1. Introduction

The use of light metals, aluminium and magnesium alloys - in particular, in the manufacture of motor vehicles grows every year. Aluminium alloys are light construction materials; their physical characteristics can be adjusted with proper chemical composition and method of manufacture, including traditional routes, like casting or plastic working (rolling, extrusion, forging), and new advanced processes, to mention as an example rapid solidification, forming in semi-solid state (thixoforming), or fabrication of metal foams. One of the most important objectives in the construction of a vehicle is safety of its use, particularly the car behaviour during accident. Accidents are simulated in the, so called, “crush tests”. The analysis of material behaviour undertaken in such studies allows proper selection of the shape of component along with the alloy composition and heat treatment. The choice of material for elements operating in the crumple zones during accidents should base not only on the mechanical properties of the alloy, but also on its ability to absorb energy. As regards the alloy chemical composition, a new family of aluminium alloys is now being developed. They contain vanadium in the range of 0.05 - 0.5 wt%, are processed by plastic working, and besides high strength and toughness, can also offer stable properties at elevated temperatures. European standards include alloys from the 6xxx series, such as EN-AW 6260, EN-AW 6008 and EN-AW 6014 with the addition of vanadium at a level of up to 0.2%. These alloys are characterized by an ability to absorb kinetic energy - the feature of material particularly useful in the assessment of properties of the structural components of vehicles subjected to strong deformation in the crumple zone in the case of accidents (low ratio of Rp0.2/Rm and very high value of the reduction of area Z) [1]. The role of vanadium in aluminium alloys, especially when this element is present in small amounts, is not sufficiently well known, and data published in the literature is sparse [2,3].

Keywords: electrodeposition, composite coatings, vanadium, SiC
introduction of vanadium causes grain refinement, reduces the conductivity and raises the recrystallization temperature [3].

The effect of vanadium content on the quality of produced metal coatings, composite nickel coatings - in particular, is not known, either. Electroplated nickel coatings are widely used in various industries. Attractive design, high corrosion resistance and good mechanical properties allow the use of such coatings for decorative, protective and technical purposes. The quality and properties of these coatings can be made even better when a composite variant of the coating is used. In the case of nickel coatings, the reinforcing phase is often composed of the SiC or Al₂O₃ particles [4-9]. The size and the amount of the introduced reinforcing phase determine the properties of the newly formed composite nickel coating. The fabrication of a composite layer characterized by new properties depends not only on the selection of optimum layer components, but also on the formation of a specific structure in the composite material.

The aim of this study was to investigate the effect of the chemical composition of aluminium alloys with the addition of vanadium and of the organic compounds used in a plating bath on the properties of composite nickel coatings deposited on the examined aluminium alloys. Full characteristics of thus produced coatings was also given.

2. Experimental

Studies of the fabrication process of electrolytic nickel coatings were conducted on aluminium alloys whose chemical composition was given in Table 1. Two solutions of different chemical composition were used. Solution 1 was a typical Watts bath containing NiSO₄·7H₂O 150 g/l, NiCl₂·6H₂O 30 g/l, H₃BO₃ 30 g/l, with the addition of 20 g/l SiC particles and C₁₂H₂₅SO₄Na (saccharin) 2 g/l. Solution 2 contained, besides the basic components and saccharin, also sodium laureate (sodium lauryl (dodecyl) sulphate) C₁₂H₂₅SO₄Na in an amount of 2 g/l. Coatings were deposited under the following conditions: current density - 4 A/dm², time - 30 minutes, solution temperature - 40°C, pH of solution - 4 ± 0.2. The whole was mixed with a magnetic stirrer at 350 rev/min and with a peristaltic pump at 40 rev/min. Electroless zinc coating was also applied before nickel plating according [10]. All solutions were prepared with analytical grade chemicals and demineralised water with a conductivity not exceeding 5 μS/cm². After the addition of the dispersed phase to the bath, the solution was ultrasonically stirred for 0.5 h and then with a magnetic stirrer for 2h.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample designation</th>
<th>Vanadium content [wt%]</th>
<th>Alloy composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>V0</td>
<td>0,0</td>
<td>AlSiMg</td>
</tr>
<tr>
<td>2</td>
<td>V04</td>
<td>0,4</td>
<td>AlSiMgV0.4</td>
</tr>
<tr>
<td>3</td>
<td>V02M</td>
<td>0,2</td>
<td>AlSiMgV0.2</td>
</tr>
<tr>
<td>4</td>
<td>R0</td>
<td>0,0</td>
<td>AlSiMgCuCr</td>
</tr>
<tr>
<td>5</td>
<td>R01</td>
<td>0,1</td>
<td>AlSiMgCuCrV0.1</td>
</tr>
<tr>
<td>6</td>
<td>R02</td>
<td>0,2</td>
<td>AlSiMgCuCrV0.2</td>
</tr>
<tr>
<td>7</td>
<td>R03</td>
<td>0,3</td>
<td>AlSiMgCuCrV0.3</td>
</tr>
</tbody>
</table>

