Improvement of Hot Galvanizing By Nickel Under Layer

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Received on:1/8/2007
Accepted on:9/12/2007

الخلاصة
الأكساء بسبيكة الزنك- نيكل تماك مقاومة عالية للتآكل, التصاقية جيدة, وخواص فيزيائية وميكانيكية متميزة . في هذا البحث طبقة النيكل تحت طبقة الغلونة(الطلاء بالتغطيس بالزنك المنصهر) . الملاحظة الأساسية التحسن في الأدائية الفيزيائية (الكلفانية) . وجود طبقة النيكل التحتية قد أنتجت الالتصاقية الجيدة وقلة المسامية وازدياد الصلادة . أن وجود طبقة النيكل تقلل السمك الخاص بالغلونة وتعزز خاصية مقاومة التآكل .

Abstract

Zn–Ni alloy based coatings have high corrosion resistance, good adherence and unique physical as well as mechanical properties. In the present work, nickel was dispersed in the under layer of hot dip zinc coating (Galvanizing). showed substantial improvement in physical as well as galvanic performance. The presence of nickel in the under layer was found to result in good adherence, less porosity and better hardness .The presence of nickel decreases the thickness of the coating and enhances the corrosion resistance character.

Keyword: Hot dip galvanizing; Zinc coating; Galvanized steel; Corrosion; Nickel coating .

1-Introduction

Hot dip galvanic coating has many advantages over other metallic coating, in terms of mode of application, longer protection and cost. Despite vast research that has been carried out on the old technology, still, there is tremendous scope for further improvement in this field. Current developments in this field include modification of pretreatment methods, bath composition, steel chemistry and various post treatment methods.

As far as the composition of hot dip zinc coating is concerned, the addition of certain element, like Al, Mg, Ni, can play an important role in improving galvanic performance. Many reports are available regarding addition of Ni, Mg, Al and Si into galvanizing bath[1,2]. However, the influence on coating structure due to presence of alloying elements in the under layer has not yet been reported clearly. Zn–Ni alloy coating systems are more efficient among the various zinc-based coating systems available in literature [1,2].

The addition of nickel into molten zinc bath has been followed in batch galvanizing processes in order to retard the growth of δ-phase [1,2]. Studies on electrodeposition of alternate layers of metals such as Zn and Ni have been reported [3]. This alloy system has six times more corrosion resistance than that of pure zinc coatings. Nickel is claimed to be a viable substitute for cadmium in marine exposures also [4,5].

Zn–Ni alloy coating possesses superior characters like high corrosion resistance, better weldability, more adherence, uniform thickness and good paintability, when compared with pure zinc coating [6]. The Ni–P alloy coating has the merit of having good corrosion resistance and adhesion characteristics. Moreover, nickel can be considered as a beneficial alloying element as it promotes zinc diffusion and forms

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compact inner alloy phases during galvanization. The present work was intended, with this background knowledge, to develop a new technique to make efficient hot dip zinc coatings containing Ni disseminated in under layers.

In the present study, a nickel-dispersed layer was formed on pretreated steel surface by electroless plating. The nickel coated steel was then subjected to hot dip zinc coating process. The hot-dip-coated specimens showed excellent galvanic performance. The results obtained in the first stage of the present work are reported in this paper.

2- Experimental Works

2-1- Surface treatment

Steel coupons of 5×5×0.1 cm cut size bearing the composition—carbon: 0.90%, manganese: 0.340%, phosphorous: 0.36%, silicon: 0.0487% and aluminum: 0.029%, were abraded with different grades of emery paper to obtain a fine and smooth surface. The coupons were then degreased using 5% sodium hydroxide solution at 50˚C and etched in 8% hydrochloric acid to ensure that the coupons were free from any superficial oxide over the surface. The coupons were then cleaned with distilled water, dried and kept ready for subsequent electroless plating.

