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Investigation of Sn-Zn electrodeposition from acidic bath on EQCM

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1. Introduction

Tin-zinc (Sn-Zn) alloys are used as sacrificial plated coatings for the protection of ferrum based metals. These coatings provide, high corrosion protection, frictional or anti-frictional properties [1], ductility and solderability to base metal in question [2-5]. Sn-Zn coatings are used in various industrial applications such as on the chassis of electrical and electronic equipment owing to low electrical contact resistance of Sn-Zn alloy [3,5,6]. Sn-Zn coatings are also used as an alternative to cadmium and nickel coatings because of their toxic and allergenic effects [2,5,7,8]. However, the first bath used for Sn-Zn alloys was the cyanide bath. New tin-zinc bath compositions were investigated due to the toxicity of cyanide baths and the difficultly to control the parameters [3,4,6]. Hence, there are different bath compositions alternative to the cyanide baths reported in industry, emphasizing the Sn-Zn ratio being the primary factor which effects the coating performance. Some studies reported that Sn-Zn coating with 70-80% Sn and 30-20% Zn in the alloy in neutral bath had the best mechanical and protective effect [3,6,7]. Sn-Zn coatings with high tin content provide permanent protection against rusting and uniform corrosion of metals [1]. At the same time, some researchers studied Sn-Zn coatings with high zinc content in slightly acidic bath [1,9]. In this study, Sn–Zn alloy with low Sn content was electroplated onto gold electrode using chronoam-

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ABSTRACT

Tin–zinc (Sn–Zn) alloy with low tin content was deposited on gold electrode and steel substrate with use of chronoamperometric technique from an acidic bath. In order to evaluate coating efficiency of Sn–Zn alloy in 0.5 M NaCl solution, open circuit potential–time curve ($E_{OCP}-t$), polarization curves, mass change of the electrode ($\Delta m-t$) using quartz crystal microbalance (QCM) were compared to those of pure Sn and Zn coatings. Anodic stripping measurements were carried out simultaneously with the mass loss of the deposit. Scanning electron microscopy (SEM) and energy dispersive X-ray spectra (EDS) analysis were performed to characterize the surface morphology. Anodic stripping experiment and EDS analysis indicated that Sn, Zn, and SnO₂ formed on the electrode surface when Sn–Zn was coated from acidic bath. Furthermore, local mapping demonstrated homogeneous distribution of Sn and Zn atoms throughout the surface.

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perometric technique from the acidic bath due to the fact that it both provides good protection for ferrum based metals and is cost effective. Coating performance of Sn–Zn alloy was examined with EQCM technique in 0.5 M NaCl solution. In addition, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were utilized to characterize surface morphology and analyze coating composition before and after Sn–Zn deposit was exposed to corrosion in 0.5 M NaCl.

2. Experimental

The EQCM measurements were carried out in a Model 400A time-resolved electrochemical quartz crystal microbalance (CH Instrument, USA) linked to a computer equipped with electrochemistry software (CHI400A). Electrochemical experiments were performed in a conventional three-electrode cell with a capacity of 4 ml. The working electrode used in QCM and anodic stripping experiments was gold AT-cut quartz crystal (CHI125A). Surface area of a gold crystal was 0.204 cm² and its nominal resonant frequency was 7.995 MHz. ST-42 carbon steel with a surface area of 0.204 cm² was also used as a working electrode in other electrochemical studies. The reference and counter electrodes were a Ag/AgCl/KCl(sat) electrode (CHI111) and a platinum rod (CHI115) respectively. Sn-Zn alloy coating was deposited from the mixture of SnSO₄·7H₂O (5 g/L), ZnCl₂·6H₂O (75 g/L), NH₄Cl (180 g/L) and pH was adjusted to 1.04 using conc. H₂SO₄. Sn and Zn coatings were carried out following bath compositions: Sn bath: SnSO₄·7H₂O (80 g/L) and 15 ml conc. H₂SO₄; Zn bath: $ZnCl_2\cdot 6H_2O~(75\,g/L)$ and $NH_4Cl~(180\,g/L).$ All reagents were analytical grade from Merck. Only one side of the gold crystal was coated with Sn, Zn and Sn-Zn alloy monitored current-mass $(i-\Delta m)$ change at a potential range of -0.6 V to -1.2 V by the use of chronoamperometric technique. The mass and theoretical thickness changes of Sn-Zn, Sn and Zn coatings on the electrode were calculated by Sauerbrey equation as follows [10]: $\Delta f = -\frac{2f_0^2 \eta \Delta m}{A \sqrt{\rho \mu}}$

where Δm is the mass change of the quartz crystal surface (g), Δf is measured frequency ($f_1 - f_0$) (Hz) shift caused by Δm , f_0 is the resonant frequency of the fundamental mode of the crystal (Hz), A is the geometric area of the electrode (cm²), μ_q is shear modulus of quartz (2.947 × 10¹¹ g cm⁻¹s⁻²) and ρ_q is the density of quartz

