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Microstructural Development of Galvanized Steels Prepared With Ni-P Electroless Deposited Pre-coatings

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Abstract

An electroless pre-coating process is investigated as a possible method to prevent the sandelin effect, whereby steels containing silicon reacts rapidly with zinc during galvanization. From the microstructural and kinetics analysis, it is found that nickel-phosphorus electroless pre-coatings effectively serve as barriers to the reaction between Fe and Zn during galvanization, regardless of the silicon content in the steel substrates. Correspondingly, the coating thickness of the galvanized steels can be well-controlled.

Keyword : Galvanizing, Coatings, Electroless deposition, Ni-P alloys, Phase transformation
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Introduction

The hot-dip galvanizing process is commonly used for applying zinc onto steels' surfaces for corrosion protection. Galvanized steels obtained therefrom are utilized in various applications ranging from building structures to automotives and electronic components. The lifetime of the coatings with a typical coating thickness of about 50-100 μm can be as high as 50 years in general environments.(1) When hot-dip galvanizing is performed on steels that contains silicon of about 0.1-0.2 wt%, the problem so-called "sandelin effect" however arises.(2-3) In this effect, silicon promotes the reaction between iron and silicon. Correspondingly, the resulting coatings are characterized by a non-uniform and excessively thick layer with dull-grey appearance.

Several methods have been investigated in attempts to prevent rapid growth of the Zn-Fe intermetallic layers during galvanization of silicon-containing steels. For examples, a small amount of Ni of 0.05-0.14% may be added to a molten zinc bath to help subside the rapid Zn-Fe kinetics(4), or alternatively a layer of Ni pre-coating may be applied on steels' surfaces prior to galvanizing to prevent Zn to interface with steel from the first place.(5-6) In addition to controlling coating thickness and uniformity, the latter approach could also provide enhancement of corrosion resistance of coatings owing to the developed intermetallic layers which comprise Zn-Ni.(7)

In this work, to effectively mitigate the sandelin effect, we further investigate the pre-coating approach by specifically examining the electroless deposition process as a method for applying Ni-P pre-coatings prior to galvanizing. The electroless Ni-P plating is attractive in its simplicity and ability to form a uniform thin coating.(6) In the study, phase transformation, microstructural development, and galvanizing kinetics are analyzed for the pre-coated galvanized steels with distinct silicon compositions. The comparison is made with those obtained from the conventional hot-dip galvanizing process.

Materials and Experimental Procedures

The Ni-P electroless deposition and hot-dip galvanizing process were conducted on two sets of steels with different compositions: (i) C 0.151 wt.%, Si 0.00502 wt.%, Mn 0.452 wt.%, P 0.00463 wt.%, Cr 0.0652 wt.%, balance Fe; and (ii) C 0.216 wt.%, Si 0.227 wt.%, Mn 0.665 wt.%, P 0.0163 wt.%, Cr 0.217 wt.%, balance Fe. They will be called herein "LS" and "HS", respectively. The steel sheet samples, cut to 4 x 2 x 0.2 cm^3, were surface polished with SiC paper, ultrasonic cleaned, degreased in 10

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wt.% NaOH at 60°C for 10 minutes, and acid pickled in 14 wt.% HCl for another 20 minutes. The samples were then immersed into the low-temperature Ni-P electroless bath (300 cc), with the formulations and conditions as shown in Table 1, for 15 minutes.

Subsequently, the samples with and without pre-coatings were pre-treated by dipping in ammonium -based flux, followed by galvanzing in a molten zinc bath, prepared from 99.995% zinc ingot, at 450°C for four different durations : 5, 10, 60, 100 sec. The drawing speed was controlled at 150 cm/min. The galvanized samples with and without pre-coatings are labelled "GN" and "GI", respectively. For examples, LS-GN-60s denotes the steel sample with the low silicon content that was applied with Ni-P pre-coating prior to galvanizing for 60 sec.

Metallography and microstructure evaluation were conducted on the cross-section of all specimens etched with 1% Nital. The chemical composition and corresponding phases of the coating layers were identified using the energy dispersive spectroscopy (EDS) and scanning electron microscopy.

