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Experimental Study on Characteristics of Hot-Dip Galvanized Coating and Effect of Magnesium Addition on Corrosion

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ABSTRACT: Steel is one of the oldest materials used in all types of fields. Steel is used in construction, in automobile and marine industries, in machineries, in plants etc. The aim of providing steel in appropriate form is to strengthen the particular member.Galvanized coating has been widely used technique to improve corrosion resistance to various components. Addition of magnesium refines the dendritic grains; reduce degree of porosity which leads to improve mechanical properties and corrosion resistance. It is difficult to add pure magnesium in HDG process due its high oxidation tendency hence magnesium is generally added to alloys or in the form of master alloys e.g. Al-Mg, Zn-Mg etc. or magnesium compound. Depend on the above behavior of the magnesium it is expected that addition of the magnesium modify zinc dendrite grains which can improve corrosion behavior of hot dip galvanized coating such as corrosion resistance, life, appearance etc.

KEYWORDS: Steel, corrosion, hot deep galvanizing

I. INTRODUCTION

Steel is the most important material used for various applications such as automobile industry, industrial machinery, marine applications etc. Steel is susceptible to the corrosion and hence generally used with a protective coating. Generally metallic coating like zinc, aluminum, or their alloys and non metallic coating, phosphates, chlorides, epoxy etc. are used as protection against corrosion for plain carbon steels [1].Due to increasing demand and cost of the steel it very important to enhance or increase corrosion resistance and the life of the hot dip galvanized coating and its resources. It is observed that alloying element addition has been providing better corrosion protection than pure HDG coating. The alloying elements like Al, Mg, Ni, Sr, Bi etc. is play an important role in improving galvanic performance i.e. corrosion resistance, its life etc. of hot dip galvanized coating [2].Alloying elements are found to increase the life of hot-dip galvanized coating hence it is importance to paid attention on modifying the metallurgical properties of the coating includes corrosion behavior, phases formed on the coating, surface morphology of coating, polarization resistance etc.

II. LITERATURE SURVEY

Zinc coatings are predominantly used to improve the aqueous corrosion of steel by two methods such as:

Barrier protection: In barrier protection, the zinc coating, which separates the steel from the corrosion environment, will first corrode before the corrosive environment reaches the steel.

Galvanic protection.: In galvanic protection, zinc is less noble or anodic to iron at ambient conditions and will sacrificially corrode to protect the substrate steel, even if some of the steel is exposed as cut edges or scratches in the coating [9].

Hot-dip zinc coating methods: Typical processing methods used in producing zinc coatings include hot-dip galvanizing, thermal spraying and electro deposition. In the hot-dip galvanizing (i.e. the immersion of a steel article in a liquid bath of zinc or a zinc alloy) by batch or continuous processing. The continuous process is more advantageous for coiled products such as sheet, wire and tube, whereas the batch process is normally used for bulk products.

In general, prior to immersion in the liquid zinc bath, the steel article to be galvanized is first cleaned to eliminate any surface oxide that may react in the zinc bath. After hot-dipping the steel reacts with the bath forming the coating, the article is withdrawn, cooled. The anatomy of a zinc coated steel part consists of
(a) The overlay or coating alloy,
(b) An interfacial layer between the overlay and the substrate steel containing a series of inter-metallic compounds.
(c) The substrate steel.

Each of these regions can be affected by the bath time and temperature, as well as the chemistry of both the bath and the substrate steel.Detailed information can be obtained from the published reviews [9].

Batch galvanizing: In the batch galvanizing process steel article to be galvanized is cleaned, degreased in an alkali solution followed by cleaning in running water and pickling in hydrochloric acid or sulfuric acid and rinsing in water and fluxed prior to immersion. In bath galvanizing process the molten hot-dip galvanizing bath is maintained at 460-480^{0}C and immersion time is in the range of 5-15 S depending upon the thickness of work piece. The two types of conventional practices used at the present time they are as follows.

A. Wet process: The wet process involves passing the article through a blanket of molten flux salts on top of the molten zinc bath to remove impurities from the surface of the steel and free from oxides. Due to the strong cleansing action of the flux blanket, it is less liable to give badly galvanized patches. In general, because of the wiping action, the wet process tends to produce thinner coatings.

