THE EFFECT OF DISPERSION PHASES OF SiC AND Al2O3 ON THE PROPERTIES OF GALVANIC NICKEL COATINGS

In this study, Ni, Ni-SiC and Ni-Al2O3 coatings were electroplated on the 2xxx series aluminium alloy. The following parameters of the electroplating process were applied: current density - 4A/dm², time - 60 minutes, and temperature - 60°C. Hard particles of submicrometric size were used. The results of the research showing the effect of the addition of hard particles (introduced into the nickel bath as a dispersed phase) on the properties of coatings, including the effect of the type of ceramic particles significantly affects the structure of produced coatings. The dispersed particles incorporated into the nickel coatings improve their abrasion resistance. Improving of the corrosion properties were observed only in the case of coatings containing silicon carbide particles.

Keywords: Nickel coatings, composite coatings, Ni-SiC, Ni-Al2O3, Galvanic coatings
2. Test materials and methods

Studies of electrodeposited nickel coatings were conducted on an EN AW-2017 aluminium alloy in the form of rolled metal sheets having an area of 1 dm². The composition of the aluminium substrate is shown in Table 1.

The nickel plating bath for composite coatings contained the following components:

- nickel sulphate, NiSO₄ 150 g/l
- nickel chloride NiCl₂ 30 g/l
- boric acid H₃BO₃ 30 g/l
- saccharin C₇H₅NO₃S 2 g/l
- SiC or Al₂O₃ particles in the amount of 0, 25, 50 g/l.
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- nickel chloride NiCl₂ 30 g/l
- ceramic particles of submicrometric size were used, i.e. silicon carbide of the D50 – 0.41μm size supplied by H.C. Starck Ceramics GmbH, and alumina particles of the D50 - 0.8 μm size supplied by NABALOX. Coatings were deposited on the aluminium substrate in an electrolytic cell of 4 dm³ capacity under the following conditions: pH of the bath - 4.0, temperature - 60°C, current density - 4 A/dm², the deposition of an intermediate zinc layer from the zincate brightening in HNO₃ 200 g/l solution - 5 minutes etching in NaOH 100 g/l solution - 10 minutes degreasing with acetone SiC or Al₂O₃ particles in the amount of 0, 25, 50 g/l.

Ceramic particles of submicrometric size were used, i.e. silicon carbide of the D50 – 0.41μm size supplied by H.C. Starck Ceramics GmbH, and alumina particles of the D50 - 0.8 μm size supplied by NABALOX. Coatings were deposited on the aluminium substrate in an electrolytic cell of 4 dm³ capacity under the following conditions: pH of the bath - 4.0, temperature - 60°C, current density - 4 A/dm², the deposition time - 60 minutes; mechanical stirring of the bath was conducted at a rotating speed of 350 rpm. The anode was nickel plate with dimension of 180×90 mm. The power source was a laboratory power supply system with the adjustable and stabilized DC voltage and adjustable (limited) current consumption.

The substrate was prepared in the following way:

- degreasing with acetone
- etching in NaOH 100 g/l solution - 10 minutes
- brightening in HNO₃ 200 g/l solution - 5 minutes
- deposition of an intermediate zinc layer from the zincate solution containing ZnO, NaOH, KNaC₄H₄O₆, FeCl₃, - 3 minutes.

To obtain high quality coatings, anode slime penetration into the cathode space was limited using polypropylene anode bags.

Coating thickness was measured by the X-ray fluorescence method using a Fischerscope X-ray XUV 773 device. On each sample 10 measurements were done. The results are average.

Zeta potential was measured with a Zetasizer Nano ZS90 device from Malvern Instruments. Using this device, the calculation of the potential is based on the determination of electrophoretic mobility, first, and application of Henry equation, next. Zeta potential is the potential that exists near the surface of a solid body or dispersed particles (emulsions) entering into contact with the electrolyte solution. It is measured at the slip boundary, which is the plane that separates this part of the interfacial space which contains ions immobilized on the surface of the solid phase and in its immediate vicinity from the remaining “fuzzy” part of the space (double electrical layer). The value of zeta potential indicates the potential stability of a colloidal system. The zeta potential of about 30mV is accepted as a threshold value defining the stability of dispersion. The zeta potential is a measure of the electrostatic interaction between particles and can be used in the assessment of the stability of dispersion, including also its stability on storage. The measurements of zeta potential were taken in two media. The first measurement was taken in solution 1 collected from the Watts bath after previous decantation and the addition of “dry” SiC or Al₂O₃ particles; the pH of this solution was 3.8. The second measurement was taken in solution 2 collected in the same manner as solution 1 but diluted with demineralized water in a 1:1 ratio. The volume of the test samples was 400ml. The multiplicity of measurements was 3. The structure of coatings was examined with Philips XL30 scanning electron microscope.