2-2- Nickel deposition

A suitable electroless bath for Ni–P alloy plating was formulated and standardized based on preliminary test results. The bath consisted of nickel sulphate: 40 g/lit, sodium hypophosphite: 25 g/lit and succinic acid: 15 g/lit. The cleaned steel coupons (Section 2.1) were directly subjected to plating without any chemical activation or sensitization. The bath pH was adjusted to 4.5 using ammonium hydroxide. The temperature of the electroless plating bath was kept at 80˚C and the deposition process was continued for 30 min [7]. Nickel was coated dispersively without formation of an effective complete monolayer.

2-3- Hot dip galvanization

After electroless nickel coating, the coupons were thoroughly cleaned with distilled water. The coated surface was slightly roughened using fine emery paper to enhance the alloying reaction between steel and molten zinc during the hot dipping process. The temperature of the molten zinc bath was kept at 450±10 ˚C, and the dipping time was fixed at 10–15 s. The excess zinc over the surface of the coupons was removed by hot air blowing.

2-4- Physicochemical characterization

The galvanized coupons were subjected to Vicker's hardness test as per ASTM E 384–899 using a shimadzu HMV-2000 instrument. The test load was 50 gf for an indentation time of 12 s at 22.9 ˚C. To determine the adhesion of coating, the coupons were bent until the two ends became parallel, and then they were returned to their original texture. Then the surface of the coupons was inspected visually to find out whether there are any cracks or defects, using a magnifying lens. Thickness measurement of the zinc coating was in analogue to ASTM standard A 525-93 [8,9].

The galvanized coupons were subjected to weldability test according to ASTM B 571-79. Porosity of the coupons was tested by modified ferroxyl test [10], as normal ferroxyl test is not suitable for zinc coating since the exposed portion of iron is cathodically protected by sacrificial action of zinc. Hence, an external anodic potential of 0.400 V was impressed on the coupons to overcome the galvanic action. The ferroxyl reagent, consisting of a solution containing potassium ferricyanide, sodium chloride and agar–agar in hot water, was applied on the surface of the coupons and inspected for Prussian blue coloration.

2-5-Electrochemical characterization

The performance of the coatings was evaluated based on OCP decay measurements and polarization studies. Longterm immersion studies were carried out to assess the potential shift characteristics of the galvanized coupons under saline conditions. Cleaned coupons were individually dipped in 5% NaCl solution kept in different beakers. The change in potential with respect to saturated calomel electrode (SCE) was measured at regular intervals for a period of 30 days. Salt spray test was carried out as per ASTM B.117 standard, using 5% sodium chloride solution at 35 ˚C, for a period of 30 days. The edges of the preweighed coupons were covered with adhesive tapes before placing the coupons in the salt spray chamber. The corroded coupons were washed with 10% ammonium persulphate ($[NH_4]_2S_2O_8$) solution at room temperature, dried and weighed.

The self-corrosion rate was calculated based on the difference in weight. Polarization studies were carried out to study the layering nature of the coating under various applied current strength. The galvanized coupons having 1 cm2-exposed area were made as the working electrodes; a platinum mesh with a large surface area was the counter electrode while SCE was the reference electrode.

The coupons were anodically polarized up to an applied current strength of 100 mA/cm^2. A 5% NaCl solution was the electrolyte during polarization studies.

3-Results and discussion

3-1- Substrate selection

The composition of steel substrate can influence significantly the hot dipping process and performance of the hot dip coating. The change in the composition of substrate not only influences the rate of attack of steel by molten zinc but also changes the mode of attack at a given galvanizing temperature [11,12].

The presence of a critical amount of Si and P in the steel substrate is necessary to control the coating weight while the presence of carbon considerably influences the rate of alloy growth [13]. In the present study, commercially available steel specimens having composition, as noted in Section 2.1, was chosen for the entire study. The elements other than iron present in the substrate were found in medium range when compared with many of the available literature. The substrate showed good coating characteristics when compared with that of other substrates initially chosen for preliminary studies.

