

STUDIES ON PERFORMANCE OF GALVANNEALED COATINGS AND OTHER TYPE OF ZINC COATINGS

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ABSTRACT

A systematic study has been performed on corrosion behaviour of unpainted galvanized and other zinc coatings in acidic (chloride and sulphurous), alkaline and salt spray exposures environments. Galvanized coating exhibits very poor resistance in acidic medium whereas in alkaline medium it performs comparatively superior than the other zinc coatings, hi salt spray exposure tests galvanized coating also performs better than the other coatings. Electrogalvanized and hot-dip galvanized coatings perform more or less equally. It has been noted from time-potential study in 0.5% NaCl solution that, galvanized coating attains the nobler corrosion potential values than the other coatings. In addition to this the evaluations of painted and bare surfaces were also performed under cyclic humid and alternate dipping/drying conditions.

INTRODUCTION

Zinc coating on ferrous substrate is applied to have an improved corrosion resistance of the substrate. Sacrificial coatings of pure zinc and other zinc alloys having metals such as nickel, cobalt, iron, aluminium, lead etc. are applied to protect the ferrous base metal⁽¹⁻⁸⁾. The life of zinc coatings is reported to improve by the alloying of elements⁽⁹⁻¹²⁾, surface treatments⁽¹³⁻¹⁸⁾, and heat treatment of the surface.⁽¹⁹⁻²¹⁾ The inter metallic layer formed during hot dip galvanizing, also playing important role on corrosion resistance of galvanized coating. One of the very effective way to alter the inter metallic layer of zinc coating is galvannealing. Galvannealing is a process where diffusion reaction between the iron substrate and zinc coating takes place in temperature range of 500°C. The diffusion of iron into results in the formation of columnar Zn-Fe crystal growing in the outward direction. The reaction is completed when zinc is totally transformed into Zn-Fe phases up to the top of the coating. The concentration of iron decreases towards the top surface and different types of inter metallic phases, namely Gamma (21-28%Fe, FeZn₄), Delta (7-12%, FeZn₁₀), Zeta (5-6%Fe, FeZn₁₃) and Eta (<0.03 %Fe, PureZn) are formed⁽²²⁾. Galvanized coatings have been reported to have better paintability⁽²³⁻²⁵⁾ improved welding characteristic⁽²⁶⁾ as well as better corrosion resistance⁽²⁷⁻³⁰⁾ in comparison to hot dip galvanized coatings. Due to these improved properties, galvanneal coatings are being increasingly used in automotive, construction and other sectors of industries. Improved corrosion resistance of galvanized coating is mainly attributed to the formation of different FeZn phase which are nobler than the pure zinc coating. A coating produced by electrogalvanized in or even by hot dip continues galvannealing process develop little or practically negligible inter metallic layer.

Literature survey has revealed that very limited informations are available on the corrosion resistance performance of galvanized coatings in different types of corrosive environments. The present work, is a part of a programme of evaluation of comparative performance of galvanized vis-a-vis other zinc coatings in acidic, alkaline and neutral environments.

Experimental :

(A) **Materials :** The following types of coatings were investigated.

Coating type	Source	Thickness	%Iron coated
Galvannealed (GA)	Factory produced	0.68gm/cm ²	9.14
Hot Dip galvanized (HDG)	Factory produced	1.4gm/cm ²	2.97
Electrogalvanized (EG)	Factory deposited	0.63gm/cm ²	Nil
Galvannealed (GA Lab)	Laboratory	1.5gm/cm ²	5.52

(B) Tests performed and procedure:

(1) Salt spray test

(a) **Salt spray test to determine the corrosion rate** - This test was carried out as per ASTM B-117 standard. 5% sodium chloride solution was taken in the bath. The temperature was maintained at 35° + -2°C. The specimens were exposed for the periods of 28 & 53 days and after removing from the chamber, they were cleaned in chromic acid solution. The corrosion rate of the zinc coatings was determined from the loss of weight of the coatings per unit area.