In the abrasion test, a Taber Abraser Model 5155 was used. The tests were carried out under the load of 1000g, applying 1000 abrasive cycles and flexible abrasive wheels marked with a symbol CS17. The environmental conditions were kept constant, i.e. the humidity of 50±5% and the temperature of 23±2°C during the test and 24 hours before the test. The measurement results were expressed by Taber Wear Index (TWI), which is the weight loss in milligrams per 1000 abrasive cycles. The lower is the value of the index, the higher is the value of the abrasion resistance of the tested material. Below the TWI index is expressed by equation 1:

\[
TWI = \frac{W_b - W_a}{N} \times 1000
\]

where:

- \(W_b\) – sample weight in mg before the test,
- \(W_a\) - sample weight in mg after the test,
- \(N\) – number of abrasive cycles

The abrasion test was conducted on five samples, which included one nickel-coated sample without the addition of ceramic particles, two nickel-coated samples containing 25g/l and 50g/l of SiC particles, and two nickel-coated samples containing 25g/l and 50g/l of Al₂O₃ particles, respectively. Three measurements were conducted on each sample and results are average.

![Fig. 1 The scheme of abrasion resistance test by the Taber method](image)

Figure 1 shows a scheme of the Taber Abrasion Test. A coated sample is placed on to a disk which is rotated at a steady speed, under the weight that is inflicted by two wheels of hard materials which one also rotated in opposite directions.

| Chemical composition of the EN AW-2017 alloy in wt% |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Si   | Fe   | Cu   | Mn   | Mg   | Cr   | Ni   | Zn   | Sn   | Ti   | Ca   | Na   | V   | Sr   | Zr   |
| 0.7383 | 0.2008 | 4.279 | 0.6429 | 0.5751 | 0.0063 | 0.0081 | 0.0721 | 0.0020 | 0.0143 | 0.0002 | 0.0004 | 0.0094 | 0.0003 | 0.00010 |
Corrosion resistance tests were carried out in a DURA HK 1000 salt spray chamber in accordance with ISO 9227: 2012 (E). Testing was conducted on samples with electroplated nickel coatings reinforced with SiC and Al₂O₃ particles added in the amount of 50 g/l and on coated samples without the addition of hard particles. The samples were exposed to neutral salt spray (NSS) for 72h and to acetic salt spray containing copper ions (CASS) for 24 hours. The sample multiplicity was 3. After the test, the samples were visually assessed in accordance with PN eN ISO 10289: 2002. The method described in this international standard is used to evaluate the appearance of metal coatings or other inorganic coatings deposited on metal substrates and subjected to corrosion testing. According to the standard, the result of surface evaluation is the performance rating, which is a combination of protection rating \( R_p \) and appearance rating \( R_A \) expressed in numbers and symbols. The protection rating \( R_p \) is a figure expressing the ability of the coating to protect the metal substrates from corrosion. In contrast, the appearance rating \( R_A \) assigns numbers and letter symbols expressing the overall appearance of the sample, including all deterioration caused by the exposure to a corrosive environment. If only the protection rating \( R_p \) is required, one can skip the appearance rating \( R_A \), in which case it is advisable to place a slash and dash to indicate that the appearance rating has been deliberately omitted. Samples were evaluated using dot charts and colour photographs contained in Annex A to this standard.

Electrochemical analysis was performed using AUTOLAB PGSTAT 302 set provided with a GPES ver.4.9 software for data recording and processing. Samples were analyzed by potentiodynamic method with potential scan rate 1mV/sec. Polarization started after ten-minute lasting setting up an open circuit potential (OCP) in stationary solution. The electrodes were nickel electroplated aluminium samples. The counter electrode was a platinum electrode, while Ag/AgCl3MKCl electrode was a reference electrode. The sample multiplicity was 3. All measurements were taken in a 3.5% NaCl solution at a temperature 25°C.

