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**COMPARISON OF THE PROPERTIES OF NICKEL COATINGS REINFORCED WITH DISPERSION SiC PARTICLES OF MICROMETRIC, SUBMICROMETRIC AND NANOMETRIC SIZE DEPOSITED ON THE 5xxx SERIES ALUMINIUM ALLOY**

**PORÓWNANIE WŁAŚCIWOŚCI POWŁOK NIKLOWYCH ZBROJONYCH CZĄSTKAMI SiC, O ROZMIARACH MIKROMETRYCZNYCH, SUBMIKROMETRYCZNYCH I NANOMETRYCZNYCH OSADZANYCH NA STOPIE ALUMINIUM SERII 5xxx**

In this study, Ni-SiC composite coatings were electroplated on the 5xxx series aluminium alloy substrate. The effect of the quantity (25g/l i 50g/l) and the size (3 $\mu$ m, 0,41 $\mu$ m and 50nm) of SiC particles introduced into the bath as a dispersed phase on properties of the coatings was tested. The influence of these parameters on thickness, microhardness, surface structure, abrasion resistance and corrosion resistance of nickel composite coatings was determined.

*Keywords:* nickel coatings, Ni-SiC, composite coating

W niniejszej pracy powłoki Ni-SiC, osadzano elektrolitycznie na stopie aluminium serii 5xxx. Przedstawiono wyniki badań dotyczące wpływu ilości (25g/l i 50g/l) oraz wielkości cząstek SiC (3 $\mu$ m, 0,41 $\mu$ m oraz 50nm), wprowadzanych do kąpeli niklowych jako faza zdyspergowana, na właściwości otrzymanej powłoki niklowej. Określono wpływ tych parametrów na grubość, mikrotwardość, strukturę powierzchni, odporność na ścieranie oraz odporność korozyjną otrzymanych kompozytowych powłok niklowych.

## 1. Introduction

In the use of aluminium as a construction material, its mechanical properties and corrosion resistance play the leading role. To improve these properties, coatings of different types are deposited on the surface of aluminium products. These are, among others, nickel coatings which confer very high quality to the coated surfaces and, therefore, are so important. Nickel plating is one of the most common surface finishing processes. The technologies of electrolytic deposition of the nickel composite coatings offer the opportunity to obtain coatings with unique properties. In coatings of this type can be embedded various dispersion particles, such as SiC [1], Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, WC, SiO<sub>2</sub> and others, although practical use in the industry is mainly limited to Ni-SiC coatings. Coatings of this type are used, among others, in the automotive industry in a new generation of motor car engines, in transport industry, in high-temperature devices, in the electronics, and generally in all those cases where the heat transfer and dissipation are necessary; they also find application in the agricultural industry, in medical equipment, and in numerous other sectors of the industry [2]. Nickel coatings are also deposited on parts of machines and equipment, whenever the durability and abrasion wear resistance are of some importance. The desired characteristics of the nickel surface layer include low roughness, low internal stress in the coating, high hardness,

high degree of the grain refinement and strong bonding with the substrate material [3]. Studies on the production of nickel coatings containing silicon carbide particles were conducted by many researchers around the world [4-7].

Silicon carbide (SiC) offers high hardness, high coefficient of thermal conductivity and satisfactory electrical conductivity. Another advantage is that the particles are relatively easily embedded in the coating during an electrochemical process [8].

