Effect of Electrolytic Condition on Composition of Zn-Ni Alloy Plating

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Abstract

Background/Objectives: The electrodepositing of Zn on the automotive parts has been adapted. However, because Zn electrodeposits needs to increase thickness for corrosion protection, it has problem of destruction of electrodeposits. Zn-based electrodeposits have been studied for corrosion protection and decreasing electrodeposits thickness. Especially; Zn-Ni electrodeposits have much attention.

Methods/Statistical analysis: In this research, The Ni content of Zn-Ni electrodeposits under various temperatures, various current densities and various electrolyte contents was estimated to understand effect of electrodeposition condition on Ni composition of specimen. The cathode resistance and diffusion coefficient can explain experimental results.

Findings: As the current density increases, the resistance in the cathode side increases. As the temperature increases, the resistance in the cathode side decreases. As the Ni content in the electrolyte increases, the resistance in the cathode side decreases. The diffusion coefficient of Ni is $0.526 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ and the diffusion coefficient of Zn is $1.2387 \times 10^{-9} \text{m}^2 \text{s}^{-1}$. The diffusion coefficient of Zn is bigger.
than that of Ni. As the resistance in the cathode side increases, mass transfer in the diffusion layer is determined by diffusion. As the resistance in the cathode side increases, the content of an element having a large diffusion coefficient increases. As the current density increases, the Ni content of Zn-Ni electrodeposits decreases.

**Improvements/Applications:** By using this paper results and prediction, it is possible to understand and predict the composition of many alloy electrodeposited coatings.

**Key Words:** Zn-Ni alloy plating, temperature, current density, electrolyte content, cathode overvoltage, diffusion coefficient.

## 1 Introduction

Alloy electrodeposition electroplates with two or more metals. If the potential of the coating is equal to the two kinds of metallic cations, it is no problem to electroplate. If the potential of the coating is small different to the two kinds of metallic cations, it is also no problem to electroplate. Even the potential of the coating is big different, if it make a metal ion complex to resistance of the ion plating, it is no problem to electroplate.

The requirements for performance of automotive corrosion resistance are increasing. Car makers are demanding all suppliers to improve the performance of automotive corrosion resistance. The electrodepositing of Zn on the automotive parts has been many used. However, because Zn electrodeposits needs to increase thickness for corrosion protection, it has problem of destruction of electrodeposits. This decreases corrosion protection. Zn electrodeposits do no satisfy performance requirements of automotive materials corrosion resistance. Therefore, there are needs to establish technology of electrodepositing deposition having excellent corrosion resistance. Recently, Zn electrodeposits have been researched for improving corrosion protection. Especially, Zn alloy electrodeposits with iron group metals have higher corrosion protection than Zn electrodeposits. There are several Zn alloy electrodeposits. Especially; Zn-Ni alloy electrodeposits have drawn a lot of attention.
Zn-Ni alloy electrodeposits are widely utilized to give good anticorrosion for steel in corrosion protection applications. Electrodeposits of Zn-Ni alloy have greatly used in high temperatures and corrosive conditions. The electrodeposition solution of Zn-Ni alloy electrodeposits can be classified into two type solution, the acid solution and alkaline solution. The Electrodeposits of Zn-Ni alloys which are deposited from the acid solution have a higher current density but not good thickness distribution of the electrodeposits. The alkaline solution used for the electrodeposits of Zn-Ni alloys contains cyanide. It is known that cyanide is toxic to environment.

In this research, the Ni content of Zn-Ni electrodeposits under various temperatures, various current densities and various electrolyte contents was estimated to understand effect of electrodeposition condition on Ni composition of specimen. The cathode resistance and diffusion coefficient can explain experimental results.\(^1\)\(^-\)\(^10\)

### 2 Experimental method

#### 2.1 Electrodepositing Condition

Table 1 shows electrolytic contents of the electrodepositing solution and electrodepositing conditions used in this experiment. Plating solution was used for first-class reagent. The source of nickel and zinc was from NiCl\(_2\)•6H\(_2\)O and ZnCl\(_2\). Triethanolamine and polyethlen glycol were the addition agents.