3-2-Process standardization

A layer of dispersed nickel was formed on the steel surface by electroless plating. A standard bath (Section 2.2) was formulated based on the performance of the respective plate/layer being suitable for efficient hot dip galvanizing process. Prior to the nickel plating, the substrate was polished to obtain a fine and smooth surface necessary for uniform coating [7,14]. Nickel was deposited by electroless plating for a deposition time of 30 min at a bath temperature of 80 ˚C. It has been reported elsewhere that the amount of phosphorous and the thickness of electroless coating are dependent on the deposition time[14].

A literature survey reveals that there is 8–9% of phosphorous content in the conventional Ni–P alloy coating [7,15]. Optimization of the coating time is necessary to control the thickness and the phosphorous content of the electroless deposit [7]. In the present work, the phosphorous content in the Ni-dispersed coating was found to be less than 1%. Hence, this low-level concentration of phosphorous in the coating can have only marginal influence during the subsequent hot dip galvanization process.

The nickel content in the electroless deposit was found to be approximately 0.5%. The amorphous Ni–P alloy phase can undergo a self-crystalline transformation to Ni and Ni3P when the temperature exceeds 300 8C [16,17]. The Ni–P binary system, as reported elsewhere, has less than 9% phosphorous after heat treatment, and it consists of crystals of nickel-rich phase and nickel–nickel phosphide eutectic [7].

The Ni-rich phase can influence subsequent galvanization processes. Considering all these factors, a suitable electroless bath was selected and standardized for the present study. The surface of the steel substrate coated with dispersed Ni was rubbed gently using an emery paper no. 2000 to make it slightly porous to facilitate the alloying reaction between the base metal and zinc. The hot dip bath temperature and the immersion time were fixed based on literature reports and the preliminary results [18,19]. After standardization, the experimental parameters were kept constant throughout the study.

3-3-Characterization of the hot dip coating

The adhesion between the zinc coating and the substrate was evaluated by bend test. No cracks or fissures were observed when the specimen was subjected to bending up to 908. The good adhesion of the coating can be attributed to the better diffusion of zinc into the steel substrate during galvanization [1]. The nickel-dispersed layer would get delocalized during dipping of the Ni-coated steel in the molten zinc bath. The alloying reaction between Fe and Zn can be facilitated due to the presence of Ni available in the under coat. The coupon having Ni-dispersed under layer had the hardness value of ≈73 VHN against ≈50 VHN, as observed in the case of pure hot dip galvanized coating (Table 1). This is due to the metallurgical improvements like grain refinement, compact layering and uniform thickness of the coating.

The thickness of the zinc coating with Ni-dispersed layer was found to be 30 Am, which is lower than that of normal commercial hot dip galvanized coating. Addition of 0.06% Ni into the zinc bath has also been reported to be effective in reducing the coating weight [20]. This can be ascribed to the preferential development of the δ-phase.

The ternary compound formation of Zn–Ni–Fe normally acts as a barrier to inward diffusion of Zn or Fe at the ζ–η boundary, preventing rapid formation of the ζ-phase that facilitates formation of more compact inner alloy phases. This can result in lowering of the coating thickness in the presence of nickel. Moreover, the present process of duplex coating is economically effective as its material cost is twice less than that of either Zn or Ni layer alone [21]. The substrate was found to be welding-compatible. The coating did not exhibit any peeling off or blister-like appearance during spot welding. All these results ensured adequate alloying and better coating strength of the galvanized layer.

The modified ferroxyl test revealed nonporous and void-free nature of the coating, as there was no typical color change (Prussian blue spots) during exposure of the galvanized coupon towards the ferroxyl reagent [10].

3-4- Electrochemical characterization

3-4-1- Potential–time relation

The galvanized steel coupons with and without dispersed nickel under layer were immersed in 5% sodium chloride solution, and their potentials were monitored with respect to saturated calomel electrode at 30 ˚C

(Fig. 1). The open circuit potential (OCP)of the galvanized coupons with and without Ni under layer showed steady but high negative potential values during initial hours of immersion in the electrolyte. The high negative OCP exhibited by the coupons can be attributed to the better alloying reaction between Zn and Fe and to the sacrificial nature of the top pure zinc layer. However, the pure zinc-coated coupon showed a potential shift towards anodic region when the duration of immersion was increased.

