

Corrosion of phosphated zinc-iron electrodeposits in neutral salt fog

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Corrosion resistance of electrodeposited zinc-iron alloys with either amorphous or crystal phosphate overlayer has been investigated by a neutral salt spray test. An amorphous phosphate layer improves the corrosion resistance of Zn-Fe coatings containing by more than 0.5% of iron. The protectiveness of that film on the alloy containing 1.5 and 2.0% of iron is equated with that of the film on a pure zinc. A crystal phosphate layer exhibits protectiveness much higher than that of an amorphous layer. The effect of the former film is observed for coatings of all compositions. A crystal phosphate coating developed on Zn-Fe alloy containing 1.5% of iron exhibits the highest protective efficiency.

Key words: corrosion, resistance, alloys

INTRODUCTION

Electrodeposits of zinc alloy with iron group metals may provide an improved corrosion resistance for protection of steel objects [1–5]. Zinc-iron alloy system deposits offer superior mechanical properties [6–8]. Steel electroplated with a single Zn-Fe alloy displays a good weldability, formability, and both high-strength and deep-drawing steels may be plated without losing the properties. Zinc-iron coatings exhibit a good paint adhesion and compatibility with cathionic electroplating. Zinc-iron alloy composition may be varied within a wide range. An alloy containing a small amount of iron (about 1%) has the same appearance as zinc and remains sacrificial with respect to a steel substrate, and it is easily chromated.

One way to improve Zn and Zn alloy corrosion resistance is to apply either an overlaying iron phosphate or a zinc phosphate conversion coating. It is known that zinc electroplates with a zinc phosphate layer followed by oiling are taken equal to corrosion resistance of cadmium coatings under a severe climate [9]. Reports on the phosphating of zinc alloys with iron group metals are not numerous. It has been determined in studying the phosphating process of zinc-cobalt electrodeposits that the phosphate layer on Zn-Co alloy has the same composition as that on a pure zinc coating, *i.e.* it is comprised of hopeit $\{Zn_3(PO_4)_2 \cdot 4H_2O\}$ crystals [10]. However, the phosphating of zinc alloy proceeds in a different manner. No special step of the coating surface activating is needed before phosphating. In addition,

the phosphate layer formed on Zn-Co alloy is thicker than that on a pure zinc. Unfortunately, papers on phosphating of zinc-iron alloy are not available.

The aim of the present work was to investigate the feasibility of applying iron phosphate and zinc phosphate coatings on the zinc-iron alloy and to determine the corrosion resistance of obtained coatings.

EXPERIMENTAL

Zinc and zinc-iron coatings were electrodeposited from chloride or sulphate-chloride electrolytes. The composition of plating baths is listed in Table 1. All coatings obtained were solid and smooth.

Table 1. Composition of plating baths and operating parameters

Electrolyte components Operating parameters	Electrolyte	
	Zn	Zn-Fe
ZnCl ₂	40–120 g/l	70 g/l
NH ₄ Cl	180–220 g/l	200 g/l
FeSO ₄ ·7H ₂ O	–	20–80 g/l
Stabilizer Limesda SNŽ-C	–	20 g/l
Brightening agent:		
Likonda ZnSR -A	30–70 ml/l	50 ml/l
Likonda ZnSR -B	3–5 ml/l	5 ml/l
PH	4.6–6.0	3.6–4.0
Temperature	Room	Room
Cathodic current density	2 A/dm ²	2 A/dm ²

The content of iron in the alloy was determined by the atomic-absorption spectroscopy method.

An amorphous phosphate coating was obtained in a Likonda FA50 solution [11]. The solution temperature was 60 °C, pH 4.2–4.5, phosphating duration 5 min.

A solution to apply a crystalline phosphate coating consisted of (mol/l): Zn^{2+} – 0.17, PO_4^{3-} – 0.34, NO_3^- – 0.4. The temperature of solution was 20 °C, pH 2.4–2.6, phosphating duration 10 min. The weight of phosphate coating was ~ 6.0 g/m².

