

Electrodeposited ZnCoNi alloys

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Ternary Zn-Co-Ni alloys were deposited by electrochemical deposition technique on to steel substrates. The effect of bath composition on the composition of the deposits, crystallographic structure, surface morphology and corrosion properties were investigated. Polarization study revealed shift of potential towards positive direction in the presence of more nickel content. SEM photomicrographs showed fine-grained deposit in the presence of nickel of 10 and 28 % in the film. All films have the same structure, but with different crystallographic orientations. It is observed that Zn-Co-Ni alloy electrodeposition is of anomalous type.

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1. Introduction

It is known that electrodeposition offers several unique advantages in the preparation of alloys (superior control of alloy composition, including formation of thin layers of alloys) and that electrochemically-formed alloy may possess different properties than those obtained by a metallurgical process [1,2]. The use of zinc alloys provides several advantages. Electrochemically, alloys have different corrosion potentials from their alloying elements. Alloys of zinc, for example, can be designed to maintain anodic protection to steel, but remain less electrochemically active than pure zinc. Thus, a zinc alloy coating can still be sacrificial to steel components, but corrodes much more slowly than zinc when exposed to a corrosive environment [3].

Zinc-alloy electrodeposited coatings and especially can those containing one of the 'iron group metals' (e.g. iron, nickel and cobalt) have found important end-uses in various industrial sectors. In particular, Zn-Ni and Zn-Co electrodeposits are promising alternatives to pure Zn. Zn-Ni alloy coatings have attracted much attention because they possess higher corrosion resistance and better mechanical characteristics in comparison with zinc and other zinc alloy coatings [4-13]. Zn-Co alloy plating is becoming more popular because of its relatively lower cost of operation compared to zinc-nickel. It offers somewhat lower levels of corrosion resistance; however, the level is still adequate and an improvement over plain zinc of the same thickness [14].

Zinc alloys also offer an important eco-friendly alternative to toxic cadmium coatings. Some researchers studied Zn-Co alloys for their anticorrosive properties [15-18]. The electrodeposition of zinc alloys with iron group metals causes the anomalous phenomenon of codeposition, whereby zinc – the less noble metal – is deposited preferentially.

Anomalous codeposition is therefore a very important phenomenon in the electrodeposition of zinc alloys.

Therefore, many literatures have reported the preparation of these alloys with high or low iron content, respectively [19-21]. Because of the aforementioned reasons, it was felt that it would be interesting to collect the properties of Zn-Co and Zn-Ni alloys in one deposit via the electrodeposition of Zn-Co-Ni alloy. Recently, Abou-Krishna et al. [22] found that ternary Zn-Ni-Co alloy electrodeposits have better corrosion resistive and brighter appearance in comparison with Zn-Ni alloy coatings.

The first aim of this work was to modify a steel substrate by electrodeposition of the Zn-Co-Ni coatings. The second objective was to study the corrosion behavior of Zn-Co-Ni alloy deposits on low carbon steel substrates evaluated in comparison to the corresponding pure Zn coating. The morphology, composition and structure of these alloys were investigated.

2. Experimental

Zn-Co-Ni alloys were obtained by electrodeposition from the solutions shown in Table 1.

Table 1. Solution composition for alloy electrodeposition.

Solution composition	ZnCoNi
ZnSO ₄ .7H ₂ O (g l ⁻¹)	45
NiSO ₄ .6H ₂ O (g l ⁻¹)	52.6-78.9-105.2-131.5
CoSO ₄ .7H ₂ O (g l ⁻¹)	143.5
C ₆ H ₅ Na ₃ O ₇ .2H ₂ O (g l ⁻¹)	25
H ₃ BO ₃ (g l ⁻¹)	25
NH ₄ Cl (g l ⁻¹)	45
Na ₂ SO ₄ (g l ⁻¹)	0.5
Solution pH	5
Deposition time (min.)	10
Temperature	Room temperature
Voltage (V)	-3

The plating time was 10 min, after which the cathode was withdrawn, washed with distilled water and dried. All these electrolytes were prepared from Merck pro-analysis grade chemicals and double-distilled water. The working electrodes were aluminum foils used for XRD and AAS measurements and AISI 4140 steel disks used for corrosion. The chemical composition of the AISI 4140 steel is 0.36C–0.80Mn–0.005Si–0.914Cr–0.30Ni–0.85Mo–0.075V–0.07S–0.143Cu–0.034P (wt-%).