Dispersion particles can improve the abrasion resistance and mechanical properties of the coating. The size of the SiC particles introduced to a solution is of the utmost importance, remembering that these particles can vary in, for example, the state of the surface. The particles of very small sizes may agglomerate, which results in their non-uniform embedding in the coating and thus in the deterioration of the mechanical properties of the coating [9]. The article describes the studies of the deposition of nickel coatings reinforced with SiC particles of micrometric, submicrometric and nanometric dimensions in solutions with two different levels of the particle content (25 and 50 g/l). The increase of particle content in the bath is accompanied by the increase of their content in the coating, but only to a certain limit. The general tendency is such that up to a certain content of particles in the coating, the properties of this coating are improved; further increase in the content of the particles either has no significant effect

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Chemical composition of EN AW – 5754 alloy expressed in % by weight

Cu	Mg	Mn	Fe	Si	Zr	Ti	Zn	Cr	Ni	Pb
0.0407	2.795	0.4151	0.3060	0.2179	0.0006	0.0165	0.0218	0.0398	0.0065	0.0034

or can even deteriorate the quality of the coating [3]. In the studies undertaken, the effect of the size and amount of the SiC particles on their content in nickel coating and on the microhardness, abrasion wear resistance, corrosion resistance, and surface structure has been determined.

## 2. Test materials and methods

Studies on electrodeposited of Ni/SiC coatings were conducted on an EN AW-5754 aluminium alloy in the form of rolled metal sheets with an area of 1dm<sup>2</sup>. The chemical composition of the alloy is shown in Table 1.

Coatings were deposited from a conventional, Watts type, nickel electroplating bath, containing NiSO<sub>4</sub>·7H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O and H<sub>3</sub>BO<sub>3</sub>, and also an organic additive reducing the internal stress in the coating. The size of the SiC particles acting as a reinforcement of the coating was as follows: micrometric particles ~3μm, submicrometric particles ~0.41μm, and nanosized particles ~50nm. The concentration of particles dispersed in a bath was 25g/l and 50g/l. The anode was a nickel plate with dimensions of 180×90 mm. Before the nickel plating process took place, aluminium had been subjected to a four-step pre-treatment, involving degreasing with acetone, etching in NaOH solution, brightening in HNO<sub>3</sub> solution, and application of a zincating interlayer. The intermediate coating was applied to improve the nickel coating adhesion to the substrate. The power source was a laboratory power supply unit with adjustable and stabilised DC voltage and controlled (limited) current consumption. The bath was agitated with compressed air.

Parameters of the coating manufacture are shown in Table 2.

TABLE 2

Parameters of the coating production

<b>pH</b>	~4.0
<b>Current density</b>	4 A/dm <sup>2</sup>
<b>Time</b>	60 minutes
<b>Temperature</b>	60°C

Coating thickness was measured under an OLYMPUS GX71 optical microscope, the structure of the coating was determined under a Philips XL30 scanning electron microscope, microhardness measurements were performed with a BUEHLER MICROMET 5103 microhardness tester under a load of 0.01HV.

The abrasion test was carried out on a Taber Abraser Model 5155 device. To smooth the surface of the sample, the test under a load of 1000 g involved first a preliminary "scuffing" of the coating obtained in 50 cycles. The weight of the sample after these 50 cycles was adopted as a starting weight, and then the coating was abraded for 1000 cycles. The test used abrasive flexible wheels, designated as CS17. The envi-

ronmental conditions were kept constant, i.e. the humidity of 50±5% and the temperature of 23±2°C during and 24 hours before the test.

Electrochemical studies were performed on an AUTO-LAB PGSTAT 302 set for electrochemical analysis using a GPES ver.4.9 software. Samples were tested by the potentiodynamic method, in the range of potential values from -0.45 to 0.45 V, with the potential scan rate of 0.01 V/s. The electrodes were aluminium samples with nickel coatings produced on their surface. A platinum electrode was used as counter electrode, while the reference electrode was Ag/AgCl 3M KCl electrode. Measurements were taken at room temperature in 3.5% NaCl solution.

## 3. Results

The surface structure of the produced nickel coatings is shown in Figs. 1-6.