B. Dry process: In the dry process after cleaning, the article is pre fluxed in an aqueous solution, dried and then dipped in the molten zinc bath. The flux used is aqueous zinc ammonium chloride with a small quantity of wetting agent added. The temperature of the pre-flux solution may range from room temperature up to 80^0 C. It is essential that the article be thoroughly dried before immersion in the molten bath.

Continuous processing: In continuous hot-dip processing, welded coils of steel are coated at speeds of up to 200 m/min. and bath temperature depends upon the composition of the bath. For galvanized zinc bath temperature is kept in between 455 - 475^{0}C. It consists of two types of coating processes are as follows.

A. Cook-Norteman process: Cook-Norteman line is similar to the batch process in that the sheet is cleaned and fluxed in line prior to immersion and is generally termed a cold line method. This process relies on a pre-dip cleaning method using aqueous alkaline degreasing, acid pickling and a final fluxing treatment to prevent oxidation. In the cold line method, most strip material must be fully annealed prior to dipping since the process does not provide for a heating and annealing step.

B.Sendzimir process: Most sheet product is made by using this process. Initially, the sheet undergoes a pre-cleaning to enhance coating adherence and prevent contaminants such as iron fines from entering the metal bath. The modern lines utilize an alkali brush system and electrolytic cleaning stage.

Post galvanizing processes:On exiting from the liquid metal pot or zinc bath, the excess liquid is forced back in to the bath by gas wiping dies that blow either air or nitrogen onto the surface of the steel. This step is designed to precisely control and maintain a uniform coating thickness and is usually monitored by on-line X-ray coating thickness measuring equipment.

III. METHODOLOGY

Coating Development and Corrosion Studies

Coatings developed in the lab: Following coating were developed as per procedure in experimental work. The chemical compositions of these coatings are given in Table 4.1.

a. (99.8 wt. % Zn)
b. Zn- 0.2 wt. % Mg.
c. Zn- 0.5 wt. % Mg.
d. Zn- 01 wt. % Mg.

Coatings	Elements in Wt.%				
	Al	Mg	Pb	Si	Zn
Pure Zn	0.11	0.003	0.035	0.03	Bal.
Zn-0.2% Mg	0.35	0.199	0.010	0.03	Bal.
Zn-0.5 % Mg	1.23	0.500	0.010	0.03	Bal.
Zn- 01% Mg	1.35	1.040	0.010	0.03	Bal.

Table 3.1.1 Chemical composition (wt. %) of hot-dip zinc coatings with varying magnesium level.

Physico-mechanical Characterization: Results obtained by visual inspection and physico-mechanical properties of the coatings are presented in detail in the following sub-sections.

Visual inspection: Images captured with digital camera of hot-dip zinc and magnesium containing zinc coatings are shown in the Fig. 32.1. Hot-dip galvanized and magnesium containing zinc coated specimens, as shown in the figures, exhibit different surface features. The surface of galvanized steel sheet has a structure that consists of large flowery dendrite grains. Zn-0.2 wt. % Mg coatings surface show fine and bright appearance, while Zn-0.5 wt. % Mg and Zn-01 wt. % Mg coatings show dull surface appearance. Zn-0.2 wt. % Mg coating shows the most fine and brightest appearance among all the coatings studied.Pure zinc coating had dull appearance. It is reported that dull spangles contain more lead or antimony and aluminum than bright spangles. Earlier researcher reported that large spangles are associated with alloy additions, which have limited solid solubility and relatively low melt/vacuum surface tension values. As the size of dull spangle increases it reduce the corrosion resistance of the coating. It was also proposed that extensive solute segregation occurs at the dendrite tip, decreasing the tip radius and thus increasing the dendrite growth velocity. The higher velocity of the primary dendrite results in dendrite spangles. Sample with dull appearance gives higher percentage of white rust than those bright appearances [28]. Magnesium seems to restrict growth of the spangles.

Thickness: The results of the coating thickness obtained are shown in the following Fig. 3.2.2.The change in the coating thickness for identical dipping conditions (15 S) of steel. The thickness of the coating increases with increasing percentage of magnesium, content in the hot-dip galvanized coating.

