steel was 480 MPa. Furthermore,   the choice of the stress in dynamic tests must not exceed 70% of the yield stress [15]. In this study 70% of the elastic zone corresponded to 1.8 mm. therefore, during dynamic bending test, the inner radius of specimen was regulated at this value. The tests were conducted at room temperature and the laboratory atmospheric pressure. The control was conducted after every 100 cycles. For the examination of the microstructure, cross-sections from the galvanized samples were mounted in bakelite and polished down to 200 Å alumina emulsion. The specimens were etched in a 2% Nital solution and observations were made by using optical microscopy and the scanning electron microscopy (SEM) associated with an EDS analyzer.

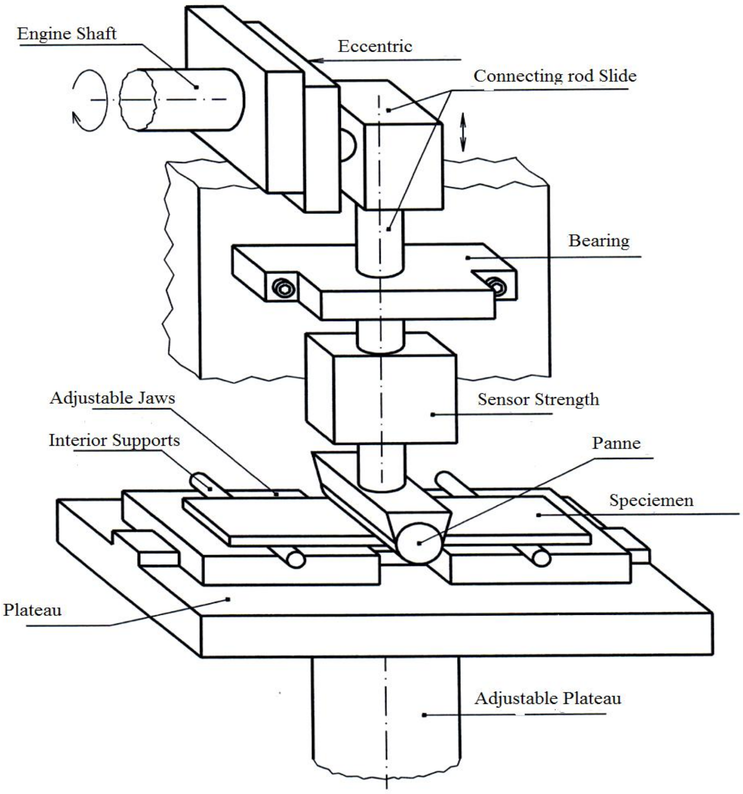


Figure 2: Experimental setup for fatigue testing.

3. Results and Discussion

In intermetallics layer Fe-Zn, fatigue cracks nucleate within a local region (figure 3) where a number of adjacent grains of nearly the same orientation have the slip characteristics of a single large grain. Indeed, G. Reumont et al. reported that cracks can initiate at grain boundaries characterized by brittle intermetallics due to the chemical impurities at the grain boundary [5]. The number cyclic not exceeds 2900 for this specimen, shown figure 3. It's clearly the cracks initiate in delta phase, in grain boundaries. The cracks initiate perpendicularly on substrate surface. After, the crack propagated along the intermetallics layer between substrate-coating interfaces. These findings suggest that the cracks are limited to the δ/ξ interface reaching the ξ phase. Hence, this study was in total agreement with Ploypech, Boonyongmaneer and Jearanaisilawong [10]. Furthermore we adopted their explanation of the observed phenomenon by the existence of a relatively high adherence between each of the two phases [10]. The differ structural of the Fe-Zn layers obtained during the galvanizing, along with the diversity in their mechanical properties can acts as crack nucleation sites contributing to subsequent crack propagation and delimitation of the coating. As a consequence of the thermal expansion coefficient (table 3) mismatch between intermetallics and iron substrates results in the creation small cracks in delta phase during cooling [1].

Table 3: Mechanical characteristics of Fe-Zn phases [5].

