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Electrodeposition and Characterization of Sn-Zn Alloy Coatings from Sulfate Based Baths

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Abstract: *Tin-Zinc alloy coatings have many applications because of their unique properties such as corrosion resistance, solderability and flexibility. In this study, the effect of current density, temperature and pH on chemical composition, cathodic current efficiency, morphology and structures of the coatings was investigated. The results illustrated that, at low current densities (<0.5 mA/cm2), the coatings were relatively pure tin, but Zn content increased with enhancing the current density. At higher currents a relatively pure Zn film was obtained. Temperature and pH also affected chemical composition of the alloy films. Zn content of the coatings was decreased by increasing the temperature, while its variation with pH had ascending-descending trend. Morphological investigation of the coatings revealed that increasing Zn content of deposits led to porous, rough and fine grained films.*

Keywords: *Sn-Zn, Electrodeposition, Cathodic current efficiency, Alloy coatings, SEM.*

1. INTRODUCTION

In today's advanced world, application of knowledge and technology for designing and manufacturing industrial parts with the aim of long-lasting and decreasing energy usage and costs is essential. Coating technologies and processes are the most important approaches in improvement of superficial properties alongside of preserving the base metal's intrinsic characteristics. Applying a monolayer or multi-layer film on the surface of a substrate can improve its corrosion, erosion and wear resistance, along with electrical conductivity, coloring capability and appearance. Therefore, the coating can be effective in longevity and applicability of the part [1-5].

Cadmium coatings were used to enhance the corrosion resistance of different components and parts in many industrial applications. Since corrosion potential of cadmium is more negative than that of steel, it can act as a sacrificial coating on the surface of steel parts. If the coating is damaged, the cadmium plating will be corroded preferentially [6-14]. Although cadmium has been extensively used as a protective coating on steel, its carcinogenic and toxic nature is a cause of concern, and its use is being restricted. Therefore, during the last decade researchers have focused on development of non-toxic coatings from cyanide free baths. Tin-zinc alloy coatings have been considered as an appropriate substitute for Cd films due to their suitable corrosion properties and soldering capabilities. These alloys frequently contain 20-30 wt.% Zn, and are produced by electrodeposition technique [15-21].

Tin based alloy coatings can be deposited by using acidic or basic solutions. According to Guaus and Burgués [22, 23], acidic baths can be based on sulfate, chloride, sulfate-chloride and acetate compositions, while alkaline solutions are cyanide, non-cyanide or methanol based. However, application of acidic baths is more common. Wang et al. [24] have studied the effect of deposition parameters on characteristics of Sn-Zn alloy coatings resulting from an acidic bath. Their results revealed that Sn content of the coatings decreased with enhancing the current density. They also found that the optimum alloy composition (i.e. 70Sn-30Zn) obtained at the current density of 5 mA/cm^2. Ashiru and Shirokoff [25] evaluated the effect of bath composition and pH on characteristics and

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corrosion properties of Sn-Zn coatings. They showed that the presence of complexing agent in the bath improved final properties of the alloy films. According to their results, corrosion resistance of Sn-Zn alloy coatings could be up to 25% better than Cd, Zn or Ni-Zn coatings. Dubent et al. [15] investigated the effect of electroplating condition on deposit composition. They used a non-cyanide alkaline bath to produce Sn-20wt.%Zn alloy coatings on steel substrates.

In spite of some research on electrodeposition of Sn-Zn alloys, the optimum condition for electrodeposition of these alloys is not clearly understood, and different bath compositions along with depositing conditions have been proposed as the optimum condition in these research works. Moreover, most of the earlier works have focused on production of Sn-20wt.%Zn alloy coatings. In the present work, Sn-Zn alloy coatings containing various percentages of Zn were electrodeposited from sulfate based baths. The effect of electrodeposition conditions (i.e. current density, pH and temperature) on chemical composition, morphology and the structure of the resultant coatings were investigated.

