

Influence of pretreatment on corrosion resistance of polymeric coating on tin–8% zinc alloy coated steel sheet

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Abstract

In this paper, results from an experimental study of different pretreatment method with polymeric coatings to improve the corrosion resistance of hot dip tin–8% zinc alloy coated steel sheet are presented. The procedure of coating and its effects on the corrosion resistance of surface were studied both theoretically and experimentally. In the presence of ferrous phosphate pretreatment, results indicate a more desirable corrosion resistance for the polymeric coating than other used pretreatment methods.

Keywords: corrosion; polymeric coating; tin–zinc alloy coating; pretreatment

Introduction

Several researches have been carried out to investigate the interaction of phosphate layer with metallic coating. Reports on the phosphating of tin alloys with zinc group metals are not numerous [1–2]. The tin metal with zinc group metals may provide an improve corrosion resistance for protection of steel objects [3–4]. Recently the Sn–Zn alloy coated steel sheet has been commonly used in manufacturing the body of liquid container tank such as automotive fuel tank [3,5,6]. Steel hot dipped with a single Sn–Zn alloy displays a good weldability, formability, and both high–strength and deep–drawing steels may be plated without losing the properties. Sn–Zn alloy composition may be varied within a wide range. The most proportion of the studied hot dip coating is composed of tin metal (about 90%) [3]. One way to improve Zn and Zn alloy corrosion resistance is to apply either an overlaying polymeric coating. It has been determined in studying the phosphating process of Sn–Zn alloy coating.

The presence of alloying elements and their chemical nature cause distinct difference in the extent of phosphatability of the surface alloy coating [7,8].

The present study aims at improving the corrosion resistance of Sn-8% Zn hot dip coated steel sheets by polymeric coating so that samples were prepared by three different pretreatments and three sorts of polymeric coatings. However, Ferrous and Tricationic phosphate solutions are used to prepare the surface before exerting polymeric coatings [8]. Therefore, phosphated and non-phosphated surfaces with three polymeric coatings as variable factors to paint the surface were studied. Finally the product of corrosion of samples was tested considering their mechanical and physical properties before and after corrosion tests.

Experimental procedure

Materials

Samples of hot dip tin-zinc coated steel sheets with coating mass 30–50 g/m² and weight percentage of Sn-8% Zn were used, which sheets were produced by the Nippon steel company. In table (1) properties of noted sheet are compared.

The surface of alloy coated steel sheets was pretreated using general alkaline solution, ferrous phosphate and Tricationic phosphate and then the surface were painted by Epoxy, Poly Urethane and Polyester separately.

Table 1

Specification of tin-8% zinc alloy coated steel sheet

Steel sheet thickness (mm)	TS (MPa)	YP (MPa)	Elongation (%)	Coating Mass (g/m ²)	Equivalent Coating Thickness (Both side)
1	270 ≤	230–350	34–46	30/30	0.011 mm

Methods

First of all, 60 samples were cut in 150 mm × 100 mm × 1 mm and then the surface of coated steel sheet was cleaned and degreased by general alkaline and straightaway was dried by a clean tissue. In following, the metallic coating was [2]

considered by scanning electron microscope (SEM) using back scattering method (BSE). Using energy dispersive X-ray spectroscopy (EDX) the type and the distribution of elements in metallic coating were evaluated. Regarding to metallic coating phases, the required pretreatment applied so that pretreatment for samples was done by three individual methods, which are listed in below [9–12]:

- Degreased by alkaline
- Degreased by alkaline and then phosphated by Tricathionic
- Degreased by alkaline and then phosphated by Fe phosphate

After pretreatment, samples were coated using three different painting materials including; Poly urethane, Polyester and Epoxy so that all samples are prepared via spraying method. Figure (1) indicates the schematic of coating layers on the surface of sample.