(b) **Salt spray effects on scratch surfaces :** This test was performed to know the ability of coatings in providing sacrificial protection to the steel surface in case presenting defects in coatings. The coatings were exposed to salt spray chamber after creating a single scribe by using a sharp knife on both surfaces of samples. These specimens were then exposed in salt spray chamber for 38 days and the appearance of brown rust was observed with time.

(2) **Immersion test :** Immersion tests were performed by exposing the samples for 6 hours in 0.012N of H₂SO₄, HCl & NaOH solutions. To understand the role of hydroxyl ions in controlling the corrosion rate of coatings, specimens were immersed in saturated lime solution, saturated lime solution +0.1M NaOH and saturated lime solution +0.1M KOH solutions for 48 hours.

(3) **Potential-time study :** This study was performed by immersing the coated specimens in 0.5% NaCl solution for 24 hours. The potentials were measured using a high impedance voltmeter. A saturated calomel electrode was used as the reference electrode.

(4) **Cyclic wet/dry humidity test :** This test was performed to determine the performance of coated surface on development of rust. Here a bunch of seven samples of sheets of size 2.5cmx5.0cm of galvannealed, painted galvannealed, electrogalvanized, painted electrogalvanized and painted hot dip galvanized was tied with nylon thread. These bunches were exposed in humidity chamber at 60°C and 85% relative humidity for cyclic wet/dry for 8 hours and then removed from the cabinet and kept in open air for 16 hours. This was continued from Monday to Friday. Over the weekend, the samples were kept in the humidity cabinet. One week of the test constituted one cycle. The observations of the surface were continued for three cycles.

(5) **Alternate dipping/drying test (GM 9511) :** This test was performed for all the

coatings described as above at is. Here, a single scribe was created on both the surfaces of coatings with the help of a sharp knife through the metallic coatings down to the steel substrate. These coupons were immersed in 5% NaCl solution for 15 minutes, followed by drying for 1 hour 15 minutes at ambient condition (25°C and 45% relative humidity). For the remaining of the day, the samples were exposed in humidity cabinet at 60°C and 85% relative humidity. This routine was followed from Monday to Friday. Over the weekend, the coupons were kept in the humidity chamber. On Monday samples were dried for 1 hour in an oven at 60°C and then placed in cold cabinet for 30 minutes. One weekday constituted one cycle.

Results and Discussion

Corrosion rate of galvanized and other zinc coatings in acidic and alkaline medium are shown in Table I.

Table I :

Corrosion rate of galvanized, electrogalvanized and hot dip galvanized coatings in 0.012 N HCl, H₂SO₄ and NaOH solution at room temperature(25°C), Exposure time = 6 hours.

Type of Coatings	Corrosion Rate (mdd)		
	HCl	H ₂ SO ₄	NaOH
GA (Plant)	718.4	601.6	14.4
EG (Plant)	364.8	424.0	28.8
HDG (Plant)	787	235	14.4
GA (Lab)	1003.2	1011.2	8.0

The result presented in the above table indicate that the galvanized coatings exhibit poorer resistance in acidic medium whereas in alkaline medium it performs comparatively better than the other zinc coatings. The results further reveal that the zinc coatings suffer accelerated corrosion in acidic than in alkaline medium. The hot dip galvanized coated strips when galvanized in the lab (GA-Lab) suffers higher acidic corrosive attack than the factory produced galvanized coating. The corrosion rate in alkaline solution for the former coating is appreciably less in comparison to the latter one. Table II shows the corrosion rate of different zinc coatings under salt spray exposures.

Table II

Salt spray test for 28 & 53 days (ASTM B 117)

Type of coatings	Corrosion Rate (mdd)		% decrease in corrosion rate
	28 days	53 days	
GA (Plant)	13.77	6.98	51.1
EG (Plant)	17.08	11.08	35.3
HDG (Plant)	20.76	13.93	33.0
GA (Lab)	18.32	-	-

It is observed from this table that the galvanized coating exhibits superior corrosion resistance than the other coatings in this test. Electrogalvanized and hot-dip galvanized coatings have almost similar resistance to corrosion. It is also observed from this-table that the percentage decrease in corrosion rate for galvanized coating is higher than the other coatings. These observations indicate that the corrosion product formed on

galvannealed coating is more impervious and protective than on the other coatings.