Before electrodeposition, aluminum foils were mechanically polished with silicon carbide emery paper, degreased in 1 M NaOH with surfactant at 70 °C during 5 min and finally rinsed with the twice distilled water (18 MΩ cm) and dried in air. Counter electrode was a Pt electrode, for the polarization and the corrosion measurements. The reference electrode used in all experiments was a saturated calomel electrode (SCE). All the potentials are referred against SCE.

The corrosive behaviors of the electrodeposited specimens were analyzed in 3 wt.% NaCl aqueous solution at room temperature in a Pyrex glass cell. The corrosion behaviors of the samples were investigated by a potentiodynamic polarization technique. Polarization and cyclic voltammetry measurements were performed with an electrochemical analyzer/workstation (Model 1100, CH Instruments, USA) with a three-electrode configuration. The exposed area of the specimens was about 1 cm². The specimens were covered with a cold setting resin and immersed into the solution until a steady open circuit potential (ocp) is reached. After equilibrium, the polarization was started at a rate of 1 mV/sn.

A Rigaku diffractometer was used to analyze the crystallographic structure of alloys. The X-ray diffractometer was operated at 30 kV and 30 mA with CuKα radiation. The film composition was determined via a Perkin-Elmer atomic absorption spectrophotometer (AAS) after dissolving the deposits in concentrated hydrochloric acid and diluting the solution with distilled water to 100 ml. The results obtained by atomic absorption spectrophotometer were shown in Table 2.

The error bars for the elemental compositions in table 2 is ±0.1%. The morphologies of the deposits were analyzed by scanning electron microscopy (SEM).

Table 2. Chemical composition of deposits.

% at electrolyte	% at deposit		
Ni	Zn	Co	Ni
23.5	92	3	5
31.5	88	5	7
38	84	6	10
43.4	62	11	28

3. Results and discussion

Zn-Co-Ni alloys were electrodeposited from the electrolyte containing different concentration levels of Nickel ions at -3 V, room temperature and pH=5 for 600 second.

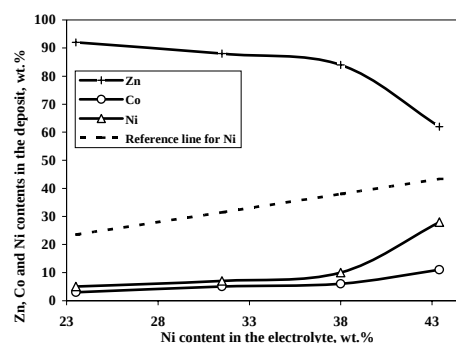


Fig.1. Influence of nickel concentration on the deposit composition.

Fig. 1 shows the influence of nickel concentrations on the deposit composition. The percentages of Co and Ni in a given deposit are lower than their percentages in the bath. A bath solution with high cobalt and nickel content produced an alloy deposit with low cobalt and nickel content indicating the preferential deposition of less noble zinc leading to anomalous codeposition. This behaviour is attributed to the formation of Zn(OH)₂ film on the cathode surface. This film suppresses the rate of deposition of cobalt and nickel [23]. These results are similar to that reported by Younan [24].

Fig. 2 shows the cyclic voltammograms (CV) of Zn-Co-Ni alloys on steel substrate. For all baths during the forward scan, a cathodic current increase could be observed as the potentials extending to -1.2 V above for all the Zn-Co-Ni alloys. These current increases were due to the formation of metals on the surface of the substrate. As the potentials were forwarded to more negative values, a drastic increase in the current profile confirmed the hydrogen evolution process that usually occurs at higher negative potentials. During the reverse scan, co-deposition of metals occurred as the potentials were scanned to lower values. However, at region 1, 2 and 3 stripping peaks indicated the dissolution of the compounds into the solutions.