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Fig. 1. SEM, EDS and local mapping analysis images for Sn–Zn alloy deposited by using chronoamperometric technique on steel substrate at –1.2 V final potential.

(2.648 g cm⁻³). The theoretical thickness ($T_{\rm f}$, cm) of the deposits was calculated from $\Delta m/\rho$ (density g/cm³).

In order to determine corrosion resistance of Sn–Zn coating, the change in deposition was recorded by comparing with pure Sn and Zn coatings and steel for 5 h in 0.5 M NaCl at room temperature by the use of open circuit potential (OCP). The OCP curves monitored for five hours. The polarization curves were taken after 5 h OCP measurements. The polarization curves were scanned at 1 mV/s adjusting potentials 200 mV more cathodic and anodic of the OCP value. Mass changes of Sn, Sn–Zn and Zn electrodes were monitored for 5 h at OCP in 0.5 M NaCl. Anodic stripping analysis was carried out at a scan rate of 10 mV/s in 0.5 M NaCl solution immediately after deposition. Morphology and composition of the coverage were examined with SEM (JEOL JSM-7000F Field Emission SEM apparatus) in the presence and the absence of 0.5 M NaCl.

3. Results and discussion

3.1. Electrodeposition process and surface morphology and compositional analysis of Sn–Zn deposit



Sn–Zn alloy was coated on one side of the gold electrode surface using chronoamperometric technique. The change in the current

Fig. 2. OCP-t curves of Sn, Sn-Zn, Zn deposits and steel substrate in 0.5 M NaCl solution.

with the change of the mass of the electrode was monitored for approximately one minute. The amount and the thickness of the coverage on the surface calculated by Sauerbrey equation were $62 \mu g$ and about 100 nm, respectively. The steel substrate was coated with Sn–Zn alloy in the same manner. The SEM image (magnification of 2000×) and EDX spectra of Sn–Zn coated steel are shown Fig. 1. According to the EDS analysis the deposit was found to contain 22.73 wt% Sn, 66.12 wt% Zn and 11.15 wt% O. EDS results indicate that Sn are coated as Sn and SnO₂ on the electrode surface from acidic bath due to the oxidation. Since Sn²⁺ ions are oxidized to Sn⁴⁺ ions in acidic medium, tin is deposited on the surface as SnO₂ as well as Sn [11]. The formation mechanism of SnO₂ can be given as follows:

$$SO_4^{2-} + 2H_2O + 2e^- \rightarrow SO_2 + 4OH^-$$

$$\mathrm{Sn}^{2+} + \mathrm{4OH^-} \rightarrow \ \mathrm{SnO_2} + \mathrm{H_2O}$$



Fig. 3. Polarization curves of Sn, Sn–Zn, Zn coatings and steel in 0.5 M NaCl after the electrode was kept at the OCP for 5 h.



Fig. 4. Mass change of Sn, Sn–Zn, Zn coatings versus time at the electrode surface in 0.5 M NaCl at OCP.

Local mapping analysis of alloy component and analysis of its EDX spectra also showed the formation of Sn, Zn and SnO_2 on the surface.

3.2. OCP and polarizing curves measurement

The open-circuit potential against time $(E_{OCP}-t)$ curves of the pure steel and Sn, Sn–Zn, Zn coatings on steel substrate measured for 5 h in 0.5 M NaCl solution are shown in Fig. 2. As seen from Fig. 2, OCP value of Sn–Zn deposit is more positive than those of Zn deposit and the pure steel and more negative than that of pure tin deposit



Fig. 5. Stripping voltammogram at $v = 10 \text{ mV s}^{-1}$ of deposit simultaneously mass changing of deposit in 0.5 M NaCl solution.

at the end of 5 h. These results indicate that Sn–Zn bath prepared from acidic bath provides good protection for ferrum based metals. Moreover, polarization curves of Sn, Sn–Zn, Zn coatings and steel in 0.5 M NaCl are shown in Fig. 3 after OCP was recorded for 5 h. As shown in Fig. 3, break down potential of Sn–Zn coating is more positive than that of Zn coating and the pure steel and more negative than that of Sn coating. These results showed that Sn (22.73 wt%)–Zn alloy coating obtained with acidic bath is more resistance than pure Zn coating.