The spreading of rust at the periphery of scribe created on different types of coated surface is shown in Table III.

Table III
Spreading of rust on the samples of GA and EG coatings.

Number of days	GA	EG
1	O.K.	O.K.
10	O.K.	O.K.
20	O.K.	O.K.
28	Few brown rust spot developed on one line.	Few brown rust spot developed on both lines.
35	20% of line covered by brown rust and brown rust also developed on surface & edges.	15 % of line covered by brown rust and few brown rust spot developed on the surface & edges.
36	30% line covered by brown rust.	20% line covered by brown rust.
37	50% line covered by brown rust.	30% line covered by brown rust.
38	75% line covered by brown rust.	50% of line covered by brown rust.

It is observed from the above table (Table III), that 75% of scribed line of galvannealed coating was covered with brown rust and 50% in case of electrogalvanized coating, after exposure of 38 days. This indicates that the galvannealed coating poorly protects the bare surfaces than the electrogalvanized coating.

Corrosion rate of GA and HDG coatings in saturated lime solution are shown in Table IV. It is observed from this table that the dissolution rates of both the coatings are almost same in saturated lime solution as well as in 0.01M NaOH solution. But, when saturated lime solution is mixed with 0.01M NaOH and 0.01M KOH, the corrosion rate of GA coating is drastically reduced. This indicates that the GA coating performs very well in highly alkaline solution having calcium ions. In case HDG coating, the corrosion rate is not much affected due to increase in alkalinity of the solution. These observations suggest that the performance of GA coating in alkaline solution having calcium ion is improved due to the presence of iron in the coating.

Table IV

Corrosion rate of galvannealed and hot dip galvanized coated samples in saturated lime, saturated lime + 0.01M NaOH and saturated lime + 0.01M KOH solution at RT (25°C), Exposure time = 48 hours.

Type of solutions	Corrosion rate (mdd)	
	GA	HDG
Saturated lime	14.1	15.0
Saturated lime + 0.01M NaOH	0.5	13.9
Saturated lime + 0.01M KOH	1.1	18.5
0.01M NaOH	14.4	14.4

Table V

Corrosion rate of galvanized coatings in saturated lime solution exposed for different Periods of time.

Number of days	Corrosion rate (mdd)	
	Galvanized	Hot dip galvanized
2	14.1	15.0
7	2.23	3.74
21	1.6	1.74

The encouraging results observed for GA in alkaline solution prompted us to investigate its performance for longer duration of exposures. The results are shown in Table V. It is observed from the table that the corrosion rate of GA and HDG decrease with increase in time of exposure. The rate of decrease in corrosion rate is higher in case of GA coating than for HDG coating. During longer period of exposure GA coating is therefore expected to perform superior than the HDG.

The superior performance of GA coating in neutral and alkaline environment and an inferior resistance in acidic solution in comparison to the pure zinc coating may be explained in terms of the corrosion polarisation Evans diagram⁽³¹⁾. In case of pure zinc, the corrosion rate is expected to be to be I_1 . When iron is present in the coating, the cathodic reaction (hydrogen ion discharge) will predominately take place on this metal. Since the exchange current density (I_0) for the discharge of hydrogen ion on iron is quite high (10^{-2} A/cm²) in comparison to zinc (10^{-11} A/cm²), observed corrosion rate in case of zinc coating having iron is expected to be quite high. This is found true in case of GA. It is to be noted here that the exchange current density for hydrogen electrode on lead is lower (10^{-14} A/cm²) than that on zinc, the alloying of zinc with lead, therefore it expected to improve the acid corrosion resistance of zinc-lead coating. (Data of exchange current density taken from J.M. West. Electro deposition and corrosion process, Van Nostrend, London (1970) cited in "The fundamental of corrosion by J.C.Scully, Pergmon press, p97).

The slower corrosion rate of GA coating in neutral and alkaline solution is attributed to sluggish cathodic reaction (oxygen reduction) on iron than on zinc.