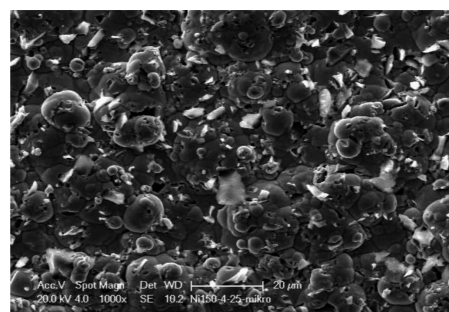


Fig. 1. Microstructure of nickel coating + 25g/l of micrometric SiC

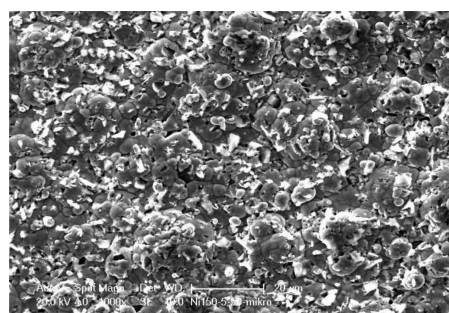


Fig. 2. Microstructure of nickel coating + 50g/l of micrometric SiC

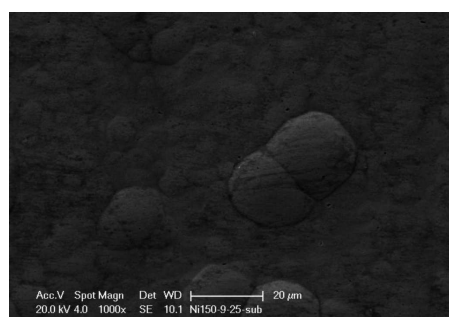


Fig. 3. Microstructure of nickel coating 25g/l of submicrometric SiC

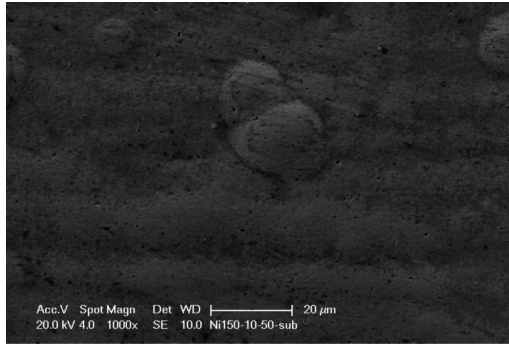


Fig. 4. Microstructure of nickel coating 50g/l of submicrometric SiC

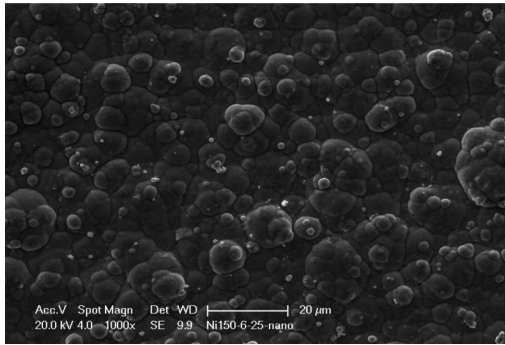


Fig. 5. Microstructure of nickel coating + 25g/l of nanometric SiC

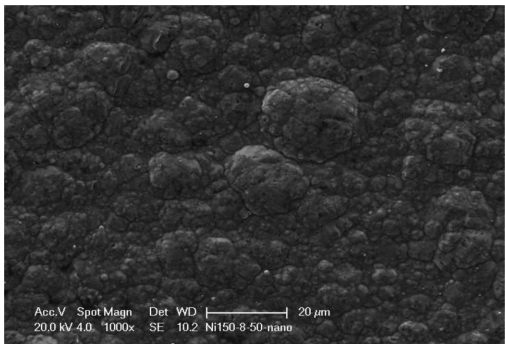


Fig. 6. Microstructure of nickel coating + 50g/l of nanometric SiC

The structure of the surface of the composite layer varies to a great extent and depends on the size of the particles that are embedded in the coating. The highest values of the surface roughness were observed in coatings with the particles of micrometric dimensions. The surface structure also differed in the case of coatings that contained particles of the same size but concentration of these particles in the bath was different. The structure of the nickel coatings reinforced with SiC particles of submicrometric dimensions was quite regular. On the other hand, in coatings containing particles of micrometric and nanometric dimensions, this structure had a “nodular” appearance. Huynh Thi Hal et al produced coatings of similar structure in their studies [10].

