THE INFLUENCE OF ELECTROLYSIS PROCESS ON THE PROPERTIES OF Zn + Ni COATINGS ON STEEL

ВЛИЯНИЕТО НА ПРОЦЕСА НА ЕЛЕКТРОЛИЗА ВЪРХУ СВОЙСТВАТА НА ПОКРИТИЯ ОТ Zn + Ni ВЪРХУ СТОМАНА

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Abstract

The main objective of this work was to define the influence of parameters of electrolysis process on the properties of Ni + Zn steel coatings. The properties of these coating were characterized by its microhardness compared with the hardness of steel matrix. Also microscopic (LM, SEM) and X-ray tests were performed followed by wear resistance tests. Following the investigation it can be concluded that the influence of type of anode and duration of the electrolysis process have an influence on properties of Ni + Zn coatings.

Keywords: electrolysis process, Ni + Zn coating, microhardness, wear resistance

Introduction

The zinc-nickel coatings have good mechanical properties and corrosion resistance. These coatings are widely used in the automotive and energy industries. Electrolytic zinc-nickel alloy coating on the steel substrate can be deposited with different types of baths. Here we distinguish acidic solutions such as chloride, sulfate, and other alkaline (e.g., cyanide) [1, 5]. On the basis of the research it can be concluded that the microstructure of the surface layer and the properties of coated layers mainly depends on the type of substrate, the technology of producing the layers and the parameters of the application process. The factors which have the decisive influence on the quality and properties of electrolytically deposited coatings are the type, composition and concentration of electrolyte additives (e.g. in the form of compounds increasing the thermal conductivity) and temperature. The authors of [4] indicate the significant difference in the structure of electrolytic coatings obtained from different alloys, especially between acidic and alkaline deposition process. In ref. [2] the coatings containing Zn and Ni, deposited electrolytically from sulphate solutions at different conditions such as bath composition, temperature, etc., were tested. It has been shown that the temperature of the bath influences the phase composition of the obtained alloys and the thickness of the layers. The current density and deposition time determines various thickness and the percentage of nickel (Ni) in the coating.

Materials for investigations

The investigations were carried out on 9 samples produced and supplied by the Bulgarian Academy of Sciences. Samples were made of ferritic steel. Three of the 9 samples were made in the form of rings, and the remaining samples were made in the form of cylinders. The dimensions of the samples is shown in Figure 1. Two alloy plating baths were used for the sample preparation: Zn + Ni - for samples numbered 1, 2, 6, 15N and 16N and Zn + Ni + NDDS (diamond nanoparticles) for other four samples. The concentration of the diamond nanoparticles in the electrolyte was 1 g/l. Nickel (Ni) or zinc (Zn) as an anode was used during the process. The time of electrolytic process was 35, 40 or 45 minutes. For the all of samples the same current density - 0.5 A/dm² was applied. The processing parameters of Zn+Ni coatings are shown in Table 1 and 2.

Figure 1. Dimensions of the samples: a) ring (1, 2, 6 – Table 1); b) cylinder (15N-21N – Table 2)
Table 1. The processing parameters of Zn + Ni coatings – ring samples

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Coating</th>
<th>Anode</th>
<th>Current density, A/dm²</th>
<th>Time, min</th>
<th>Thickness of the coating, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Zn + Ni</td>
<td>Ni</td>
<td>0.5</td>
<td>45</td>
<td>5.2</td>
</tr>
<tr>
<td>2</td>
<td>Zn + Ni</td>
<td>Ni</td>
<td>0.5</td>
<td>35</td>
<td>3.6</td>
</tr>
<tr>
<td>6</td>
<td>Zn + Ni</td>
<td>Zn</td>
<td>0.5</td>
<td>40</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 2. The processing parameters of Zn + Ni coating – cylinder samples 15N – 19N and 21N

