The comparative study of the corrosion stability of Zn-Ni-Co alloy coatings deposited from chloride and sulphate baths

ABSTRACT

The ternary Zn–Ni–Co alloy coatings were electrodeposited on steel from chloride and sulphate baths. The deposition was carried out galvanostatically at different current densities at ambient temperatures from additively free baths with different ratios of Ni and Co. Corrosion behaviour of these coatings was evaluated from polarization measurements in 3% NaCl. The deposition current density exhibited small influence on the corrosion potential and corrosion current density of alloys obtained from both chloride and sulfate baths. On the other hand, [Co²⁺]/[Ni²⁺] ion ratio showed a significant influence on corrosion behaviour of ternary alloy coatings, and this influence was more pronounced with alloys deposited from chloride baths. It was shown that increased corrosion protection of steel can be achieved by electrochemical deposition of ternary alloys that contained lower amount off the alloying elements, while the composition of the ternary alloy can be optimized by proper choice of the type and composition of the deposition bath.

Keywords: electrochemical deposition, Zn-Ni-Co alloys, coatings, corrosion stability, polarization measurements.

1. INTRODUCTION

Due to its various excellent properties steel is used at a wide scale in many industries. Its main drawback is the corrosion stability, both in atmospheric conditions and in the more severe environments. Thus, steel protection has drawn a lot of attention for many decades. Depending on the application, various methods are used for steel protection: cathodic and anodic protection, metallic coatings, inorganic and organic coatings, application of inhibitors and passivators, etc. [1]. Each of these methods is applied according to numerous factors, such as the type of the application, the type of the corrosion agents, i.e. environment, the expected service life, the cost of production, and so on. All coatings are mainly aimed in providing barrier to the transport of corrosive species to the steel substrate. Considering metallic coatings, they could be divided in two groups: noble coatings, whose main action is a barrier type of protection and sacrificial coatings, that besides the barrier protection, sacrificially dissolve, thus providing also a galvanic protection. Metallic coatings could be deposited in many different ways, depending on the cost of production, type of application, the number of produced parts, environmental considerations: spraying, chemical deposition, electrodeposition, cementation, physical and chemical vapor deposition. Among metallic coatings zinc coating have been mostly used in the steel protection. In order to enhance coating service life zinc has been alloyed, mostly by the iron group elements (Ni, Co and Fe) [2–8]. It has been evidenced that a thin Zn-Ni alloy coating containing 10–15 wt. % Ni could provide several time longer protection than a pure Zn coating [9–13]. The Zn-Co alloy coatings also improve zinc stability, and these coatings are applied either as low Co content ones (~1wt. %) or with higher Co amount (10–15 wt. % Co) [14–18]. In order to further improve the corrosion stability of both Zn-Ni and Zn-Co coatings the combination of both of these alloying elements in a ternary alloy coating has emerged recently as a promising possibility [19–22]. This combination could enable the utilization of beneficial properties of both binary coatings in a single, ternary alloy...
coating. However, these alloy coatings have not been studied as much as binary alloy coatings [23-25]. In this work the corrosion stability of ternary Zn-Ni-Co alloy coatings will be analysed. Since alloy properties depend, among other plating parameters, on the type of the plating bath and deposition current density the aim of this work will be a comparative study of the corrosion stability of ternary Zn-Ni-Co alloy coatings electrodeposited from chloride and sulphate plating baths at different current densities and at different ratio of alloying elements in the bath.

2. EXPERIMENTAL

Ternary Zn-Ni-Co alloy coatings were deposited on steel galvanostatically, at different deposition current densities, at 25°C from chloride and sulfate baths of the following composition:

a) Chloride bath: 0.38 mol dm⁻³ ZnCl₂, 0.24 mol dm⁻³ H₂BO₃, 3.85 mol dm⁻³ KCl, and with different amounts of alloying elements, 0.34 mol dm⁻³ NiCl₂·6H₂O and 0.04 mol dm⁻³ CoCl₂·6H₂O or 0.20 mol dm⁻³ NiCl₂·6H₂O, and 0.18 mol dm⁻³ CoCl₂·6H₂O.

b) Sulfate bath: 0.38 mol dm⁻³ ZnSO₄, 0.24 mol dm⁻³ H₂BO₃, 0.10 mol dm⁻³ Na₂SO₄, and with different amounts of alloying elements, 0.345 mol dm⁻³ NiSO₄ and 0.035 mol dm⁻³ CoSO₄ or 0.20 mol dm⁻³ NiSO₄ and 0.18 mol dm⁻³ CoSO₄.