Figure 7 shows the results of measurements of the nickel coating thickness. The greatest thickness was obtained in the coating reinforced with SiC particles of micrometric dimensions (with 25 g/l of SiC the thickness was 31.4  $\mu\text{m}$ , while with 50 g/l of SiC the thickness was 29  $\mu\text{m}$ ). For coatings with particles of submicrometric and nanometric dimensions,

the coating thickness was in the range of 25–28  $\mu\text{m}$ . The number of SiC particles in the nickel plating bath had no major effect on the thickness of the obtained coatings, the difference amounted to some 2  $\mu\text{m}$  only.

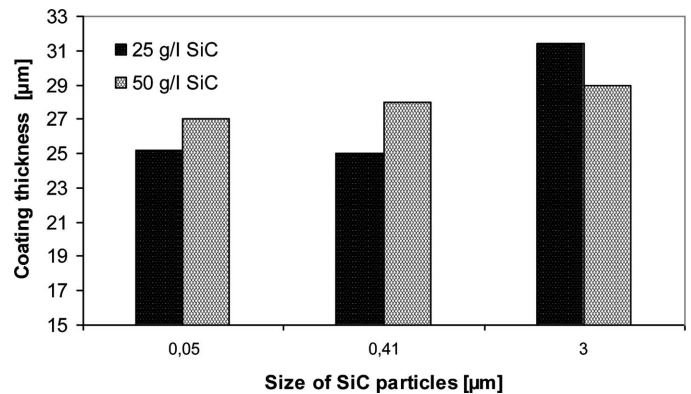


Fig. 7. Relationship between the thickness of produced nickel coating and the size of SiC particles used as a reinforcement

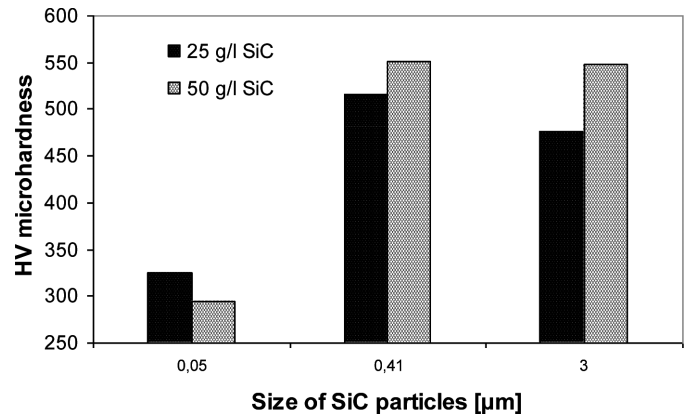


Fig. 8. Relationship between the microhardness of produced nickel coating and the size of SiC particles used as a reinforcement

Figure 8 shows the microhardness of nickel coating as a function of the size of the SiC particles dispersed in a bath. According to the data given in literature [11–13], microhardness of coatings produced from baths containing the hard particles of micrometric dimensions amounts to about 460 units, for the coatings with particles of submicrometric dimensions, this value is somewhat lower and amounts to about 420 units, while for the coatings with embedded particles of nanometric dimensions this value reaches the level of about 300–360 units. However, as it has been observed (Fig. 3), the microhardness does not depend only on the size of the particles reinforcing the coating, but also on their concentration in the bath and on the amount of particulate embedded in the coating, and this, in turn, depends mainly on the method and rate of stirring, so not always these parameters can be compared with each other. There is also another relationship according to which with the increasing microhardness of the coating, its resistance to abrasion wear increases, too.

