Chromate Coating of Zinc-Aluminum Plating on Mild Steel

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Abstract. The chromate coating on zinc-aluminum deposits has been studied. Zinc-aluminum deposition from noncyanide bath was carried out at current density $3-3.5 \text{ A/dm}^2$, plating voltage ~ 1.25 V, temperature $18-20 \,^{\circ}\text{C}$, for $15 \,\text{min}$. The effect of aluminum chloride on the rest potentials of golden, colourless and non-chromated zinc-aluminum alloy deposits was observed. It was found that rest potential was slightly increased with the increase in the concentration of aluminum chloride, only in the case of golden chromating. The rest potential of colourless chromated zinc-aluminum deposits on mild steel were observed to have no correlation with aluminum chloride concentration. The abrasion resistance of colourless chromating was better than golden chromating.

Keywords: zinc-aluminum deposition, chromating, rest potential, chromate coating, mild steel chromating

Introduction

Steel sheets coated with zinc or aluminum alloy are successively coated with a metal layer containing iron, cobalt and nickel at 0.1-10 mg/m² and a chromate layer containing > 25 mg (as chromium) Cr^{+6}/m^3 at 10-150 mg/m². The coated steel sheets so obtained have good adhering property (Tomiyasu and Ikishima, 2000).

The aqueous bath for chromating of zinc or zinc-alloy surface contains Cr⁶⁺ions, Cr³⁺ions, and nitrate ions at the chromium ion/nitrate molar ratio of 2.1-5.5, and cations of nickel, cobalt, zinc and aluminum at the cations/nitrate molar ratio of 0.05-1. The chromating bath preferably contains the Cr³⁺/Cr⁶⁺ molar ratio of 0.25-0.67, and optionally includes minor phosphate ions and fluoride-containing anions. The conversion bath is suitable for chromating of zinc-coated steel sheets at 10-100 mg chromium/m² for resistance to darkening and white corrosion, as well as for the similar coating on zinc-aluminum alloy surface without pretreatment by metal flash coating. The wet chromate coating is dried without rinsing. The typical aqueous bath for chromating includes zinc nitrate at nitrate/total chromium molar ratio of 5.5, and is suitable for chromating of galvanized steel sheets, or of zinc-55% aluminum alloy coating (Matsubara and Kato, 1999).

Steel sheets coated with a zinc-(25-75%) aluminum alloy are coated with a chromating compound and dried without washing with water to form a chromate film. The film contains 10-40 mg chromium/m² and 1.0-3.0 g organic resin/m² and has a phosphate/chromium ratio of 0.5-4.0. The sheets are suitable as

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building materials and for electrical appliances (Yamaji *et al.*, 1997).

The durability of passivation in zinc electroplating has been studied using weak acid zinc bath free from cyanide and ammonia for zinc plating, and yellow and non-coloured passivating solutions for passivation process. At the running voltage of 1.1 V, amperage of 1 A, pH 5-5.4, at room temperature, best plating results were obtained from the zinc bath. The plated sample was washed in distilled water and then dipped in dilute HNO₃ for two seconds to make the zinc plated surface active toward accepting final passivating film. The sample was then dipped in passivating solutions. Chromate film developed on the zinc surface, which protected it against corrosion, as well as gave it an attractive appearance. It was found that yellow passivation at the dipping time of one min at room temperature with the passivating solution composition of CrO₃, 50g/l; H₂SO₄, 1 ml/l; HNO₃, 3 ml/l gives best corrosion resistance, but had weak abrasion resistance. On the other hand, colourless passivating solution comprising CrO₃, 2 g/l; KF, 4 g/l; HNO₃, 3 ml/l gives good abrasion resistance with weak corrosion resistance (Haque et al., 2003a). Electrodeposition of zinc is done on iron to provide protection against corrosion and to enhance appearance. Colouring of zinc-electroplates through chromating has been reviewed (Haque et al., 2003b).

