



Improvement of hot-dip zinc coating by enriching the inner layers with iron oxide

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Abstract

The performance of hot-dip galvanic coating formed on steel not only depends on the alloy composition of the superficial layer but also significantly, on the composition of the inner alloy layers at the coating/substrate interface. Further, the presence of barrier oxide layers, if any can also improve the performance of galvanic coating. In the present work, the effect of inner iron oxide barrier layer formed prior to hot-dip galvanization was investigated. A continuous and adherent iron oxide layer was formed on steel by anodic oxidation of the steel substrate. Although the wettability of oxide surface by liquid zinc was initially poor, the increase in dipping time and the transition of the oxide layer to unstable form due to the presence of Cl^- ion in the flux facilitated localized growth of Fe–Zn alloy phases. The inhibitive nature of the oxide layer was temporary, since the presence of Cl^- induces micro cracks on the oxide surface thereby facilitating better zinc diffusion. The modification of the substrate structure during galvanization was found to influence the galvanizing process significantly. The present study predicts scope for application of this process for protection of rusted steel specimens too.

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1. Introduction

Hot-dip galvanizing is the oldest and economical method used to apply zinc based coatings on steel in order to provide sacrificial protection against corrosion. The formation of inter-metallic phases or alloys during galvanization depends on diffusion rate of the

zinc into the substrate and the subsequent alloying reaction between iron and zinc [1,2]. The bonding strength between the substrate and the coating mainly depends on the surface feature of the metal substrate. Conventional hot-dip process involves laborious steps like degreasing, pickling, fluxing and heating of the substrate before galvanization. Any traces of impurities present on the steel surface can adversely affect the coating quality. The coating structure and its performance can be improved by bath alloying or through various pre and post treatment processes [3–5]. Rusted

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steel surface normally contains iron oxides and hydroxides, a quasi-stable oxide layer. Iron oxide has different usage including development of pigments and semiconductors [6–10]. It has been reported that iron rich inner layer have greater resistance to corrosion than pure zinc layer in normal galvanized coatings [11–15]. Reports are also available on corrosion resistant characteristics of Fe–40Al inter-metallic surfaces due to prior oxide formation. The oxidizing behavior of the alloying elements in the surface, if any, can form adherent oxide layers having effective protection characteristics.

The present study was designed to investigate the influence of preformed oxide layer during galvanization. In the present work, the usual pre-treatment procedures applied on steel substrate prior to galvanization were avoided and the oxidized surface of the steel substrate was galvanized as such, instead. The present approach generates the scope of making efficient use of partially rusted steel.

2. Experimental methods

2.1. The substrate

The composition of the steel substrate can significantly influence the process and performance of the hot-dip zinc coating [16]. The presence of certain elements like C, Si and P can influence the coating weight and also the rate of the alloying growth. In the present case we were keen on the substrate that it should contain alloying elements that favour formation of uniform oxide layer. Based on the preliminary results obtained, a commercially available low carbon steel (Indian ISI Standard, IS: 10748) was selected and used as the substrate for the entire study. The steel used in the present study had the composition—carbon: 0.090%, manganese: 0.340%, phosphorous: 0.036%, silicon: 0.0487% and aluminium: 0.029%.

2.2. Iron oxide formation

The steel coupons of cut size 5 cm × 5 cm × 0.1 cm were abraded with 200 grade emery papers to remove thick and loosely adhered surface oxides formed on the surface. The steel coupons were cleaned using water to remove dirt and grits. The coupons were

kept anodically polarized, by impressing an anodic current of 10 mA/cm², in NaCl solution for 10 min to form iron oxide on the surface. The coupons were then dried, sprinkled with fluxing solution (ZnCl₂/NH₄Cl) and kept at a temperature of 500 ± 10 °C in a muffle furnace for 3 min. No other mechanical or chemical treatments were applied in between the processes. The thickness of the oxide layer was predicted to be less than 10 μm over the steel surface. Duplicate studies were carried out in order to ascertain the reproducibility. There was no considerable variations.

2.3. Galvanic coating

The coupons having a surface layer of iron oxide were dipped in a molten zinc bath containing 0.1% Ni. The presence of Ni in the galvanizing bath can improve the adhesion of the zinc coating facilitating the diffusion of zinc during galvanization [1,17]. The temperature of the molten zinc bath was kept at 550 ± 5 °C and the dipping time was 40 s. The coupons were taken out and the excess zinc on the surface was removed by blowing hot air. The same bath condition and dipping time were employed for pure zinc coating of the steel coupons but the steel coupons were degreased using 5% NaOH solution, pickled in 8% HCl solution and fluxed in (ZnCl₂/NH₄Cl) solution before hot-dipping. The physical properties like adhesion, thickness and porosity of the coupons were evaluated and compared with that of the pure zinc coating. The weight of the zinc consumed during each cases of the process were also determined. Duplicate studies with similar type of the coatings were also carried out in order to ascertain the reproducibility. All coatings showed similar results with negligible variations.

2.4. Structural analysis

The characteristics of the Fe–Zn inner alloy layers and the presence of oxide layer on the galvanized coupons were evaluated layer-by-layer. The coupons were anodically dissolved layer-by-layer intermittently by impressing a constant current load of 5 mA/cm². The dissolution process was successively continued until no more zinc was found in the coating. The electrolyte was 3% NaCl solution and the solution was changed after each successive step of dissolution. The product formed

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