The steep fall in corrosion rate of galvanized coating in saturated lime solution having NaOH or KOH is probably owing to the precipitation of insoluble salt of iron-calcium and zinc on the coating surface⁽³²⁾. The corrosion product formed on the surface of GA coating under this condition is being characterised and the exact nature of the product will be reported separately.

The result of spreading of rust on coating under cyclic humidity exposures test is shown in Table VI.

Table VI
Observations on spreading of rust during cyclic humidity exposure tests.

Type of coatings	Observations after number of cycles		
	1st	2nd	3rd
GA	Cut edges covered with brown rust. Top surface rusted.	As in 1st cycle	Cut edges fully covered with brown rust. Top surface covered with brown rust.
GA-painted	As above except top surface OK	As in 1st cycle	Edges covered with brown rust. Top surface rusted.
EG	Top surface white rusted, brown rusting on edges.	As in 1st cycle	
EG-painted	No brown rusting either on edges or on surface.	As in 1st cycle	As in 2nd cycle
HDG-painted	No brown rusting at any place.	As in 1st cycle	As in 2nd cycle

It is observed from the above table that the GA coating has failed in controlling the corrosion of cut edges for painted as well as unpainted surface. EG and HDG coatings on the other hand, are quite effective in this aspect.

To observed the spreading of rust on scribed surface on coatings, the experiment were performed under alternate dipping/drying test. The results are shown in Table VII. It is evident from the table that GA coatings have very poor performance in controlling the corrosion at the scratch and cut edges. However, the HDG and EG coatings have an edge over the GA.

Table VII
Observations on spreading of rust on scribed surface on coatings during alternate dipping / drying test.

Types of coatings	Observations after number of cycles		
	1st	2nd	3rd
GA	Few brown rust stain developed on scratch line. Few on edges & lower portion of the surface.	56% brown rust on scratch surface.	Scratch line covered with 100% brown rust.
GA-Painted	Few brown spot developed on the scratch line.	Brown spot appeared on scratch line, cut edges & down portion of the panel	Scratch line covered with brown rust. Few tiny blister formed on the surface.
EG	Brown rust (BR) appeared on scratch line and lower portion.	30% BR on lower portion and scratch line has slight BR.	50% scratch line covered with BR.
EG-Painted	BR appeared on scratch line	Scratch line has no BR.	30% scratch line covered with BR. Blister formed on grey surface & coating peeled off from white painted surface.
HDG-Painted	White rust developed on scratch line.	White rust.	Pew BR on scratch line. Blisters formed on grey side & coating peeled off from white surface.
HDG	White rust developed on scratch line.	White rust.	Scratch line covered with BR.
GA(Lab)	BR appeared on scratch line	50% BR on scratch line.	Scratch line covered with BR.

Table VIII

Time potential study in 0.5% NaCl solution for different coatings.

Time	Potential (-mv) (SCE)			
	GA (Plant)	EG (Plant)	HDG	GA (Lab)
Initial	0.798	0.954	0.968	0.838
1 hour	0.824	0.994	0.990	0.850
5 hour	0.855	1.001	1.018	0.901
24 hour	0.854	1.003	1.018	0.944

The variation in corrosion potential with the passage of time shown in Table VIII. It is evident from this table that during the exposure of coatings for 24 hours, GA attains the nobler corrosion potential values than the other coatings. HDG and EG produce the potential of the same order. The superior performance of the GA coating, therefore, is attributed to the development nobler potential of the coating.

Conclusions

- (1) HDG and EG coatings, having identical thickness, provide same degree of protection to the steel substrate.
- (2) GA provides very poor corrosion resistance in acidic solution. In alkaline and neutral corrodents, however, the coatings perform excellently well.
- (3) In saturated lime solution having extra addition of alkali, GA performs superior than the EG or HDG coatings..
- (4) GA has poor ability to protect cut edges or paint underneath corrosion in comparison to EG or HOG.
- (5) The superior performance of GA in neutral and alkaline solution is attributed to the attainment of nobler potential of this coating than EG or HDG.
- (6) Inferior performance of GA in acidic environment is due to the higher exchange current density of iron present in the coating than the zinc.

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