Potassium salt based alkaline bath for deposition of Zn–Fe alloys

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Abstract

A new alkaline bath was proposed based on highly concentrated potassium hydroxide for electrodeposition of Zn–Fe alloys. Triethanolamine was used as the complexing agent to eliminate precipitation of ferrous hydroxide and to enable the co-deposition of Zn and Fe. The conductivity value of the proposed baths is 161–188% higher than that of a known formula. From cathodic linear sweep voltammograms the co-deposition of Zn and Fe in the proposed bath is applicable. Zn–Fe alloys with different compositions were achievable by tuning the deposition variables such as the ion ratio Zn/Fe and the deposition current density. The co-deposition of Zn and Fe is an anomalous type under a small current density and switches to the regular one under a larger current density. The transition current density was found to be 0.075 and 0.05 A cm \(^{-2}\) for Baths 1 (ion ratio Zn/Fe=13) and 2 (Zn/Fe=25), respectively. A mechanism based on adsorbed Fe-TEA barrier-layer was proposed to explain this transition. There is a more than 40% enhancement in cathodic current efficiency by using the proposed Bath 2 versus the known formula. Comparing with Zn coating, the deposited Zn–Fe layer reveals 10% nobler corrosion potential, \(-0.987 \text{ vs. } -0.897 \text{ VSCE}\), and two times smaller corrosion current density, 42.0 vs. 19.7 \(\mu\text{A cm}^{-2}\). The proposed baths are much easier for bath control during deposition.

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1. Introduction

In the past two decades, many efforts were devoted to develop steels and their coatings with higher corrosion resistance [1–15]. The excellent properties of coatings by Zn-iron group alloy make them very promising, specifically for the application such as in automobiles. The electrodeposition of Zn–Fe alloy was usually conducted in acidic baths such as chloride bath [3], sulfate bath [4,5], sulfate-chloride bath [6,7], aqueous acetate bath [8]; as well as in some alkaline baths either cyanide bath or non-cyanide bath [9,10]; and in methanol bath [11]. In most cases, co-deposition of Zn–Fe followed the anomalous type deposition [12], in which the less noble element Zn deposited in preference to the nobler Fe. The anomalous deposition can be inhibited by using non-aqueous ionic liquid or cyclic voltammetry deposition instead of the DC method [13,14]. In general, the alkaline baths exhibit uniform distribution of current but resulted in low current efficiency; the acidic baths show high current efficiency but the current distribution is not good enough.

Since iron-group elements such as Fe, Co, and Ni tend to form hydroxide precipitates in alkaline media, a complexing agent is required in the bath to inhibit. The cyanide baths using toxic cyanide and ammonia raise many problems, including the loss of ammonia at high operating temperature, problems in maintaining the deposition process and effluents from the cyanide baths. Sree and Ramachar reported an alkaline pyrophosphate Zn–Fe bath [15]. Narasimhamurthy and Sheshadri developed a non-cyanide bath based on sodium salt. They used triethanolamine (TEA) as the complexing agent to replace ammonia [12]. The use of TEA was not only to eliminate precipitation of ferrous hydroxide in the strong alkaline media but also to enable the co-deposition of Zn and Fe. Crotty made a comparison of alkaline baths with potassium and sodium salts for plating Zn [16], and found that the electrolyte based on potassium salt possesses higher conductivity but the cost of chemicals is slightly higher. After a literature survey, we found that the traditional alkaline baths for the alloy deposition of Zn-iron group (Fe, Co, Ni) are mainly dilute solution of sodium hydroxide. It was the main purpose of this
study to develop a novel alkaline Zn–Fe bath based on highly concentrated potassium hydroxide solution. This is not just a straightforward substitution of NaOH using KOH. Constituents and concentrations were completely different and much effort was required to optimize the deposition conditions.

In this study, the electrodeposition parameters, such as the ion ratio Zn/Fe and the current density were tuned to obtain Zn–Fe alloys with different compositions. Furthermore, the conductivity of the proposed baths, cathodic current efficiency, the chemical composition, phases (lattice structure), anti-corrosion property and surface morphology of the electrodeposited Zn–Fe alloy layers obtained from the potassium hydroxide baths containing TEA were rigorously studied.