All the coatings for the salt-spray tests were deposited on carbon steel panels 100 x 50 x 1 mm in size. The thickness of zinc and zinc-iron coatings was 10 μ m. It was prepared in five specimens with coatings of different composition.

A neutral 5% NaCl solution was sprayed in a salt-spray chamber at 35 ± 1 °C [12]. The degree of corrosion damage was assessed by evaluating the surface area covered with corrosion products. The percentage of defective area was converted to rating numbers. The rating numbers and the corresponding specimen surface areas covered with corrosion products are listed in Table 2.

Table 2. The intervals of the specimen surface area covered with corrosion products and the corresponding rating numbers

The surface area (S), %.	Rating number
without corrosion	10
$S \leq 0,1$	9
$0,1 < S \leq 0,25$	8
$0,25 < S \leq 0,5$	7
$0,5 < S \leq 1,0$	6
$1,0 < S \leq 2,5$	5
$2,5 < S \leq 5$	4
$5 < S \leq 10$	3
$10 < S \leq 25$	2
$25 < S \leq 50$	1
$50 < S$	0

RESULTS AND DISCUSSION

Corrosion tests of non-passivated Zn-Fe coatings in a salt-spray chamber show that the iron present in a zinc coating improves the corrosion resistance beginning even from 0.3% (Fig. 1). Variation of iron content from 0.3 to 0.8% does not actually change the coating resistance. An alloy containing 1.5% Fe has a much lower corrosion resistance to a salt fog effect. It may be possible that such a variation is conditioned not by a direct iron quantity effect, but by structural differences of the coatings. Zinc and zinc-iron coatings containing from 0.3 to 0.8% of

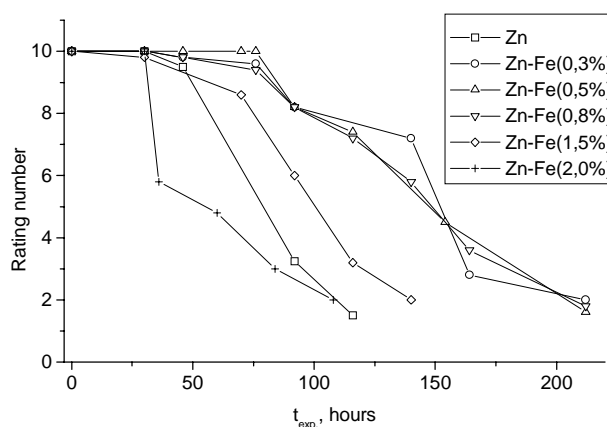


Fig. 1. Corrosion of non-passivated zinc and zinc-iron coatings with different iron amount in a neutral salt fog. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

Fe were both smooth and bright. Meanwhile, the surface of Zn-Fe coatings containing 1.5 and more per cent of iron were semibright. Such coatings have a rougher surface and could be more porous. This worsens coating corrosion resistance.

The data on coating corrosion performance, evaluating the area of phosphate coating surface covered with zinc corrosion products should provide information about the protective properties of phosphate film. However, the phosphate film is very quickly decomposed in a salt fog, and the data obtained give no information about the influence of Fe content in alloy on the protective efficiency of the phosphate film (Fig. 2). A conclusion may be made from this chart that corrosion protectiveness of the coatings with a crystal phosphating layer is much higher than that of the coatings with amorphous layer.

The data on the corrosion performance of coatings, when the time of appearance and the area covered with corrosion products of the base metal, are much more informative. In this case, the rating involves a summary result, viz. corrosion resistance of the metal coating and protectiveness of the phosphate layer.

