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Investigation of microstructure and corrosion behaviour of prior nickel deposited galvanised steels

Kuntal Sarkar, Avik Mondal, Anindita Chakraborty*, Mohit Sanbui, Nitu Rani, Monojit Dutta

Research and Development, Tata Steel, Jamshedpur, India

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ABSTRACT

Structure and performance of hot dip galvanised coating can be improved by incorporation of different alloying elements like Al, Ni, Pb etc. in the coatings. Zn-Ni alloy based coating systems have already been proved to have high corrosion resistance along with improved adherence, weldability, mechanical properties etc. In the present study, the microstructural development of prior nickel coated galvanised coating is studied. The initial nickel coating thickness is about 6 μm and the galvanising time is varied from 3 to 10 s. Nickel-zinc delta and gamma phases are formed within the coating and iron diffusion is considerably suppressed. Corrosion performances of prior Ni coated galvanised coating and conventional galvanised coatings have been evaluated with the help of electrochemical analysis techniques. The potentiodynamic polarization study shows that both the coatings have similar active dissolution behaviour. The EIS analysis reveals that the passivation behaviours of two different coatings are largely different for prolonged immersion in the electrolyte solution. The prior nickel coated galvanised alloy coating has been observed to develop a stable thin passive layer of oxide which is duplex in nature and the resistance to corrosion is increasing with immersion time. The exposure of nickel rich intermetallic layers with prolonged immersion is also acting as barrier to corrosive ions penetration and increasing the corrosion resistivity. On the contrary the pure galvanised samples first show increasing (up to 10 days) and then decreasing (10 to 20 days) resistance to corrosion due to the initial formation of the oxide film followed by its dissolution.

1. Introduction

Zinc based coatings are the most widely used coating systems on steel. The applications of zinc based coatings are enormous starting from automotive, construction, white goods, plumbing and irrigation. Different types of hot dip coatings such as galvanised, galvannealed, zinc-aluminium alloy coating, zinc-aluminium-magnesium coating etc. have been developed commercially over last few decades. The structure-property relationship of these coatings as well as development of further improved processes and new products have been the core area of research. Depending upon the process requirement and/or final applications, there are several approaches to further improve the coating compositions, microstructure and coating properties [1].

The use of prior coating before galvanising is one such approach over existing processes to improve coating quality in terms of surface finish and corrosion properties. Prior deposition of copper and copper-tin coatings on high strength steels was found to reduce the number of bare spots during continuous galvanising of Dual Phase (DP) steels [2–4]. The prior-copper coatings deposited by flash process as well as by electrodeposition process were effective in enhancing the coating corrosion performance [4–6]. Similarly, prior-nickel coating was found to be effective in suppressing the selective oxidation of DP steels reducing the number of bare spots after galvanising [7]. The pre-layer of copper or nickel was used as a diffusion barrier to the alloying elements in steel to prevent surface segregation and selective oxidation. Copper coating was also explored as a potential solution to suppress the Fe-Zn phase formation during batch galvanising [8–10]. Prior-coating of nickel and nickel-phosphorous could control the Fe-Zn reaction for high silicon reactive steels [11–13]. The initial nickel coating thickness has profound effect on the final phase formation in galvanised coatings. It was investigated by the same group [14–16] that there exists a threshold or critical thickness of nickel beyond that nickel-zinc intermetallic phases instead of iron-zinc start to form within the galvanised coating.

The corrosion behaviour in presence of prior copper or nickel layer is reported to have improved over the conventional galvanised coatings. It was reported that electroless coating of nickel layer [17] and pulse-electrodeposited nickel layer [18] resulted in uniform and void free

* Corresponding author.
E-mail address: anindita.c@tatasteel.com (A. Chakraborty).

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coating. It was reported that the OCP of the Prior nickel coated galvanised alloy coating shifted towards more anodic region with prolonged immersion time in aqueous Sodium Chloride solution indicating the initial sacrificial nature of the top η (pure zinc) layer followed by increasing barrier protection of highly stable oxide film formed on the surface. Sa-nguanmoo et al. [18] studied the difference in corrosion characteristics of prior nickel pulse electro-deposited galvanised coating and a conventional galvanised coating on low carbon cold rolled steel. The coating with Ni-based intermediate layers showed less amount of red rust formation than the conventional galvanised coating in salt spray testing. Additionally, the polarization study revealed the increasing corrosion resistance and shifting of E_{corr} towards more anodic region due to the exposure of Ni rich layers with prolonged immersion in electrolyte solution. Evidence of improvement in corrosion performance in presence of nickel are also reported by other researchers, e.g., Ramanauskas et al. [19,20].

The objective of the present research is to investigate the microstructure and property relationship of prior nickel coated galvanised steels. The coating phases are formed by electrodeposition of nickel followed by galvanising. The composition and morphology of these coating phases as well as the steel/coating interface were studied using Glow Discharge Optical Emission Spectroscopy (GDOES), Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS). The corrosion performance and the mechanism of corrosion during prolonged immersion in electrolyte solution were studied with the help of time dependent Electrochemical Impedance Spectroscopy analysis.

