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A. KOZIK^{*,#}, M. NOWAK^{*}, M. GAWLIK^{*}, M. BIGAJ^{*}, M. KARAS^{*}**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 (SiC or Al₂O₃) and content (0, 25, 50 g / l) of these particles, were discussed. Based on extensive investigations, it was found that 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

1. Introduction

The development of science and technology calls for new materials with improved technical parameters. Common coatings are no longer sufficient for the more and more demanding industrial practice, and this fact is the source of rapid development of composite materials. The composite material is formed of at least two components, and the characteristic feature is that its properties are superior and/or new in relation to the properties of each of the components used separately. Composite electrolytically deposited coatings are based on a metal matrix, in which particles of other materials (metallic or non-metallic) are dispersed. Various types of dispersed particles such as SiC, Al₂O₃, TiO₂, WC, SiO₂, Si₃N₄ [1-4] are incorporated in the coating. Their presence improves the abrasion resistance and mechanical properties of the coating. Composite coatings can have practical application, provided the required stability under operating conditions, including proper corrosion resistance, is achieved.

Silicon carbide (SiC) offers high values of hardness, combined with equally high coefficients of thermal and electrical conductivity [5]. Alumina (Al₂O₃) has, in turn, satisfactory mechanical and physical properties, combined with good corrosion resistance. Its high hardness, high dielectric properties and thermal conductivity make it an excellent material for a wide range of applications [6].

In the use of aluminium as a construction material, its mechanical properties and corrosion resistance play the most important role. To improve these properties, nickel coatings are deposited on the aluminium surface. They considerably improve the quality of the coated surface, and therefore are of great practical importance. Composite nickel coatings are used in many different applications, to mention only the

automotive industry with a new generation of engines for vehicles and motorcycles, transport industry, high-temperature devices for the electronics where the heat dissipation effect is necessary, the agricultural industry, medical facilities, and many other similar sectors of industry [7]. Nickel coatings are also produced on parts of machines and equipment in all those cases where providing long performance life and high wear resistance is the most necessary condition.

The quality of the deposited nickel coatings depends on the parameters of the manufacturing process, such as the concentration of individual bath constituents, temperature, time, cathodic current density, pH of the solution, and also the size, quantity and zeta potential of the dispersed particles introduced into the bath. Significant impact on the quality of the resulting coatings has also the bath mixing technique [8].

For nickel electroplating, Watts bath is most commonly used [1, 9-12]. It consists of the three basic components: nickel sulphate, nickel chloride and boric acid. A bath like this can be modified with the addition of various types of surfactants, which change the coating appearance (brighteners, anti-pitting agents, surface tension reducing agents) and reduce internal stresses formed in the coating. Studies of the effect of the addition of various types of organic substances on the quality of nickel coatings reinforced with Al₂O₃ particles were carried out in IMN OML Skawina [13].

The aim of this paper is to describe the deposition of nickel coatings reinforced with particles of the ceramic phases of SiC and Al₂O₃, added in two different amounts to the electrolyte, i.e. 25 g/l and 50 g/l, as opposed to the deposition of coatings without the addition of the dispersed phase. The effect of the type and content of hard particles on the thickness, surface structure, microhardness, wear resistance and corrosion resistance of the resulting nickel coatings was compared.

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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.

Ceramic particles of submicrometric size were used, i.e. silicon carbide of the D50 – 0.41 μm 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 mean value.

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:

$$TWI = \frac{W_b - W_a}{N} * 1000 \quad (1)$$

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 resistance was tested 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.

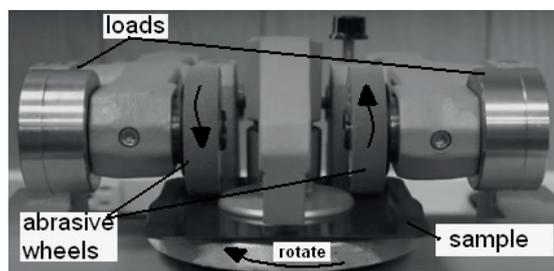


Fig. 1 The scheme of abrasion resistance test by the Taber method

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.

TABLE 1

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 (RA), 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

Figure 2 shows the results of the measurements of the nickel coatings thickness.