Table 1. Formulation of the electroless Ni-P baths operated at 65°C

Chemical	Formula	Concentration
Nickel Sulfate	$NiSO_4.6H_2O$	0.15 M
Sodium Hypophosphite	$NaH_2PO_2.H_2O$	0.38M
Tri-Sodium citrate	$Na_3C_6H_5O_7$	0.16 M
Ammonium Sulfate	$(NH_4)_2SO_4$	0.23 M
Thiourea	$SC(NH_2)_2$	0.8 ppm
pH		9

Results and Discussion

All specimens were successfully prepared. For both LS-GN and HS-GN sets of specimens, the pre-coatings are determined to be approximately 6 μm thick prior to galvanizing. Figure 1 and 2 illustrate the cross-sectional microstructure of the specimens. In general, for LS-GI, LS-GN, HS-GI, and HS-GN, the microstructure consists of a steel substrate and a zinc layer that sandwich at least a couple of intermediate layers. Unlike the typical columnar structure found in the intermediate layers of the conventional galvanized steels (e.g., LS-GI and HS-GI), the LS-GN and HS-GN specimens exhibit rather compact intermediate layers. In all sets of specimens, the intermediate layers' thicknesses appear to increase monotonically with galvanizing duration. The original Ni-P pre-coating layers are found to remain in the structure generally, but the thicknesses are also reduced over galvanizing time.

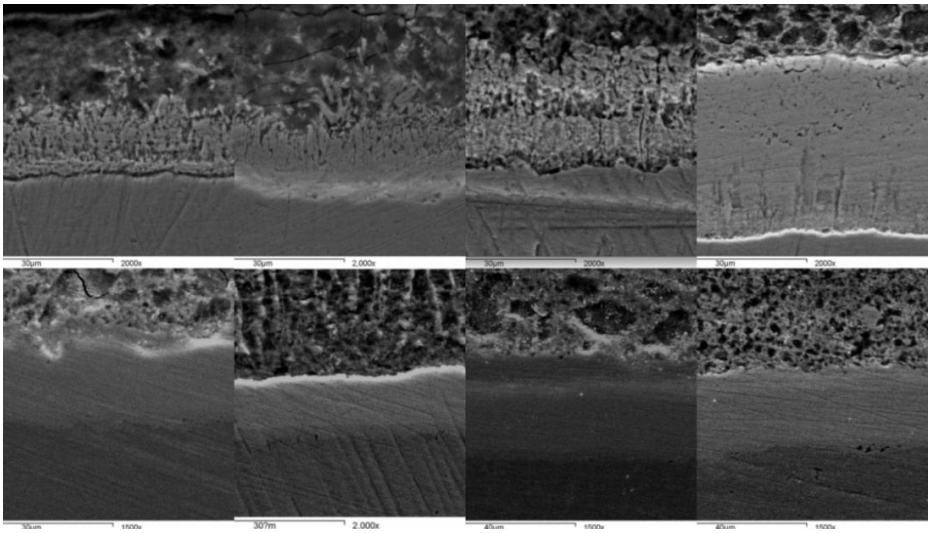

Figure 1. SEM micrograph of JIS SS400 low silicon steels (LS-GI) hot-dip galvanized for (a)-(d) 5, 10, 60 and 100 s respectively, and low silicon steels with Ni-P pre-coating (LS-GN) hot-dip galvanized for (e)-(h) 5, 10, 60 and 100 s respectively.