The corrosion behaviour of zinc-iron coatings containing 0.3% of iron does not actually differ from that of non-passivated coatings of the same composition, i.e. an amorphous phosphate layer does not improve the protective properties of the coating (Fig. 3). Meanwhile, an amorphous phosphate film on the zinc-iron alloy containing either 0.5 or 0.8% of iron considerably changes the coating corrosion behaviour. Corrosion damages of the same level appear on phosphate coatings 35–75 h later than on non-passivated ones exposed in a salt-pray chamber (Figs. 4 and 5). The amorphous phosphate layer

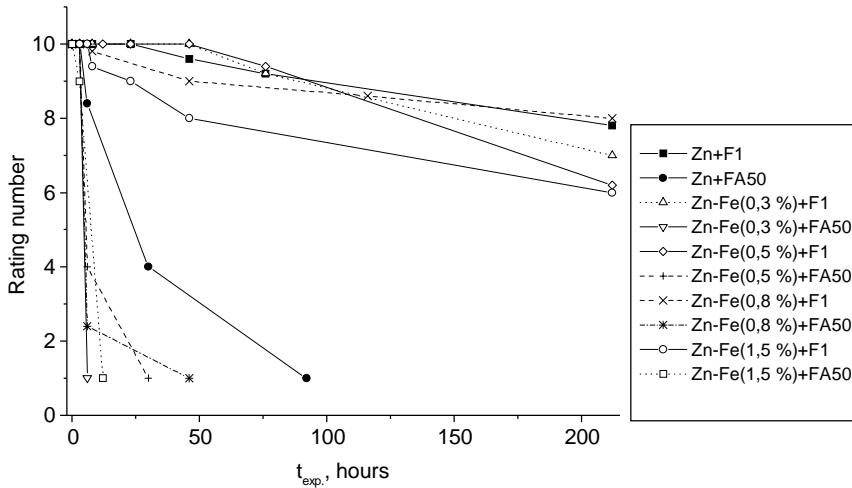


Fig. 2. Corrosion of zinc and zinc-iron coatings of different iron amount in a neutral salt fog. The coatings were passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with coating corrosion products

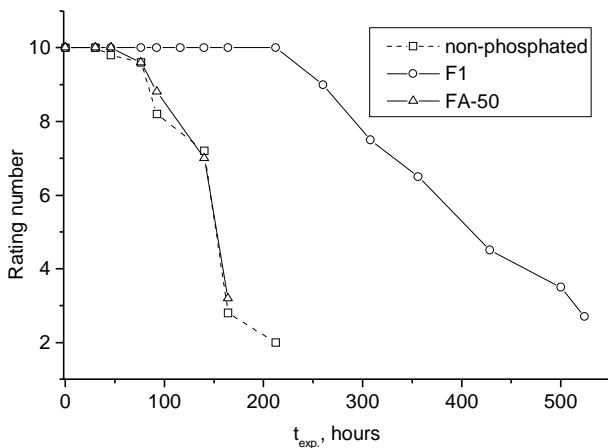


Fig. 3. Corrosion of zinc-iron coatings containing 0.3% of iron in a neutral salt fog. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

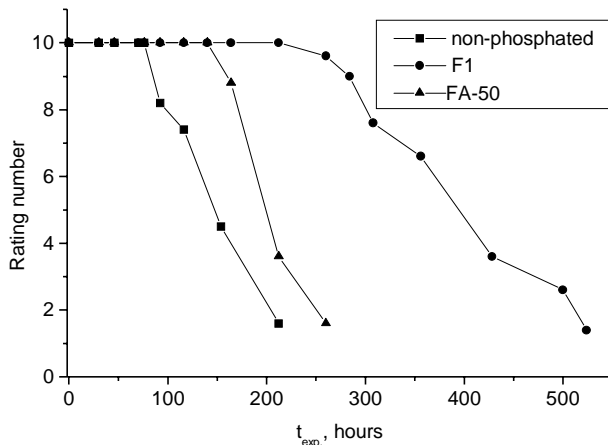


Fig. 4. Corrosion of zinc-iron coatings containing 0.5% of iron in a neutral salt fog. The coatings were either non-passivated or passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

developed on a Zn-Fe alloy with the content of iron 1.5 and 2.0% delays the appearance of the same corrosion signs by 96–165 and 70–174 hours, respectively.