2. EXPERIMENTAL

2.1. Preparation of the Substrates

St 37 steel plates with an exposed area of 4 cm2 were used as the cathode. Before electrodeposition, all the substrates were mechanically abraded using emery papers from 120 to 2000 grit. After rinsing with distilled water, the substrates were ultrasonically cleaned in an acetone bath at room temperature for 10 min. Degreasing was performed in an alkaline solution (containing NaOH, Na_2CO_3, and $Na_3PO_4.12H_2O$) at 70 °C for 15 min. Afterward, acid pickling was done by using 20 % HCl solution at room temperature for 1 min. The substrates were transferred to electrodeposition bath immediately after activation.

2. 2. Electrodeposition of Sn-Zn Coating

In order to prepare Sn-Zn alloy coatings, a double electrode cell, sulfate based baths and DC current were used. The anode was a stainless steel sheet (316L) with an effective area of 4 cm^2. The distance between the anode and the cathode was 3 cm.

Bath composition and deposition condition have been presented in Table 1. It is worth noting that, for preparing these baths high purity chemicals (Merck grade) were used. Bath pH was adjusted by small addition of either 1M NaOH or 1M H_2SO_4 solutions.

Current efficiency of Zn electrodeposition was calculated according to the following equation [26]:

$$CE_{Zn} = \frac{P_{Zn}E_f}{P_{Zn}+P_{Sn}R} \qquad (1)$$

where P_{Zn} and P_{Sn} are weight percentages of Zn and Sn in the coatings, E_f is the efficiency of alloy deposition, and R is the ratio of equivalent weights of Zn to Sn.

2. 3. Characterization of the Coatings

Morphology and chemical composition of the coatings were studied by using a CAMSCAN MV2300 scanning electron microscope (SEM) equipped with ROUTEC energy dispersive spectroscope (EDS). Average chemical composition of the coatings was determined by EDS analysis at low magnifications from at least five different areas of the coatings surface.

X-ray diffraction (XRD) technique was used to evaluate the structure of the coatings. For this purpose, Philips X Pert Pro apparatus with Cu-K_α(λ=1.542 A), step size of 0.02°, step duration of 0.4 s and 2θ range of 10-110° was employed. The resultant patterns were analyzed by using X-pert high score software.

3. RESULTS AND DISCUSSION

3. 1. Effect of Current Density

Effect of electrodeposition current density on chemical composition of Sn-Zn alloy coatings is shown in Fig. 1. Temperature and pH of the bath were 30°C and 4, respectively. It's clear that at

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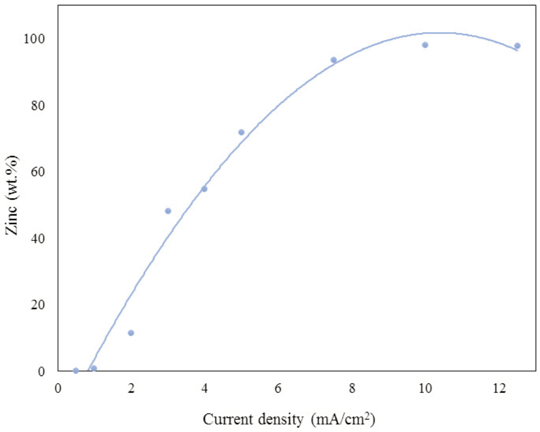
low current densities (<0.5 mA/cm^2), the deposit is relatively pure tin. However, the amount of zinc in deposits increases with enhancing the current density, and at high current densities (> 10 mA/cm^2) almost pure zinc film is obtained. A wide range of alloys with different chemical compositions can be produced by variation of current density in this study, which is in contrast to Vitkiva et al. [11] results. Increment of zinc content of the coatings with raising the current density is similar to Kazimierczak et al. [19] results, but unlike the Dubent et al. [15], and Ashiru and Shirokoff [25] observations in the alkaline baths.