Fe-zn Phase	***Micro hardness under 0.25 N(VHN)***	***Young's Modulus (GPa)***	***Linear expansion coefficient ($10^{-6}K^{-1}$)***
Fe	150	210	11.30
Γ	-	134	-
δ	285	140	21.78
ξ	112	117	23
η	70	75	29.3

A galvanized component thus contains a pre-existing crack network which leads to the consideration of whether the reliability of the component is affected or not. The typical morphology of a galvanized steel coating can be seen in figure 4. This figure shows that thickness of brittle phase (δ + ξ) to almost equal 58 um for an immersion time 1 min (figure 4.a), increase roughly 72 um when the immersion time was increase to 2 min (figure 4.b). Then it continued to rise reaching 76 um at the immersion time 3 min (figure 4.c).The detailed characteristic phases present are shown in tables 4a, 4b, and 4c. The η phase would correspond to almost pure zinc. This phase was located over the intermetallic compounds ξ and δ whose formulae were respectively, $FeZn_{13}$ (94%Zn) and $FeZn_7$ (88% to 93%Zn). Both compounds had columnar structure and are brittle. Finally, in intimate contact with the steel, there is a very thin brittle phase, Γ($FeZn_3$).

Table 4a: Results of the EDS analysis of the phases composing the coating of Fig.4(a).

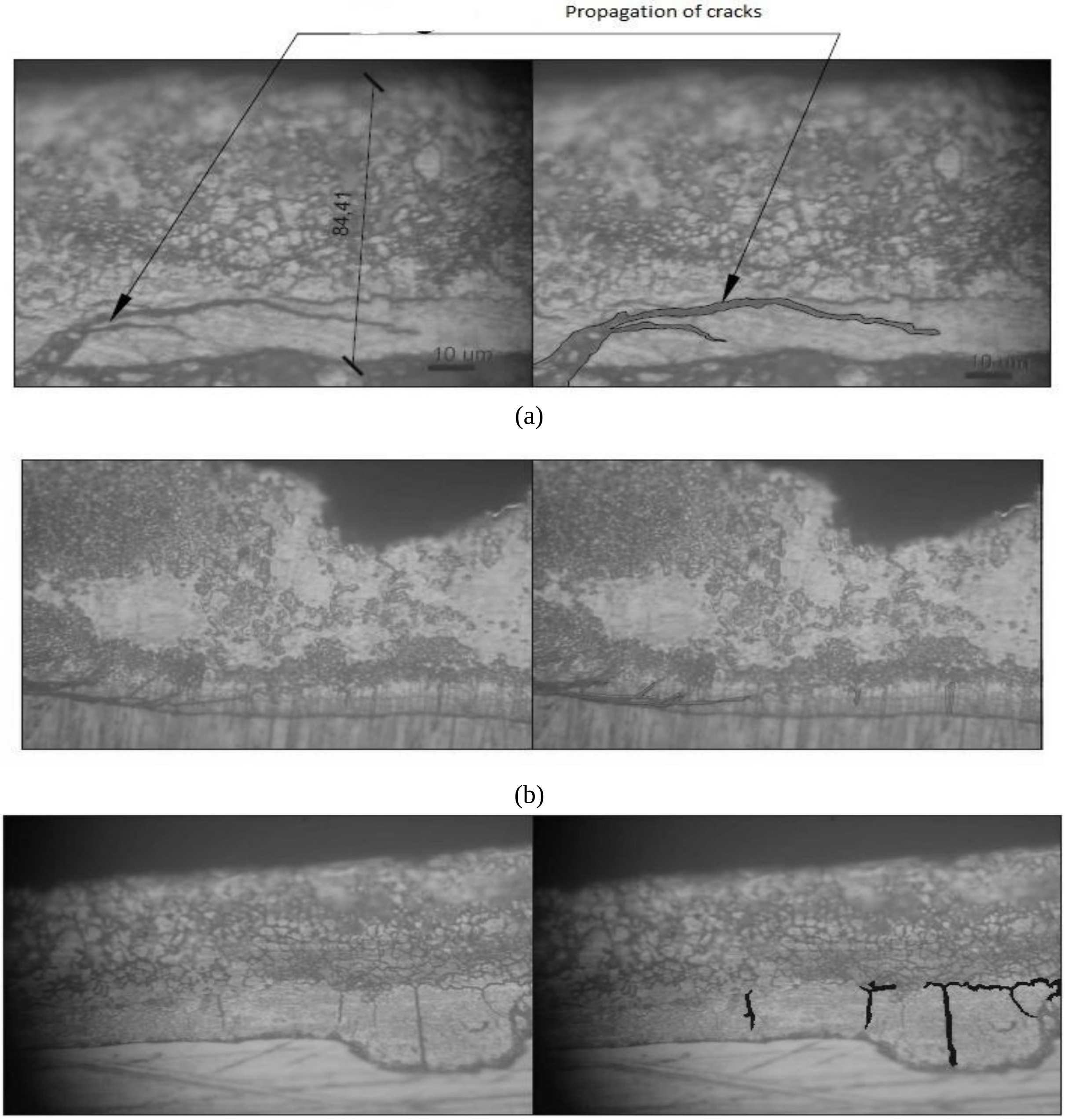
Point in fig.a.	Fe (wt%)	Zn (wt%)	Phas	Thickness (µm)
1	17.865	82.135	Gamma	2
2	11.729	87.981	Delta	10
3	5.523	94.477	Zeta	48
4	0.100	99.900	Eta	24
			Total thickness (µm)	84