It is clear from the figure that the higher the amount of zinc dissolves during the course of exposure, the more the magnitude of the anodic potential shift. In the case of nickel-dispersed galvanized coating, the nickel present in the coating would promote better diffusion of zinc during galvanization that facilitates preferential development of the y-phase, resulting in more compact inner alloy layers [20]. (Thinner individual layers in the multilayer coatings are normally associated with more active (i.e., highly negative) potentials than that of thicker layers [3].

During prolonged immersion in the electrolyte, the pure zinc-coated coupon showed a drastic anodic shift in the OCP due to faster dissolution of zinc from the inner alloy layers. Moreover, the corrosion products adherently formed on the coating were found to be porous promoting aggressiveness. Only a marginal potential shift was noticed in the case of the galvanized coupon having dispersed Ni in under layers.

This can be attributed to the fact that the combination of Ni and Zn on the surface of steel provides both sacrificial protection and resistance to chloride attack [3]. The nickel rich under layer can be predicted to prevent penetration of aggressive ions like Cl^- and ClO_4^- towards steel when the coupons are exposed to saline atmosphere. The smooth and bright surface of the coupon can reduce the rate of corrosion in high chloride environment. Since zinc is more electronegative than iron, which is more electronegative than nickel, the mixed potential of this type of coating can yield better corrosion resistance to steel substrates [3].

3-4-2-Polarization

The layering nature of metallic coatings can be envisaged based on polarization experiments. The polarization trends of different galvanized steel coupons are shown in Fig. 2. The corrosion potential values revealed that the surface was efficiently covered with zinc coating without any large-size pores that can cause anodic potential shift.

The coating having nickel under layer showed substantial resistance towards anodic polarization (Fig. 2). The presence of nickel in the coating always facilitates diffusion of zinc into the steel substrate during galvanization, forming more compact inner alloy layers. This attributes to the better alloying reaction between Fe and Zn. At an applied current strength of 100 mA/cm^2, there was a potential difference of 300 mV between the two types of the coating. Although corrosion potential of nickel on steel is nobler when compared with steel substrates, nickel can provide some degree of protection by acting as a barrier to aggressive ions [3].

The uniformity of the coating, compact-layering structure, low surface energy of bright crystals due to their smooth surface and smaller amount of surface segregation can enhance the polarization tolerance of the coating [22]. The penetration of Cl^-or ClO_4^- ions can also be prevented effectively by the under layer nickel coating. In the present case also, the presence of nickel in the under layer could have yielded such good coating characteristics, resulting in very low polarization.

The anodic potential shift observed in the case of other coupons having pure zinc coating can be attributed to gradual dissolution of zinc from inter alloy phases, especially at high current densities at or above 100 mA/cm^2.

3-5- Long-term performance evaluation

3-5-1- Salt spray test

The corrosion product formed initially on the galvanized coating during salt spray test was white rust, indicating the onset of corrosion. The delay in formation of white rust reveals better corrosion resistance of the coating. Formation of white corrosion products [8] on the pure zinc coating was observed within 2 days of exposure in the salt spray fog, indicating beginning of corrosion, and the area was fully covered with the white rust in a short span of 7 days.

The initial white rust formation can be attributed to the faster dissolution tendency of zinc under saline condition. The degree of penetration of aggressive ions (e.g., chloride) through the coating in the fog depends on the whole layer corrosion potential activity and the deposit properties in terms of thickness, porosity and uniformity of the coating [3].

The changes on the galvanized coupons observed during the salt spray test are presented in Table 2. In the case of nickel-dispersed coating, the surface was found scarcely covered with white rust during initial 5 days of exposure. The under layer of dispersed nickel can yield better coating characteristic, as discussed above.