The values of the (TWI) Taber wear index obtained during the test are shown in Figure 9. The presented results indicate that the best abrasion wear resistance is obtained in a nickel coating reinforced with SiC particles of micrometric dimensions. The largest loss in weight during the test was suf-



ferred by the sample with nickel coating containing nanoscale particles of silicon carbide. The reason may be the fact that only very few of the SiC particles of nanometric dimensions had the chance to get embedded in the coating. This phenomenon can be explained by referring to the research of H.K. Lee et al [14] on the zeta potential. Zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. H.K. Lee et al noticed that SiC particles with micrometric size are more negative than SiC particles with nanometric size in the zeta potential, indicating that micrometric SiC particles were easily adsorbed by the positive ions.

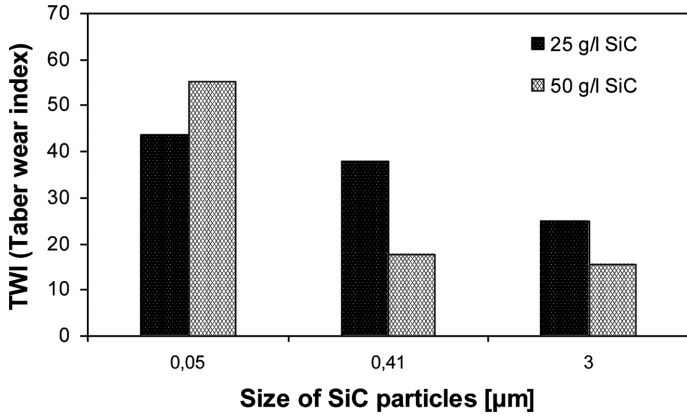


Fig. 9. Relationship between the abrasion wear resistance of produced nickel coating and the size of SiC particles used as a reinforcement

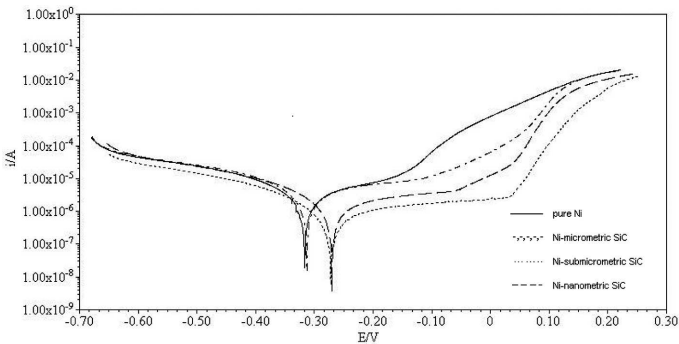


Fig. 10. Polarisation curves of nickel coatings produced with the SiC particles content of 25 g/l

Based on the analysis of polarisation curves (Fig. 10, 11) it can be concluded that nickel coating reinforced with hard particles of SiC has more cathodic character than the coating non-reinforced with hard particles.

Comparing the polarisation resistance values ( $R_p$ ) (Table 3), it is clear that higher resistance offers the nickel coating containing SiC particles. This value increases with the decreasing SiC particle size and with the increasing number of the hard particles in a solution. Compared with pure nickel coating, coatings containing SiC particles are also characterised by a lower value of the corrosion current (Table 3) (the only exception is coating with SiC particles of the submicrometric size, produced with a content of 25 g/l of particles in the solution). The lowest value of the corrosion current was achieved for coatings produced from a solution containing 25g/l of SiC particle of submicrometric size. Also in the case of coatings made from a solution containing hard particles in an amount of 50 g/l (Table 3), the coating with the particles of submicrometric size was characterised by the lowest value of corrosion current. Coatings containing composite particles were also characterised by a lower value of the corrosion potential compared with the coating made of pure nickel. The lowest value of  $E_{corr}$  had the coatings containing particles of nanometric size (25g/l SiC -  $E_{corr}$  = -261 mV, 50 g/l SiC -  $E_{corr}$  = -270mV). These results indicate that, with regard to the conclusions drawn by Cai et al [15], SiC particles can change the surface structure of a nickel coating or act as a physical barrier to prevent the initiation and propagation of corrosion centres.