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Coating</th>
<th>Anode</th>
<th>Current density, A/dm²</th>
<th>Time, min</th>
<th>Thickness of the coating, µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>15N</td>
<td>Zn + Ni</td>
<td>Zn</td>
<td>0.5</td>
<td>35</td>
<td>6.54</td>
</tr>
<tr>
<td>16N</td>
<td>Zn + Ni</td>
<td>Zn</td>
<td>0.5</td>
<td>45</td>
<td>4.23</td>
</tr>
<tr>
<td>17N</td>
<td>Zn + Ni + NDDS</td>
<td>Zn</td>
<td>0.5</td>
<td>35</td>
<td>3.20</td>
</tr>
<tr>
<td>18N</td>
<td>Zn + Ni + NDDS</td>
<td>Zn</td>
<td>0.5</td>
<td>45</td>
<td>4.94</td>
</tr>
<tr>
<td>19N</td>
<td>Zn + Ni + NDDS</td>
<td>Ni</td>
<td>0.5</td>
<td>35</td>
<td>2.60</td>
</tr>
<tr>
<td>21N</td>
<td>Zn + Ni + NDDS</td>
<td>Ni</td>
<td>0.5</td>
<td>45</td>
<td>4.66</td>
</tr>
</tbody>
</table>

Results

The main objective of the study was to determine the effect of the processing parameters on the properties of electrolytic Zn + Ni coatings and the durability of the connection between the coating and the substrate. Experimental work included: microhardness measurements on the surface and ground samples, light (LM) and scanning electron microscopy (SEM) and X-ray investigations. In addition, the wear resistance tests were carried out.

Microhardness

Microhardness investigations of the coatings and the substrate sample were carried out using Innovatest hardness tester (Vickers hardness). During the test, samples no 1, 2 and 6 were used. The hardness measurements (HV 0.1) were performed every 0.5 mm. The results of the surface microhardness (film hardness) is shown in Figure 2. Measurement of microhardness (HV 0.01) of the steel substrate was made in ten randomly selected areas. The results of microhardness of the substrate are presented in Figures 3 and 4.

Figure 2. The average microhardness, HV 0.1, measured on the surface of the samples 1, 2 and 6

Figure 3. The average microhardness, HV 0.01, measured on the base of the samples 1, 2 and 6

Figure 4. The average microhardness, HV 0.01, measured on the base of the samples 15N – 19N and 21N

Light optical microscopy of investigated coating

The Zn+Ni layers was tested using metallographic microscope Leica DM4000M. In order to identify the layers, investigation first were carried out on non-etched samples (Figures 5-8). In order to reveal the microstructure of the substrate, metallographic examinations were carried out on 3% nital-etched samples. Selected photomicrographs of etched specimens are shown in Figures 9-10.

Figure 5. Microphotograph of sample 1 – the base with the layer
SEM investigations of coating

Electrodeposited layers were investigated using SEM. The test was performed both for the ring and cylinder samples. The results of SEM analysis is shown in Figures 11-14. Additionally, the analysis of the chemical composition of the coatings were carried out using EDS microanalysyer, (acceleration voltage 20 kV). The results of analysis of chemical compositions is presented in Figures 15-17.
The coating phase analysis using X-ray diffraction

X-ray diffraction phase analysis (Bragg-Brentano geometry) was performed to identify the phases presented in each sample. The effective penetration depth did not change. The measurements were carried out with the angle of incidence \( \alpha = 3^{\circ} \). Analysis of the phase composition of the Zn + Ni layers on ferritic steel was carried out using on D500 X-ray diffractometer (Siemens) using Cu Ka radiation with a length of radiation = 1.54 Å and radiation penetration depth of 3.16 mm. The examples of diffraction path are given in Figures 18-19.