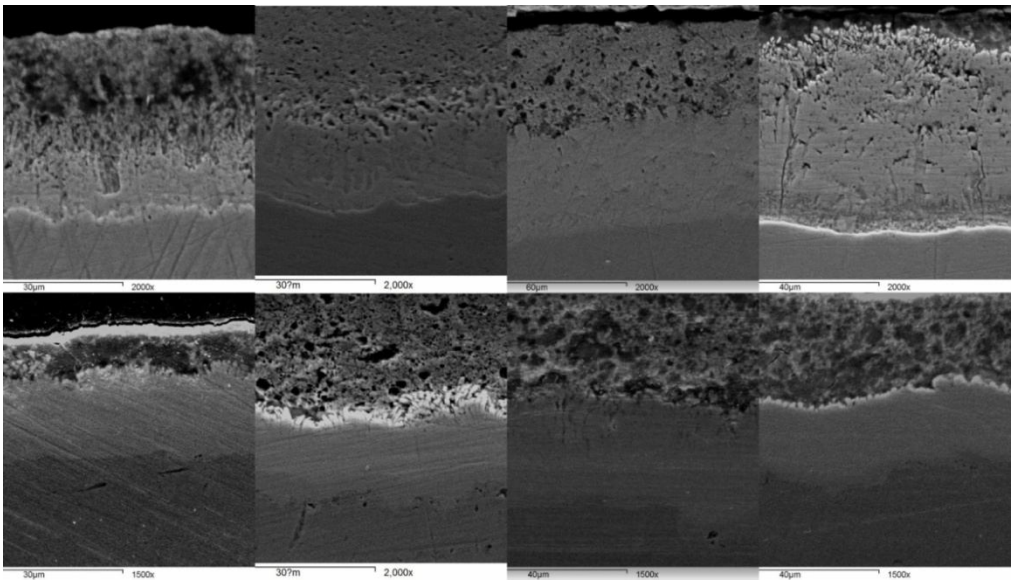

Figure 2. SEM micrograph of JIS SS400 high silicon steels (HS-GI) hot-dip galvanized for (a)-(d) 5, 10, 60 and 100 s respectively, and high silicon steels with Ni-P pre-coating (HS-GN) hot-dip galvanized for (e)-(h) 5, 10, 60 and 100 s respectively.

Figure 3 summarizes the coating layer thicknesses of the specimens in various sets, as deduced from the micrographs. It can be observed that, the pre-coatings can effectively help prevent the rapid growth of the coating upon galvanization. This is clearly observed for galvanizing durations above 5 sec where the total coating thicknesses of the LS-GN and HS-GN specimens are significantly thinner than those of the LS-GN and HS-GN. Interestingly, the coating thicknesses of the specimens in the LS and HS sets are comparable, suggesting that the sandelin effect has been effectively suppressed.

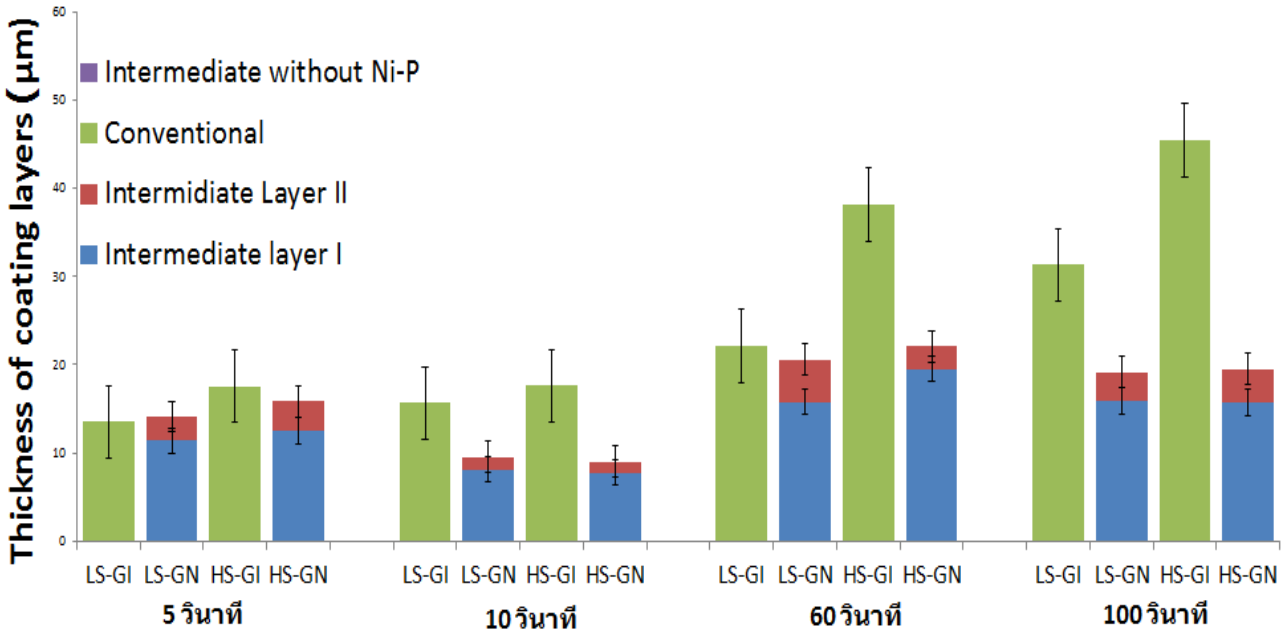

Figure 3. The thickness of the intermediate layers in the galvanized specimens hot-dipped for various durations.

Table 2 presents the chemical compositions and phase structures of different sets of specimens in details. The analysis was conducted at 4 regions, namely the Ni-P layers, the central of the intermediate layers, the intermediate layer close to the zinc layer, and the zinc layer. The conventional galvanized specimens (LS-GI and HS-GI) exhibit the typical intermediate layer comprising of Γ, δ, and ζ phases.[7] As for the specimens with the pre-coatings (LS-GN and HS-GN), the compositions of Zn, Ni, and Fe in the intermediate layers suggest a formation of Γ+β, Γ, and δ phases, according to the ternary phase diagram.[8]

Table 2. Chemical compositions and phases of the specimens with Ni-P pre-coating following hot-dip galvanizing for 10 seconds.