2. Experimental

Shown in Table 1 are the bath compositions and the operating conditions for the electrodeposition of Zn–Fe alloys. All solutions used were freshly prepared using analytical grade chemicals and double-distilled water. The baths were prepared using potassium hydroxide to a concentration of 6.6 M (≈30 wt.%) with an alkalinity of pH > 14. The Zn-removed galvanized steel sheet was used as the cathode. The galvanized steel sheet was immersed in 50 vol.% HCl to remove the Zn layer until a smooth and metal bright surface appeared. It was then washed with de-ionized water and ethanol followed by drying. The deposition area of the cathode sheets was fixed at 1 cm². In this study, the Pt-coated Ti gauze was used as an un-dissolvable anode or a counter electrode for electrodeposition or electrochemical characterization, respectively. The deposition was done at a constant current mode for 5 min followed by water rinse and drying.

The electrochemical characterization was acquired using an electrochemical workstation (Model 604A, CH Instruments, USA) with a three-electrode configuration. The tested electrolyte, maintained at 25 °C, was purged with Ar for 1 h prior to testing. The sweep rate was 1 mV s⁻¹. The cathodic linear sweep voltammogram (CLSV) of the individual metals and the Zn–Fe bath was conducted using Fe sheet and Hg/HgO (6.6 M KOH) as the working electrode and the reference electrode, respectively. The corrosion tests were done using a deaerated 3.5 wt.% NaCl solution and SCE (saturated calomel electrode) as the testing electrolyte and the reference electrode, respectively.

The cathodic current efficiency (CCE) was calculated by resultant weight gain versus theoretical weight gain obtained from Coulumb charges supplied. The conductivity of the baths was measured using a Suntex Conductivity meter SC-170.

The surface morphology and chemical composition of the deposited films were studied using a field emission electron probe microanalyzer (FEEPMA, JXA-8500M, JEOL) with the aid of a ZAF program [17]. The crystal structure of the deposits was characterized by grazing incidence X-ray diffraction (GIXRD) using Cu Kα₁ radiation of wavelength 0.154056 nm (Mac MXP-18).

![Fig. 1. The cathodic linear sweep voltammograms of baths with individual metallic ion and Zn–Fe ions.](image-url)
3. Results and discussion

In order to develop the novel Zn–Fe bath based on alkaline potassium salt, it was a good policy to refer to the formula in the literature [9]. The concentration of KOH, 6.6 M (≈ 30 wt.%), was chosen because it has the highest conductivity among all concentrations, and its water vapor pressure equilibrates with 60% atmosphere humidity, which is typical of sub-tropical climate. After some trials, it was found that ZnSO₄ and Na₂SO₄ could not be dissolved into this KOH solution, other Zn salts should be alternatively chosen. Since ZnO is commonly used to prepare zinicate solution, it was very straightforward to choose it as the Zn ion source. Ferrous sulfate was also chosen as the Fe ion source, since it is very cheap and stable. The conductivity of the bath is high enough, as to be delineated below, so that a secondary electrolyte, such as Na₂SO₄ is not required. The concentration of FeSO₄ (0.01 M) and TEA (0.2 M) were the same as the optimum values proposed in the literature [9]. The additives in conventional baths such as ascorbic acid, toxic cyanides, volatile ammonia and others were avoided on purpose in this study.

The conductivity of a bath is un-predictable thus should be obtained by measurement. Table 1 also shows the conductivity results, the conductivity data of the proposed baths, 515–567 mS cm⁻¹, and that of the reference bath (Bath R, 197 mS cm⁻¹) which was taken from literature as a reference [9]. This has a 161–188% higher value. Comparing the values between the two proposed baths, it is manifested that conductivity decreases about 9% while the Zn ion concentration in the bath is increased from 0.13 M to 0.25 M. It revealed that higher metal ion concentration in the bath did not necessarily lead to higher bath conductivity. High bath conductivity leads to lower power consumption and generates less amount of heat during the deposition process.

