

Effect of Aluminum on Microstructure and Thickness of Galvanized Layers on Low Carbon silicon-Free Steel

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Abstract

In hot dip galvanizing, several parameters such as chemical composition of coating bath, immersion time and surface roughness of specimens could affect microstructure and properties of coating. In this article, the effect of aluminum content, immersion time and surface roughness on structure and properties of alloy layers have been investigated. Specimens of low carbon silicon-free steel with different surface roughness were galvanized in pure zinc bath and bath containing various amounts of aluminum for different times. It was found that the morphology of deposits was changed from layered to columnar state when 0.025wt%Al was added into coating bath. By increasing Al content up to 0.05wt%Al the adherence of the layers was improved but these thicknesses were decreased due to reduction of diffusion rate.

Keywords: Hot Dip Galvanizing, Aluminum, alloy layers.

1- Introduction

Hot dip galvanizing is a process by which an adherent, protective coating of zinc and zinc/iron compounds could be developed on the surfaces of iron and steel products. The protective coating usually consists of several layers. Various layers which are formed on substrate are composed of iron-zinc compounds. These, in turn, may be covered by an outer layer of zinc. Some properties of these layers are shown in Table 1¹⁾. As already indicated, these alloys show very poor ductility. They are very hard and brittle. When a sheet of such coated steel is deformed into various shapes, the probability of shear cracks developing will be high. This behavior seriously limits formability of the coated sheet²⁾.

The formation of reactive coating microstructures on Si-containing steel sheets has been a problem for galvanizers. Sandlin³⁾ was the first who reported that it was the silicon in steel that caused excessively galvanized coatings to be formed on steel samples. Foct et al.⁴⁻⁶⁾ have proposed that a thin layer of liquid zinc saturated with silicon on the steel surface cause the loose and over thick coating to be formed during galvanization. Hot dip galvanizing of reactive steels has been problematic because the presence of Si significantly increases the coating thickness and yields a gray appearance and a poor adherence^{7, 8)}. During the last decades, it has been established that,

depending on the steel geometries and composition, the growth of alloy layers may be controlled by both the chemical composition of the molten zinc and the physical operating parameters⁹⁻¹²⁾. On the one hand, it was shown that the addition of low amounts of certain elements such as Al¹¹⁻¹⁶⁾ can contribute to the problem resolution by inhibiting the zinc-steel reactivity.

On the other hand, it was found that besides the additives obtaining an acceptable product requires a suitable adjustment of physical parameters^{8, 9, 11, 12)}, in particular the immersion time^{12, 16)} which controls the thickness of the alloy layer.

In this article the effects of aluminum content, immersing time and surface roughness on formation and control of alloy layers have been investigated jointly, that over previous papers do not be in this manner. Sheets of low carbon silicon-free steel with different surface roughness were galvanized in pure zinc bath and bathes containing various amount of Al for different times.

2- Experimental procedures

Plates of UKSt37-2 steel with dimensions of 60×30×3 mm and the chemical composition that is listed in Table 2 were prepared. In order to prepare samples with different surface roughness, two different surface treatments were used. Some plates were sandpapered with different emery papers up to 600 grade and the remaining were sand blasted with Cr₂O₃.FeO particles of 0.5-2 mm at air pressure of 70 psi for 5 minutes. Prior to galvanizing, the plates were degreased in NaOH 60g/l at 60 °C for 10 minutes, rinsed with distilled water, and were deoxidized by using HCl 30 Vol% at an ambient temperature for 5 minutes and were finally rinsed with distilled water again. The plates were then

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immersed in an aqueous solution consisting of 50%wt ZnCl₂.2.5NH₄Cl at 70°C for about 10 minutes to activate the surface. The galvanized coatings were obtained by immersing the plates in zinc bath containing varied aluminum contents of 0, 0.025, 0.05 %wt. for 3, 5 and 10 minutes. In all cases the bath temperature was maintained at 450°C. The pure zinc bath was prepared by melting zinc ingot (99.99%wt.Zn). Baths with different aluminum content were prepared by adding predefined amounts of Zn-3.5%Al alloy in pure zinc bath. The bath composition was determined by spectroscopy method. The samples were characterized using optical microscope, scanning electron microscope (LEO 440i) and EDX (Oxford 7059). The effects of aluminum content, immersing time and surface roughness on structure and properties of alloy layers were investigated. The characteristics of various phases were identified using hardness values of alloy layers (Table1). The applied load of 10g has been used during hardness measurements by using a M400

G1 microharness testing machine.

