



Study the Effect of Immersion Time and Zinc Bath Temperature on Coating Thickness and Generated Phases in Hot Dip Galvanizing

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Abstract: In this paper, hot dip galvanizing (HDG) process was studied to understand the growth and generation phases between Iron and zinc and the changes or behavior in zinc coating thickness at different immersion time and zinc bath temperature. Hot dip galvanizing specimens prepared at temperatures in range of (450 to 650)°C in steps of 50°C and at different immersion time. The specimens were examined by using optical microscopy and scanning electron microscopy/energy dispersion spectroscopy.

Keywords: Hot dip galvanizing, coating thickness, galvanizing temperatures, Electron microscopy, zinc coating

I. Introduction

Hot-dip galvanizing is known as the real technique used to apply zinc coating on steel to give protection security against corrosion [1]. During hot dip galvanization, the steel substrate is totally submerged in a bath comprising of at least 99 % pure liquid zinc. The bath temperature is kept up at around 450°C. The zinc metal then reacts with the iron on the steel surface to shape a zinc/iron intermetallic alloy. The articles are withdrawn slowly from the galvanizing bath and the overplus zinc is removed by draining, vibrating or centrifuging. The articles are cooled in air instantly after withdrawal from the bath [2]. Can be recognizing two kinds of processes: continuous and batch processes. The continuous galvanizing process includes the application of zinc onto steel sheets, wires and tubes by passing them consistently through a bath of molten zinc at high speeds, while the batch galvanizing process includes the use of a zinc coating to the surface of steel parts after they have been manufactured [3]. This technique has been adopted as a well proven feasible process since 1800 soon after the exploration of iron and zinc. The exploration of the process was attempted in 1742 when a French Chemist Melouin presented a paper on hot dip galvanizing, and the process received commercial momentum with patents mainly in the 1830's [4]. Hot dip galvanized steel has been widely utilized as a part of industrial fields such as automobiles, electrical home appliances or construction due to their excellent corrosion resistance characteristics [2]. Dirt, oils, lubricants, greases, and different polluting influences, as well as normal oxidation products such as mill scale or rust, may be deposited on the steel during fabrication, transportation, or storage. These impurities must be removed so that iron and zinc may intermix to form the galvanized coating [5]. These surface contaminants are normally removed to be galvanized by cleaned, pickled and fluxed prior to immersion. The part is first degreased usually in an alkali solution. Oils, greases, and other compounds are removed in this step, followed by rinsing in water are performed primarily to ensure that acid and iron contaminants carried from the pickling bath with the work are prevented from adversely impacting the fluxing and galvanizing operations [6], pickling to remove adhering mill scale, rust and oxide films on the surface of the article by immersion in either in hydrochloric or sulfuric acid, and rinsing in water [7]. The last step in the surface preparation is an immersion in flux solutions to dissolve any oxide films formed on the steel after pickling but before galvanizing and to ensure that a clean metal surface contacts the molten zinc. Flux solution consists of zinc chloride and ammonium fluoride [5]. Many factors affecting the product quality such as bath temperature, immersion time, bath composition, withdrawal speed [8]. A hot-dip galvanized coating consists of a series of layers. Beginning from the steel surface, each layer is an iron-zinc alloy with increasingly lower iron substance [9]. These phases are: Gamma (Γ) phase has an iron composition range of 23.5±28.0 wt. % content at 450°C. In the basic crystal lattice the Γ phase is very similar to the structure α (Fe) (both crystallizing in bcc), Gamma1 (Γ_1) phase, has a face centered cubic lattice structure with an iron of 17±19.5 wt. % content at 450°C, Delta (δ) phase, the delta phase has iron content range of 7 ± 11.5 wt % and a hexagonal unit cell, Zeta (ζ) phase has an iron content of approximately 5±6 wt., Eta (η) phase the outer phase being a zinc-rich solid solution with approximately 0.04% iron. Zinc crystallizes hexagonal system (hcp) [10].

II. Experimental procedure:

The work includes preparing specimens to test the galvanizing thickness and the metallurgical phases across the zinc layer with various dipping time and bath temperature. So, seven periods of immersion time selected (0.5 , 1 , 2 , 5 , 10 , 15 and 20 minutes) and the bath temperatures were (450 , 500 , 550 , 600 and 650°C). Therefore the total number of samples were (35) specimens made of low carbon steel with chemical analysis shown in Table (1). The dimensions of each specimen were (1.5 X 20 X 80 mm) and there is an alumina crucible used to contain the molten zinc with a purity of (99.99999).