Shown in Fig. 1 are the cathodic polarization curves of the individual metals and the Zn–Fe alloy. From the voltammogram, it is manifested that the co-deposition of Zn and Fe is applicable. The addition of TEA not only decreases the difference in reduction-potential between Zn and Fe to enable the co-deposition of Zn and Fe but also prevents precipitation of Fe(OH)₂ in such a highly alkaline solution.

Fig. 2(A) and (B) are typical surface morphology of the electrodeposited Zn–Fe alloy from Bath 1 (ion ratio Zn/Fe=13), 50 mA cm⁻² and Bath 2 (ion ratio Zn/Fe=25), 200 mA cm⁻², respectively. They are uniform and compact. The former one composes of platelets with size 1 to 10 μm, the later one composes of granules with size 0.5 to 3 μm. The cross-sectional view of the resultant layer from Bath 2, 200 mA cm⁻² is demonstrated in Fig. 2 (C). The thickness of the resultant layer is about 14 μm. Fig. 3 indicates the chemical composition of the deposited layers and the resultant cathodic current efficiency (CCE) from Baths 1 and 2, respectively. The composition reference line (CRL, the dashed one) which depicts the Fe % in the baths was drawn in the figures for comparison. It is obvious that the Fe content in the deposits increases with increasing deposition current density or decreasing Zn/Fe ion ratio in the bath. The deposition of Zn–Fe alloy is an anomalous type under small current density, but switches to the regular type as deposition current density increases over a certain transition value. The transition current density is the point where the CRL line meets the composition line. It is about 0.075 (interpolation from Fig. 3) and 0.05 A cm⁻² for Baths 1 and 2, respectively. The change in deposition type is also found in acidic Zn–Fe sulfate bath containing TEA, but the mechanism is not clear [4]. The anomalous deposition in which the less noble element Zn is deposited preferentially than the nobler Fe has been explained by many theories [18]. Most people believe that it is attributed to the formation of Zn(OH)₂ film on the cathode surface because of the rise in pH around the cathode film while H₂ evolution occurs [19]. It is this film which suppresses the deposition of Fe. However, the existing explanation does not take into account the role of complexing agent. We tried to propose a mechanism to explain this transition. Fig. 4 schematically depicts the deposit/diffusion-layer/bath interfaces. The reduction potential of TEA-Fe complex ion
should be higher than that of zincate ion \((\text{Zn(OH)}_4^{2-})\) while \(\text{Zn(OH)}_2\) film is formed. There exists an electrical resistance \((R)\) on the diffusion-layer composed of the Fe-TEA complex and zincate ions, thus a corresponding potential barrier \((\Phi)\). The barrier resistance \(R\) and barrier potential \(\Phi\) are further dissociated into those of TEA-Fe \((R_{\text{Fe}}, \Phi_{\text{Fe}})\) and those of zincate \((R_{\text{Zn}}, \Phi_{\text{Zn}})\). Because the Fe/Zn ion ratio of Bath 1 was higher than that of Bath 2, the \(\Phi_{\text{Fe}}\) value of Bath 1 should be higher. It is the reason why Bath 2 reveals lower transition current density. The depositing current density \((J)\) will impose an ohmic potential, which is equal to \(\Phi=R_{\text{Fe}}J+R_{\text{Zn}}J\). If \(R_{\text{Fe}}J\leq\Phi_{\text{Fe}}\) then the Fe-TEA complex is stable, the portion of reductive Fe is less, thus Zn deposited preferentially. However when \(R_{\text{Fe}}J>\Phi_{\text{Fe}}\) the Fe-TEA is destabilized, the imposed voltage exceeded that of the total barrier potential, thus the deposition shifts to a regular type.

The cathodic current efficiency (CCE) of the proposed baths is about 16–24% depending on the bath composition and the current density. Higher Zn/Fe ratio in the bath results in slightly higher CCE. Higher metal content in the bath thus lowers \(H_2\) evolution during deposition and contributes to CCE. Compare with the reported values in literature [9], 10–17%, our best CCE value is more than 40% higher. It reveals that the \(H_2\) evolution rate is lower by using our proposed baths.