Hot-Dip duration	Sample	Ni-P				1					2					3				
		Fe	Zn	Ni	P	Fe	Zn	Ni	P	Pha	Fe	Zn	Ni	P	Pha	Fe	Zn	Ni	P	Pha
		[%atomic]				[%atomic]					[%atomic]					[%atomic]				
5	LS-GI-5s	N	N	N	N	14.	85.	0	0	Γ	7.0	92.	0	0	δ	0	100	0	0	η
	LS-Gm-	7.0	0	84.	8.8	0	86.	13.	0	Γ+β	6.2	93.	0	0	ζ	4.6	95.	0	0	η
	HS-GI-	N	N	N	N	6.4	93.	0	0	Γ	5.3	94.	0	0	ζ	0	100	0	0	η
	HS-GN-	3.0	5.8	82.	8.8	0	85.	14.	0	Γ+β	0	97.	2.5	0	Γ1	0	100	0	0	η
10	LS-GI-	N	N	N	N	10.	89.	0	0	δ	7.7	92.	0	0	δ	0	100	0	0	η
	LS-Gm-	3.2	2.5	86.	7.7	1.8	85.	12.	1.8	n/a	0	97.	2.3	0	Γ_1	0	97.	2.0	0	η
	HS-GI-	N	N	N	N	7.9	92.	0	0	δ	5.6	94.	0	0	ζ	0	100	0	0	η
	HS-GN-	1.8	0	95.	0	0	87.	12.	0	Γ+β	1.0	98.	0	0	ζ	0	100	0	0	η
60	LS-GI-	N	N	N	N	10.	89.	0	0	δ	6.2	93.	0	0	ζ	0	100	0	0	η
	LS-Gm-	3.1	9.5	79.	8.1	0	87.	12.	0	Γ+β	6.7	93.	0	0	ζ	0	100	0	0	η
	HS-GI-	N	N	N	N	6.0	93.	0	0	δ	1.2	98,	0	0	η	0	100	0	0	η
	HS-GN-	3.3	4.7	83.	8.0	0	87.	12.	0	Γ+β	0	90.	9.4	0	Γ1	0	100	0	0	η
100	LS-GI-	N	N	N	N	11.	88.	0	0	δ	6.5	93.	0	0	ζ	0.9	99.	0	0	η
	LS-Gm-	4.9	0	84.	10.	0	86.	13.	0	Γ+β	0	87.	12.	0	Γ+β	0	100	0	0	η
	HS-GI-	N	N	N	N	11.	88.	0	0	δ	6.9	93.	0	0	ζ	0	100	0	0	η
	HS-GN-	4.0	15.	72.	7.4	0	87.	12.	0	Γ+β	0	92.	7.0	0	Γ1	0	100	0	0	η

The kinetics of the growth of the intermediate layers may be represented by a power-law growth equation: $Y= Kt^n$, where Y, K, t, and n are coating layer thickness, growth rate constant, reaction time, and growth-rate time constant, respectively. From the coating thickness data shown in Figure 3, the growth-rate time constant, n, of specimens LS-GI, LS-GN, HS-GI, HS-GN are determined to be 0.33, 0.15, 0.36, 0.15, respectively. This clearly indicates that the types of kinetics controlling the layer growth of the systems with and without the pre-coatings are fairly distinct. Specifically, the kinetics that control the interaction between Ni-P and Zn exhibits somewhat lower rates than those of the Fe and Zn interaction, regardless of Si constituents in the steel substrates.

Conclusions

Electroless Ni-P pre-coatings effectively serve as barriers to the reaction between Fe and Zn during galvanization. Particularly, the corresponding thicknesses of the intermediate coating layers prepared with the electroless pre-coating route are somewhat smaller than those prepared by the conventional galvanizing process. Such kinetics impeding effect is independent of the Si constituents in the steel substrates. Furthermore, the intermediate layers of the galvanized coatings prepared with Ni-P pre-coatings also compose of Zn-Ni, expectedly exhibiting relatively high corrosion resistance. The electroless pre-coating is therefore a potential approach to effectively prevent the sandelin effect and in parallel provide enhancement of coatings' durability.

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