Materials and Methods

Chemicals. The chemicals used with their sources included: zinc chloride (Qingadao Sunchiment, China), aluminum chloride and potassium dichromate (Riedel-de Haën, Germany), chromium trioxide (Oxychem, USA), sulphuric acid (BDH, England), nitric acid and hydrochloric acid (E-Merck, Germany), and maintenance, 2222 and wetting, 1111 (Dico, Germany). All other chemicals, namely, sodium hydroxide, sodium silicate, sodium phosphate, sodium chloride, sodium fluoride, ethanol, and sodium carbonate were of technical grade or better.

Electrodeposition procedure. Zinc-aluminum bath was used for the electrodeposition of zinc-aluminum on mild steel. Bath was prepared from zinc chloride, aluminum chloride and sodium chloride. The composition of the bath camprised of zinc chloride, 150 g/l; sodium chloride, 200 g/l; aluminum chloride, 0-25 g/l; maintenance, 2222, 1 ml/l; and wetting, 1111, 30 ml/l. The concentration of aluminum trichloride was varied from 0-25 g/l. The electrodeposition was carried out at the current density of 3-3.5 A/dm², voltage 0.75-1.25 V, temperature 30-35 °C for 15 min.

Cathode. The mild steel substrates, 2×1 inch² were employed as the cathode. Surface preparation of cathode, before plating, involved the following procedure: specimens were polished, buffed, degreased with ethanol, cleaned electrolytically, rinsed, pickled, and rinsed thoroughly.

Anode. Two plates of zinc metal having dimensions of 6×2.5 inch² were used as the anodes. The surface of anodes was covered with glass wool to avoid entery into the plating bath of any oxides developed at the anodes.

Chromate coating on the mild steel samples deposited with zinc-aluminum. After electroplating, the samples were rinsed with distilled water, immersed in 10% nitric acid for few seconds, thoroughly rinsed in distilled water, and immersed in the chromating solutions.

Golden chromating. The golden chromate coating was formed when the zinc-aluminum plated samples were dipped in the bath containing potassium dichromate, 125-150 g/l and sulphuric acid, 20-25 g/l, pH 1.25-1.3 at 18-20 °C for one min.

Colourless chromating. Colourless chromate coating was formed when the zinc-aluminum plated samples were dipped in a bath containing chromic acid, 5-6 g/l, sodium fluoride, 5-6 g/l, and conc nitric acid, 2-3 ml/l, pH 1.77 at 18-20 °C for one min.

Rest potential. Rest potentials of the colourless chromated zinc-aluminum deposited plates, golden chromated zinc-aluminum deposited plates, and only zinc-aluminum deposited plates were measured versus mild steel specimen and platinum electrode in 5% sodium chloride solution.

Results and Discussion

Mild steel specimens were electroplated with zinc-aluminum alloy. The concentration of aluminum chloride was varied from 0-25 g/l. The changes occurring in the pH of the plating bath, on varying the concentration of aluminum chloride, were also noted (Table 1), which showed that with the increase in the concentration of aluminum chloride, the pH of the plating bath decreased gradually.

The zinc-aluminum coated mild steel specimens were divided into three groups: in the first group, the plates were not chromated; in the second group, the plates were immersed in golden chromated solution comprising potassium dichromate (125-150 g/l) and sulphuric acid (20-25 g/l), at pH 1.25-1.3 and temperature 18-20 °C for one min; and in the third group plates were colourless chromated in the solution comprising chromium trioxide (5-6 g/l), sodium fluoride (5-6 g/l), and conc nitric acid (2-3 ml/l), at pH 1.77 and 18-20 °C for one min. The effect of aluminum chloride concentration on rest potentials for golden, colourless, and without chromated zinc-aluminum deposits were observed, which have been summarized in Figs. 1 and 2.