Table (1) chemical analysis of steel specimens and standards steel C1004.

Name	C	Cr	Cu	Mn	Ni	P	S	Si
Tested sheets	0.06 max			0.25 max		0.04 max	0.04 max	0.35 max
C1004	0.047	0.0153	0.032	0.199	0.0104	0.013		0.0175

The process of galvanizing achieved by heating the crucible to required temperature and immersion time the specimen inside molten zinc waiting for a specific time then the specimen pullout. Where the immersion levels in zinc bath was 60 mm for all specimens also, before galvanizing process the specimens degreased, pickled and fluxed with solution of ammonium fluoride and zinc chloride salts as fluxes to achieve good wet ability between steel surface and molten zinc. After complete the galvanizing process for specimens as shown in Figure (1) the thickness is measured



Figure (1) the specimens of steel after completed galvanizing process

Mounting the strip by acrylic epoxy then refine the section by grinding and polishing and finally etching by immersion in (5 mL HNO₃+100 mL H₂O) for 1 minute. This etched section tested using optical microscope as shown in Figure (2) the zinc layer measured directly

The phases generated across the zinc layer estimated by test the sections by TESCAN (VEGA3-LMU) scanning electron microscope and the micro chemical analysis done using Oxford (MAX3) Energy-dispersive X-ray spectroscopy detector.

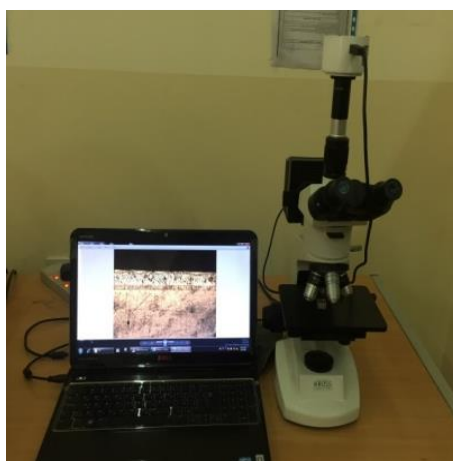


Figure (2) optical microscope used to measured zinc layer thickness

III. Results and discussion

The results of galvanizing specimens were tabulated in table (2) which represents the thickness of all 35 specimens with different times and temperatures.

Table (2) galvanizing layers thickness for different immersion times and molten zinc bath temperatures.

Bath Temp. °C	450	500	550	600	650	Average
Time (min.)	Thickness (μm)					
0.5	103.3	28.2	75.2	47.7	57.6	62.4
1	77.8	28.2	103.0	50.0	83.9	68.6
2	61.8	81.7	121.0	56.1	95.1	83.1
5	93.3	105.7	123.3	59.1	43.1	84.9
10	108.9	192.7	188.1	74.4	33.6	119.6
15	161.0	196.1	215.2	52.7	30.9	131.2
20	176.9	266.5	286.3	43.9	28.2	160.4

Figure (3) represent and explain the thickness values tabulated in table (2). The average values of produced zinc layer thickness proportional directly with immersion time in zinc bath and the relation formula can be fitted as forth order polynomial equation (equation 1) which gives most accurate curve fitting value.

$$T = 63.65 + 4.95t + 0.324t^2 - 0.043t^3 + 0.00133t^4 \dots\dots (1)$$

Where: T is thickness in micrometers, t is time in minutes

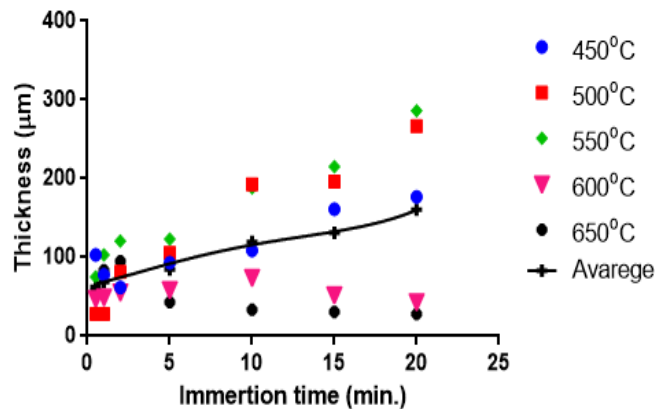


Figure (3) show the average zinc layer thickness for galvanizing process at different time (0.5 – 20 min) and molten zinc bath temperature (450-650°C).