<table>
<thead>
<tr>
<th>Table 1. Electrolytic contents</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ZnCl(_2)</strong></td>
</tr>
<tr>
<td><strong>NiCl(_4) . 6H(_2)O</strong></td>
</tr>
<tr>
<td><strong>KCl</strong></td>
</tr>
</tbody>
</table>
2.2 Test specimen

The electrodeposition used a hull cell. The anode used pure Zn. Cathode used low carbon steel. As a pretreatment before plating, it was mirror-polished to 1 µm diamond paste. The test specimens were degreased in 5% NaOH solution. It was washed with water. The acid solution (60°C and 10wt% H2SO4) was treated with 5 seconds. The plating solution in the plating bath capacity of 1l was used a glass cell filled with 500ml. Table 2 shows chemical composition of cathode specimen.

<table>
<thead>
<tr>
<th>C</th>
<th>P</th>
<th>Mn</th>
<th>Ni</th>
<th>S</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.013</td>
<td>0.30</td>
<td>0.04</td>
<td>0.028</td>
<td>0.03</td>
<td>bal.</td>
</tr>
</tbody>
</table>

2.3 Analysis

The observation of surface morphology used SEM (Model: Hitachi S-4300SE). Measuring Ni content of the coating layer used EDX (Model: Hitachi S-4300SE).

3 Experimental Results

3.1 variation of Ni content

3.1.1 Variation of Ni composition with the current density

Figure 1 shows the Ni content of specimen with the current density at 1M of Ni content in the electrolyte. The Ni content with increasing the current density decreases. The Ni content in 1A/dm² and 30°C is 24wt%, 20.79wt% in 3A/dm² and 20.38wt% in 6A/dm².
Figure 1: Ni content with increasing current densities at 30°C

Figure 2: shows the Ni content with increasing the current density at 40°C. The Ni content with increasing the current density decreases. The Ni content in 1A/dm² and 40°C is 41.3 wt%, 36.83 wt% in 3A/dm² and 26.68 wt% in 6A/dm².

Figure 2: Ni content with increasing current densities at 40°C

Figure 3: shows the Ni content with increasing the current density at 50°C. The Ni content with increasing the current density decreases. The Ni content in 1A/dm² and 50°C is 50.71 wt%, 43.37 wt% in 3A/dm² and 42.5 wt% in 6A/dm².

Figure 3: Ni content with increasing current densities at 50°C
The resistance in the cathode with increasing the current density increases. As the resistance in the cathode increases, mass transfer in the diffusion layer is determined by diffusion. As the resistance in the cathode increases, the content of an element having a large diffusion coefficient increases. The Zn content with increasing the resistance in the cathode increases.

The diffusion coefficient of Ni is $0.526 \times 10^{-9} \text{m}^2\text{s}^{-1}$; the diffusion coefficient of Zn is $1.2387 \times 10^{-9} \text{m}^2\text{s}^{-1}$. Zn diffusion coefficient is bigger than Ni diffusion coefficient [9-10].

### 3.1.2 Variation of Ni composition with temperature

Figure 4 indicates the Ni content with increasing temperature at 1M of Ni content in the electrolyte. The Ni content with increasing temperature increases. The Ni content of specimen in 30$^\circ$C and 1A/dm$^2$ is 20.79wt%, 36.83wt% in 40$^\circ$C and 43.37wt%.

![Figure 4: Ni content with various temperatures at 1A/dm$^2$](image)

Figure 5 shows the Ni content with increasing temperature. The Ni content with increasing temperature increases. The Ni content of specimen in 30$^\circ$C and 3A/dm$^2$ is 20.38wt%, 26.68wt% in 40$^\circ$C and 42.5wt%.