Corrosion tests of pure zinc coatings phosphated were carried out for comparison (Fig. 8). An amorphous phosphate film on pure zinc prolongs the time of corrosion damages from 83 to 171 hours.

It follows from the results obtained that the amorphous phosphate layer on Zn-Fe alloy containing more than 0.5% of iron improves the capability

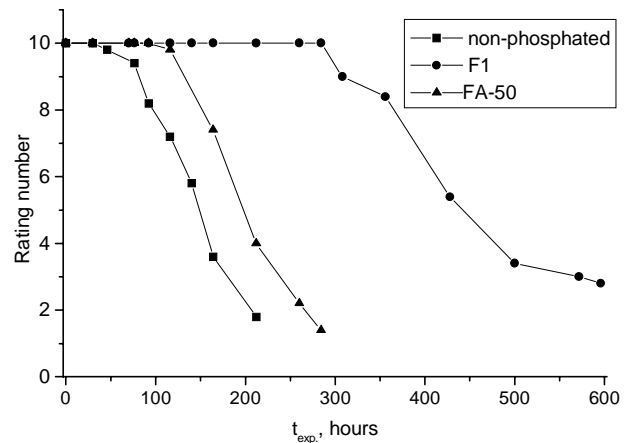


Fig. 5. Corrosion of zinc-iron coatings containing 0.8% of iron in a neutral salt fog. The coatings were either non-passivated or passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

of the coating to protect steel from corrosion. The protective properties of the film on the alloy containing either 1.5 or 2.0% of iron are equated with those of the film on pure zinc. The efficiency of phosphate layer on an alloy with a smaller content of iron is lower.

A crystal phosphate layer improves the protective properties of zinc-iron coatings better than does an amorphous layer. This may be seen from the data on corrosion of the coatings when estimating the specimen surface area covered with corrosion products of the base metal and the coating corrosion products (Figs. 2–7). A prominent effect of crystal phosphate is observed for tested alloys of all compositions. A crystal phosphate coating developed on

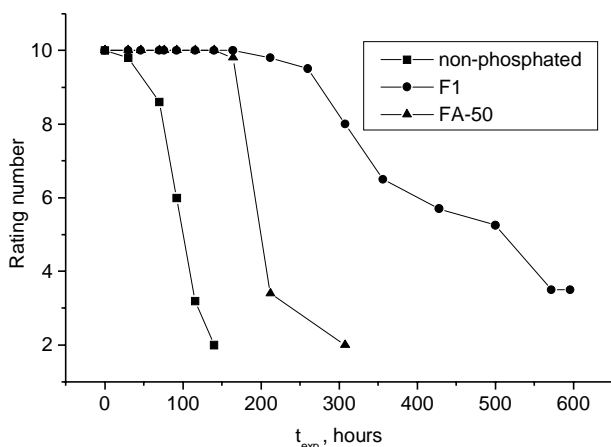


Fig. 6. Corrosion of zinc-iron coatings containing 1.5% of iron in a neutral salt fog. The coatings were either non-passivated or passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

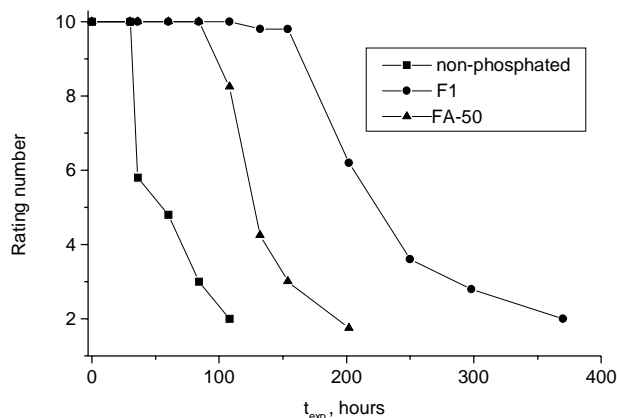


Fig. 7. Corrosion of zinc-iron coatings containing 2.0% of iron in a neutral salt fog. The coatings were non-passivated or passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