### 3. Results and discussion

Thickness of nickel coating without the dispersed phase particles was 22 µm; in other coatings it increased to about 25 µm.

In Table 2, the average measured values of the zeta potential are compared. In both solutions, the absolute value of zeta potential was much lower for the SiC particles than for the Al₂O₃ particles. Hence the conclusion follows that SiC particles are more likely to form agglomerates, which will naturally make their incorporation into a nickel matrix much more difficult. For both SiC and Al₂O₃ particles, the absolute value of zeta potential was less than 30 mV, which allows considering them as unstable.

<table>
<thead>
<tr>
<th>Type of solution</th>
<th>Zeta potential [mV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 1</td>
<td>SiC: -0.081, Al₂O₃: -4.84</td>
</tr>
<tr>
<td>Solution 2</td>
<td>SiC: -4.80, Al₂O₃: -13.23</td>
</tr>
</tbody>
</table>

Figures 3-5 show the appearance of surface structure of the resulting nickel coatings.
Fig. 4. Surface structure of nickel coating reinforced with SiC particles added in an amount of: a) 25 g/l, b) 50 g/l

Structure varies depending on the type of ceramic particles embedded in the coating. The surface structure of nickel coatings reinforced with SiC particles is quite regular and uniform, slightly resembling the surface structure of coatings without the addition of ceramic particles. It appears that the SiC particle is covered by a layer of Ni matrix. A similar surface structure of Ni-SiC coatings received the authors in article [14]. Srivastava et al. suggested that this may be due the Ni$^{2+}$ ion would have formed a sheath on SiC and the particle with the adsorbed ion got reduced and codeposited on the cathode. In contrast, the surface structure of nickel coatings reinforced with alumina particles is more developed with clearly visible agglomerates of Al$_2$O$_3$ particles. On fig. 4b is much less visible Al$_2$O$_3$ phase than on fig. 4a, despite its doubled content in the electrolyte. A similar phenomenon was also observed by Kim et al. [15]. In their work increasing the content of the ceramic phase in the electrolyte caused an increase in the content of this phase in the coating but only to a certain limit, above which was a content decrease of hard particles in the coating. This is due to the fact that in electrolytes of low content of ceramic phase, the number of nickel ions adsorbed on this phase was small, which resulted in the small amount of co-deposited particles.

The results of Taber abrasion tests are shown in Figure 6.

Fig. 5. Surface structure of nickel coating reinforced with Al$_2$O$_3$ particles added in an amount of: a) 25 g/l, b) 50 g/l

The highest abrasion resistance was obtained in the nickel coating reinforced with SiC particles, deposited in a bath containing 50 g/l of these particles (TWI 17.6). The bath containing 25 g/l of SiC particles has yielded the TWI value of 37.9. The weight loss during the test was most prominent in the sample of nickel coating without the addition of reinforcing particles (TWI 44.5). The whole of these results prove that the abrasion resistance of composite coatings is about two times higher than that for coatings without hard particles. An exception is the sample 25g/l SiC. The reason might be the smaller number of SiC particles embedded in the coating, or particles “detaching” from the coating during the abrasion test. A similar weight loss tendency was observed in coatings reinforced with alumina particles. Nearing studies conducted authors of article [16]. Comparing the abrasion resistance of Ni and Ni-SiC coatings they found that abrasion resistance of composite Ni-SiC coatings is about 37.5% higher than the coating of pure nickel one.

The results of the salt spray tests are shown in table 3 and 4.

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>7</td>
</tr>
<tr>
<td>Ni-SiC</td>
<td>8</td>
</tr>
<tr>
<td>Ni-Al$_2$O$_3$</td>
<td>8</td>
</tr>
</tbody>
</table>
The results of corrosion resistance studies in acetic salt spray with the addition of CuCl₂ (CASS) according to PN-EN ISO 10289:2002

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Corrosion Rp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1</td>
</tr>
<tr>
<td>Ni-SiC</td>
<td>3</td>
</tr>
<tr>
<td>Ni-Al₂O₃</td>
<td>0</td>
</tr>
</tbody>
</table>

The coating was exfoliated from the substrate material

According to the PN-EN ISO 10289:2002 standard, test in a neutral salt spray (NSS) (tab. 3) has shown that the coating containing SiC and Al₂O₃ particles have improved corrosion resistance (protection rating Rp - 8) compared to the coating without the inclusion of the ceramic phase (Rp - 7). In the case of test in acid salt spray with the addition of copper ions (tab. 4) assessment of the coating was possible only in the case of Ni and the Ni/SiC layer. Ni/Al₂O₃ coating peeled. Studies have shown that the Ni-SiC coating is more resistant to acidic salt spray in comparison with coating without inclusions of dispersed phase.