Considering standard electrode potentials versus standard hydrogen electrode (Eqs. 2-4) [26], it can be roughly concluded that zinc is more active than hydrogen and tin under the used electrodeposition condition.

$$2H^+ + 2e = H_2 \qquad E^0 = 0.0\ \text{mV} \tag{2}$$

$$Sn^{2+} + 2e = Sn \qquad E^0 = -0.13\ \text{mV} \tag{3}$$

$$Zn^{2+} + 2e = Zn \qquad E^0 = -0.76\ \text{mV} \tag{4}$$



fect of current density on Zn content of the alloy coatings, electrodepositing at T=30°C ar

Fig. 1. Effect of current density on Zn content of the alloy coatings, electrodepositing at T=30°C and pH=4.

The cathode potential becomes less noble (more negative), and the overpotential grows with increasing the current density. Therefore, conditions for deposition of less noble metal (Zn) are prepared. There is an upper limit for deposition rate of a metal. At a given current density, deposition rate of more noble metal (Sn) is closer to its limiting value than that of less noble one (Zn) [26, 27]. Thus, the proportion of Zn in the alloy films increases with enhancing the current density. The calculated current efficiency for Zn deposition also confirms the obtained results (Fig. 2).

Fig. 3 exhibits morphology of the alloy

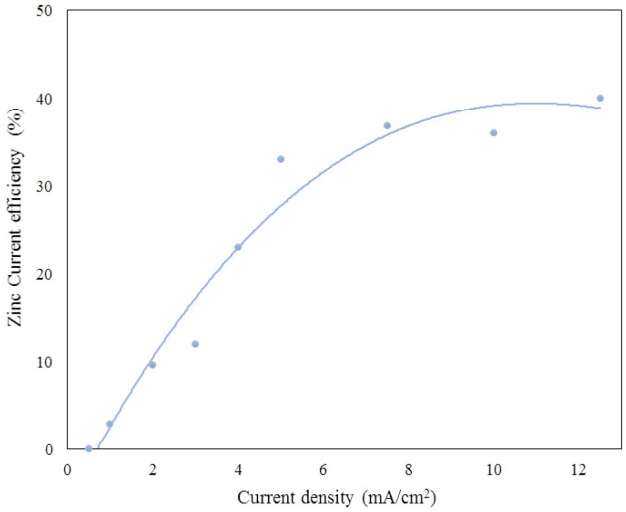


Fig. 2. Effect of current density on the cathodic current efficiency of zinc ion reduction.