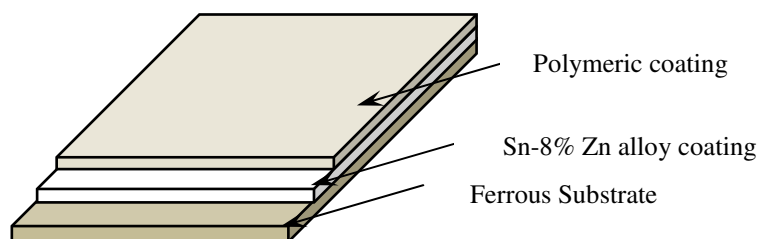


Figure 1: Different coating layers on the ferrous steel sheet after preparation

Table (2) compares the used pretreatment and painting processes in detail for all samples. The interaction of pretreatment with Sn–Zn alloy coating and also with polymeric coating was considered by corrosion resistance tests and mechanical tests. Samples were subjected to salt spray test (SST), moisture resistance test and Gasoline resistance test to evaluate their corrosion resistance. Finally, the mechanical properties of polymeric coating layer were considered via different common tests such as adhesion test, impact test, cupping test, chipping test and hardness test [13,14].

Table 2

Different methods of sample making

No	Painting	Alternative for pretreatment	Process
1	PS	Degreasing (4 samples) / Fe phosphate (4 samples) / Tricationic (4 samples)	Spray (solvent base)
2	EP	Degreasing (4 samples) / Fe phosphate (4 samples) / Tricationic (4 samples)	Spray (solvent base)
3	PU	Degreasing (4 samples) / Fe phosphate (4 samples) / Tricationic (4 samples)	Spray (solvent base)

EP: epoxy / PS: polyester / PU: polyurethane

Results

Figure (2) indicates various phases in the metallic coating layer which are observed by the SEM using a Tescan model VG20805731R.

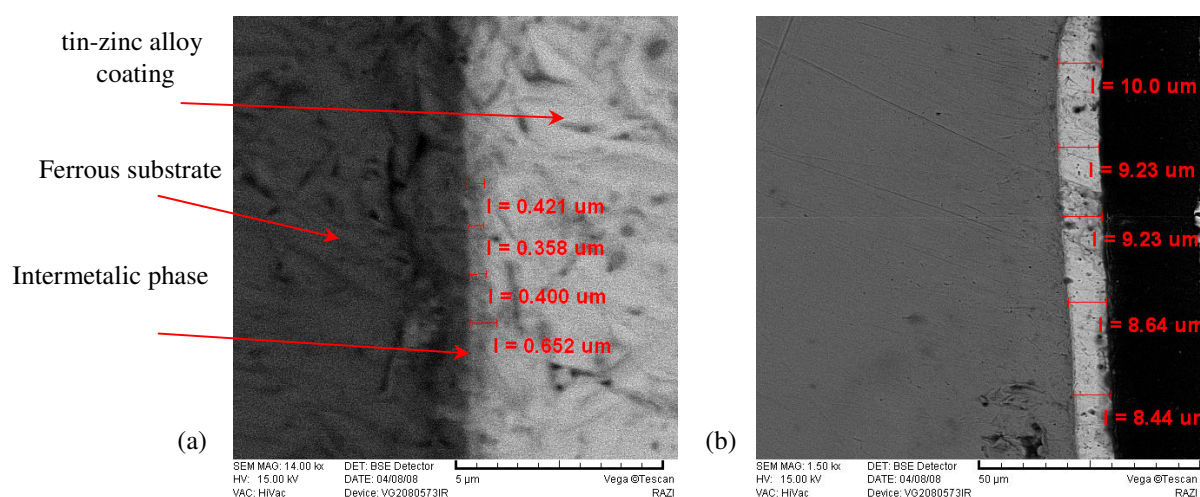


Figure 2: SEM test for considering the metallic coating, a) cross sectional of micrograph of intermetallic layer using BSE, b) cross sectional of micrograph of entire coating using BSE

As can be seen in figure (3) dark points are zinc enriched phases which distribute in the coating as secondary phase; meanwhile, table (3) compares the composition of dark points. Figure (2) illustrates the cross-sectional of coating by showing thickness of intermetallic layer.