Two sets of measurements of rest potential were recorded. In one case, the contact between the two electrodes was closed for a short period of time, and the rest potential on the multimeter (DT-830 B) display was noted. In some cases, this method gave wide dispersion in the rest potential. The rest potential was measured versus mild steel and the results so obtained have been shown in Fig. 1. In the second case, the contact between the electrodes was closed for a finite period of time (ten seconds), and the stable value of the rest potential ver-

Table 1. The effect of aluminum chloride concentration on the
pH of the plating bath

Concentration of aluminum chloride (g/l)	pH of the bath
).0	5.30
2.5	4.93
5.0	3.79
7.5	3.56
0.0	3.60
2.5	3.29
5.0	3.00
7.5	3.31
0.0	3.09
2.5	3.17
5.0	2.80

sus platinum electrode, after this interval, was noted and the observations so recorded have been shown in Fig. 2.

The influence of aluminum chloride concentrations and the rest potentials for golden chromated, colourless chromated, and plates without chromated versus mild steel specimens are shown in Fig. 1. It may be noted that with the increase in

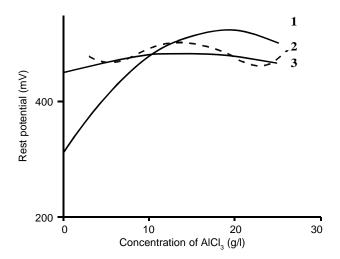


Fig. 1. Effect of concentration of aluminum chloride on restpotential versus mild steel in 5% sodium chloride solution; (1) golden chromating on zinc-aluminum deposited mild steel, (2) colourless chromating on zinc-aluminum deposited mild steel, (3) non-chromating on zinc-aluminum deposited mild steel.

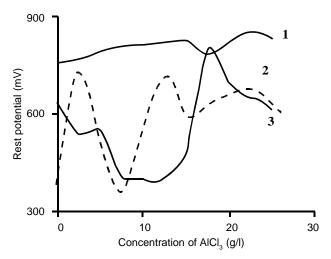


Fig. 2. Effect of concentration of aluminum chloride on rest potential versus platinum in 5% sodium chloridesolution; (1) golden chromating on zinc-aluminum deposited mild steel, (2) colourless chromating on zinc-aluminum deposited mild steel,(3) non-chromating on zinc-aluminum deposited mild steel.

the concentration of aluminum chloride from 0-5 g/l, the rest potential for golden chromating first rose slowly and then nearly remained constant on the further addition of aluminum chloride. There was no correlation between the rest potential for colourless chromating and the concentration of aluminum chloride. The rest potential of the without chromated zinc-aluminum alloy electroplated versus mild steel also remained constant with the increasing concentration of aluminum chloride.

The relationship between the concentration of aluminum chloride and the rest potentials for golden, colourless, and plates without chromating versus platinum electrode are shown in Fig. 2. It may be noted that there was a slight increase in the rest potential for golden chromating with the increase in the concentration of aluminum chloride. There was no correlation between the rest potential for colourless chromating and the concentration of aluminum chloride (Fig. 2.) In the case of plates without chromating, the rest potential increased after 12.5 g/l aluminum chloride up to the concentration increase of 18 g/l, which then decreased with further addition of aluminum chloride.

The appearance of the plates was good enough. Bright alloy deposits were obtained. Abrasion resistance of golden chromating was very poor as compared to the abrasion resistance of colourless chromating.

Conclusions

Results obtained in the present study show that:

(a) abrasion resistance of colourless chromating was more than with golden chromating;

(**b**) the rest potential of the golden chromated zinc-aluminum deposits was increased slightly with the increase in aluminum chloride concentration;

(c) the rest potential for colourless chromated zinc-aluminum deposits had no correlation with aluminum chloride concentration;

(d) the rest potential of non-chromated zinc-aluminum deposits on mild steel specimens was maximum at the aluminum chloride concentration of 17.5 g/l; and

(e) the appearance of the deposits was good.

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