Zn-Ni alloy coating made of chloride electrolyte

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INTRODUCTION

Resistance of zinc coatings towards the corrosion processes is well known so these coatings were the first choice of protection for a long time during the production of the steel constructions. As technology developed and demands for thinner coatings but with much higher corrosion stability increased, zinc coatings were not satisfactory enough anymore. Research showed that alloy coatings based on zinc and other elements of iron triads can satisfy these conditions very well. There are many factors influencing features of deposited coatings based on double and in recent time even triple alloys based on zinc. Those factors are mostly concentration of metal ions, chemical composition of electrolytes that caused deposition and current density. [Esih 2010; Gamburg 2011; Vujićić 2002]

In this paper, coatings based on Zn-Ni alloys made of chloride electrolyte were tested. Depending on conditions (current density and deposition time), coatings of different sizes and with different amount of Ni in each coating were prepared. The samples were tested in salt spray chambers according to BS EN ISO 10289:2001 standard. The best results showed coatings which were over 10 μm thick and which contained up to 15% of Nickle. There were no signs of corrosion even after 2160 hours of being in salt spray chambers.

Abstract: Electrodeposition coating based on Zn-Ni alloys was made of chloride electrolyte which contains 142.56 g/dm³ NiCl₂x6H₂O; 109.03 g/dm³ ZnCl₂; 30.9 g/dm³ H₃BO₃; 223.65 g/dm³ KCl; 40.99 g/dm³ CH₃COONa. As the result coatings of different sizes and different amount of Ni in each coating were prepared. The samples were tested in salt spray chambers according to BS EN ISO 10289:2001 standard. The best results showed coatings which were over 10 μm thick and which contained up to 15% of Nickle. There were no signs of corrosion even after 2160 hours of being in salt spray chambers.

EXPERIMENTAL

For electrochemical deposition of Zn-Ni based coatings chloride electrolyte was used. In table 1. The composition of chloride electrolyte is showed in Table 1.

Table 1. Chemical composition of electrolytes for deposition of coating Zn-Ni alloys

<table>
<thead>
<tr>
<th></th>
<th>NiCl₂x6H₂O</th>
<th>ZnCl₂</th>
<th>H₃BO₃</th>
<th>KCl</th>
<th>CH₃COONa</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol/dm³</td>
<td>0.6</td>
<td>0.8</td>
<td>0.5</td>
<td>3</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Electrolyte used is prepared using chemicals of p.a. purity. Tiles from plane construction steel were used as working electrodes for deposition of Zn-Ni based coatings. Electrode of high cleanliness Nickle (99.9%) was used as an auxiliary electrode during deposition of alloys. Relation between the surface of working and auxiliary electrode was 1: 2. Before the deposition, working electrodes were processed with abrasive paper, granulation 800 and 1200, degreased in NaOH solution then in ethanol and etched in 10% HCl solution. Between every phase of preparation, electrodes were washed with distilled water. Electrochemical cell for
deposition was laboratory glass of 500 cm³ of volume. Current density which is used for deposition was 1; 2 and 3 A/dm², the temperature of solution was 35°C and pH was 4.5. Time of deposition was 10, 15, 20 and 35 minutes to get the coatings of different sizes and with different amounts of Ni. Chemical composition thickness of Zn-Ni alloys were done in SurTec Eurosjaj d.o.o. Konjic, na Fischerscope® XRAY XDL-B laboratory. The results are showed in table 2.

Table 2. The thickness of Zn-Ni alloy and the amount of Ni in coating

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Sample label in salt chamber</th>
<th>Working conditions</th>
<th>Thickness of coating, μm</th>
<th>Amount of Ni in coating, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R</td>
<td>49 i=2A/dm² τ=20 min</td>
<td>5.805</td>
<td>10.79</td>
<td></td>
</tr>
<tr>
<td>4R</td>
<td>50 i=1A/dm² τ=20 min</td>
<td>9.326</td>
<td>11.93</td>
<td></td>
</tr>
<tr>
<td>2P</td>
<td>47 i=2A/dm² τ=20 min</td>
<td>8.126</td>
<td>12.13</td>
<td></td>
</tr>
<tr>
<td>1K</td>
<td>43 i=1A/dm² τ=20 min</td>
<td>5.273</td>
<td>13.60</td>
<td></td>
</tr>
<tr>
<td>2K</td>
<td>45 i=2A/dm² τ=20 min</td>
<td>10.180</td>
<td>14.34</td>
<td></td>
</tr>
<tr>
<td>3K</td>
<td>46 i=3A/dm² τ=20 min</td>
<td>12.62</td>
<td>17.89</td>
<td></td>
</tr>
<tr>
<td>1KT</td>
<td>40 i=2A/dm² τ=10 min</td>
<td>5.036</td>
<td>11.27</td>
<td></td>
</tr>
<tr>
<td>2KT</td>
<td>41 i=2A/dm² τ=15 min</td>
<td>7.111</td>
<td>11.49</td>
<td></td>
</tr>
<tr>
<td>6KT</td>
<td>42 i=2A/dm² τ=35 min</td>
<td>14.97</td>
<td>14.86</td>
<td></td>
</tr>
</tbody>
</table>

Testing in salt spray chamber was done in SurTec-Eurosjaj d.o.o. Konjic. Chamber is JW-150-NS Salt Spray Chamber type. Testing lasted for 2160 hours. Conditions of testing in chambers were following: test space temperature was 35 °C; moisturizer of compressed air temperature was 45-50°C; compressed air pressure was 7-1,4 bars; solution was 5% NaCl; condensate pH in 25°C was 6,8 while electrical conductivity of distilled water in 25°C was < 20 μS/cm.