3- Results

3-1- Galvanized coating in pure zinc bath

The structure of alloy layers, which were developed in pure zinc bath during 3, 5 and 10 minutes, is shown in Fig.1. As indicated, the total thickness of the galvanized coating was increased while that of the η layer was decreased with increasing immersing time. It is also shown that increasing immersion time causes the thickness of the ζ layer to increase first and decrease by further increasing immersing time. Increasing immersing time from 3 to 5 minutes has no significant effect on layer thickness, but increasing further from 5 to 10 minutes causes the thickness of the δ layer to increase (Table3).

The structure of deposited layer on sandblasted plate is shown in Fig.2. Comparing Fig.2 with Fig.1.a reveals that increasing the surface roughness of the plate causes the thickness of the coating to be considerably increased (Table3).

Table1. Properties of alloy layers of hot dip galvanized steels ¹⁾

Layer	Alloy	Iron wt%	Melting point °C	Crystal structure	Diamond pyramid microhardness	Alloy characteristics
Eta(η)	Zinc	0.03	419	Hexagonal	70-72	Soft, ductile
Zeta (ζ)	FeZn13	5.7-6.3	530	Monoclinic	175-185	Hard, brittle
Delta(δ)	FeZn7	7-11	530-670	Hexagonal	240-300	Ductile
Gamma(γ)	Fe Zn10	20-27	670-780	Cubic	Thin, hard, brittle
Steel	Iron	1510	Cubic	150-175	...

Table2. Chemical composition of steel plates (wt %)

%C	%Si	%Mn	%S	%P
0.085	0.003	0.47	0.01	0.01

Table3. Thickness and hardness of different galvanized layers

Bath	Immersion time (min)	η		ζ		δ		total Thickness (μm)
		Thickness (μm)	HV	Thickness (μm)	HV	Thickness (μm)	HV	
Pure Zn	3	25	70	10	178	20	268	50
	5	18	71	22	182	20	249	60
	10	10	70	10	180	40	270	65
Pure Zn after blasting	3	30	75	45	185	20	252	100
Zn-0.025wt%Al	3	8	72	-	184	-	280	65
	5	8	71	-	-	-	270	65
Zn-0.025wt%A l after blasting	3	8	-	-	180	-	290	100
Zn-0.05wt%Al	3	45	72	-	-	-	-	45
	5	-	72	-	181	-	-	70
	10	20	70	90	184	-	-	110
Zn-0.05wt%Al after blasting	3	60	71	50	181	-	-	110

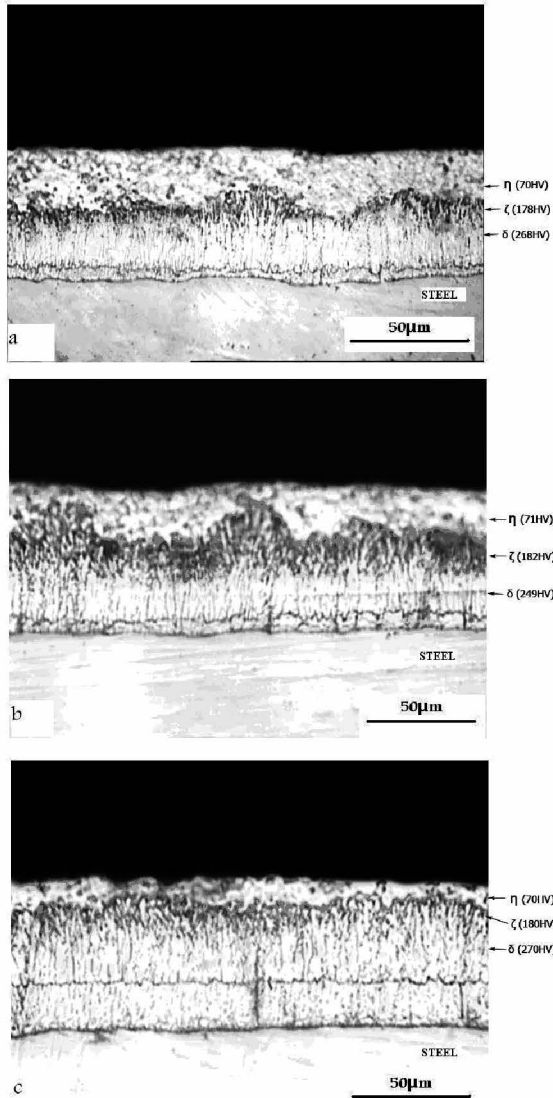


Fig.1. Structure of alloy layers developed in pure zinc bath after (a) 3 minutes (b) 5 minutes (c) 10 minutes.