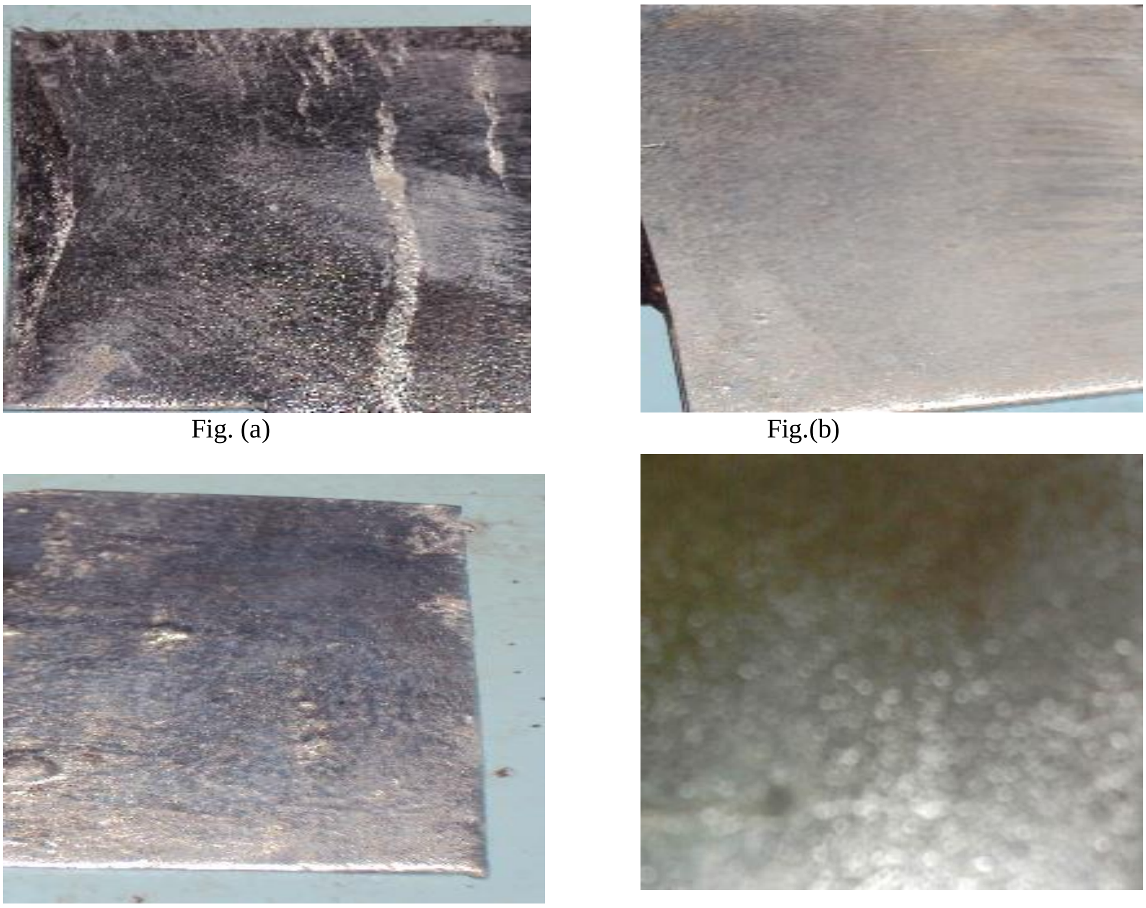


Fig. (a) Fig.(b)

Fig. (c) Fig. (d)

Fig. 3.2.2 Surface appearance of coatings (a) Pure zinc, (b) Zn-0.2 wt. % Mg,
(c) Zn-0.5 wt.% Mg, (d) Zn-01 wt. % Mg.