After testing, the samples were taken out of salt chamber and visually evaluated according to BS EN ISO 10289:2001 standard. The appearance of red corrosion is not noted even after 2160 hours of being in salt spray chamber. According to the assessment of protection and look Rp/RA was 10/8sC. Sample 46 shows the appearance of white corrosion after 720 hours of testing but on on the surface area smaller than 0,25%. There were no visible defects. The amount of corrosion products was moderate. It is mostly about corrosion product made of anodic coating. The appearance of red corrosion is not noted even after 2160 hours of being in salt spray chamber. According to the assessment of protection and look Rp/RA was3/2mF.
peeling. According to the assessment and look Rp/RA equaled 6/5mE.

Table 4. The test results from salt spray chamber

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness of coating, µm</th>
<th>Amount of Ni in coating, %</th>
<th>Start of the test</th>
<th>End of the test</th>
<th>White corrosion (hours)</th>
<th>Red corrosion (hours)</th>
<th>Assessment of protection and look</th>
</tr>
</thead>
<tbody>
<tr>
<td>40/1KT</td>
<td>5,036</td>
<td>11,27</td>
<td>28.09.2015</td>
<td>05.10.2015</td>
<td>168</td>
<td>192</td>
<td>-</td>
</tr>
<tr>
<td>41/2KT</td>
<td>7,111</td>
<td>11,49</td>
<td>28.09.2015</td>
<td>06.10.2015</td>
<td>96</td>
<td>192</td>
<td>-</td>
</tr>
<tr>
<td>42/6KT</td>
<td>14,97</td>
<td>14,86</td>
<td>28.09.2015</td>
<td>28.12.2015</td>
<td>720</td>
<td>2160 (no corrosion)</td>
<td>10/8sC</td>
</tr>
<tr>
<td>43/1K</td>
<td>9,273</td>
<td>13,60</td>
<td>28.09.2015</td>
<td>03.11.2015</td>
<td>480</td>
<td>864</td>
<td>3/2mF</td>
</tr>
<tr>
<td>45/2K</td>
<td>10,180</td>
<td>14,34</td>
<td>28.09.2015</td>
<td>28.12.2015</td>
<td>720</td>
<td>2160 (no corrosion)</td>
<td>10/8sC</td>
</tr>
<tr>
<td>46/3K</td>
<td>12,62</td>
<td>17,89</td>
<td>28.09.2015</td>
<td>28.12.2015</td>
<td>720</td>
<td>2160 (no corrosion)</td>
<td>10/6mE</td>
</tr>
<tr>
<td>47/2P</td>
<td>8,126</td>
<td>12,13</td>
<td>28.09.2015</td>
<td>16.11.2015</td>
<td>720</td>
<td>1176</td>
<td>6/5mE</td>
</tr>
<tr>
<td>48/3P</td>
<td>5,951</td>
<td>13,71</td>
<td>28.09.2015</td>
<td>08.10.2015</td>
<td>120</td>
<td>240</td>
<td>-</td>
</tr>
<tr>
<td>49/1R</td>
<td>2,805</td>
<td>10,79</td>
<td>28.09.2015</td>
<td>02.10.2015</td>
<td>48</td>
<td>96</td>
<td>-</td>
</tr>
<tr>
<td>50/4R</td>
<td>9,326</td>
<td>11,93</td>
<td>28.09.2015</td>
<td>06.10.2015</td>
<td>96</td>
<td>192</td>
<td>-</td>
</tr>
</tbody>
</table>

CONCLUSION

Samples with Ni part of 8-15%, which had the red corrosion appear earlier than the expected for this type of coating, after 720 hours of testing did not passed the testing despite the thickness of the coating. As a result, red corrosion appeared much earlier than expected. The rest of the samples that had the thickness of Zn-Ni alloy coating higher than 10 µm and the needed part of Ni 15%, fully satisfied the salt spray chamber test. That means they did not show any signs of red corrosion appearance in the testing time of 2160 hours.

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Summary/Sažetak

Izvedena je elektrodepozicija prevlaka na bazi legura Zn-Ni iz hloridnog elektrolita sastava 142,56 g/dm³ NiCl₂₆H₂O;
109,03 g/dm³ ZnCl₂; 30,9 g/dm³ H₃BO₃; 223,65 g/dm³ KCl; 40,99 g/dm³ CH₃COONa. Dobivene su prevlake različite
rezultate su pokazale prevlake debljine preko 10 μm i sadržajem nikla do 15%. Nisu pokazivali pojavu korozije ni nakon
2160 sati provedenih u slanoj komori.