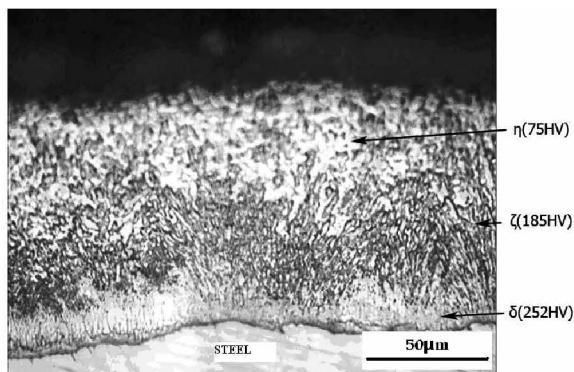


Fig.2. Structure of alloy layers developed in pure zinc bath after 3 minutes in sandblasted plate.

3-2- Galvanized coating in Zn-0.025wt%Al bath

The structure of galvanized coating developed in Zn-0.025wt%Al bath is shown in Fig.3. Comparing

Fig.3a with Fig.1a reveals that by adding 0.025%Al in pure zinc bath the morphology of alloy layers is changed from continuous to columnar structure and ζ phase is dispersed discontinuously between δ phase columns. By increasing immersing time to 5 minutes, the ζ phase is changed to δ phase and as a result the final structure of coating consists of only δ columns (Fig.3b).

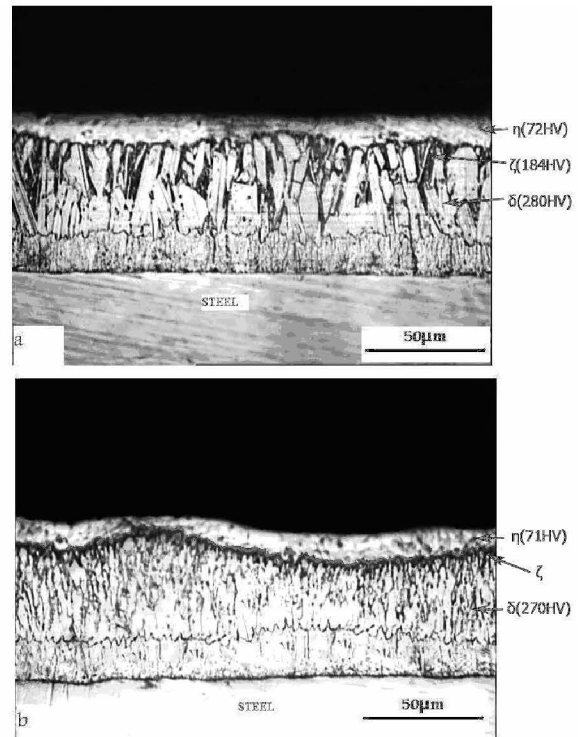


Fig.3. Structure of alloy layers developed in Zn-0.025wt%Al bath after (a) 3 minutes (b) 5 minutes.

The structure of galvanized coating on sandblasted plate in Zn-0.025wt%Al bath is shown in Fig.4, as indicated, sandblasting prior to galvanizing results in a columnar structure and in thicker layers (Table3).

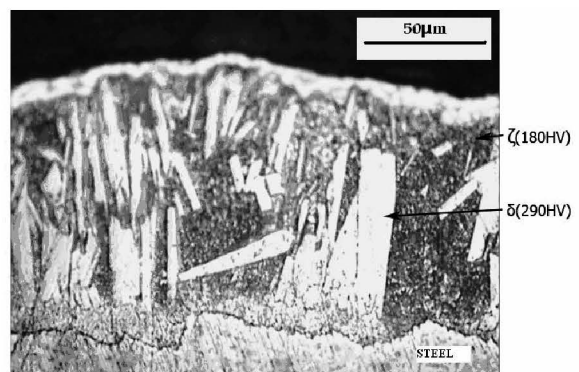


Fig.4. Structure of alloy layers developed in Zn-0.025wt%Al bath after 3 minute in sandblasted plate.

3-3 Galvanized coating in Zn-0.05wt%Al bath

The structure of alloy layers of galvanized coatings for different immersing times in Zn-0.05wt%Al bath are shown in Figs.5 and 6.