Fig.3.2.3 Effect of magnesium on hot-dip zinc coating

Effect of magnesium on hot-dip zinc coatingthickness with increasing Mg content the thickness of coating goes on increasing**.**

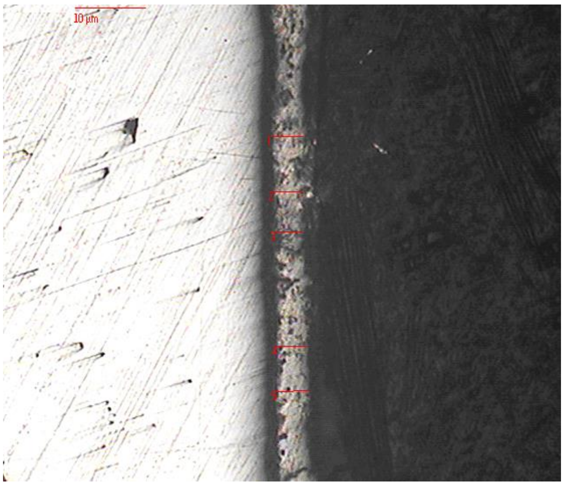


Fig. a

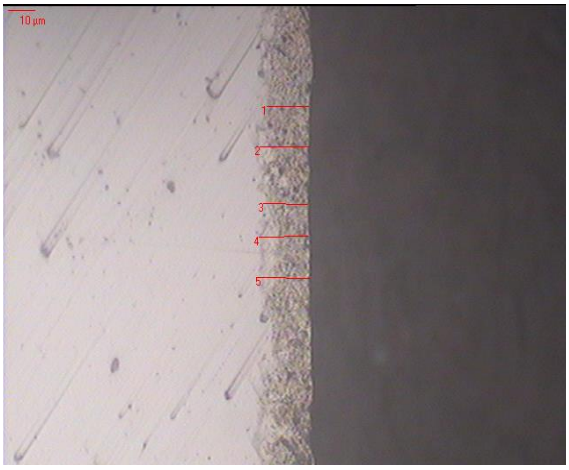


Fig.b

Fig.a Pure Zn coating		**Fig.b Zn-0.2% Mg Coating**	
Line 1	11.49	Line 1	15.48
Line 2	10.24	Line 2	18.04
Line 3	10.00	Line 3	16.44
Line 4	10.87	Line 4	18.39
Line 5	11.49	Line 5	18.39
Average thickness in µm	**10.74**	Average thickness in µm	**17.35**

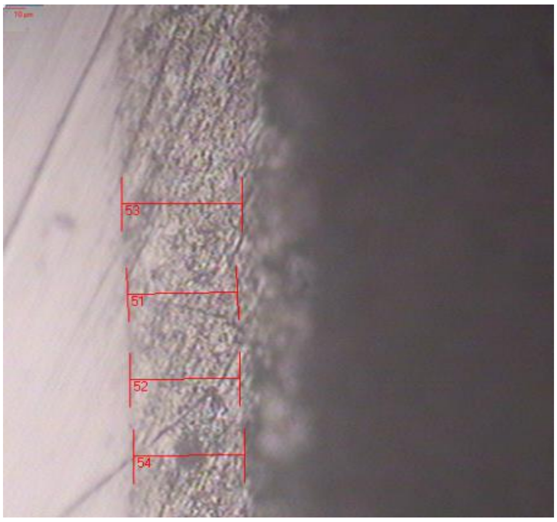


Fig.c

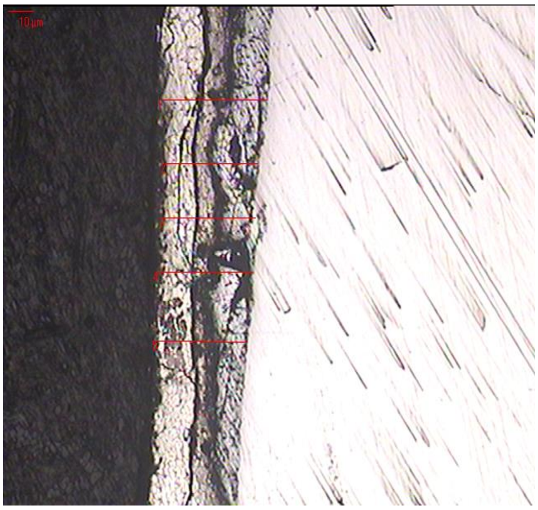


Fig.d

Fig. c Zn- 0.5% Mg coating		**Fig. d Zn-01% Mg Coating**	
Line 1	28.75	Line 1	40.96
Line 2	28.75	Line 2	36.12
Line 3	29.56	Line 3	35.80
Line 4	29.04	Line 4	37.01
Line 5		Line 5	35.12
Average thickness in µm	**29.53**	Average thickness in µm	**37.03**

Fig.3.2.3 Effect of magnesium on hot-dip zinc coating thickness with increasing Mg content the thickness of coating goes on increasing (a) Pure Zn coating, (b) Zn-0.2%Mg, (c) Zn-0.5%Mg, (d) Zn-01%Mg.