In general, the thickness of produced zinc layer increased because the zinc diffusion becomes faster with longer immersion time and higher temperature. Where the minimum thickness values around 60 micrometer and the maximum was around 160 micrometer. But this thickness values represent the average values with different immersion time and bath temperature. To understand the given results of the produced thickness, the time and temperature must be specified. In figure (4) it can be seen there are a huge variation of layer thickness values for each bath temperature.

At bath temperature of 450°C the thickness of zinc layer behavior can be estimated that at very short immersion time the steel strip low temperature chill the attached molten zinc at dipping moment. Therefore the interaction between two metals changed from liquid-solid to solid-solid diffusion where there is minimal phases generated at time of 30 second and one minute from figure (5-a,b) the thickness can be calculated as 53 , 44 μm and the phase (Zeta 6%Fe) is generated with thickness of 2.7 , 3.72 μm.

Increasing dipping time to 2 minutes as in figure (5-c) shows generating a new phase (Delta 10%Fe) with average thickness of 4.3 μm where the Zeta phase continue to growth to a thickness of 24 μm. Those generated phases do not liquefy at 450°C, therefore they lead to add continues thickness to galvanized surface to the zinc pure layer. Thus, the total galvanized layer thickness at time of two minutes increased to 67 μm.

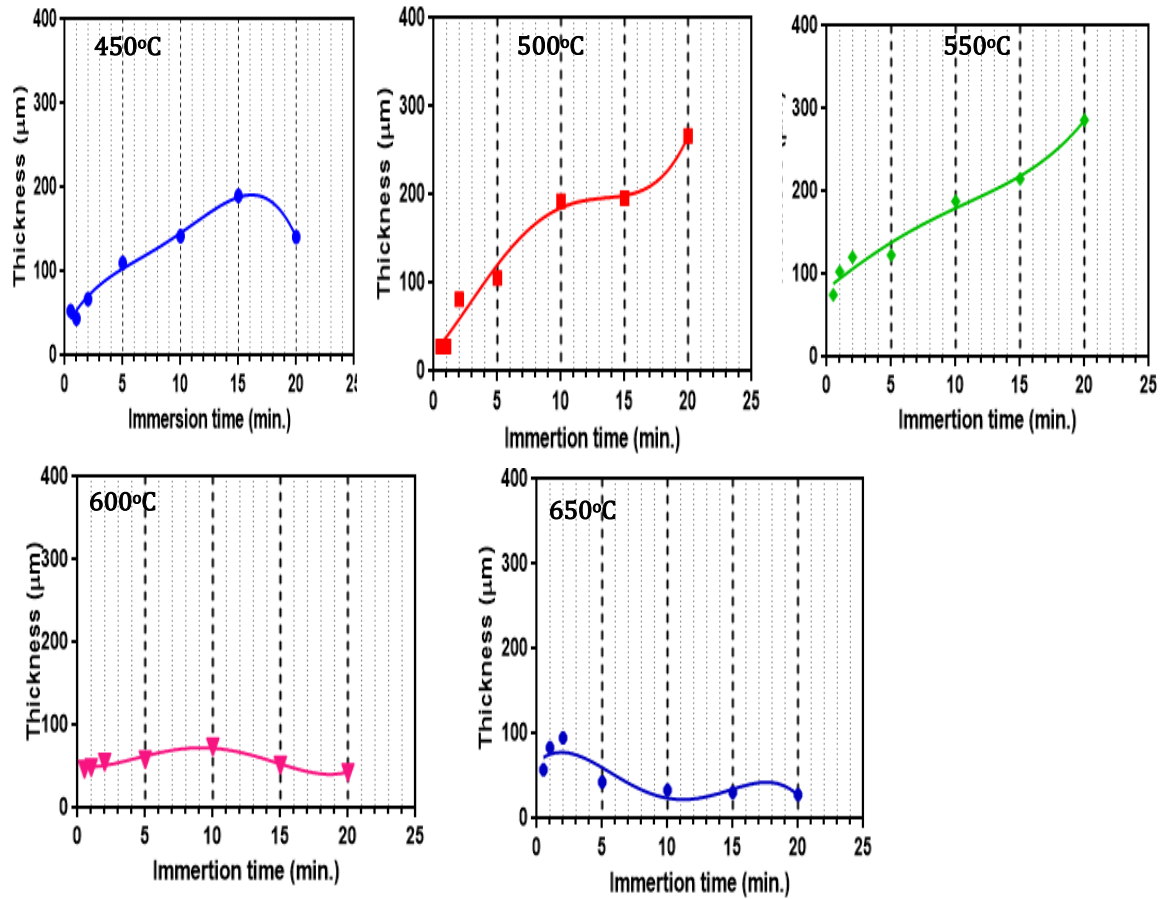


Figure (4) show Change in galvanized layer thickness with different dipping time and different temperatures.

