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Effect of prior electro or electroless Ni plating layer in galvanizing and galvannealing behavior of high strength steel sheet

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ABSTRACT

Galvanization (GI) and galvannealing (GA) of high strength (HS) steel surface is very prone to develop uncoated spots in coating. Sometimes, GA coating may lead to inferior mechanical performance than GI coating as different brittle (Zn-Fe) intermetallic phases are formed in the coating. In this study an innovative prior Ni plating followed by hot dip galvanization and galvannealing process was thought of to obtain good quality of alloy coating. Adherence of molten zinc on the surface of high strength steel sheet improved significantly by prior Ni coating. SEM-EDS and XRD techniques were used for depth analysis of all coatings. The presence of pure zinc phase was confirmed almost entire depth of the coating when GI coating was formed on HS steel substrate without any prior metallic coating whereas the presence of alloy phase was confirmed up to some depth of the coating when GI coating was obtained on HS steel surface with prior Ni coating. The GA coatings with prior Ni plating primarily compose of the desirable $Ni_{5.225}Zn_{41.8}$ phase. Interdiffusion of Zn and Fe is controlled by Ni layer to get desirable alloy coating. The GI coatings with prior Ni plating layer provides better resistance against chloride attack and GA coating ensured significance improvement in performance than GI coating. The best GA coating was formed on the steel substrate with prior Ni coating by electrodeposition process. This GA coating showed 3–4 times improvement in performance against aggressive chloride attack, lowest powdering and excellent phosphatability with respect to the GA coating on the steel substrate without any prior Ni plating.

1. Introduction

Steel sheets use in motor cars must satisfy resistance against corrosion. Coating plays a vital role to ensure longer life of the automobiles [1–3]. The life of the steel substrate can be improved by many coating technologies available, like hot-dip [4–6], electro or electroless deposition [7–13], spraying [14–16] and surface passivation by phosphating [17–19] etc. Since early development of zinc coating on steel substrate by dipping in molten zinc to provide corrosion protection to steel, still this coating has an edge over other metallic coatings processes because of its ease of application process, capability to provide sacrificial as well as barrier protection with longer protection guarantee with cheaper coating cost. Galvanization of steel sheet can be done continuously by dipping in liquid zinc in the presence of small amount of other alloying components like Al, Mg [20–25]. Reaction between steel substrate and zinc is mainly controlled by Al content in molten zinc. This reaction stops totally if aluminum content is >0.2 wt% with the formation of a thicker and stronger Fe_2Al_5 intermetallic compound as an inhibition layer [21]. For better safety and fuel efficiency [26–30], automakers are looking for high strength steel. Several high strength steel grades have been developed by addition of alloying elements like Si, Al in steel. Mn and Si have a tendency to segregate to top surface during annealing operation and form different oxides. Thereby, poor zinc coating on HS steel surface happens as the oxides hinder zinc adhesion on steel resulting uncoated spots [31–37].

Several research works have been done to resolve the zinc coatability issue of HS steel by internal oxidation of Si and Al [38–40]. Internal oxidation process got some success to resolve the zinc coatability problem of HS steel but the problem still persists. Hence, researchers have tried to explore an alternative route to resolve this chronic problem and got good success to improve zinc coating performance by prior Ni coating [41]. Prior Cu coating was tried as a replacement of fluxing operation for steel tube galvanization with a great success. Excellent GI coating was obtained on the substrate of steel tube by prior Cu flash coating [42]. The authors also tried Cu flash [43–44] coating as an option to resolve the coatability issue of high strength steel. The Zn-Ni alloy coating by electrodeposition process was developed to improve surface quality of steel for automotive application with limited success as the process is slow and complicated. In this scenario an innovative prior Ni plating followed by a quick hot dip galvanizing and galvannealing process was employed to obtain good quality of alloy coating.

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Table 1
Basic composition of steel in wt%.

C	Si	Mn	P	Al	Ti	Nb	B	Cr	N
0.003	0.015	0.40	0.045	0.04	0.04	0.42	~0.001	0.044	<0.004

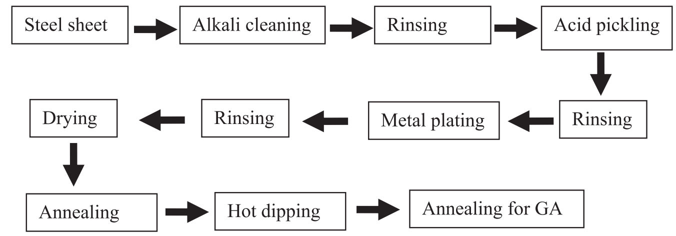
Table 2
Condition for metal plating.