A double distilled water and p.a. chemicals were used for baths preparation.

The working electrode was prepared prior to electrodeposition by mechanical cleaning, degreasing in an alkaline solution and pickling in a mild acid solution. The zinc panel (99.999) was used as a counter electrode in electrodeposition and saturated calomel electrode (SCE) as a reference electrode.

Corrosion stability of electrodeposited binary and ternary alloy coatings was determined by ZRA Gamry potentiostat/galvanostat.

3. RESULTS AND DISCUSSION

3.1. The corrosion stability of Zn-Ni-Co alloy obtained from chloride baths

The corrosion stability of Zn-Ni-Co alloy coatings on steel was determined by polarization measurements in 3 % NaCl. The anodic and cathodic polarization curves (Tafel curves) for some alloy samples deposited from chloride bath with ([Co²⁺]/[Ni²⁺]) = 0.1 are presented in Fig. 1. All polarization curves were recorded after one hour of exposure in the 3 % NaCl solution, to make sure that the stable value of open circuit potential was established.

The values of corrosion potentials, $E_{corr}$, and corrosion current densities, $j_{corr}$, determined from Figure 1 are shown in Table 1. The data given in Table 1 are mean values of 3-5 measurements. The small variations of both $E_{corr}$ and $j_{corr}$ values could be seen from Fig. 1 and Table 1. This could be explained by almost negligible differences in chemical content of these alloy coatings. It was shown that ternary Zn-Ni-Co alloys are deposited anomalously, meaning that zinc, as less noble metal, deposits preferentially, and the content of Ni an Co, as alloying elements, is smaller in the alloy coating than in the plating bath [26,27].

**Figure 1.** Polarization curves in 3% NaCl for Zn-Ni-Co alloy coatings deposited at different current densities from chloride bath, [Co²⁺]/[Ni²⁺] = 0.1.

**Table 1.** The corrosion potentials, $E_{corr}$, and corrosion current densities, $j_{corr}$, for Zn-Ni-Co coatings deposited at different current densities from chloride baths with different ion ratios

<table>
<thead>
<tr>
<th>[Co²⁺]/[Ni²⁺]</th>
<th>$j_{corr}$/ A dm⁻²</th>
<th>$-E_{corr}$/ V</th>
<th>$j_{corr}$/ μA cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>1.02</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.02</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>1.09</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>1.00</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>1.11</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.810</td>
<td>45</td>
</tr>
<tr>
<td>0.9</td>
<td>2.0</td>
<td>0.79</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>0.80</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>0.80</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>0.82</td>
<td>65</td>
</tr>
</tbody>
</table>
In this kind of electrodeposition the content of the alloying element (Ni and Co) is nearly constant in a wide range of deposition current densities [26]. The chemical content of alloy coatings deposited from bath with small ion ratio \([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.1\) was ~3 wt. % Co and ~10.5 wt. % Ni for all analyzed ternary deposits [27]. The only coating that exhibited high corrosion rate (98 \(\mu\text{A cm}^{-2}\)) is the one deposited at the highest current density, 10 \(\text{A dm}^{-2}\), which was not completely homogenous since it was powdery at the edges. The same was obtained for alloy coating deposited at the same current density from sulfate bath, so this current density was not further examined.

The example of the influence of the \([\text{Co}^{2+}] / [\text{Ni}^{2+}]\) ion ratio in the plating bath on the corrosion stability of electrodeposited ternary coatings is shown in Figure 2, for Zn-Ni-Co coatings deposited at 3 \(\text{A dm}^{-2}\), as an intermediate current density.

![Figure 2. Polarization curves in 3% NaCl for Zn-Ni-Co alloy coatings deposited at 3 A dm\(^{-2}\) from different [Co\(^{2+}\)]/[Ni\(^{2+}\)] ratios](image)

Slika 2. Polarizacione krive u 3% NaCl za Zn-Ni-Co legure taložene sa 3 A dm\(^{-2}\) iz hloridnih rastvora, sa različitim odnosom jona \([\text{Co}^{2+}] / [\text{Ni}^{2+}]\)