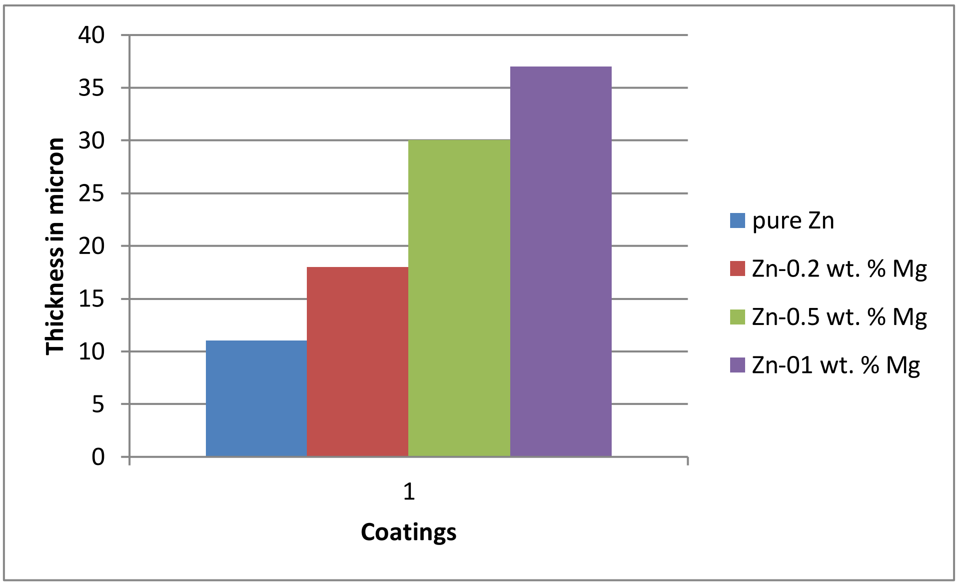
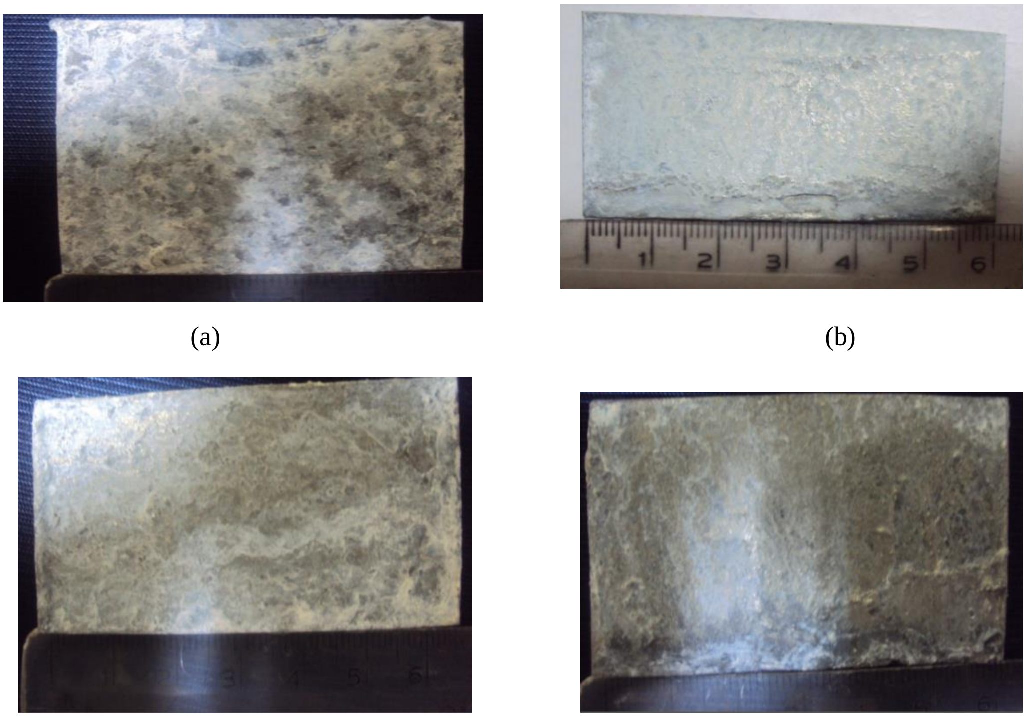


Fig.3.2.4 Effect of magnesium on hot-dip zinc coating thickness; with increasing Mg content the thickness of coating goes on increasing.