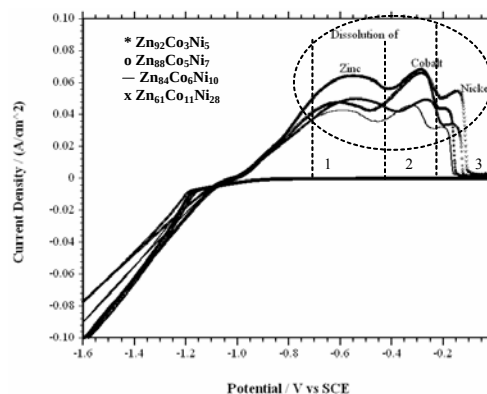


Fig. 2. Cyclic voltammetry of AISI steel electrode in the sulphate solution at room temperature. Scanning rate: 1 mV/s.

In Fig. 2 it can be seen from the cyclic voltammetry curves that the addition of Ni in the electrolyte, caused a decrease of the dissolution peak (region 1). This peak corresponds to the preferential dissolution of zinc, so the decrease of dissolution peaks can be related to the composition of the dissolved deposit. Peak (region 2) and (region 3) correspond to the dissolution of cobalt and nickel, respectively.

The XRD patterns of the electrodeposited Zn-Co-Ni films are given in Fig. 3. It is clearly seen that Zn-Co-Ni alloys have only the η (101) reflection. Adding Ni and Co atoms in the zinc matrix firstly shifted towards to more small reflection angles then shifted towards to more big angles of Zn (101) reflection. The strongest (101) reflection was observed at $\text{Zn}_{61}\text{Co}_{11}\text{Ni}_{28}$ film. An increase of (101) peak was observed when nickel level in the film was increased to 28 %. The increase of this peak may be attributed to the increase of the thickness of the coating obtained when the nickel concentration in the bath increased.

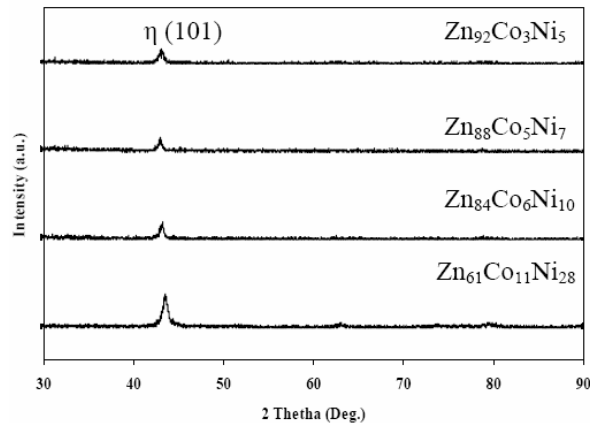


Fig. 3. XRD patterns of the Zn-Co-Ni coatings.

Fig. 4 shows the SEM images of different electrodeposits. It is observed that the deposits are generally composed of fine grains. The metallic luster and the brightness of the deposit increased with the increasing of the nickel. In the presence of 10 % Nickel in the film, an appreciable change was observed in the deposit morphology. For the deposits containing 10 and 28 % Ni, a deposit with even larger grain size was observed. The presence of more cobalt and nickel in the zinc matrix apparently modified the growth of zinc nuclei, leading to the fine-grained deposits. This result is in accord with the previous studies [25-27].

