A New Sacrificial Corrosion Protection Mechanism for High Performance Zinc/Aluminum Flake Coating Systems and Applications

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Introduction

Zinc/Al Flake Coating with High Corrosion Protection Performance
Popular in Automotive and Construction Industries
Introduction

Important to Form Basic Zinc Chloride (Insulator)

\[ \text{Zn} \xrightarrow{\text{H}_2\text{O}} \text{Zn}^{2+}, \text{OH}^- \]

\[ \text{ZnO} \]

\[ \beta \text{Zn(OH)}_2 \] Protective, insoluble

\[ 4\text{Zn(OH)}_2 \cdot \text{ZnCl}_2 \] Protective, insoluble

\[ 6\text{Zn(OH)}_2 \cdot \text{ZnCl}_2 \] Protective, insoluble

\[ \text{ZnO} \] Less protective, insoluble

\[ \text{Zn(OH)}_2(\text{CO}_3)_2 \] Protective, insoluble

Minimize ZnO formation!

Stop! Stop! Stop! Stop!

Introduction

Corrosion Product on Coating Film

Relationship with Corrosion Resistance

New & Current Product Comparison

Investigation:

<table>
<thead>
<tr>
<th>Cycles to Red Rust [hr]</th>
<th>SST</th>
<th>CCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>40</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>60</td>
<td>800</td>
<td>800</td>
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<tr>
<td>80</td>
<td>1800</td>
<td>1800</td>
</tr>
<tr>
<td>100</td>
<td>2800</td>
<td>2800</td>
</tr>
<tr>
<td>120</td>
<td>3800</td>
<td>3800</td>
</tr>
<tr>
<td>140</td>
<td>4800</td>
<td>4800</td>
</tr>
<tr>
<td>160</td>
<td>5800</td>
<td>5800</td>
</tr>
<tr>
<td>180</td>
<td>6800</td>
<td>6800</td>
</tr>
<tr>
<td>200</td>
<td>7800</td>
<td>7800</td>
</tr>
<tr>
<td>220</td>
<td>8800</td>
<td>8800</td>
</tr>
<tr>
<td>240</td>
<td>9800</td>
<td>9800</td>
</tr>
<tr>
<td>260</td>
<td>10800</td>
<td>10800</td>
</tr>
<tr>
<td>280</td>
<td>11800</td>
<td>11800</td>
</tr>
<tr>
<td>300</td>
<td>12800</td>
<td>12800</td>
</tr>
</tbody>
</table>

New Type (2C2B)

Current Type (2C2B → V-C-T)

Current Type (2C2B)

0 500 1000 1500 2000 2500 3000

Time to Red Rust [hr]
Experiment (Sample)

Test Samples

Table 1. Summary of Zinc/Aluminum Flake Coating Systems

<table>
<thead>
<tr>
<th>Sample</th>
<th>Base Coat</th>
<th>Top Coat</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Main Components</td>
<td>Thickness [μ]</td>
<td>Main Components</td>
<td>Thickness [μ]</td>
</tr>
<tr>
<td>B-1</td>
<td>Zn, Al, Si</td>
<td>8 - 10</td>
<td>No topcoat</td>
<td>-</td>
</tr>
<tr>
<td>B-1 + T</td>
<td>Zn, Al, Si</td>
<td>8 - 10</td>
<td>Si, O</td>
<td>1 – 2</td>
</tr>
<tr>
<td>B-2</td>
<td>Zn, Al, Si</td>
<td>8 - 10</td>
<td>No topcoat</td>
<td>-</td>
</tr>
<tr>
<td>Zn-Ni Alloy</td>
<td>Zn, Ni (17%)</td>
<td>8 - 10</td>
<td>No topcoat</td>
<td>-</td>
</tr>
</tbody>
</table>

Experiment (Process)

Coating Process of Base Coat

- Degrease
- Blast
- Base Coat
- Bake 500°F (260°C) 30 min
- Base Coat
- Bake 500°F (260°C) 30 min

Top Coat Process

- Top Coat
- Dry 212°F (100°C) 15 min
Experiment (Evaluation)