The phases of the electrodeposited Zn–Fe alloy are very complicated depending on the chemical compositions [4,20]. The electrodeposited Zn–Fe alloys have metastable structures.
and many phases coexist over a wide range of composition. Adaniya et al. reported that the phases of electrodeposited Zn–Fe alloys include: η phase (100–81% Zn), δ1/γ phase (89–70% Zn), γ phase (87–48% Zn) and α phase (62–0% Zn) [19]. Fig. 5 demonstrates a typical XRD pattern of the electrodeposited layer using Bath 1, 100 mA cm\(^{-2}\). Instead of a wide-angle X-ray diffraction, the GIXRD (grazing incidence X-ray diffraction) was used in this study to eliminate substrate signals. Among the studied ranges, phases of the alloy mainly compose of a Zn-terminal η phase (JCP: 04-0831) and a ζ phase (Zn—7% Fe, JCP: 65–4676). Only relative intensities of the two phases change among the deposited layers with different compositions. As the Zn content in the deposits increases the signals belonging to the η phase becomes more intense.

Fig. 6 shows the corrosion property of Zn coating and that of a deposited Zn–Fe alloy from Bath 1, 200 mA cm\(^{-2}\) in a deaerated 3.5 wt.% NaCl aqueous solution. The corrosion potential (\(E_{\text{corr}}\)), corrosion current density (\(I_{\text{corr}}\)) of Zn coating and the Zn–Fe alloy coating are \(-0.987\) V\(_{\text{SCE}}\), \(42.0\) μA cm\(^{-2}\) and \(-0.897\) V\(_{\text{SCE}}\), \(19.7\) μA cm\(^{-2}\), respectively. Compared with Zn coating, it is found that the corrosion potential of the deposited Zn–Fe alloy is 10% nobler (\(-0.987\) versus \(-0.897\) V\(_{\text{SCE}}\)); and the corrosion current is
more than two times smaller (42.0 to 19.7 $\mu$A cm$^{-2}$). It is thus further concluded that the deposited Zn–Fe alloy coating possesses superior anti-corrosion behaviors than that of Zn coating.

The proposed potassium hydroxide based electrolyte shows lots of advantages, including much higher conductivity, non-toxicity, higher cathodic current efficiency, simple and easier to maintain. The water vapor pressure of the proposed baths being equilibrium with ambient humidity makes them much easier to maintain by just auditing and adjusting of the Zn/Fe ion ratio and bath conductivity without humidity control. The use of potassium hydroxide will be extendable to non-cyanide alkaline baths of Zn–Ni or Zn–Co systems. It is clear that although Bath 1 possesses higher conductivity than that of Bath 2, the deposition using Bath 2 results in slightly higher cathodic current efficiency due to its higher metal content in bath. There must be a tradeoff between the conductivity and efficiency. Besides, electrodeposition by repeatedly using baths with different Zn/Fe ratios, composition modulated co-deposition layers with different amount of Fe contents inside out is readily possible by using our bath design.

4. Conclusions

A novel alkaline Zn–Fe bath based on highly concentrated potassium hydroxide is proposed and proved feasible for the co-deposition of Zn–Fe alloy layer on steel substrates. The conductivity of the proposed baths is 161 to 188% higher than that of the conventional alkaline bath based on dilute NaOH. The proposed formulae are much simpler in composition, easier to maintain, non-toxic, lower power consumption and less heat generation during the electrodeposition process comparing with the conventional formula. Zn–Fe alloy deposits with different compositions are tunable by the ion ratios Zn/Fe in the bath and the deposition current density. The co-deposition of Zn and Fe is an anomalous type under small current density and switches to the regular one at 0.075 and 0.05 A cm$^{-2}$ for Baths 1 (ion ratio Zn/Fe = 13) and 2 (Zn/Fe = 25), respectively. A mechanism based on adsorbed Fe-TEA barrier-layer was proposed to explain this transition. The maximum cathodic current efficiency attained is 24%, which is more than 40% improved over that of the best alkaline bath in literature. The corrosion potential of the deposited Zn–Fe alloy is 10% nobler and the corrosion current is two times smaller than those of Zn-only coating. Thus the deposited Zn–Fe alloy layers provide superior anti-corrosion properties than those of Zn-only coating. From the environmental-protection point of view, the proposed baths are very promising.

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