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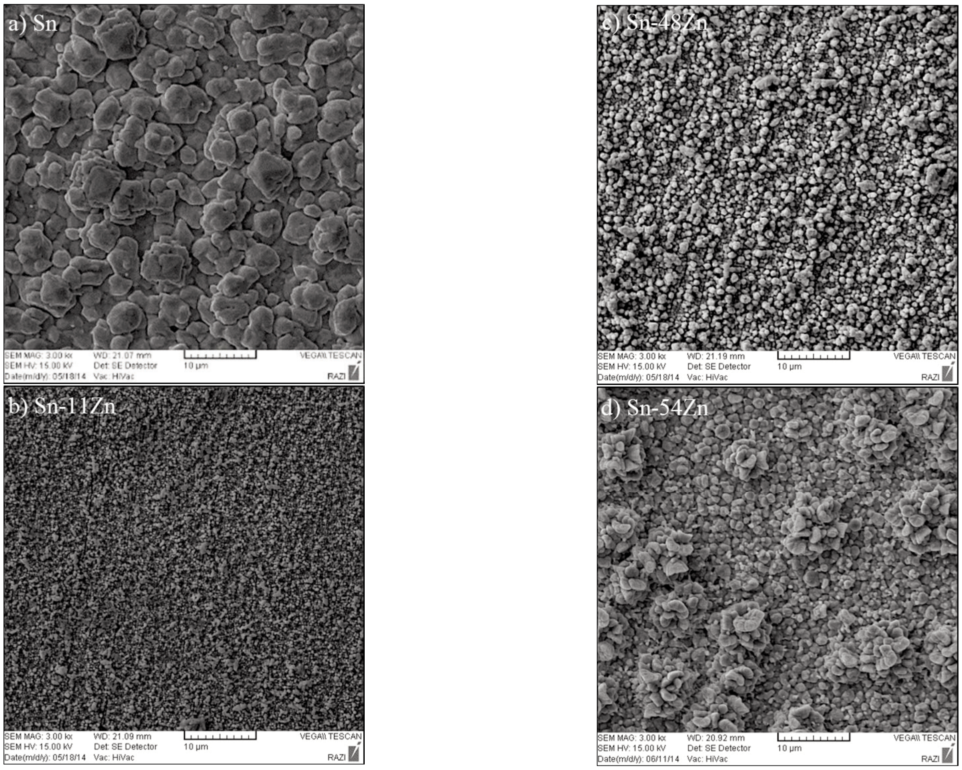
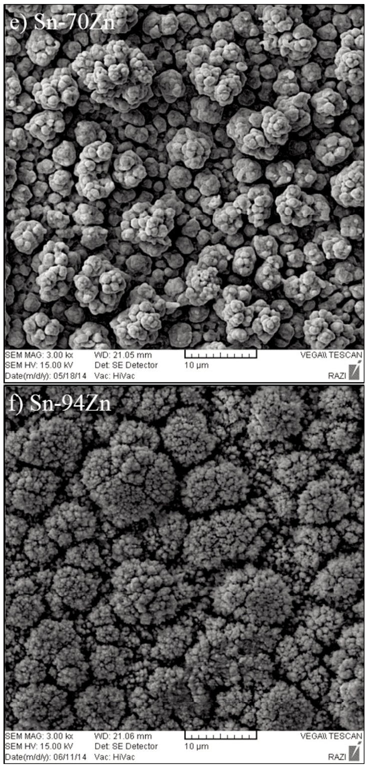
coatings depositing at different current densities. As it can be seen, relatively pure tin film (Zn content < 1wt. %, Fig. 3a) has a coarse grain morphology. While at first morphology becomes finer by increasing the current density and Zn content of the coatings, it becomes rough and micro porous at higher current densities. Roughness is the result of high reduction rates of





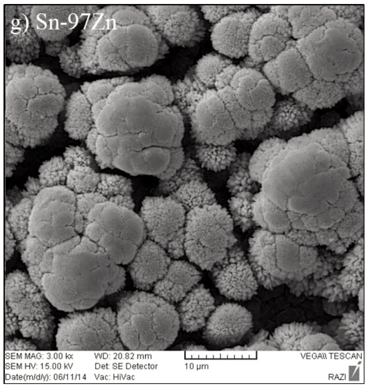


Fig. 3. Effect of current density on the morphology of Sn- Zn alloys (a) 1mA/cm^2 (b) 2 mA/cm^2 (c) 3 mA/cm^2 (d) 4 mA/cm^2 e) 5 mA/cm^2 (f) 7.5 mA/cm^2 (g) 10mA/cm^2.

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metallic ions [25]. Formation of porous films can be due to fast reduction of metal ions upon arrival to the cathode surface at high current densities, which limits migration and penetration of ad-atoms to the blank places. Therefore, porosity of the coatings is increased [28].

3. 2. Effect of Plating Bath Temperature

Variation of the coatings Zn content as a function of bath temperature has been illustrated in Fig. 4. Current density and pH were adjusted at 5 mA/cm2 and 4, respectively. Zn content of alloy coatings decreases from about 70 to 17 wt.% with increasing the bath temperature from 30 to 50°C. Similar trend has also observed in other studies [15, 25]. Mobility of metallic ions, and as a result, concentration of metallic ions around the cathode, rises with increasing the bath temperature. Preferential deposition of more noble metal (i.e. Sn) is encouraged by increasing the metallic ions concentration at the cathode-solution interface [28]. This can be also a reason for lower partial current efficiencies of Zn deposition at higher temperatures (Fig. 5). Moreover, it is clear from Fig. 5 that total current efficiency is reduced by enhancing the temperature. Hydrogen reduction overpotential at the cathode surface is decreased, and greater part of the applied current is consumed for hydrogen reduction by increasing the bath temperature.