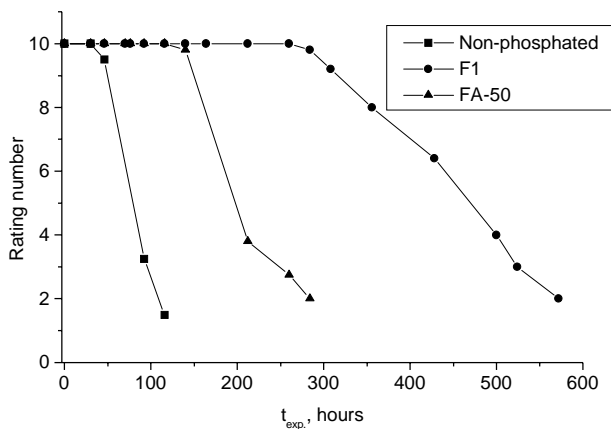


Fig. 8. Corrosion of zinc coatings in a neutral salt fog. The coatings were either non-passivated or passivated in a crystal (F1) or an amorphous (FA-50) phosphating solution. Ratings were determined by the specimen surface area covered with corrosion products of the base metal

a Zn-Fe alloy containing 1.5 % of iron is noted for the highest protective efficiency. It by 180–450 hours delays the appearance of corrosion of the same degree (Fig. 6). A crystal phosphate layer on pure zinc has a similar effect (Fig. 8).

CONCLUSIONS

An amorphous phosphate layer improves the corrosion resistance of Zn-Fe coatings containing more than 0.5% of iron. The protectiveness of the film on an alloy containing either 1.5 or 2.0% of iron is equated with that of the film on pure zinc.

A crystal phosphate layer exhibits a much higher protectiveness than does the amorphous one. The effect of the former film is observed for coatings of all compositions. A crystal phosphate coating developed on a Zn-Fe alloy containing 1.5% of iron exhibits the highest protective efficiency.

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**FOSFATUOTŲ CINKO–GELEŽIES DANGŲ
KOROZIJA NEUTRALIAME DRUSKOS RŪKE**

S a n t r a u k a

Amorfinės fosfatinės dangos padidina Zn–Fe dangų, kurių sudėtyje yra daugiau negu 0,5% Fe, korozinį atsparumą. Fosfatuoto lydinio, kurio sudėtyje yra 1,5–2,0% Fe, korozinis atsparumas yra artimas fosfatuoto gryno Zn koroziniam atsparumui.

Kristalinių fosfatinių dangų atsparumas korozijai yra didesnis už amorfinių fosfatinių dangų korozinį atsparumą. Apsauginis fosfatinių dangų efektas stebimas, esant įvairiai Zn–Fe lydinio sudėčiai. Didžiausias fosfatuotų Zn–Fe dangų korozinis atsparumas nustatytas esant Zn–Fe lydinyje 1,5% Fe.

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**КОРРОЗИЯ ФОСФАТИРОВАННЫХ
ЦИНК-ЖЕЛЕЗО ГАЛЬВАНОПОКРЫТИЙ В
НЕЙТРАЛЬНОМ СОЛЕВОМ ТУМАНЕ**

Р е з ю м е

Аморфные фосфатные покрытия увеличивают коррозионную стойкость электролитических Zn–Fe покрытий, содержащих более 0,5% железа. Коррозионная стойкость на сплавах, содержащих 1,5 и 2,0% железа, сопоставима с защитными свойствами фосфатированного цинка.

Кристаллические фосфатные покрытия отличаются большей коррозионной стойкостью по сравнению с аморфными. Вышеупомянутый эффект наблюдается для всех видов Zn–Fe сплавов. Кристаллические фосфатные покрытия на Zn–Fe сплавах, содержащих 1,5% железа, отличаются наибольшей коррозионной стойкостью.