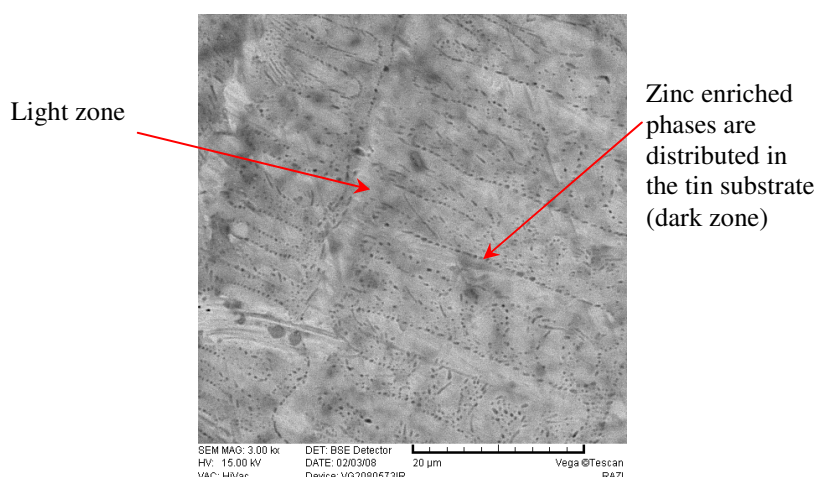


Figure 3: SEM micrograph shows the surface of metallic coating using BSE

Table 3

Element analysis of dark points in tin–zinc alloy coating

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Iron	K series	1.10	1.07	1.56
Zinc	K series	55.79	54.42	67.87
Tin	L series	45.62	44.50	30.57

The result of EDX for light zone of coating and whole of coating are shown in figure (4), figure (5) and figure (6) and the quantitative evaluation of elements for zones are indicated in table (3), table (4) and table (5).