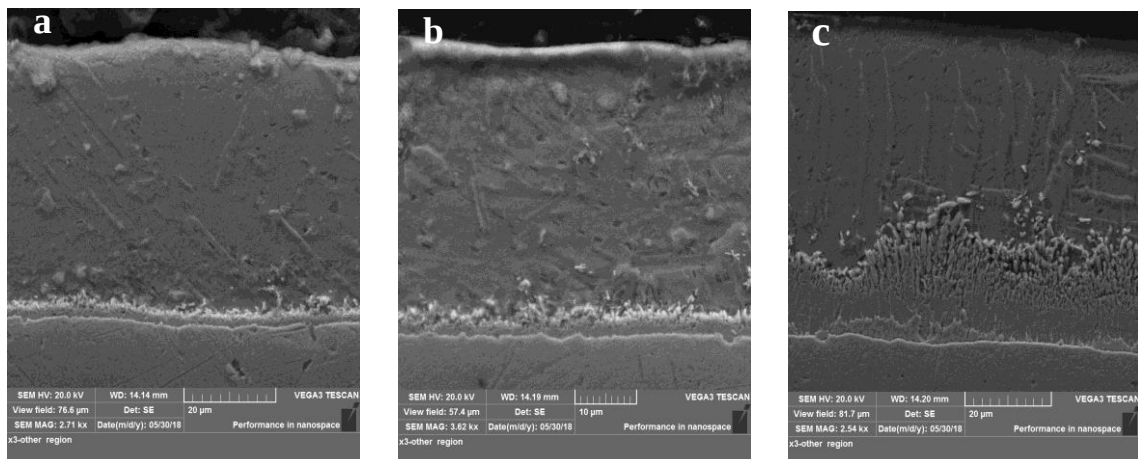


Figure (5) show SEM images for sectioned galvanized layer for specimens with different immersion times (0.5, 1, 2 minutes) at 450°C.

Beyond 5 minutes the thickness increased because the solidified chilled zinc layer will dissolved again due to equilibrium of steel strip temperature with surrounding molten zinc therefore the diffusion return to Liquid-solid and phases which will generate phases with faster manner which resist melting in 450°C as indicated in Fe-Zn phase equilibrium diagram.

Therefore the thickness of galvanized layer increased to 110 μm at dipping time of 5 minutes. Increasing dipping time lead to continuous diffusion in phases as Gamma, Delta and Zeta as shown in figure (6-b) where the dipping time was 10 minutes and here the phases separated clearly beginning with Gamma phase with thickness of 10 μm attached to steel surface followed by Delta phase with thickness of 10 micrometer and finally Zeta phases with thickness of 40 micrometer.

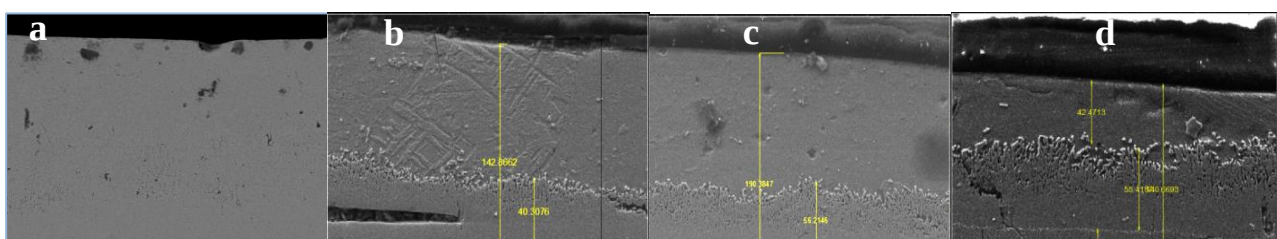


Figure (6) show SEM images for sectioned galvanized layers specimens with different immersions times (5, 10, 15 and 20 minutes) at 450°C.