Corrosion Study: Pure zinc and magnesium containing zinc coated steel specimens were studied for electrochemical corrosion behavior.

Salt spray exposure: Salt spray test measures the ability of various types of coatings to withstand in corrosive-cum-humid environment. The tests were conducted as per ASTM B-117(03). The panels were visually examined and the variation in the protection was further examined with EIS. Phases formed on the specimen were analyzed with XRD and surface morphology of the specimen was studied with SEM.



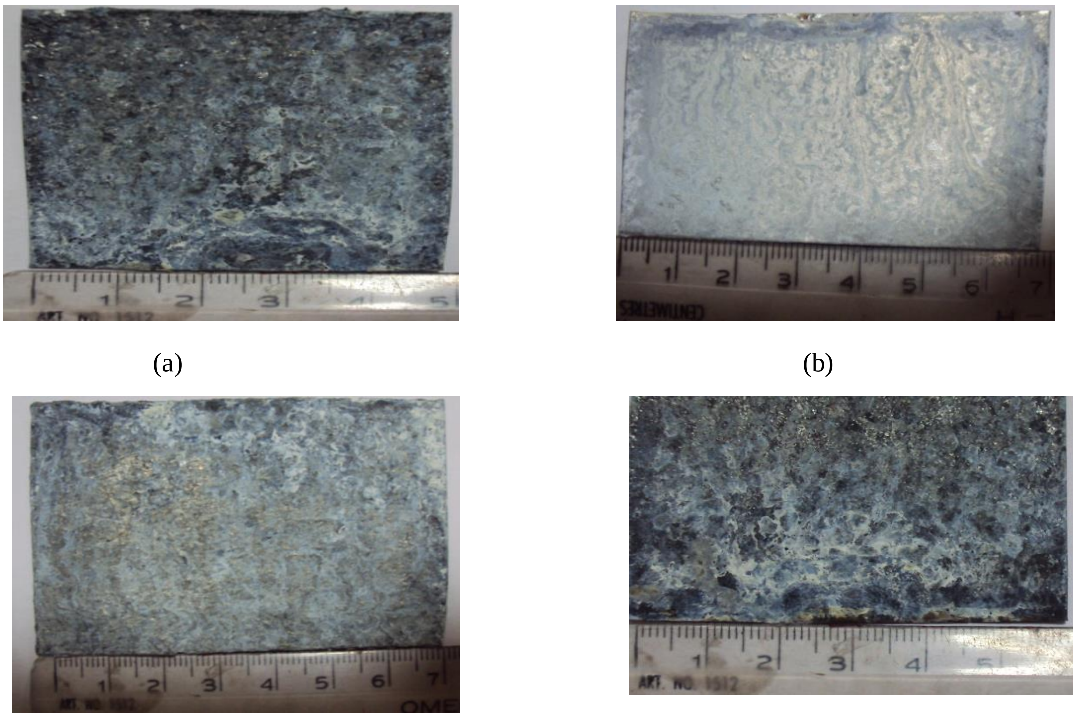
(a) (b)

(c) (d)

Figs. 3.3.1 Photographs obtained on hot-dip zinc coated panels after 50 h of salt spray exposure: (a) Zn; (b) Zn-0.2 wt. % Mg; (c) Zn-0.5.wt. % Mg; (d) Zn-01 wt.% Mg; showing the start of white rust formation on the surface of specimens.