No specific requirements of corrosion resistance are imposed on the composite nickel coatings, and therefore the results described above should serve only as an example of the investigations of the corrosion behaviour of these coatings, providing a general information about the corrosion resistance under the conditions of exposure to the effect of both neutral salt spray and salt spray with the addition of copper ions. Similar tests were carried out on nickel coatings reinforced with particles of SiC, B and PTFe [17].

In Table 5 and Figure 7, the results of electrochemical tests are shown. Comparing the obtained results of these tests it was found that the lowest corrosion current density has occurred in the composite coating with the silicon carbide content of 50 g/l (0.5576 mA/cm²), i.e. in the coating of a more cathodic character and characterized by much higher polarization resistance compared to the coating without hard particles. In a similar way behaved the coating deposited at a concentration of 25 g/l SiC (Icorr – 0.1083 mA/cm², Rp – 7146 [Ω]). Improvement of the corrosion resistant of Ni/SiC coatings were also observed by C. Cai et al. [18] Coatings produced in solutions containing alumina particles were more anodic in nature than the coatings without the addition of the reinforcing ceramic particles and showed much lower polarization resistance (223.9 Ω and 817.5 Ω for coatings deposited at a concentration of 25 g/l Al₂O₃ and 50 g/l Al₂O₃, respectively). Also M. Trzaska et al. [19] have not found increase in corrosion resistance of Ni/Al₂O₃ coatings, compared with a pure nickel coating in NaCl environment.

The basic condition for high corrosion resistance of materials is their homogeneity, while the manufactured composite coatings are characterized by a heterogeneous structure. In contact with the corrosive solution, microcells are formed in them, leading to a non-uniform and eventually selective corrosion [20]. The corrosive destruction of nickel coatings frequently occurs along the grain boundaries. If defects are present in the interface areas between the nickel matrix and the particles of dispersed phase, the corrosive solution penetrates into them and crevice corrosion progresses [21]. These facts can explain a relatively high value of the corrosion current density obtained in the composite coatings produced in a bath containing 25g/l Al₂O₃.

The results of electrochemical test in 3.5% NaCl

<table>
<thead>
<tr>
<th>Without ceramic particles</th>
<th>SiC 25 g/l</th>
<th>50 g/l</th>
<th>Al₂O₃ 25 g/l</th>
<th>50 g/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Icorr [µA/cm²]</td>
<td>1,028</td>
<td>0,1083</td>
<td>0,5576</td>
<td>1,6185</td>
</tr>
</tbody>
</table>

Fig. 7. Polarization curves of nickel coatings with different type and amount of ceramic particles

4. Conclusions

• The main challenge during the manufacture of composite coatings is to effectively incorporate into their structure a satisfactory number of the ceramic phase particles and avoid agglomeration of these particles.
• For both types of particles, the absolute value of zeta potential was less than 30 mV. This is the limit value below which the particles are considered unstable. A comparison of the SiC and Al₂O₃ particles shows that silicon carbide particles exhibit stronger tendency to agglomeration and therefore their incorporation into the coating may be more difficult.
• The thickness of all composite coatings was approximately 25 µm.
• Abrasion resistance of composite coatings is about two times higher than that for coatings without hard particles.
• According to PN-EN ISO 10289:2002, composite Ni/SiC coatings are characterized by the corrosion resistance superior to coatings without the addition of the reinforcing ceramic phase particles. Ni/Al₂O₃ coatings improve the corrosion resistance of nickel coatings only in neutral salt spray environment.
• Coatings containing SiC particles are more cathodic in nature and show much higher polarization resistance than the coatings without the addition of hard particles. In contrast, coatings deposited in the solutions containing...
alumina particles are more anodic in nature and characterized by the polarization resistance definitely inferior to coatings without the addition of hard particles.

- Coatings containing SiC particles are of a more cathodic nature and show much higher polarization resistance than coatings without the hard particles. In contrast, coatings deposited from the solutions containing alumina particles are more anodic in nature compared to coatings without the particles of a ceramic phase and show much lower polarization resistance.

REFERENCES