Gamma phase is a weak to HNO_3 where it appear as space between Delta and Steel surface and it can be assure this space was Gamma phase as shown from the same joint but etched using NaOH with distilled water as shown in figure (7). Increasing dipping time to 15 minutes show thicker galvanized layer, where this thickness composed of 16 μm of Gamma layer, 22 μm of delta phase and 56 μm of Zeta phase followed by 90 μm of pure zinc and the total thickness of the coat layer was approximately 190 μm .

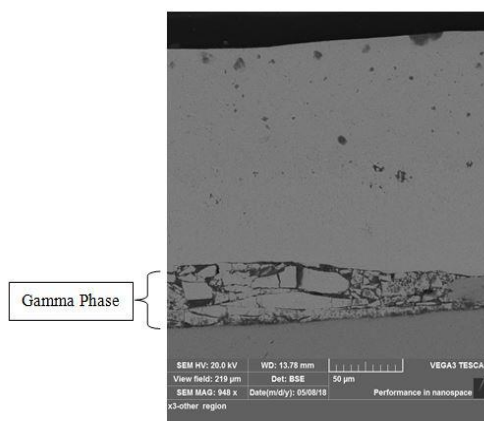


Figure (7) Gamma phase shown in bottom of galvanized layer using NaOH (10gram in 100ml distilled water)

Beyond dipping time of 15 minute the thickness of galvanized layer decreased to 140 μm where the thickness of the pure zinc layer thickness decreased to 50% from 90 μm at 15 minute where the thickness was 42 μm at 20 minutes of dipping time as shown in figure (6-d), and the other phases remain identical to dipping time of 15 minute.

By taking the mean values of galvanized layer thickness for different temperatures as shown in table (3). Increasing temperature to 500°C and 550°C gives similar behavior in layer thickness to galvanizing in 450°C but generally the resulted coating thickness is thicker than that founded in 450°C. The cause of that related to higher activity of diffusion for zinc in Iron lead to generate more phases which not dissolved in bath temperature and growth more than founded in 450°C.

Table (3) show averages zinc layer thickness for galvanized specimens with different immersion times.

Temp.°C	450	500	550	600	650
Thickness μm	106	128	159	55	53

But increasing temperatures to 600°C and 650°C lead to dramatically decrease in galvanized layer thickness about three times less than 500°C and 550°C and the reason for this related to the lower viscosity value at higher temperatures for molten zinc. Therefore, at withdrawal moment of steel strip from molten zinc bath the remaining melted zinc will drop to bath and a thin layer of pure zinc will coat the generated phases on the surface. The second reason lead to thinner coating layer at high temperature (600°C and above) that the generated phases will dissolved again in molten zinc as shown in figure (8) where the molten zinc will penetrate the phases at grain boundaries and finally will separate the phases grains which migrates far of surface toward molten zinc and dissolved there which cause decrease in bath zinc purity.

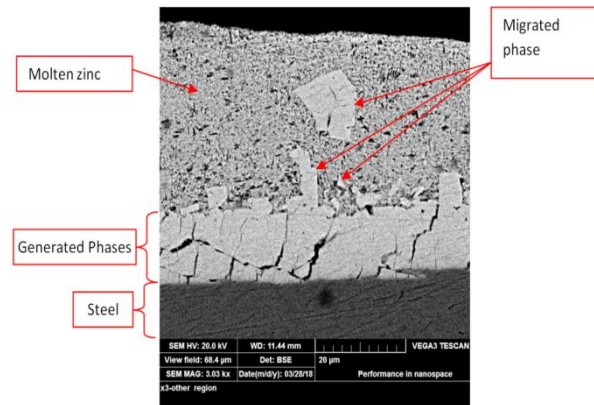


Figure (8) SEM (BSE) for galvanized steel strip at bath temperature of 650°C and immersion time of 15 minute.

IV. Conclusion

- In hot dip batch galvanizing process at low temperatures (450 to 550°C) increasing dip time lead to thick galvanizing layer.
- At 600°C and above for molten zinc bath, the thickness of galvanized layer decreased dramatically compared to low galvanizing temperature.
- In high galvanizing temperature increasing immersion time does not help in increasing coating thickness, but it may decrease coating layer due to dissolving generated phases and make most of coat layer compound of complex phases from Iron and zinc instead of pure zinc layer.

V. References

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