The differences in corrosion stability of deposits obtained from two plating baths are clearly seen in Fig. 2 and Table 2. The corrosion potential of alloy coating deposited from bath with higher ion ratio \(([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.9)\) is ~0.8 V vs. SCE, whereas it is almost 300 mV more negative for coating deposited from bath with lower ion ratio \(([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.1)\). The corrosion current densities of these two deposits also differ a lot, and \(I_{\text{corr}}\) of the coating deposited from the bath with higher ion content is more than twice smaller, indicating its greater corrosion stability (Table 1). The content of alloying elements in coatings deposited from bath with high ion ratio \(([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.9)\) was several times higher than in deposits obtained from the bath with small ion ratio. It ranged from ~8 wt. % Co and ~6 wt. % Ni for coating deposited at small current densities of 1 and 2 \(\text{A dm}^{-2}\), it is ~11 wt. % Co and ~6.2 wt. % Ni for coating deposited at 3 \(\text{A dm}^{-2}\), and 14 wt. % Co and 7.8 wt. % Ni for coating deposited at higher current density, 8 \(\text{A dm}^{-2}\) [27]. So, the increased amount of alloying elements was beneficial for increased protective properties of these alloy coatings.

### 3.2. The corrosion stability of Zn-Ni-Co alloy obtained from sulphate baths

The corrosion behavior of Zn-Ni-Co ternary alloy coatings was also determined for deposits obtained from sulfate baths with different ratio of alloying elements. The \(E\) vs. \(\log j\) dependences for ternary alloy coatings deposited from sulfate bath with lower ion ratio \(([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.1)\) at different current densities are shown in Figure 3.

![Figure 3. Polarization curves in 3% NaCl for Zn-Ni-Co alloy coatings deposited at different current densities from sulfate bath, [Co\(^{2+}\)]/[Ni\(^{2+}\)] = 0.1](image)

Slika 3. Polarizacione krive u 3% NaCl za Zn-Ni-Co legure taložene sa različitim gustinama struje iz sulfatnih rastvora, \([\text{Co}^{2+}] / [\text{Ni}^{2+}] = 0.1\)

The small influence of the deposition current density on the corrosion stability of ternary coatings was observed also in deposits obtained from sulfate bath with small ion ratio. Namely, corrosion current densities varied negligibly, and there was only an oscillation of the corrosion potential (Figure 3, Table 2), which was the consequence of the small differences in chemical content of these deposits [28]. However, the ratio of alloying elements showed considerable differences in the corrosion stability of Zn-Ni-Co alloy coatings, as can be seen from Figure 4.

When \([\text{Co}^{2+}] / [\text{Ni}^{2+}]\) was increased to 0.5 there was only a small change in Tafel curve, but for greater ion ratio of 0.9 there was a more pronounced influence on the coating corrosion stability. The corrosion potential shifted to more positive value and corrosion current density increased (Table 2). The \(E_{\text{corr}}\) and \(I_{\text{corr}}\) values for deposits obtained from sulfate baths at different \([\text{Co}^{2+}] / [\text{Ni}^{2+}]\) ion ratio, and at different deposition current densities is shown in Table 2.
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containing small amounts of alloying elements and deposited from sulfate baths. Optimal deposit parameters could be: [Co^{2+}]/[Ni^{2+}]=0.1 while deposition current could be varied, since it showed a negligible influence on the corrosion stability. Based on the data presented in Table 1 and Table 2 it can be concluded that at least three times more efficient protection was achieved with deposits obtained from sulfate bath. Moreover, the lower amount of the alloying elements and higher deposition currents could be used with this bath, which is of great interest for practical considerations. However, more work has to be done in order to further evaluate and discuss optimal working conditions primarily related to morphology and quality of the deposits and prolonged corrosion behavior, as well.

4. CONCLUSIONS

It was shown that it is possible to obtain protective ternary Zn–Ni–Co alloys on steel by galvanostatic electrochemical deposition from both chloride and sulphate additives free baths. Deposition parameters, deposition current density, [Co^{2+}]/[Ni^{2+}] ion ratio and bath type, exhibited influence on the protective features of Zn–Ni–Co alloys. The deposition current density exhibited small influence on the corrosion potential and corrosion current density of alloys obtained from both chloride and sulphate baths. On the other hand, [Co^{2+}]/[Ni^{2+}] ion ratio showed a significant influence on corrosion behaviour of alloys deposited from chloride bath, while it was not observable with sulphate baths. Zn–Ni–Co alloys obtained from the sulphate bath showed more efficient steel protection in 3% NaCl, probably due to optimal content of Co in the alloy. The efficient protection of steel by electrochemically deposited Zn–Ni–Co alloys can be achieved by proper choice of the type of the deposition bath, content of alloying elements and deposition current density.

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5. REFERENCES

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