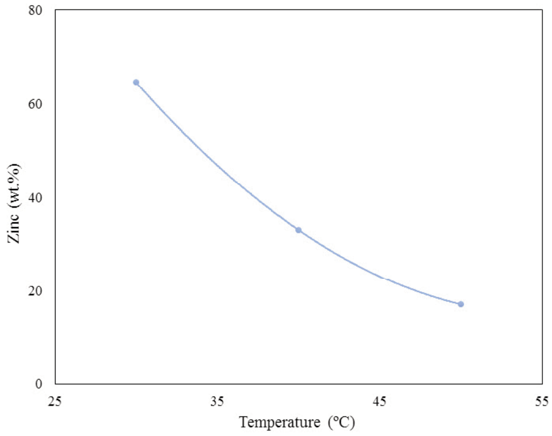

Fig. 4. Zn content of the alloy coatings as a function of bath temperature.

Effects of plating bath temperature on the morphology of the alloy coatings are shown in Fig. 6. Coatings with different morphologies have been obtained at various temperatures. At 30°C, surface of 70Zn-30Sn alloy coating is rough, porous and consisting of fine grains (Figs. 3a and 6a). Alloy coatings with coarser grains, but smoother and compacter morphologies are

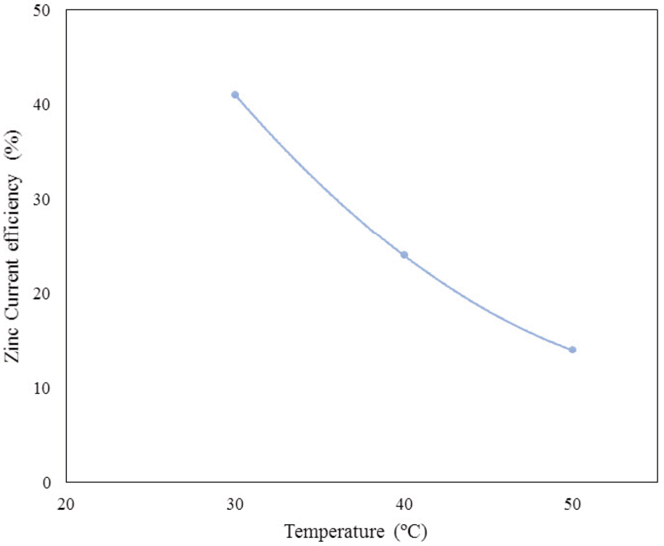

Fig. 5. Effect of plating bath temperature on partial current efficiency of Zn deposition.

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obtained by increasing the bath temperature and Sn content. Similar trend has also been reported by other researchers [1, 18]. This could be due to higher hydrogen reduction overpotential on tin rich layer as compared to zinc rich ones, producing at low temperatures. Coarser grain structure can be attributed to the low number of buds that formed on the surface in the early stages of the plating process (Due to high emissions of hydrogen).