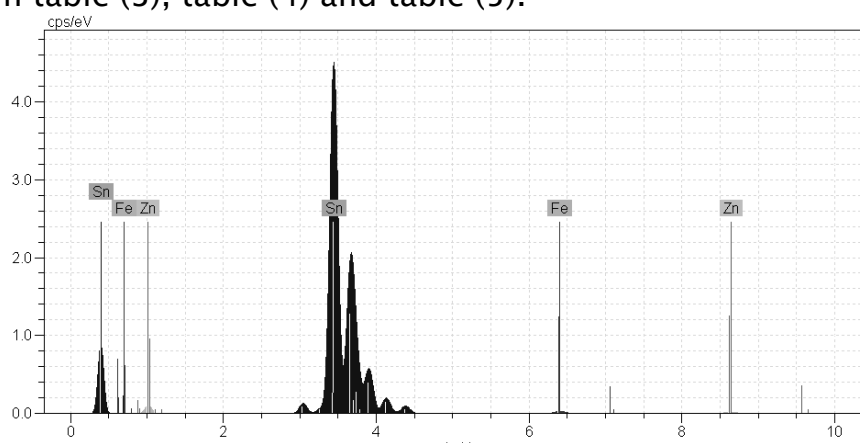


Figure 4: EDX spectra of light zones in metallic coating

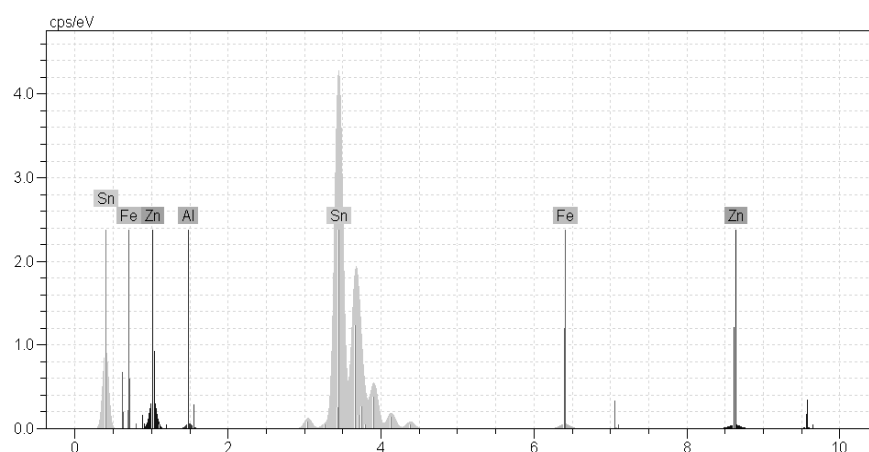


Figure 5: EDX spectra of intermetallic layer in metallic coating

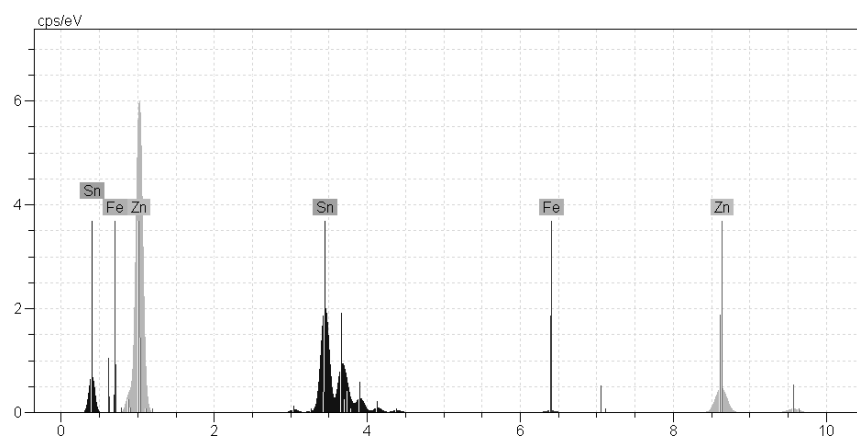


Figure 6: EDX spectra of dark zones in metallic coating

Table 4

Element analysis of tin-zinc alloy coating

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Aluminum	K series	0.29	0.28	1.14
Zinc	K series	4.78	4.55	7.73
Tin	L series	98.22	93.3	87.39

Table 5

Element analysis of light zone in tin-zinc alloy coating

Element	Series	unn. C [wt.-%]	norm. C [wt.-%]	Atom. C [at.-%]
Iron	K series	0.85	0.81	1.69
Zinc	K series	1.42	1.36	2.42
Tin	L series	102.38	97.83	95.89

It can be clearly seen that table (6) shows the results of thickness and hardness measurement for all samples. It should be mentioned that the figure are the average of thicknesses which are rounded off.

Table 6

Results of thickness and hardness measurement

Sample	Thickness (μm)	Hardness (Sec)
	Degreased / Fe / Tricationic phosphate	Degreased / Fe / Tricationic phosphate
EP	55	140
PU	65	33.3
PS	60	75

The results of cupping and chipping tests of samples before and after corrosion tests are also demonstrated in the table (7).

Table 7

The results of cupping and chipping test

No	Painting	Pretreatment	Cupping before SST	Cupping after SST	Chipping
1	EP	degreasing	8mm	3.5mm	Grade 2
	PU		10.5mm	5mm	Grade 2
	PS		12 mm	6mm	Grade 4
2	EP	Fe phosphate	9mm	7.5mm	Grade 2
	PU		10.2mm	8mm	Grade 2
	PS		12mm	9mm	Grade 2
3	EP	Tricationic	8.5mm	5.6mm	Grade 2
	PU		10.2 mm	7.5mm	Grade 2
	PS		11 mm	8mm	Grade 2

In terms of measurement, Grade zero (0) is recorded as adhesion test result for all samples. Table (8) shows the result of SST, moisture test and gasoline resistance test for samples.

Table 8

The results of salt spray, moisture resistance and gasoline resistance tests

No	Painting	Pretreatment	Salt spray test (hours)	Moisture resistance (hours)	Gasoline resistance
1	EP	degreasing	552	1000	V.M
	PU		672	480	no
	PS		504	480	F.C
2	EP	Fe phosphate	576	1000	no
	PU		794	480	no
	PS		576	480	F.C
3	EP	Tricationic	552	1000	F.C
	PU		770	480	V.M
	PS		552	480	F.C

V.M: very much change, F.C: Few Change, no: no change

Discussion

Corrosion of the coatings

In order to relate the effect of phosphating process with the corrosion resistance of Sn-Zn alloy coating, some of their mechanical properties were considered both before and after corrosion tests.

It was demonstrated in [15] that by changing the corrosive atmosphere the reaction of coating is changed. Thus, with regard to aggressiveness of different atmospheres of different tests in which the samples were exposed different results were obtained. The atmosphere of SST presents the highest rate of variations, a factor which is known to favour the effective corrosion process of alloy coating.

The real atmosphere of part application as underbody part is also more aggressive than would be expected from the laboratory test atmosphere. For this reason it was decided to additionally expose the samples for more than first corrosion products on the surface.