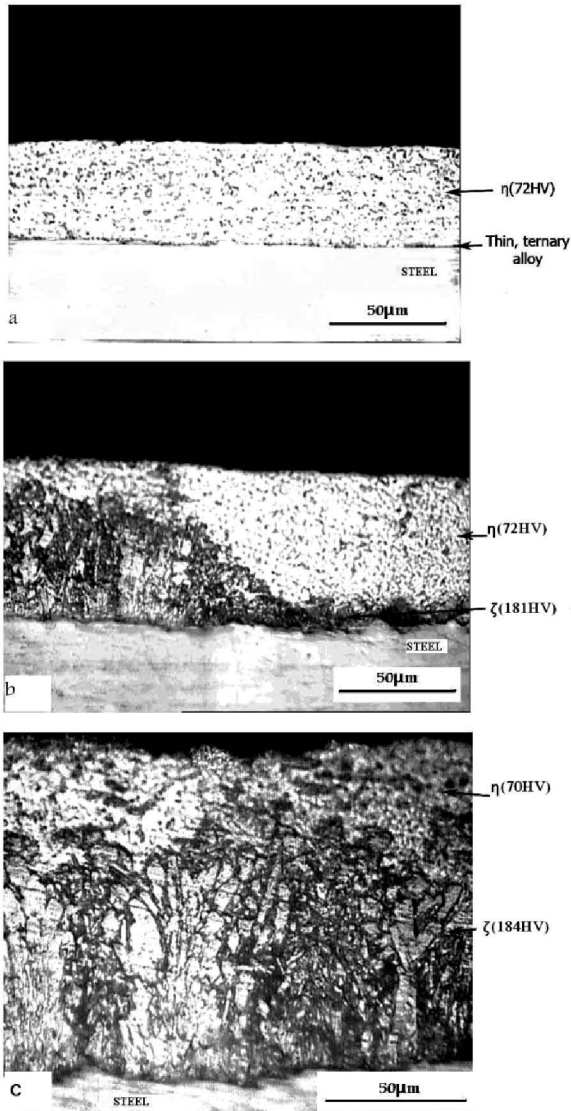


Fig.5. Structure of alloy layers developed in Zn-0.05wt%Al bath after (a) 3 minutes (b) 5 minutes (c) 10 minutes.

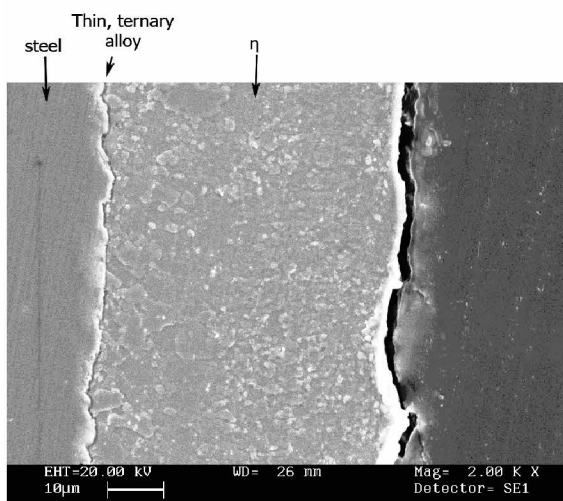


Fig.6. SEM micrograph obtained in Zn-0.05wt%Al bath after 3 minutes.

Increasing aluminum content of the coating bath to 0.05wt% has a significant effect on alloy layers structure as shown in Fig.6. As indicated, there way no sign of alloy layers when the plate was immersed into 0.05wt%Al containing bath for 3 minutes and coating was composed of η layer and a very thin layer between η layer and substrate. Chemical composition of later thin layer was determined as 35wt%Al, 35wt%Fe and 30wt%Zn using EDX method. Increasing immersing time from 3 to 5 minutes results in incomplete formation of ζ layer on substrate. This was completed and grown on all over the whole surface, when immersing time was further increased to 10 minutes.

The structure of galvanized coating on sandblast plate in Zn-0.05wt%Al bath for 3 minutes is shown in Fig.7. It is shown that alloy layers have grown on substrate.

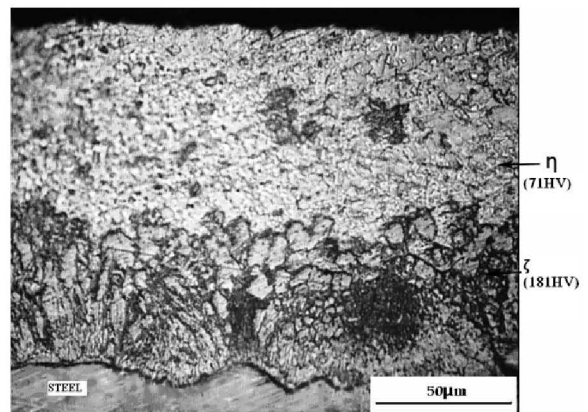


Fig.7. Structure of alloy layers developed in Zn-0.05wt%Al bath after 3 minutes in sandblasted plate.