Figure 18. Sample 6 - diffraction path in Bragg–Brentano geometry and constant angle of incidence \( \alpha = 3^{\circ} \). Visible feature lines derived from the nickel coating and the base – steel; Radiation Cu Ka

Figure 19. Sample 18N - diffraction path in Bragg–Brentano geometry and constant angle of incidence \( \alpha = 3^{\circ} \). Visible feature lines derived from the nickel coating and the base – steel; Radiation Cu Ka
Wear resistance

The wear resistance tests were performed on T05 tester (Figure 20). During the test, a rectangular sample (1) with dimensions of 4x4x20 mm were mounted in the sample holder (4) with a semicircular insert (3), ensuring adequate contact between the sample and the stainless steel ring (2) heat treated to 55 HRC, rotating with constant speed of 136 rpm/min. The tester was equipped with a microprocessor control and measurements systems (5). During the test, such parameters as power, time and depth of wear (abrasive) were recorded.

Figure 20. Schematic view of the block–on–ring tester; 1 – wear sample, 2 – steel ring, 3 – hemispherical insert, 4 – sample holder, 5 – microprocessor control and measurement system

The weight loss of the sample was measured after 2000s. The friction coefficient was calculated as the ratio of the mean force during the whole period of the test and load test sample, amounting to 157 N (Table 3). The weight loss, expressed in %, and friction coefficient are summarised in Figure 21 and 22. The dependence of the depth of wear (abrasive) as a function of time is presented in Figure 23. Surfaces topography of the samples after the wear tests are shown in Figures 24-26.

Table 3. The results of the wear resistance test of investigated samples

<table>
<thead>
<tr>
<th>No of sample</th>
<th>Mass before test, m1, g</th>
<th>Mass after test, m2, g</th>
<th>Δm, g</th>
<th>Δm, %</th>
<th>Friction coefficient, -</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.44778</td>
<td>1.44490</td>
<td>0.00288</td>
<td>0.20</td>
<td>0.577</td>
</tr>
<tr>
<td>2</td>
<td>1.63356</td>
<td>1.62878</td>
<td>0.00478</td>
<td>0.29</td>
<td>0.633</td>
</tr>
<tr>
<td>6</td>
<td>1.45635</td>
<td>1.44795</td>
<td>0.00840</td>
<td>0.58</td>
<td>0.506</td>
</tr>
</tbody>
</table>

Figure 21. The loss of mass of the samples after 2000 seconds

Figure 22. Friction coefficient of the investigated samples

Figure 23. The depth of wear of the samples as a function of the time

Figure 24. Surface topography of sample 1 after 2000 seconds wear test

Figure 25. Surface topography of sample 2 after 2000 seconds wear test
The analysis of the results

Among the first group of samples (ring-shape samples), the highest coating thickness - 5.2 µm - were obtained for sample 1 and slightly lower value - 3.6 microns for sample 2 (Table 1). For both samples, the anode was formed of nickel and coating times were respectively 45 and 35 min. On the basis of the results obtained it can be concluded that with increasing the duration of the process the thickness of the layer increased. Sample 6 (Zn anode) was characterised by the layer with thickness of 5.2 µm using process time of 40 min. The processing parameters for the sample 6 do not allow for confrontation with the results obtained for other samples (1 and 2).

Among the second group (cylinder samples) the maximum thickness - 6.54 µm was obtained for sample 15N. The lowest coating thickness - 2.60 µm was recorded for sample 19N (Table 2). The coating thickness for these samples was the same (35 min). However, for sample 15 N and 19N zinc and nickel anode were applied, respectively. Moreover, the electrolyte used during the coating process of sample 19N consisted of nanodiamonds particles.

Comparing the results obtained for samples 15N and 16N it can be found that using the zinc anode, the same current density of 0.5 A/dm², but at different time of electrolysis we obtain different layer thickness (Table 2). It can be concluded that increasing the time of the process didn’t affect the increase of the thickness of the resulting layer (thicker layer was obtained for the sample 15N – processing time 10 minutes shorter than for the sample 16N).