3.3. Mass change

The mass losses of Sn, Sn–Zn, Zn deposits with time in 0.5 M NaCl were followed up to 5 h using EQCM at OCP. The slopes of



Fig. 6. SEM images and EDX spectra for Sn-Zn deposit after 5 h immersion in 0.5 M NaCl solution.

curves are proportional to corrosion rates of the coatings [3,12]. As seen from Fig. 4, the total mass losses of Sn, Sn–Zn and Zn deposit are $-9.3 \mu g$, $-16.3 \mu g$ and $-23.05 \mu g$, respectively at the end of 5 h. These results show that Sn–Zn deposit is more resistance than pure Zn deposit. Moreover, there was a rapid mass loss observed for the Sn–Zn coverage for the first 6000s because of the dissolution of Zn in the deposit. The mass loss was observed to decrease after 9000s due to decrease in the amount of Zn in the deposit.

3.4. Potentiodynamic anodic stripping

Potentiodynamic anodic stripping was carried out simultaneously with the mass change of coated surface to elucidate the coverage of Sn-Zn layer upon the surface. Anodic stripping experiment was carried out using the gold working electrode. Fig. 5 shows simultaneous anodic stripping curve and mass change for Sn-Zn deposit. The deposited film was stripped in the reverse direction (in anodic direction) in 0.5 M NaCl after Sn-Zn alloy was coated under the same conditions (temperature, pH and mass change of deposit) in order to show the presence of SnO₂ in the deposit. The peaks heights of the anodic stripping curve can also be used to estimate proportion of tin and zinc in deposit [5]. As shown by Fig. 5, anodic stripping starts with the dissolution of Zn(P1) and is followed by the dissolution of Sn (P2). Anodic dissolution peaks of metallic Zn and Sn are observed at -0.725 V and -0.394 V. The stripping peak P3, corresponding to Sn^{+4} ion (-0.073 V), shows the presence of SnO_2 in deposit. Moreover, as seen from mass change in Fig. 5, Zn ratio is higher than the other constituents in the deposit. Mass change curve indicates that the mass loss of Zn in deposit is $-32 \mu g$ up to -0.675 V it was Zn which is mainly consumed in the deposit. Mass loss of Sn is $-8.2 \mu g$ up to -0.38 V in the deposit. These results show that mass change and anodic stripping experiment verify that the coverage obtained from the acidic bath was rich in Zn and Sn was coated on the surface as Sn and SnO₂.

3.5. SEM and EDS analysis

SEM image of Sn–Zn deposit and its EDX spectra were presented in Fig. 6 again after Sn–Zn coated steel had been exposed to corrosive medium for 5 h in 0.5 M NaCl solution. The SEM image taken at a magnification of $50000 \times$ demonstrates that there are various sizes SnO₂ nano particles in deposit and Zn and Sn undergoes corrosion in 0.5 M NaCl at the end of 5 h. EDS analysis result after a corrosion time reveals that oxide and chloride layers are formed on the surface. According to EDS analysis, zinc oxide and zinc chloride can be found as corrosion products of zinc in 0.5 M NaCl on the surface [13,14].

4. Conclusions

Sn–Zn alloy was electroplated with chronoamperometric technique from acidic bath. The investigation of the corrosion resistance of Sn–Zn coating compared to Sn and Zn coating by the use OCP and polarization curves showed that Sn–Zn coatings coated from acidic bath provide good protection to the steel matrix. Moreover, according to QCM result, Sn–Zn alloy coating with low tin content is more resistance than pure Zn coating. According to potentiodynamic anodic stripping and EDS results, the coverage was found to contain Sn, Zn and SnO₂ in the deposit and the amount Zn in the deposit was higher than the other components. SEM pictures showed the presence of SnO₂ nanoparticles in the deposit. Low Sn content Sn–Zn coating by the use of an acidic bath gave highly satisfactory results regarding to the protection of steel from the corrosion process.

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