(a)
(b)
(c)
(d)
(e)
(f)
(g)

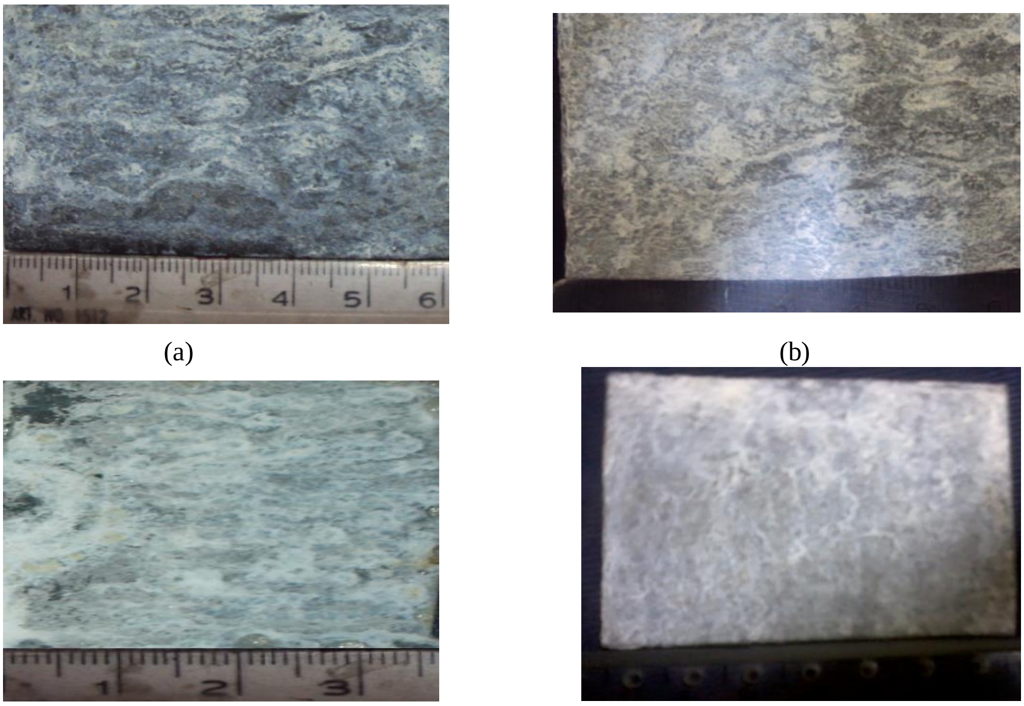
(h)



(a) (b)

(C) (d)

Figs. 3.3.2 Photographs obtained on hot-dip zinc coated panels after 130 h of salt spray exposure: (a) Zn; (b) Zn-0.2 wt. % Mg; (c) Zn-0.5.wt. % Mg; (d) Zn-01 wt. % Mg; showing the entire surface covered with white rust on the specimens.



(a) (b)

(c) (d)

Figs.3.3.3 Photographs obtained on hot-dip zinc coated panels after 300 h of salt spray exposure: (a) Zn, (b) Zn-0.2 wt. % Mg; (c) Zn-0.5.wt. % Mg; (d) Zn-01 wt. % Mg.

(a) (b)

Figs. 3.3.4 Photographs obtained on hot-dip zinc coated panels after 400 h of salt spray exposure: (a) Zn-0.2 wt. % Mg; (b) Zn-0.5.wt. % Mg; (c) Zn-01 wt. % Mg.