The surface of the coupons with nickel under layer was found brighter, as the corrosion resistance characters of bright spangles are better than that of dull spangles. After 20 days of exposure in the salt fog, the surface of the pure zinc coating was found fully covered with brown rust, revealing the failure of the galvanic coating. But the galvanic coating containing nickel had very low brown rust, indicating good corrosion resistance.

The corrosion products formed on the surface of pure zinc coating under the fog were instantaneously removed by fresh colloids, avoiding probable barrier action of the rust. Hence, the corrosion of pure zinc coating would get accelerated under the continuous salt spray condition. However, in the case of the coating containing nickel, the nickel chloride formed during such exposure was found to be more stable and adherent in NaCl environment.

The dispersed nickel under layer could inhibit the concentration of free iron [23] at the galvanized surface, minimizing the brown rust formation. But in the case of normal pure zinc coating, the simultaneous dissolution of zinc from the interalloy layers causes a substantial potential shift. The OCP of the coupons were also monitored during exposure to salt fog parallely. During the initial hours of exposure, both the types of coupons showed high negative and steady OCP values.

The shift in OCP was more pronounced in the case of pure zinc-coated coupons when compared with Ni containing galvanized coupons. Fig. 3 illustrates the trend of OCP shift observed during the salt spray test. The time of exposure was fixed as 30 days, consistent with many other available reports and the factor that the surfaces were considerably covered with brown rust. The coupons were thoroughly washed, dried and weighed, and the self corrosion rates were determined. The presence of Ni in the interlayer was found to have considerable effect in reducing the rate of corrosion.

4-Conclusions

The presence of nickel in under layers of hot dip galvanic coating improves significantly the galvanic performance as well as the physical properties including weldability and hardness of the coating. The presence of Ni in hot dip baths reduces substantially the thickness and corrosion rate of galvanized coating.

The presence of Ni in the under layer facilitates diffusion of Zn, a phenomenon required for good alloying reaction that facilitates formation of effective interalloy phases. The penetration of aggressive ions, like Cl^- and ClO_4^- , towards the steel substrate is effectively suppressed by the presence of Ni. The hot dip zinc coating containing nickel exhibits steady OCP decay when immersed in saline electrolyte or exposed to salt fog.

It also exhibits least polarization during steady state anodic polarization experiment even under a high current load as high as 100 mA/cm^2. The smooth and nonporous surface of the coating, as achieved in the present method, can prevent condensation of moisture over the coating and minimize corrosion rate.

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Table 1 Test result of hot dip galvanized steel with and without dispersed Ni under layer

Coating system	Hardness (HVN)	Thickness (μm)	Adhesion	Porosity	Spot weldability	Mean coating weight (g/m^2)
Nickel+zinc-coated coupons	73	30	Better	Nonporous	Good	275
Pure zinc-coated coupons	57	45	Good	Less porous	Good	340

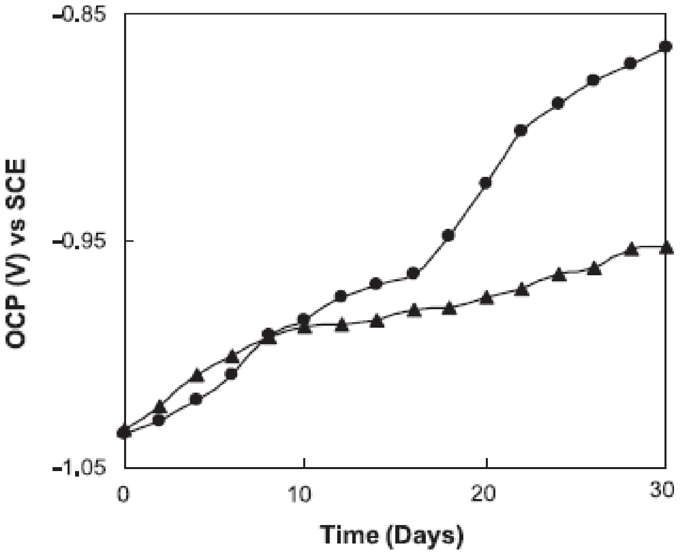

Fig. 1. The OCP decay curves of galvanized coupons during long-term immersion test. Medium: 5% NaCl at 30 8C, stagnant condition. (●)—pure zinc coating; (▲)—with dispersed Ni under layer