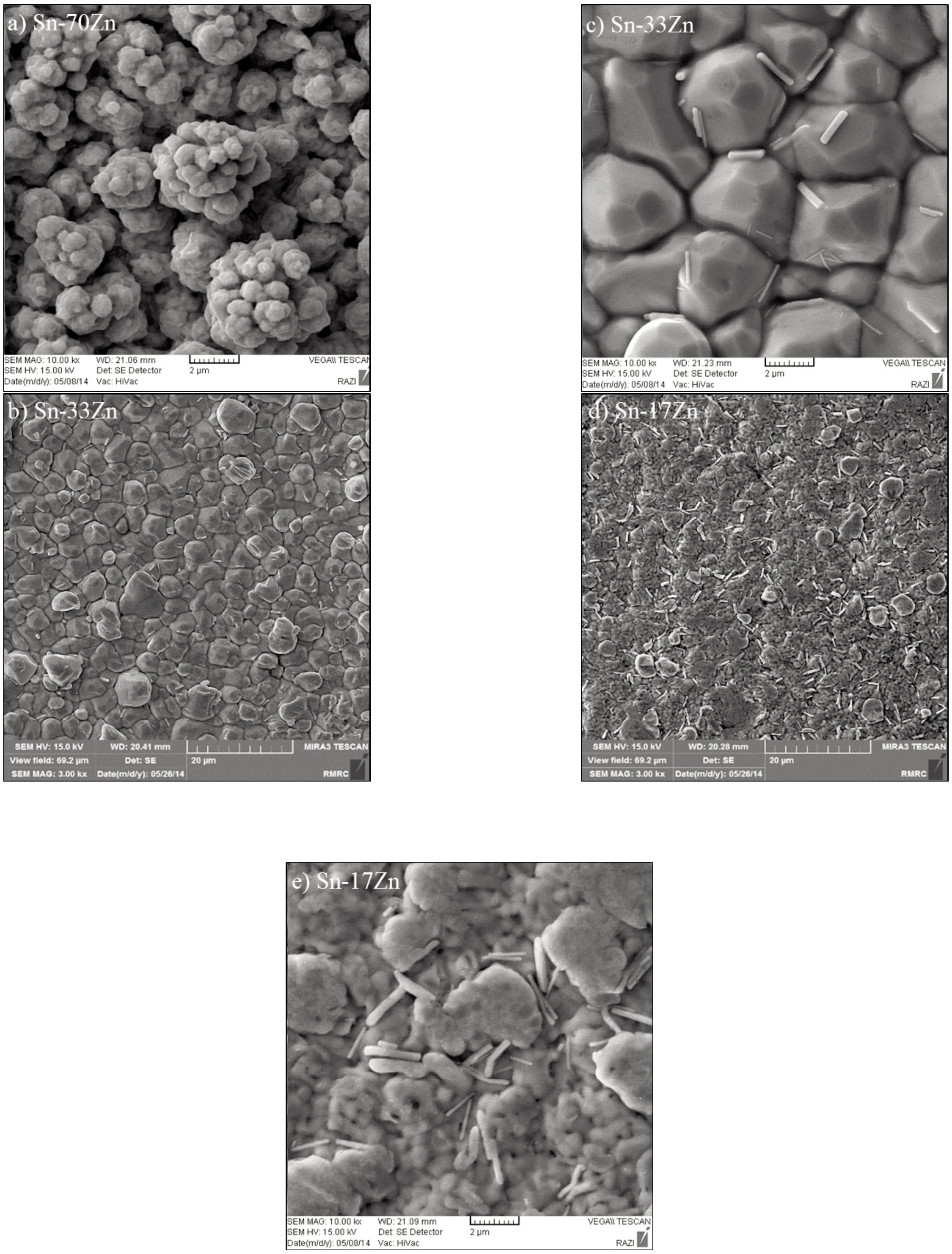

Fig. 6. SEM micrographs from surface of Sn-Zn coatings prepared at (a) 30 (b, c) 40 and (d,e) 50 °C.

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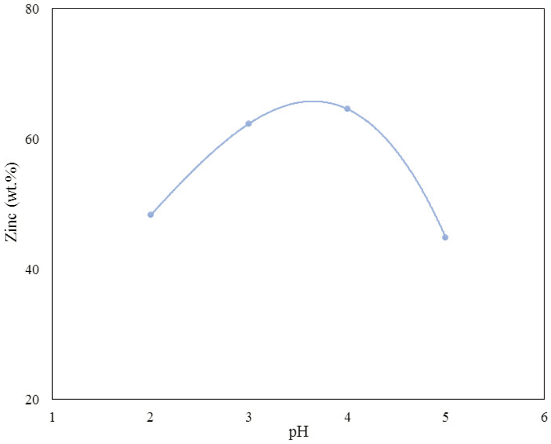

Fig. 7. Zn content of alloy coatings as a function of bath pH.