Plating	Salt content (g/L)	Acid content (ml/L)	Time (s)	Temperature (°C)
Ni	$NiSO_4$: 300, $NiCl_2$: 45	H_3BO_3: 40	300	27–30
Ni-P	$NiSO_4$: 50, NaH_2PO_2: 25	glycolic acid: 30	360	85–90

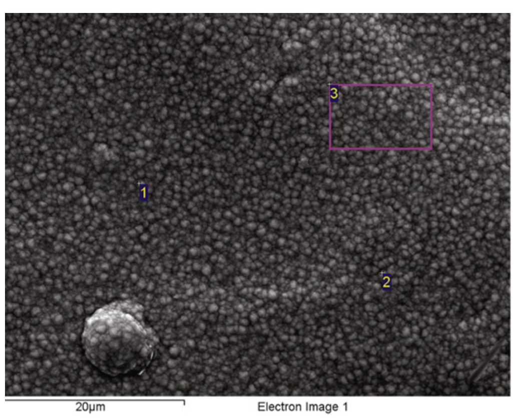
Being nobler to iron Ni can be used as a prior metallic coating layer to get better zinc coating on the surface of high strength steel. The objective of present research work is to understand the role of prior Ni or Ni-P plating as an inner layer before dip in molten zinc bath of high strength steel sheet to resolve the issue of bare spot problem and improvement in corrosion performance. The process optimization to obtain such a good quality alloy coating were also studied to manufacture excellent quality galvannealed coating on the surface of high strength steel sheet.

2. Experimental procedure

The high strength steel sheet was collected from plant for the experimentation. Table 1 represents the composition of steel sheet used for experimentation in weight percent. ASTM E 415-99a [45] was adopted to analyze the steel composition.

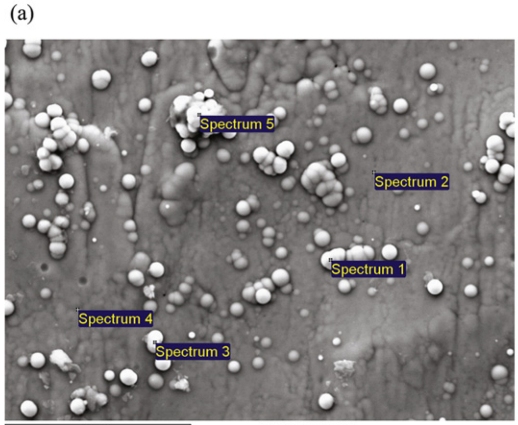


The process followed has been shown above as flow diagram. The steel sheet was cut to pieces of size (200 mm × 120 mm) as per requirement for GI and GA operation in a hot dip simulator (HDS). To remove contaminants like oil from steel substrate, alkali treatment was done in 40 wt% alkali solution at 70 °C for 120 s. All the specimens were washed in tap water to remove alkali chemicals from the steel substrate. Thereafter, pickling treatment was conducted in 16 vol% HCl acid solution at 70 °C for 5 s to ensure complete removal of oxides. Steel sheet specimens were washed using tap water to ensure complete removal of acid from steel surface. Pure Ni or alloy of Ni-P plating was done on the substrate of high strength steel sheets by electro or electroless deposition process. Electrodeposition of Ni on the steel surface was performed by applying external direct current power source. Steel sheet was used as cathode for this type plating process. Ni ions in the solution are reduced by electron and deposited on the cathode surface. No external power supply was adopted for electroless deposition process. In this case, the reduction of nickel ions happened by the reducing agent added in the solution. Phosphorous co-deposited on the steel surface along



Pt	Fe	Ni
1	3.37	96.63
2	3.54	96.46
3	3.57	96.43

(a)



Pt	Fe	Ni	P
1	5.41	82.02	12.56
2	6.40	82.64	10.96
3	4.55	83.76	9.47
4	5.82	83.72	10.46
5	4.90	81.52	13.58

(b)

Fig. 1. Morphology and EDS at the top surface after (a) Ni and (b) Ni-P flash coatings.