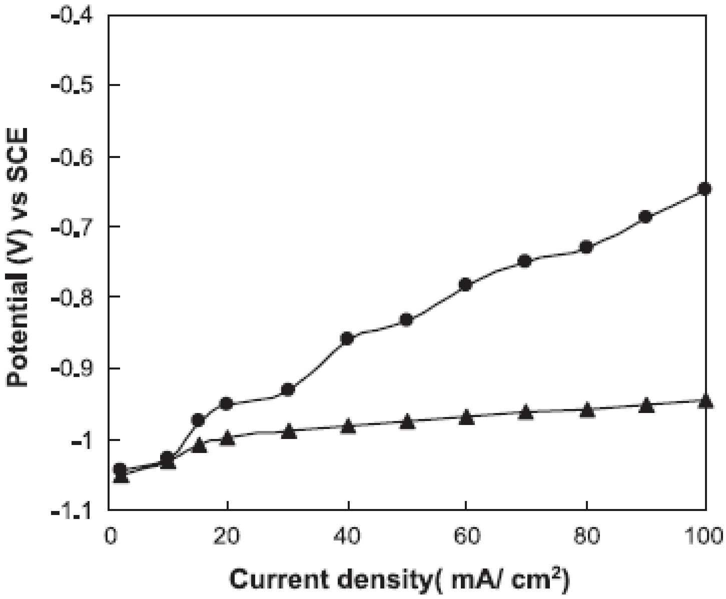

Fig. 2. The anodic polarization trends of galvanized coupons. Medium: 5% NaCl at 30 8C. (●)—pure zinc coating; (▲)—with dispersed Ni under layer.

Table 2 The visual observation of the galvanized coupons noted during salt spray test

Coating system	Number of days of exposure			Self corrosion rate[a] (g/cm^2/h)
	5	20	30	
Nickel+zinc-coated coupons	20% WR	90% WR	20% BR	2×10^{-6}
Pure zinc-coated coupons	75% WR	30% BR	80% BR	10×10^{-6}

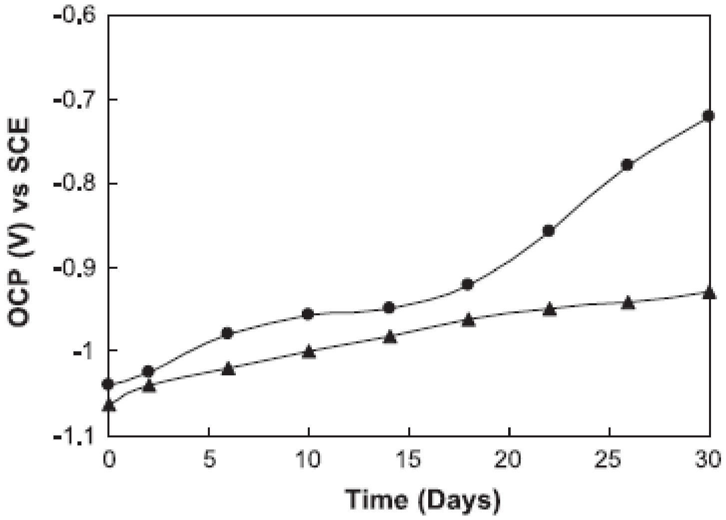

Fig. 3. The OCP decay curves of galvanized coupons during salt spray test. Medium: 5% NaCl at 35˚C. (●)—pure zinc coating; (▲)—with dispersed Ni under layer.