3. 3. Effect of pH

Effect of plating bath pH on chemical composition (Zn content) of the alloy coatings is represented in Fig. 7. Current density and temperature were adjusted at 5 mA/cm2 and 30° C, respectively. It is clear that Zn content of the alloy coatings increases with enhancing bath pH. However, there is a maximum for Zn content of the coatings, and after a specific pH, Zn percentage of the alloy films decreases. Reduction of Zn is difficult at low pH values because of high concentrations of hydrogen and fast reduction of that (because of higher activity of Zn than hydrogen activity, reduction of Zn occurs at low rates). Hydrogen evaporation rate is decreased, and Zn deposition is facilitated by increasing bath pH. Therefore, Zn content of the alloy deposits increases. Decreasing of Zn content of the alloy coatings at high pH values can be due to the formation of white zinc hydroxide around the cathode (Eq. 5) [18, 22].

$$Zn^{2+}+2OH^{-}=Zn\,(OH)_2,\ K_{sp}=3.0\times10^{-16} \qquad (5)$$

Effect of plating bath pH on morphology of the resultant coatings is shown in Fig. 8. Roughness and porosity of the coatings increase with raising the elecetrodeposition bath pH up to 4 (Figs.8a,b and 3a), but smoother and compacter alloy coatings are produced at higher pH (Fig. 8c).

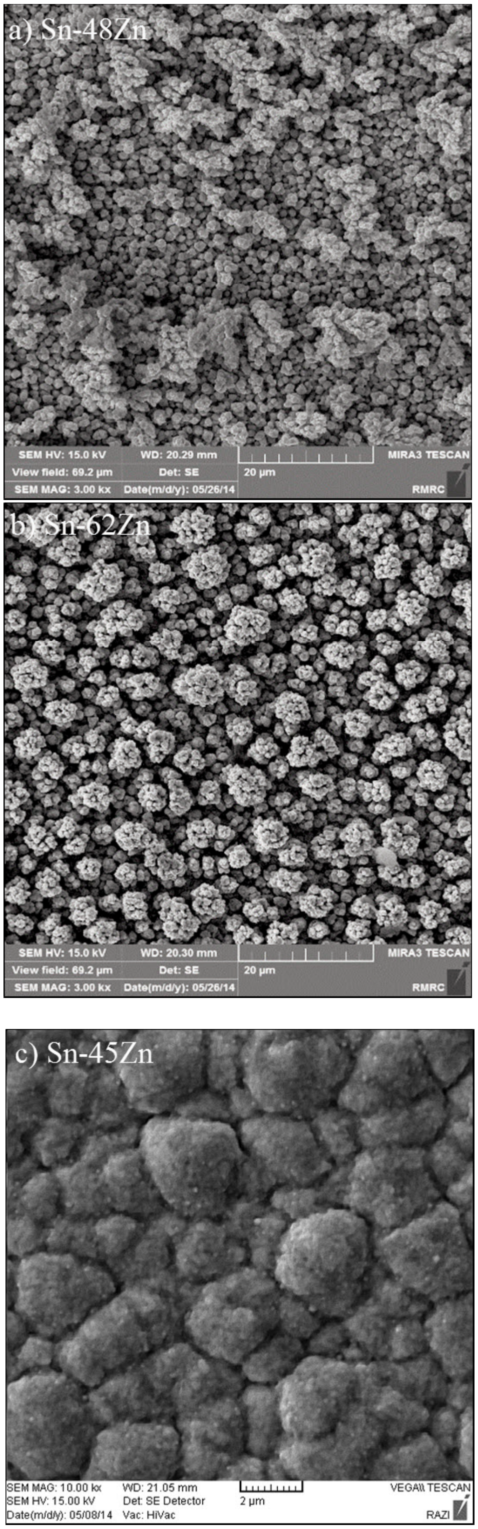

Fig. 8. Effect of pH on the morphology of Sn- Zn alloy coatings. (a) pH=2, (b) pH=3 and (c) pH=5.

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Morphological changes of the alloy coatings with pH can be related to their Zn content. The coatings with lower percentage of Zn have a smoother morphology.