Table 4b: Results of the EDS analysis of the phases composing the coating of Fig.4(b)

Point in fig. b	Fe (wt%)	Zn (wt%)	Phase	Thickness (µm)
1	26.473	73.527	Gamma	2
2	10.913	89.087	Delta	14
3	6.120	93.880	Zeta	58
4	0.050	99.950	Eta	40
			Total thickness (µm)	114

Table 4c: Results of the EDS analysis of the phases composing the coating of Fig.4(c).

Point in fig.c.	Fe (wt%)	Zn (wt%)	Phase	Thickness (µm)
1	17.850	82.150	Gamma	2
2	10.542	89.458	Delta	16
3	4.990	95.010	Zeta	60
4	0.040	99.960	Eta	61
			Total thickness (µm)	139



(a)

(b)

(c)

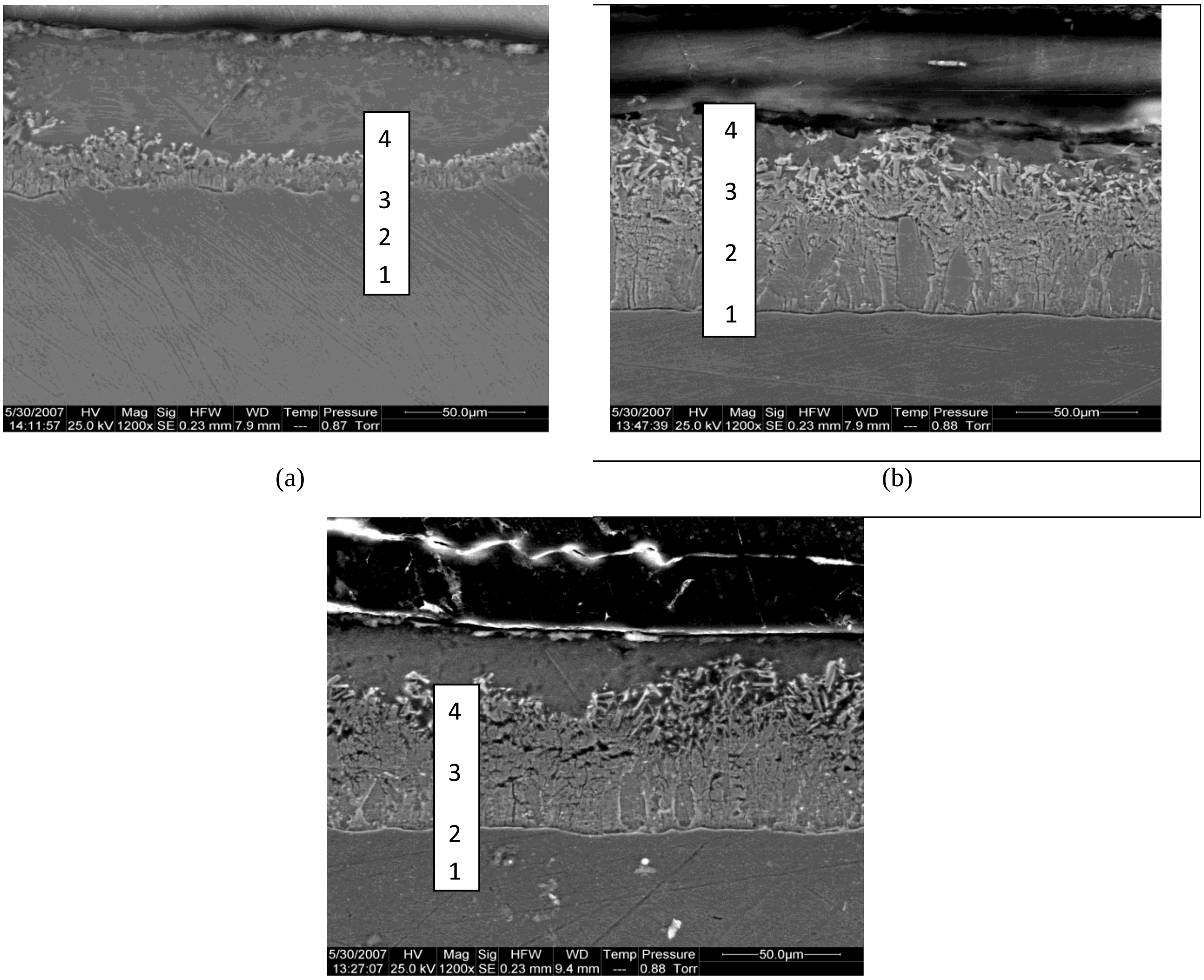
Figure 3: Light optical micrograph of galvanized coating after appearance of cracks.

The number of cycles, given in table 5, depends on the thickness of brittle phases (δ and ξ). However, the minimum total thickness obtained in condition (a), where the temperature of liquid zinc was 450 °C, the immersion time was 1 min and the withdrawal speed was 4 m/ min. The number of cycles was 2900.

Table 5: Effect of the layer thickness on the mechanical behavior of zinc coatings.

	Thickness of ξ+δ (µm)	Total thickness (µm)	Number of cycles
(a)	58	84	2900
(b)	72	114	2200
(c)	76	139	2100

The decrease in fatigue resistance appeared to be a consequence of the formation of cracks in the coating during fatigue cycling. However, it would be unlikely associated with the pre-existing crack network. The thickness of the coating and the differing morphologies of the phases in the coating were shown to have an important effect on the propagation of the cracks. It was concluded that the best physical parameters for preventing fatigue crack propagation is one that prolongation fatigue life of layers in the galvanized coatings. Within this perspective, it would be very beneficial to work on reducing the zinc layer so that the zinc consumption drops in the life expectancy of the coating increases.



(a) (b)

(c)

Figure 4: SEM micrograph of the coating obtained with different physical parameters, (a) 450°C, 1 min, 4m/min; (b) 450°C, 2 min, 4 m/min; (c) 450 °C, 3 min, 4 m/min.

Conclusion

The present study aimed at investigating fatigue of the intermetallic layer and crack behavior in galvanized steel. Cracks seemed to initiate in the delta phase, at the grain boundaries. The employed galvanizing process parameters resulted in the formation of thinner brittle layers in the galvanized coatings, which would imply lesser consumption of zinc layer. Finally, this study was another attempt to reach the optimum conditions of the galvanization process.

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