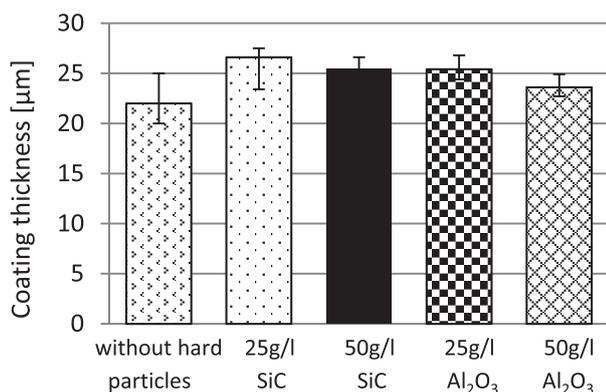


Fig. 2. Thickness of the obtained nickel coatings

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 2

The zeta potential of SiC and Al₂O₃ particles used for bath preparation

Type of solution		Zeta potential [mV]
Solution 1	SiC	- 0.081
	Al ₂ O ₃	- 4.84
Solution 2	SiC	-4.80
	Al ₂ O ₃	-13.23

Figures 3-5 show the appearance of surface structure of the resulting nickel coatings.

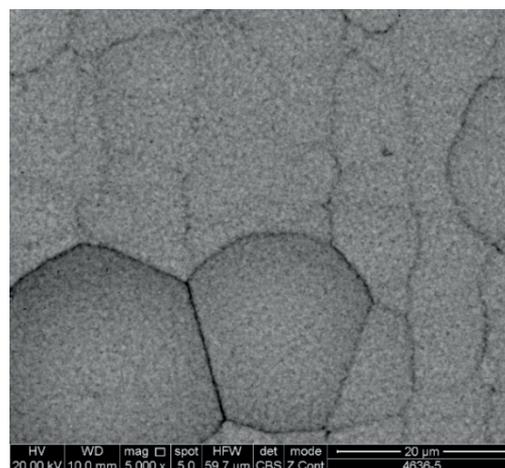
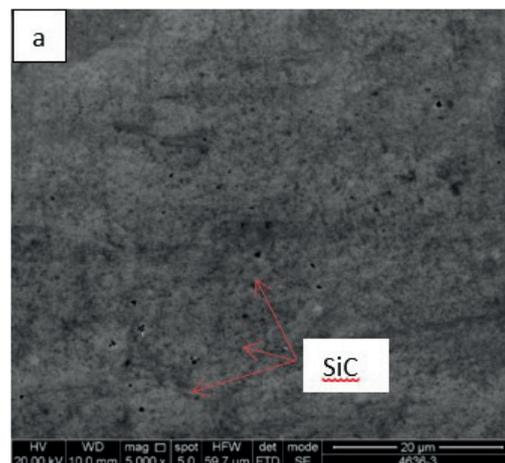


Fig. 3. Surface structure of nickel coating without the dispersed phase particles



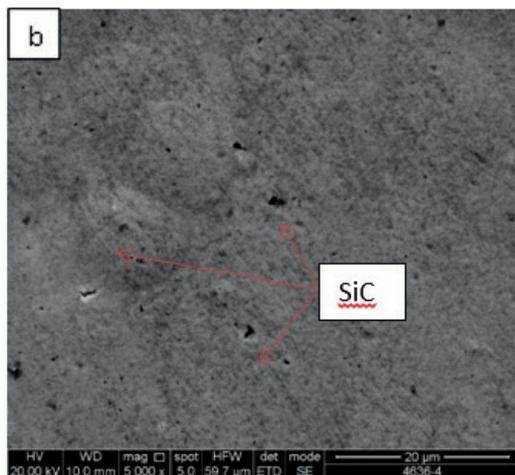


Fig. 4. Surface structure of nickel coating reinforced with SiC particles added in an amount of: a) 25 g/l, b) 50 g/l