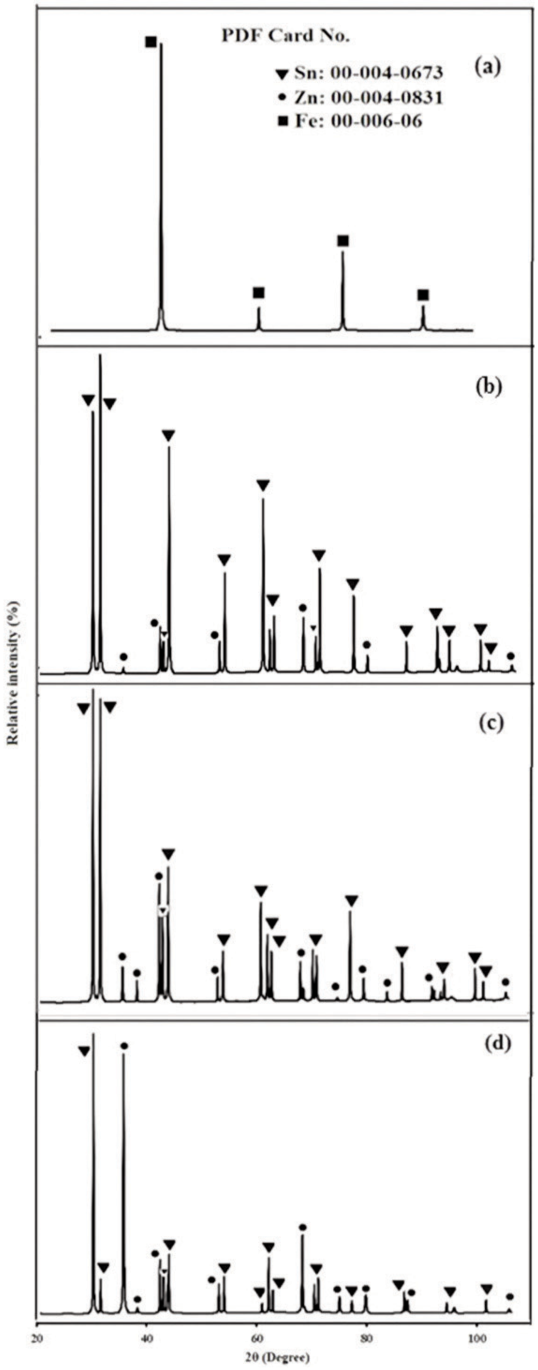

Fig. 9. XRD pattern (a) steel (base metal) and alloy coatings with Zn content of (b) 11%, (c) 33%, (d)70 %.

3. 4. Structure of Coatings

Fig. 9 illustrates the XRD patterns of steel substrate (9a), Sn-11Zn (9b), Sn-33Zn (9c) and Sn-65Zn (9d) alloy coatings. Substrate peaks cannot be seen in XRD patterns of the coatings, due to the suitable thickness of these films. Both Zn and Sn peaks are present in XRD patterns of the alloy coatings. The intensity of these peaks varies with chemical compositions. Presence of both Zn and Sn peaks in XRD patterns of all the alloy coatings means that the alloys consist of a mixed Zn and Sn phases rather than a single phase solid solution, as also reported by other investigators [1,5,19,22]. This result is in accordance with the tin-zinc phase diagram, indicating very low mutual solubility of these elements [28 -30].

4. CONCLUSION

In the current study, Sn-Zn alloy coatings on st37 steel substrates were prepared by using electrodeposition technique. The results illustrated that, at low current densities (<0.5 mA/cm2), the coatings were relatively pure tin, while Zn content would increase with increasing the current density. At higher currents a relatively pure Zn film was obtained. Temperature and pH also affected chemical composition of the alloy films. Zn content of the coatings was decreased by increasing the temperature, while its variation with pH had ascending-descending trend. Morphological investigation of the coatings revealed that increasing Zn content of deposits led to porous, rough and fine grained films.

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