The microstructure of the composite coatings was examined with (SEM) Philips XL30 scanning electron microscope. The thickness of coating was determined by X-ray fluorescence using the FISHERSCOPE X-RAY XUV 773 device. The Vickers microhardness was measured with a Buehler Micromet. Corrosion tests were performed in an AUTOLAB PGSTAT model 302 test kit made by EcoChemie BV with GPES ver. 4.9 software for the experiment control, and for the data collecting and analysis. The polarisation of samples was carried out at 25°C in a naturally aerated NaCl solution at a concentration of 3.5%. The working electrode was nickel-coated electrode with an area of 1.8 cm², the reference electrode was an Ag/AgCl/3M KCl electrode, and the counter electrode was a platinum electrode. The polarisation rate was 0.001 V/s. Tests and studies started after a 10 minute stabilisation period of the stationary open circuit potential. As a result of the studies, polarisation curves were plotted in a logarithmic system, in which the respective values were used to calculate the corrosion potential - Ecorr, corrosion current - Icorr, and polarisation resistance - Rp.

3. Results and discussion

Composite nickel coatings were reinforced with the ceramic SiC phase with an average particle size of approx. 7.3 μm. Figure 1 shows the size and shape of the ceramic particles. Based on the SEM image analysis, it was found that the SiC powder particles are sharp-edged in shape. It was also found that the powder fraction contains both fine ceramic particles as well as very large sizes exceeding 15 μm. The voltage waveforms were analyzed during the growth of the coating. In the case of bath containing saccharin only (Fig. 2), lowering of the process bias voltage was observed with the increased content of vanadium for both the AlSiMg alloy and AlSiMgCuCr alloy. This relationship was not observed after the addition of sodium laureate to the plating bath (Fig. 3).

During the deposition of composite nickel coatings on the surface of aluminium alloys it was found that when the bath contained saccharin only, numerous defects were formed on the coating surface due to the presence of hydrogen evolved in the process (Figs. 4 and 5). The defects were eliminated by the use of sodium laureate addition. In view of the large number of surface defects it was decided not to continue the studies using the solution with the sole saccharin and focus attention on the process of producing coatings from a solution containing its composition both saccharin and sodium laureate. Therefore, this article presents only the results of studies of the coatings produced with the use of two organic additives, ignoring the results obtained on defective coatings. The diagram in Figure 6 shows thickness of the nickel coatings obtained on each of the examined alloys. The thickness of coatings amounted to approx. 33 to 48 μm. Coating of the largest thickness amounting to 48.3 μm was obtained on the alloy designated as R0. The smallest thickness of 33.9 μm was obtained on the alloy designated as R03. The results of the analysis of the coating thickness lead to the conclusion that in the case of AlSiMg alloy, the increasing vanadium content promotes the thickness growth in the resulting composite nickel coating. An inverse relationship is observed in the AlSiMgCuCr alloy, where coating of the largest thickness...
has been formed on the alloy without the addition of vanadium. Vanadium content in the aluminium alloy increasing from 0.1 to 0.3% reduces the thickness of the growing coating.

Fig. 1. SEM image of the ceramic particles of SiC a) and size of these particles b)

Fig. 2. Voltage waveforms observed during manufacture of nickel coatings from the solution without sodium laurate

Fig. 3. Voltage waveforms observed during manufacture of nickel coatings from the solution with sodium laurate

Fig. 4. The surface of composite nickel coating produced without the addition of sodium laurate on AlSiMg alloy - visible are numerous surface defects

Fig. 5. The enlarged view of defect found in composite coating produced without the addition of sodium laurate

Microscopic examinations (Figs. 7-13) have proved that coatings obtained on aluminium substrates are continuous and characterized by good adhesion to the substrate. There are no defects like discontinuities or delamination of coating. The distribution of the ceramic phase in the metal matrix is fairly uniform. Respective images show individual particles of different sizes embedded in a metal matrix. Detailed analysis of the images did not show the phenomenon of the particles agglomeration. There was no clear impact of the vanadium content in aluminium alloys on a percent fraction of the ceramic phase in composite coating.