■ Corrosion Protection Evaluation

1) CCT:
   Salt spray (5% NaCl, 50°C) 17 hrs → dry (70°C) 3 hrs → salt spray (5% NaCl, 50°C) 2 hrs → natural dry (25°C) 2 hrs

2) SST: 5% NaCl, 35°C

3) Salt water immersion test: 5% NaCl, 25°C, exposed to the atmosphere

■ Corrosion Product Evaluation
- X-ray diffractometry (XRD)

■ Surface Condition Evaluation
- SEM-EDS

■ Time-Dependent Changes in Natural Potentials
Natural potentials measured in 5% NaCl solution

Results and Discussion (Corrosion Resistance)
- CCT -

<table>
<thead>
<tr>
<th>Cycles Sample</th>
<th>0cy.</th>
<th>20cy.</th>
<th>40cy.</th>
<th>80cy.</th>
<th>120cy.</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td></td>
<td></td>
<td>Red Rust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-1 + T</td>
<td></td>
<td></td>
<td>Red Rust</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-Ni</td>
<td>Red Rust</td>
<td>Red Rust</td>
<td>Red Rust</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Corrosion Resistance: B-2 > B-1+T > B-1 > Zn-Ni
### Results and Discussion (Corrosion Resistance)

#### - SST -

<table>
<thead>
<tr>
<th>Sample</th>
<th>0h</th>
<th>1000h</th>
<th>1500h</th>
<th>2000h</th>
<th>2500h</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>B-1 + T</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Zn-Ni</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

*Corrosion Resistance: B-2 > B-1+T > B-1 > Zn-Ni*

#### - NaCl Immersion Test -

<table>
<thead>
<tr>
<th>Sample</th>
<th>0h</th>
<th>24h</th>
<th>240h</th>
<th>480h</th>
<th>720h</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>B-1 + T</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>Zn-Ni</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
</tbody>
</table>

*Fig. Salt water immersion test results*
Results and Discussion (XRD NaCl Immersion Test)

**Fig. 2.** XRD Pattern of Each Film Before and After 24-Hour NaCl Immersion Test

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Basic Zinc Chloride Was Mainly Formed in B-1, B-2 and Zn-Ni.

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Results and Discussion (XRD Intensity Changes) - NaCl Immersion Test -

**Fig. 4.** XRD Intensity Changes of Corrosion Product and Zinc (NaCl Immersion Test)

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**Basic Zinc Chloride Intensity Change:**

B-2 > B-1 > B-1+T > Zn-Ni
Results and Discussion (XRD Intensity Changes) - CCT -

Fig. 6. XRD Intensity Changes of Corrosion Product and Zinc (CCT)

Basic Zinc Chloride Intensity Change: B-2 > B-1 > B-1+T > Zn-Ni

Results and Discussion (XRD Intensity Changes) - SST -

Fig. 8. XRD Intensity Changes of Corrosion Product and Zinc (SST)

As consistent as in CCT
XRD Trends in Salt Water Immersion Test

- Basic Zinc Chloride Formation on Each Film in Immersion Test

![Graph showing amount and speed for B-1, B-1+T, B-2, and Zn-Ni](image)

Results and Discussion (SEM Image)

Fig. 9. SEM Image of Each Film After 240-Hour SST

- Granular Crystals of Basic Zinc Chloride

Granular Crystal Ratio: B-1 > B-1+T > B-2
Results and Discussion (Natural Potential)

Fig. 10. Time-Dependent Change in Natural Potential of Each Film

- Potential was stable with basic zinc chloride.
- B-2 formed basic zinc chloride at early stage.
- Characteristic in between Zn-Ni & Zn plating
- Potential increased with formation of basic zinc chloride.

Results and Discussion (Pattern Diagram)

Fig. 11. Corrosion Protection Mechanism of Zn/Al Flake Coating

- Corrosion Reaction Controlled by Basic Zinc Chloride
Summary

- Important Factors for Achieving High Corrosion Resistance

- Control excessive zinc dissolution

- Film with high corrosion resistance

- Finer crystals

- Formation of basic zinc chloride during initial stage of corrosion

Thank you for your attention!