As mentioned earlier, mechanical tests were used to consider the interaction of pretreatment with alloy coating so that different pretreatments account for different consequences in mechanical properties of samples before and after corrosion tests. It should be noted that the interaction of corrosion products with paint and alloy coating in micro-scale can be considered by SEM and X-ray as future work.

As a matter of fact, the thicker polymeric coating can cause to the higher rate of corrosion resistance and the more desirable mechanical properties [15,16]. To avoid unsatisfactory results, the thickness of polymeric coatings were controlled between a specific rang. In this research, the thickness of polymeric coatings for all samples is between 55 μm to 70 μm . The higher level of coating hardness accounts for lower level of penetration. According to this assumption three types of polymeric coating in the basis of their hardness from 33 to 195 seconds were studied.

The adhesion test results as well as the impact test results before corrosion tests are similar for three types of pretreatment. The results of cupping and chipping tests demonstrate desirable results, although depending on the sort of pretreatment they show little differences. On the other hand after SST, the results of cupping test accounts for decreasing in rate of adhesion between organic and alloy coating. The fact that after SST the degree of corrosion experienced by the ferrous phosphated samples was less than obtained by the other pretreatments. According

[9]

to results, the type of pretreatment has little effect on humidity resistance of samples. So the chloride existing in the atmosphere of SST accelerates the corrosion process via favouring the cathodic reduction reaction of hydrogen ions on the alloy coatings.

These results, which were to be expected because of greater electro-potential compatibility between Fe phosphate with alloy coating than other pretreatments.

In agreement with the corrosiveness data obtained, it is confirmed that there is greater deterioration of painting for the tricationic phosphated and non-phosphated samples respectively under near real condition of using (see table (8)). So that differences in results of SST are graphically compared in figure (7).

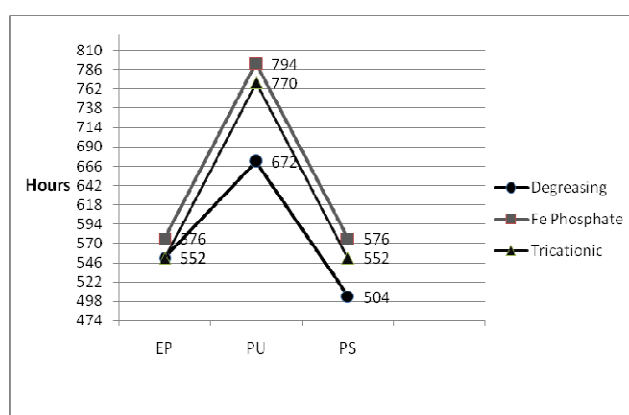


Figure 7: Graphical comparison among the SST results

Regarding to the application of Sn-Zn coating, the properties of polymeric coating targeted to standard criteria which are shown in table (9) [3,5,6,17]. Thence, the appropriate rate of corrosion resistance should be equal or more than 720 hours up to first red stain after SST. Accordingly, the theoretical consideration shows following results concerning the corrosion resistance of polymeric coatings terming to their pretreatment.

Table 9

Predefined criteria range for a desirable paint

Criteria range								
Salt spray test	Moisture resistance	Gasoline resistance	Hardness	Thickness	Adhesion	Cupping	Chipping	Impact
720 hours	480	F.C	At least 30 Sec	at least 40 μm	grade 0	8 mm	Grade 2	Min: 18 lb.in

A t-test analysis on these results shows that for the ferrous-phosphated samples there is p=90% assumption possibility that corrosion resistance is between 436 hours and 860 hours. When comparing Tricationic-phosphated samples, p=90% that SST are between 412 hours and 836 hours (see figure 8).