![Figure 5: Ni content with various temperatures at 3A/dm$^2$](image)
Figure 6 shows the Ni content with increasing temperature. The Ni content with increasing temperature increases. The Ni content of specimen in 30°C and 6A/dm² is 20.38wt%, 26.68wt% in 40°C and 42.5wt%.

![Graph of Ni content vs. temperature]

Figure 6: Ni content with various temperatures at 6A/dm²

The resistance in the cathode with increasing temperature decreases. As the resistance in the cathode decreases, the content of an element having a large diffusion coefficient decreases. The Zn content with decreasing resistance in the cathode decreases.

3.1.3 Variation of Ni composition with the Ni content in the electrolyte

Figure 7 shows the Ni content with the Ni content in the electrolyte at 50°C. The Ni content with increasing Ni in the electrolyte increases. The Ni content of specimen in 0.1M and 1A/dm² is 7.43wt%, 11.34wt% in 0.5M and 50.71wt% in 1M.

![Graph of Ni content vs. Ni content in electrolyte]

Figure 7: Ni content with various Ni content in the electrolyte at 50°C
Figure 8 shows the Ni content with the Ni content in the electrolyte at 50°C. The Ni content with increasing Ni in the electrolyte increases. The Ni content of specimen in 0.1M and 1A/dm$^2$ is 3.16wt%, 11.39wt% in 0.5M and 43.37wt% in 1M.

Figure 8: Ni content with various Ni content in the electrolyte at 50°C

Figure 9 shows the Ni content with the Ni content in the electrolyte at 50°C. The Ni content with increasing Ni in the electrolyte increases. The Ni content of specimen in 0.1M and 1A/dm$^2$ is 0.6wt%, 12.5wt% in 0.5M and 42.5wt% in 1M. Generally, the less noble metal Zn with increasing resistance in the cathode electrolyte is plated more. As the Ni content in the electrolyte increases, the resistance in the cathode decreases. The Ni content with increasing resistance in the cathode electrolyte decreases.

Figure 9: Ni content with various Ni content in the electrolyte at 50°C

The resistance in the cathode with increasing Ni in the electrolyte decreases. As the resistance in the cathode decreases, the content of an element having a small diffusion coefficient increases. The Ni content with decreasing resistance in the cathode electrolyte increases.
3.2 Surface observation

Figure 10 shows the surface morphology with the current density at 0.5M and 50°C. The surface size with increasing the current density increases.

![Image of surface morphology with current density](image1)

![Image of surface morphology with current density](image2)

Figure 10: Surface shape of Zn-Ni electrodeposits at (a) 2 A/dm² and (b) 4 A/dm²

4 Conclusions

The Ni content of Zn-Ni electrodeposits under various temperatures, various current densities and various electrolyte contents was estimated to understand effect of electrodeposition condition on Ni composition of specimen. The cathode resistance and diffusion coefficient can explain experimental results.

The resistance in the cathode with increasing the current density increases. As the resistance in the cathode increases, mass transfer in the diffusion layer is determined by diffusion. As the resistance in the cathode increases, the content of an element having a large diffusion coefficient increases. The Zn content with increasing the resistance in the cathode increases.

The diffusion coefficient of Ni is $0.526 \times 10^{-9} \text{m}^2\text{s}^{-1}$; the diffusion coefficient of Zn is $1.2387 \times 10^{-9} \text{m}^2\text{s}^{-1}$. Zn diffusion coefficient is bigger than Ni diffusion coefficient.

The resistance in the cathode with increasing temperature decreases. As the resistance in the cathode decreases, the content of an element having a large diffusion coefficient decreases. The Zn content with decreasing resistance in the cathode decreases.
The resistance in the cathode with increasing Ni in the electrolyte decreases. As the resistance in the cathode decreases, the content of an element having a small diffusion coefficient increases. The Ni content with decreasing resistance in the cathode electrolyte increases.

5 Acknowledgment

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References