4- Discussion

The results of Table 3 revealed that the total thickness of the galvanized coatings increases and that of the η layer decreases with time. During immersion time of plates in pure zinc bath for 3 minutes, diffusion between Fe and Zn atoms is negligible and as a result, the total thickness of the alloy layers which were developed on substrate is low. By increasing diffusion time for 5 minutes, the thickness of the ζ layer increases. This compact layer retards the diffusion between Fe and Zn atoms and subsequently the thickness of internal alloy layers remains constant. On the other hand, by further increasing immersion time for 10 minutes the thickness of the compact ζ layer decreases, and as a result, diffusion rate between Zn and Fe atoms is accelerated and therefore the thickness of internal alloy layers increases (Table3). Increasing surface roughness of plates causes the reaction area between Zn and Fe to increase and consequently the total thickness of the alloy layers increases (Table3). Addition of aluminum to the coating bath decreases the thickness of alloy layers. Aluminum has a greater affinity with iron than zinc, so immediately after immersing the steel into the coating bath, instead of a

zinc-iron compound an aluminum-iron intermetallic compound (Fe_2Al_3) forms within 0.15 second²⁾. This alloy (also known as a barrier or inhibition layer) is extremely thin and retards the zinc-iron reaction. By the time the strip leaves the bath (2-4 seconds later) some zinc is taken into this layer and changes its nature from which occurs in the absence of Zn to a ternary alloy which is very thin and is composed of approximately 45% Al, 35% Fe and 20-30% Zn ($\text{Fe}_2\text{Al}_{5-x}\text{Zn}_x$). Zinc and solid iron form a binary alloy in aluminum-free bath; the diffusion rate is now dependent on the transport characteristics of zinc through the barrier created by the aluminum-iron compound. The reaction between zinc and iron is delayed, and the net result is that the final thickness of the alloy layer is much less than when it is being formed in Al-free pure zinc coating bath^{2, 17-24)}. Galvanized coating produced in 0.025wt%Al bath consists of alternative discontinuous columns of ζ and δ phases. The intermetallic Fe-Al-Zn inhibitor layer that is formed on substrate is very thin. This layer breaks down after immersing in the coating bath in some areas and diffusion between Zn and Fe results in the formation of ζ phase in such areas. By increasing immersing time and diffusion of Fe, the ζ phase disappears and instead δ phase is gradually developed. By increasing immersing time further to 5 minutes, the ζ columns is being changed to δ phase and as a result the final structure of the coating consists of only δ columns. The remained Fe-Al-Zn layer on substrate breaks down and by diffusion of Fe atoms the ζ phase grows in this area; and in this manner the columnar structure containing alternative layers of ζ and δ structure is developed on the substrate. This mechanism is clearly shown in Fig.4. The intermetallic alloy layer is produced all over the surface when the sheets are immersed in Zn-0.05wt%Al bath for 3 minutes. This layer acts as a barrier to diffusion of Fe and Zn atoms and prevents the other alloy layers from being developed. But by increasing immersing time from 5 to 10 minutes, this inhibition layer breaks down completely, and as a result the ζ layer is developed on the substrate. Sandblasting increases the surface roughness of the plates. Consequently, the contact surface area between substrate and molten zinc increases, on the other hand, the intermetallic Fe-Al-Zn layer retards the diffusion between Fe and Zn. ζ layer grows on the substrate by immersing sandblast plate in Zn-0.05wt%Al bath after 3 minutes. Hardness of η phase did not change with an increase in the immersion time or aluminum addition. For the steel galvanized in the 0.025wt%Al bath, during 3 minutes, the higher surface roughness seems to increase the hardness of the δ phase (Table3).

5- Conclusions

- Addition of 0.025wt% aluminum in pure galvanizing zinc bath changes the morphology of

alloy layers from continuous and compact to columnar and discontinuous state.

- In Zn-0.05wt%Al bath after 3 minutes a very thin intermetallic layer is developed on the substrate, and alloy layers do not form. This inhibition layer breaks down after 5 and 10 minutes and alloy phases are developed on the substrate.

- The thickness of coating increases by sand blasting before galvanizing. This process can be used when thick coating is needed.

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