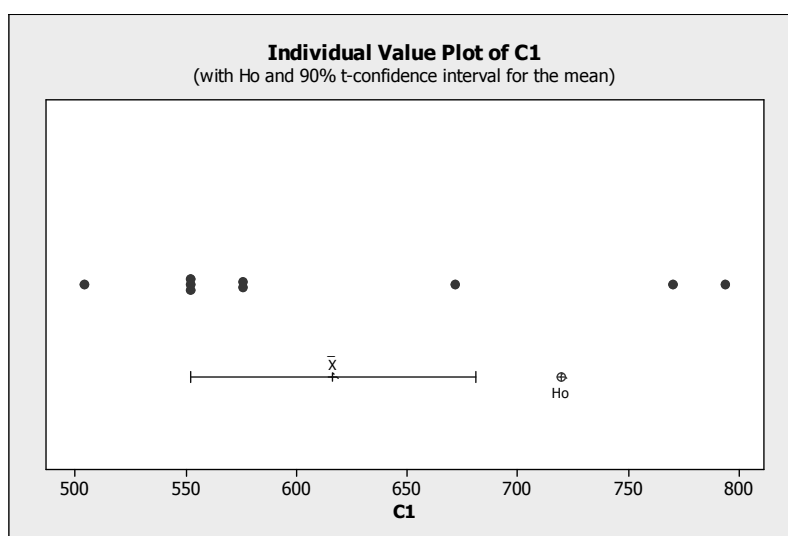


Figure 8: The t-test student distribution of SST results

As can be seen, the figure 9 illustrates the cumulative probability plot including percentile points for corresponding probabilities of SST results. The middle line is the expected percentile from the distribution based on maximum likelihood parameter estimates. The left and right lines represent the lower and upper bounds for the confidence intervals of each percentile. The samples demonstrate 104 hours

comparing standard variance as well as 0.776 Anderson–Darling (AD). Thence, it is probably better to choose the ferrous pretreatment in lieu of other used pretreatment methods.

Among the considered polymeric coatings in this research, PU with ferrous phosphate shows the most effective role to improve the corrosion resistance of Sn–Zn alloy coated steel sheets. Ferrous phosphate seems far satisfactory as pretreatment although Tricationic phosphating can be used as secondary choice for Sn–Zn alloy coating.

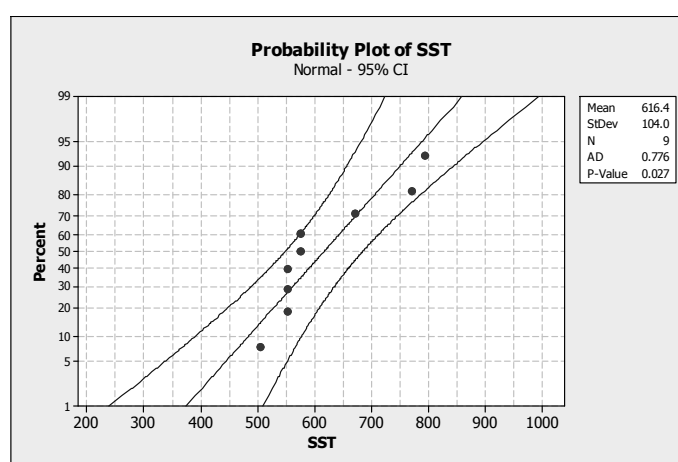


Figure 9: Probability plot of SST results for three groups of phosphated samples

The corrosion mechanism

As results of SEM, the main proportion of Sn–Zn bimetal alloy coating is composed of tin element and the zinc enriched phases are distributed in the eutectic phase of tin–zinc coating (see figure (10)) [18]. As a matter of fact in the noted eutectic phase the zinc phase is distributed among the tin dendrites of tin so that zinc as secondary phase plays the role to improve the corrosion resistance of the coating by cathodic protection.

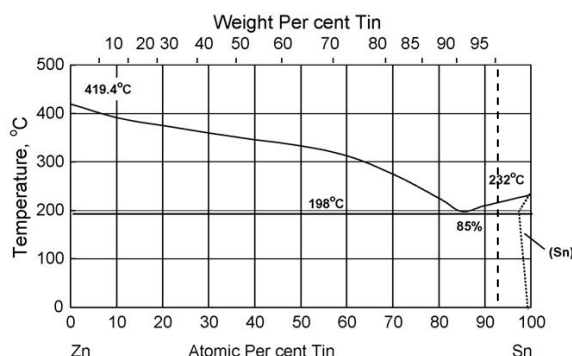


Figure 10: The equilibrium phase diagram of tin-zinc

As can be seen in figure (2), there is an Intermetallic layer between alloy coating and ferrous substrate with thickness around 0.4 μm .