2. Experimental

2.1. Sample preparation

Cold rolled Interstitial Free (IF) steel substrate was used for this work. The composition of the substrate steel is shown in Table 1.

The as-received steel substrates were cut in 110 × 200 mm^2 size. They were degreased with 2.5 wt% alkali solution in distilled water at 60 °C for 40 to 60 s, followed by rinsing with distilled water. It was then pickled with 10% HCl solution at 60 °C for 5 to 10 s followed by final rinsing with distilled water.

The nickel coating was applied on the steel substrate by electroplating process. The electroplating bath was prepared with $NiSO_4$, $NiCl_2$ and H_3BO_3 solution of pH around 4, where pure nickel was used as anode and steel substrate as cathode. The bath solution was always maintained in homogeneous condition by constant stirring. The voltage and current for electroplating were maintained at 0.5 V and 2.3 mA/cm^2 respectively during the deposition process. The temperature of bath was at 80 °C during the plating process. The electro plating time was constant for all samples to give rise to nickel coating thickness of 6 ± 0.5 μm.

The galvanising experiments were performed in a Hot Dip Process Simulator (HDPS) using pure zinc bath. Samples were first nickel plated and heated to about 480 °C in inert atmosphere followed by hot dipping. The zinc bath temperature was maintained at 460 °C. The galvanising time was varied from 3 to 10 s. Samples without any prior nickel coating were also prepared following same galvanising conditions for the purpose of comparison. All the experiments were repeated thrice.

Table 1
Steel composition (wt%).

Element	C	P	S	Si	V	Cr	Fe
Wt%	0.0028	0.0105	0.0109	0.013	0.013	0.0158	Rest

2.2. Characterization of coating

2.2.1. Analysis of depth profile

GDOES technique (Model: Leco GDS850A) was used to determine the elemental concentration profile throughout the depth of the coating. A DC lamp of 4 mm diameter was used to perform all the tests. The galvanised coating was characterised using 'ZnGalv method' and the prior electroplated nickel coating was characterised by 'Plating method'. The applied voltage and current were 700 V and 30.9 mA for 'ZnGalv method' and 700 V and 20.9 mA for 'Plating method'.

2.2.2. Cross sectional composition analysis

Coated samples of 1 × 1 cm^2 area were mounted in Bakelite. After common metallographic sample preparation, the Scanning Electron Microscope study was performed to understand the morphology of different phases of the coating. The compositional analysis was done by Energy Dispersive Spectroscopy (EDS).

2.2.3. Corrosion measurement

Potentiodynamic polarization tests and time dependant Electrochemical Impedance Spectroscopy (EIS) over a prolonged time (up to 20 days) were performed on coated samples. All the electrochemical measurements were accomplished by Gamry potentiostat (Reference 3000). Flat cell of three-electrode system was used for all the electrochemical studies where the coated sample acts as working electrode (WE), the saturated calomel electrode (SCE) as reference electrode (RE) and platinum mesh as counter electrode (CE). The exposed specimen area of 1cm^2 was fixed for all the electrochemical experiments. All the experiments were performed at room temperature (25 °C) after the stabilization of Open Circuit Potential (OCP) for 15 min to obtain an OCP fluctuation < 5 mV for the period of 5 min.

2.2.3.1. Potentiodynamic polarization test. The potentiodynamic polarization tests were conducted in 3.5 wt% aqueous Sodium Chloride solution (NaCl) solution. After stabilizing the OCP, Tafel tests were performed at a scan rate of 0.5 mV per second in the potential range of 250 mV more negative potential than the corrosion potential (E_{corr}) to 1500 mV more positive potential than the E_{corr} potential to get the Tafel diagram.

2.2.3.2. Electrochemical impedance spectroscopy (EIS). Time dependant impedance studies of the coatings were conducted in 3.5 wt% aqueous Sodium Chloride solution (NaCl). The EIS experiments were performed for same samples after each 5 day duration to understand the change in barrier properties with time. These were recorded up to 20 days of immersion. A sinusoidal perturbation of ± 10 mV was applied at OCP from the frequency range of 100 kHz to 10 mHz and ten points were recorded in every one decade. The experimental data was fitted with Zview 2.0 software to calculate the values of electrochemical parameters.

3. Results and discussion

3.1. Coating composition and microstructure

The elemental concentration profiles for conventional galvanised and prior nickel coated galvanised coatings for 3 s were analysed by GDOES as shown in Fig. 1(a&b). The conventional galvanised steel has the total coating thickness of around 18 μm (Fig. 1(a)) whereas that of prior nickel coated steel is around 20 μm (Fig. 1(b)), considering the 50–50 wt% crossover point. The thickness of pure zinc layer at the top surface, which is due to the drag force and subsequent wiping, is nearly same for both the samples, i.e. about 5 μm. The conventional batch galvanised coatings comprised of different iron-zinc intermetallic layers. The layers are iron-zinc gamma, iron-zinc delta and iron-zinc zeta phases and overlay zinc, sequentially from the interface to the top