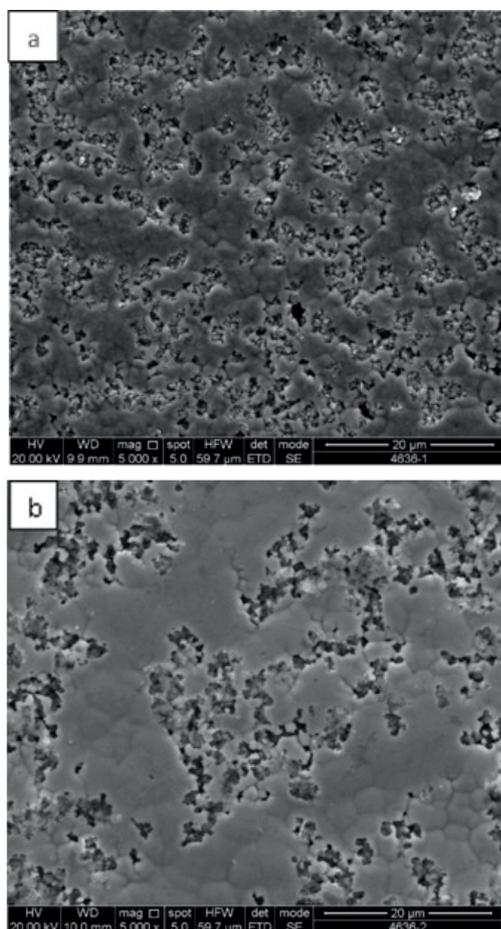


Fig. 5. Surface structure of nickel coating reinforced with Al₂O₃ particles added in an amount of: a) 25 g/l, b) 50 g/l

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 Ni²⁺ 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 Al₂O₃ particles. On fig. 4b is much less visible Al₂O₃ 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.

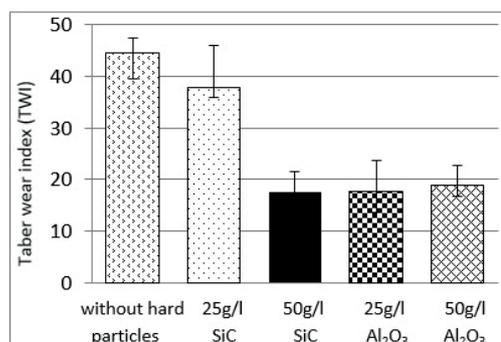


Fig. 6. The abrasion resistance of electroplated nickel coatings depending on the type and amount of hard reinforcing particles

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 3
The results of corrosion resistance studies in neutral salt spray (NSS) according to PN-EN ISO 10289: 2002

Type of coating	Corrosion
	R _p
Ni	7
Ni-SiC	8
Ni-Al ₂ O ₃	8

TABLE 4

The results of corrosion resistance studies in acetic salt spray with the addition of CuCl_2 (CASS) according to PN-EN ISO 10289: 2002

Type of coating	Corrosion
	R _p
Ni	1
Ni-SiC	3
Ni-Al ₂ O ₃	0 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 R_p- 8) compared to the coating without the inclusion of the ceramic phase (R_p - 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 $\mu\text{A}/\text{cm}^2$), 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 ($I_{\text{corr}} - 0,1083 \mu\text{A}/\text{cm}^2$, R_p - 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.

TABLE 5

The results of electrochemical test in 3.5% NaCl

	Without ceramic particles	SiC		Al ₂ O ₃	
		25 g/l	50 g/l	25 g/l	50 g/l
I_{corr} [$\mu\text{A}/\text{cm}^2$]	1,028	0,1083	0,5576	1,6185	0,4556

E_{corr} [mV]	-318	-267	-283	-393	-467
R _p [Ω]	4924	7146	8021	223,9	817,5

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

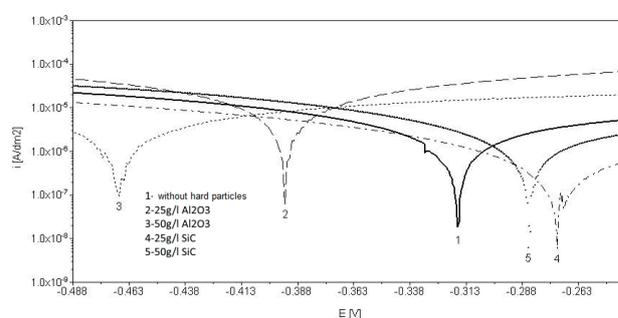


Fig. 7. Polarization curves of nickel coatings with different type and amount of ceramic particles

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.

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