The Intermetallic layer fairly plays the role of impregnable layer, so ferrous substrate and Intermetallic layer has little effect on constitutes of phosphated layer. The zinc enriched phase among the tin dendrites is more susceptible to be corroded [15–18]. Under atmospheric condition, the surface of the metallic coating is covered with a thin passive layer. During alkaline degreasing, this metal–O passive layer dissolves to form metal–OH. The amorphous metal–OH layer formed on the surface induces the phosphate nucleation (table (10)) [2]. Therefore, in pretreatment process; phosphate solution makes constitute with the tin element and also zinc. In regard to electro potential of tin and zinc elements, it's clear that zinc is more active than ferrous [19]. And tin is more noble than ferrous (substrate), thus a very thin layer of tin–zinc coating is partially corroded by the phosphate solution initially and then the phosphate constitute is formed. In [15–18] it was demonstrated that in eutectic alloy coating the velocity of corrosion depending on the element and phase distribution is changed alternatively.

Table 10

Phase constitutes of Tricationic phosphate coatings on zinc [7,11,12]

Ion	Phosphate bath	Phase composition
Fe ⁺²	Fe ₃ H ₂ (PO ₄) ₄ ·4H ₂ O	Zn ₃ (PO ₄) ₂ ·4H ₂ O
	(Fe –heureaulite, monoclinic)	Zn ₂ Fe(PO ₄) ₂ ·4H ₂ O Fe ₂ H ₂ (PO ₄) ₂ ·4H ₂ O
Mn ⁺²	(Mn.Fe) ₄ H ₂ (PO ₄) ₄ ·4H ₂ O	Zn ₃ (PO ₄) ₂ ·4H ₂ O Mn ₂ H ₂ (PO ₄) ₄ ·4H ₂ O
	(Hureaulite, monoclinic) with Mn– Fe (Ashilary)	(Mn–heureaulite, monoclinic)
Zn ⁺²	Zn ₂ Fe(PO ₄) ₂ ·4H ₂ O	Zn ₂ (PO ₄) ₂ ·4H ₂ O (Phosphophyllite, monoclinic)
		Zn ₃ (PO ₄) ₂ ·4H ₂ O (Hopeite, thombic)

It should be noted that, based on inhomogeneous distribution of zinc metal in the tin coating, the speed of corrosion during phosphating process for each phase can be considered as future study. Therefore, product of corrosion due to ion penetration through painting causes decreasing in the rate of paint adhesion.

In [18] it was demonstrated that the corrosion of the interdendritic phases in the eutectic alloy coatings leads to an increased prospect of a crevice developing beneath the delaminating organic coating (see figure 11). Hence corrosion activity becomes more pronounced in the metallic coatings produced here. According to the results of cupping tests the impact of organic coating delaminating due to corrosion product on the alloy coating was shown (see table 8).

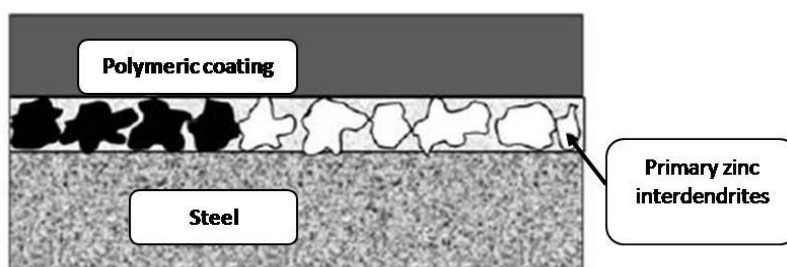


Figure 11: Schematic showing the removal of primary zinc phase from a alloy coating following exposure to corrosion tests

Conclusions

Overall, in this research the objective is to focus on investigating the influence of pretreatment on corrosion resistance of Sn-8% Zn coated steel sheet. This is demonstrated clearly in the present theoretical and experimental analyses, in which the ferrous pretreatment is effective to increase the corrosion resistance of coated sheet and also a more compatibility with polymeric coating. It must be mentioned that, despite the trivial differences among the experimental results of samples, the predicted results from the theory show encouraging agreement with experimental values.

Acknowledgments

The authors wish to thank Young researchers club of Islamic Azad university of Saveh branch, Bahman Motor Company and Nippon steel company for the use of the facilities and financing the project.

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