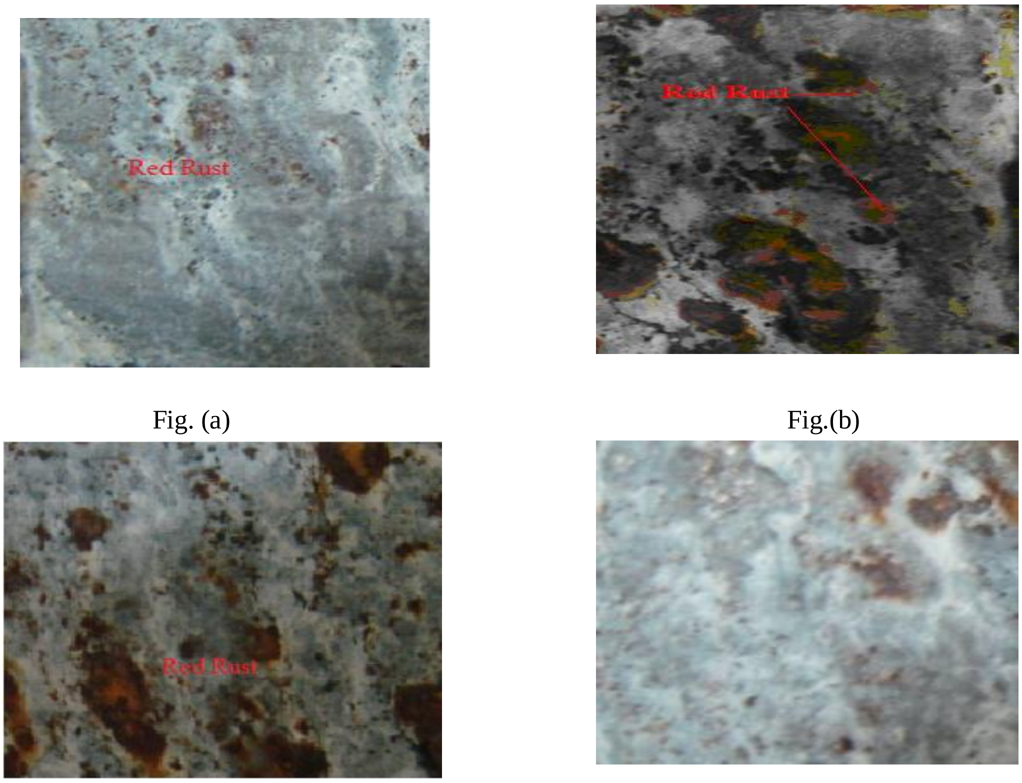


Fig. (a) Fig.(b)

Fig. (c) Fig. (d)

Fig. 3.3.5 Time for the appearance of the first red rust on various hot-dip zinc coatings (a) Pure Zn; 250 hr (b) Zn- 0.2% Mg; 400 hr (b) Zn-0.5% Mg; (c) Zn-01% Mg 370hr. With increasing magnesium content the time for red rust formation goes through a maximum at 0.2-0.5 wt. % Mg.

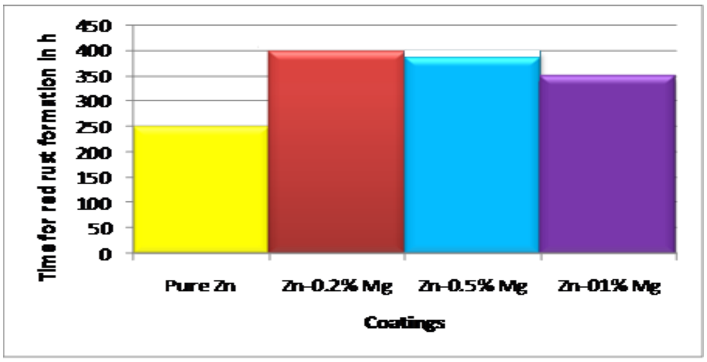


Fig. 3.3.6 Time for the appearance of the first red rust on various hot-dip zinc coatings, with increasing magnesium content the time for red rust formation goes through a maximum at 0.2-0.5 wt. % Mg.

IV. CONCLUSIONS

Surface appearance of coatings containing magnesium is brighter and smoother than pure zinc coating.salt spray studies show higher corrosion resistance in case of magnesium containing zinc coatings than magnesium free zinc coating. It is observed that Mg in the Zn-Mg coating is distributed mainly near the dendroid portion of the dendritic crystal. This is caused by precipitation of Mg coming out of the Zn crystal grain during solidification. Microstructure observation shows that in the Zn-Mg coating, the dendroids extended in the form of intermetallics compound Mg_2Zn and $Mg_2Zn_{11,}$ due toformation of intermetallics compound near dendrite crystal the surface hardness of Zn-Mg layer is higher than Zn layer without Mg.The present study shows that magnesium addition in the HDG increase the wet ability of the grains in coating. Smaller spangles are formed with Pb addition of 0.01 wt. % and with increasing Pb, spangles became larger. Magnesium seems to behave differently with respect to surface brightness. It is observed that increasing lead content of the zinc coating increases the number of dull spangles and reduces the number of bright spangles. On the other hand, magnesium enhances the brightness of the coating up to certain extent and then decreases the brightness of the coating. It is seen that with magnesium addition up to 0.2-0.5 wt. %, fine and bright coating surface. However, as the magnesium addition goes beyond 0.5 wt. %, the coating becomes dull.

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