Samples17N-19N and 21N were coated with a Zn + Ni + NDDS layer. During the process two types of anodes were employed - zinc anode for 17N and 18N and nickel anode for samples 19N and 21N (Table 2). In both cases, with increasing the time of the process the thickness of the layer increased. The greatest layer thickness - 4.94 µm was recorded for sample 18N (zinc anode, process time 45 min) and the lowest -2.60 µm- for sample 19N (anode nickel, process time 35 min) (Table 2).

Comparing the results of surface microhardness, obtained for samples 1 and 2 (coating time 45 and 35 minutes, respectively) it can be concluded that the average value of microhardness for both samples is comparable (Figure 2). In Figures 3 and 4 the results of the microhardness of samples substrate were presented (1, 2 and 6). These results are very similar what means the substrate test samples were made from the same grade of steel. The highest average microhardness was recorded for sample 21N – 262.56 HV; the lowest one was recorded for sample 15N – 219.77 HV (Figure 4).

The results of microhardness of sample coatings 1, 2 and 6 indicate the increase of microhardness in comparison with the microhardness of substrates before coatings.

The changing of processing parameters of the electrolysis process, such as material from which the anode was made (nickel or zinc) and the duration of the process (35, 40 or 45 minutes) allowed for different properties of the coatings. On the basis of light microscopy investigations it can be assumed that the deposited layers are characterised by different adhesion to the substrate, thickness and quality. These layers are characterized by fragility and susceptibility to mechanical damage. SEM investigations showed that investigated coatings are characterised by numerous cracks and delamination (sample 1 – Figure 11) or almost complete chipping of the applied layer (Sample 2). The deposited layers had a different adhesion to the substrate. The SEM results show that better properties were obtained for the cylinder samples.

The EDS microanalysis allowed for identification in investigated samples the following elements: Fe, Ni, Zn, Cr, W, Mn and C. Nickel was detected in all samples, Zn – only in samples numbered 2, 16N, 19N and 21N. Due to the poor quality of the coating on sample 6, it has not been analyzed.

On the basis of X-ray examinations it can be assumed that coatings on samples 1, 2, 15N-21N consist of Ni. The coating which was preset on sample 6 consisted of Ni and the traces of FeZn10 and NiZn21 (Figure 18).

The highest weight loss after wear tests - 0.58% - was observed for the sample 6 (Table 3, Figure 21). The deposition time of the coating (zinc anode) on the surface of the sample was 40 minutes. The smallest weight loss - 0.2% - was recorded for sample 1 (nickel anode, deposition time 45 minutes). Following the results in can be concluded that increasing the time of the process allow for decreasing in weight loss during wear tests.

Moreover, with increasing the time of coating process, friction coefficient decreased. The lowest friction coefficient - 0.506 - was obtained for sample 6, the greatest one - 0.633 – was reported for sample 2 (Table 3, Figure 22). The difference in friction coefficient of sample 1 and 2 is 0.056. It can be assumed that extending the duration of the process contributed to the increasing of friction coefficient. The topography of specimens after wear test is presented in Figures 24–26. The dominant damage mechanism of specimens shown in Fig. 24-26 is abrasive mechanism (cracks and wrinkles occurred). The adhesive mechanism in combination with the transverse cracking was observed in the area of sample where the applied layer has been wiped.

Conclusions

On the basis of the results obtained the following conclusion can be drawn:
1) Thickness of the layer depends on the time of electrolysis process, chemical composition of electrolyte and the type of anode.
2) Adhesive parameters of the layer, its hardness and the thickness of the layer depend on type of anode.
3) Investigated layer are characterized by poor adhesive to the substrate; they, are also brittle.
4) Investigated layers are characterized by almost the same friction coefficients.
5) The dominant damage mechanism of specimens is abrasive mechanism.

Acknowledgments

The financial support of the Ministry of Science and Higher Education under AGH contract no 11.11.110.299.

References