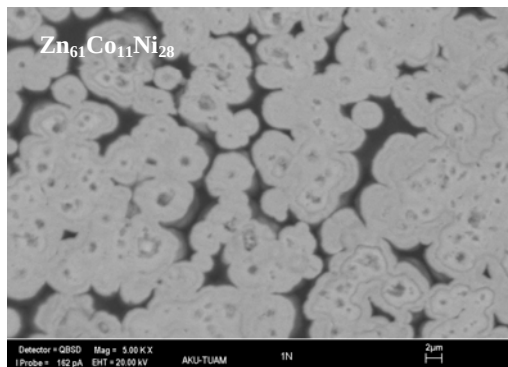
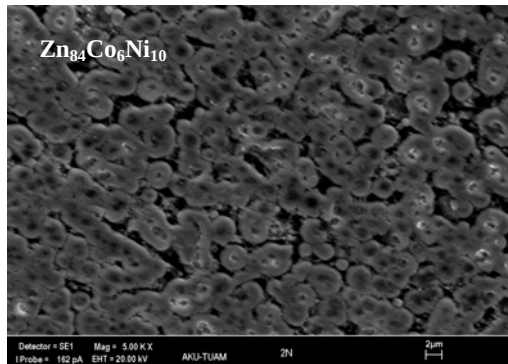
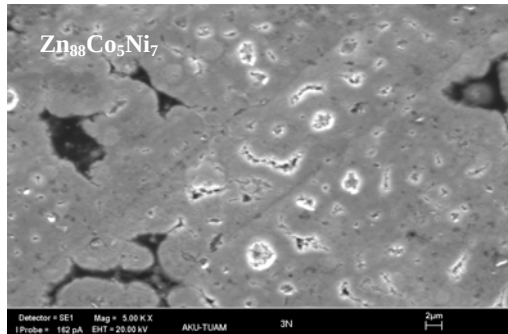
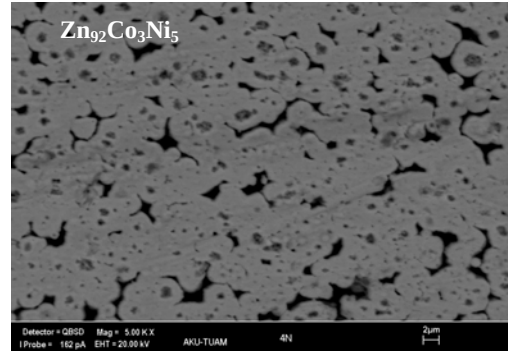


Fig. 6. SEM images of electrodeposited Zn-Co-Ni coatings.

Fig. 5 shows the corrosion property of Zn-Co-Ni alloys and in a 3 wt. % NaCl aqueous solution. As can be seen in the figure, biggest decrease in the anodic current density was observed in the coating containing Ni at 28%.

The corrosion potential (E_{corr}) of the smallest corrosive at Ni 28% coating and the biggest corrosion resistive coating Ni 5 % alloy are -1.01 VSCE and -0.921 VSCE, respectively. Compared with $\text{Zn}_{92}\text{Co}_3\text{Ni}_5$ coating, it is found that the corrosion potential of the deposited at $\text{Zn}_{61}\text{Co}_{11}\text{Ni}_{28}$ alloy is 10% nobler. Increase of nickel content up to 28 wt. % reduced the reactivity of the zinc alloys and, thereby, ZnCo alloys presented a lower degree of corrosion. The increase of nickel content in the deposits is caused a finer grain size and an increase in corrosion resistance of Zn-Co-Ni alloys due to formation of high nickel γ -alloy phase and cobalt codeposition [22].

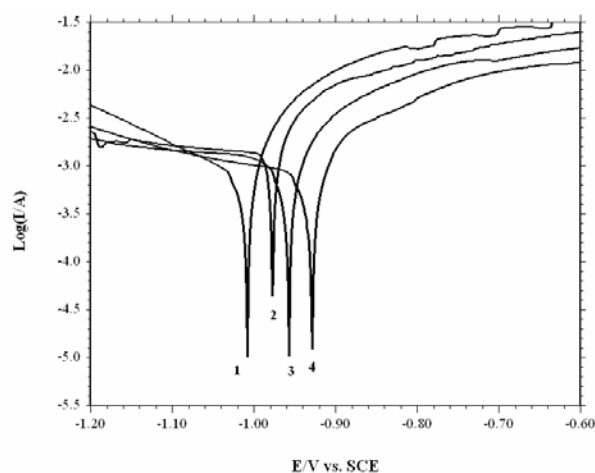


Fig. 5. Linear sweep voltammograms of the electrodeposited Zn-Co-Ni alloys on AISI 4140 substrates.

4. Conclusions

Zn-Co-Ni coatings were obtained from different sulfate baths, and the corresponding electroplating behavior and the corrosion were investigated using cyclic voltammetry and linear sweep voltammetry methods. The baths is non-toxic, easily soluble in water and hence require no treatment of the effluent. The increase of nickel content in the deposits is caused a finer grain size and an increase in corrosion resistance of Zn-Co-Ni alloys due to formation of high nickel γ -alloy phase and cobalt codeposition.

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