Fig. 6. Thickness of nickel coatings produced on the 6xxx series aluminium alloys with vanadium addition

Fig. 7. Microstructure of nickel coating produced on sample V0

Fig. 8. Microstructure of nickel coating produced on sample V04
Corrosion tests performed by the potentiodynamic method on composite nickel coatings have proved that in the AlSiMg alloy the increase of vanadium content causes a minimal (comprised within the measuring error) increase in the corrosion current density as compared with the vanadium-free alloy (the results are shown in Fig. 14 and Table 2). The polarisation resistance increases from the value of 1240 \( \Omega \) (alloy without vanadium) through 1470 \( \Omega \) (alloy with 0.2% vanadium) to 1619 \( \Omega \) (alloy with 0.4% vanadium), indicating a slight improvement in the protective properties of coatings. In the case of AlSiMgCuCr alloy, the increase of vanadium content reduces the corrosion current density. The increase of polarisation resistance is also observed in samples containing 0.2 and 0.3% vanadium compared to alloy without the addition of this element. The only exception is sample containing 0.1% vanadium. It shows a drop of polarisation resistance compared to the alloy without the addition of vanadium. Electrochemical studies have shown that vanadium content increasing in the AlSiMgCuCr alloy increases the resistance of protective coatings deposited on this alloy.

The results of studies of the Vickers microhardness of coatings are shown in Table 3. From the results obtained it can be concluded that in the case of AlSiMg alloy the addition of vanadium in an amount of 0.2 wt% promotes the increase of coating microhardness from the value of 447HV0.05 to 480.2 HV0.05, while the addition of vanadium in an amount of 0.4% increases the microhardness values to 496,6HV0,05. In the case of AlSiMgCuCr alloy, no significant differences in the composite coating microhardness were observed after adding the vanadium in an amount of 0.1-0.3 wt%.
The results of potentiodynamic tests made in 3.5% NaCl solution

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Results of electrochemical tests</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Icorr [µA/cm²]</td>
<td>Rp [Ω]</td>
<td>Ecorr [mV]</td>
</tr>
<tr>
<td>V0</td>
<td>0.104</td>
<td>1240</td>
<td>-266</td>
</tr>
<tr>
<td>V04</td>
<td>0.116</td>
<td>1619</td>
<td>-265</td>
</tr>
<tr>
<td>V02M</td>
<td>0.127</td>
<td>1470</td>
<td>-273</td>
</tr>
<tr>
<td>R0</td>
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<td>1335</td>
<td>-256</td>
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<td>R01</td>
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<td>R02</td>
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<td>-263</td>
</tr>
<tr>
<td>R03</td>
<td>0.057</td>
<td>1412</td>
<td>-246</td>
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</tbody>
</table>

Microhardness of composite coatings

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Microhardness HV 0,05</th>
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</thead>
<tbody>
<tr>
<td>V0</td>
<td>447,0</td>
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<tr>
<td>V02M</td>
<td>480,2</td>
</tr>
<tr>
<td>V04</td>
<td>496,6</td>
</tr>
<tr>
<td>R0</td>
<td>487,2</td>
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<tr>
<td>R01</td>
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<tr>
<td>R02</td>
<td>483,0</td>
</tr>
<tr>
<td>R03</td>
<td>488,6</td>
</tr>
</tbody>
</table>

4. Conclusions

Based on the results of studies of the manufacturing process of composite nickel coatings reinforced with SiC particles deposited on aluminium alloys containing vanadium addition, it was found that high-quality coatings can be obtained when the addition of saccharin and sodium laurate is introduced to the plating bath. Tests and examinations have shown that all coatings produced on the aluminium alloy substrate were continuous and characterized by good adhesion to the substrate. Defects like discontinuities or coating delamination were not detected. The distribution of the ceramic phase in the metal matrix was uniform. Microscopic examinations did not reveal the phenomenon of the ceramic particles agglomeration. There was no clear effect of vanadium content in aluminium alloys on the ceramic phase content in the composite coating. Electrochemical studies showed the increasing resistance of protective coatings deposited on the AlSiMgCuCr alloy with the increasing vanadium content in this alloy. In the case of AlSiMgCuCr alloy, the increase of vanadium content has reduced the corrosion current density. Higher polarisation resistance was also observed in samples containing 0.2 and 0.3% vanadium compared to alloy without the addition of this element.

Acknowledgments

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