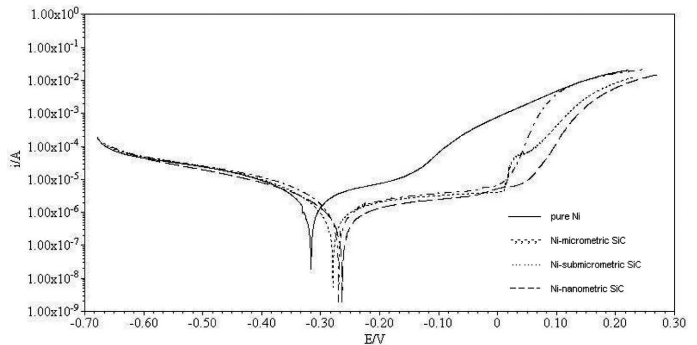


Fig. 11. Polarisation curves of nickel coatings produced with the SiC particles content of 50 g/l

TABLE 3

The results of electrochemical studies of coatings produced from the solution containing 25 g/l and 50g/l of SiC particles

Coating Parameter	Pure nickel	Ni-SiC micro	Ni-SiC submicro	Ni-SiC nano	Ni-SiC micro	Ni-SiC submicro	Ni-SiC nano
		25g/l SiC			50g/l SiC		
		$E_{corr}$ [mV]	-304	-292	-276	-261	-274
$i_{corr}$ [ $\mu A/cm^2$ ]	0.80	0.99	0.29	0.52	0.50	0.49	0.56
$R_p$ [ $\Omega$ ]	4408	5371	6149	10366	5659	9303	13846

#### 4. Conclusions

1. Nanometric SiC particles are much more difficult for embedding in a nickel matrix than the submicrometric and micrometric particles, which is manifested if in nothing else at least in the increased surface roughness. Therefore, the main challenge during the deposition of coatings reinforced with SiC particles is to get the appropriate number of particles embedded in the coating and avoid agglomeration of particles dispersed in the solution. The particle agglomeration is highly influenced by the method and speed of mixing the electrolyte. Mixing is particularly difficult in the case of nano-sized particles, and for this reason the method of mixing can greatly affect the results obtained.
2. The largest thickness was achieved in the coating containing micrometric particles, the smallest – in the coating with nanometric particles, but the difference between these coatings was maximum  $7\mu\text{m}$ .
3. Microhardness of nickel coatings containing hard particles ranges from 300 – 550 units depending on the size of the particles embedded in the coating. Satisfactory microhardness was obtained in coatings containing both submicrometric and micrometric particles, as it was nearly two times higher than the microhardness of "pure" nickel coating, which according to the literature reaches the value of about 300 units.
4. The best abrasion resistance was offered by the coating comprising particles of micrometric dimensions, the worst abrasion resistance index had the coating with nano-scale particles, but it should be remembered that the obtained results could be affected by the mixing technique.
5. High corrosion resistance of coatings containing hard particles is probably due to the non-conductive characteristics of SiC particles that inhibit the formation of corrosion centres. From the obtained results it can be seen that the highest polarisation resistance, two times higher than that of the coatings containing particles of micrometric and submicrometric size, has been obtained in coatings reinforced with SiC particles of nanometric dimensions.

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#### REFERENCES

- [1] I. Dobosz, E. Rudnik, L. Burzyńska, Archives of Metallurgy and Materials **56**, 3 (2011).
- [2] B. Szeptycka, Kompozyty (Composites) **1**, 2 (2001).
- [3] B. Szeptycka, A. Skrzyniowski, Kompozyty (Composites) **3**, 8 (2003).
- [4] L. Burzyńska, E. Rudnik, K. Cwięka, of Metallurgy and Materials **54**, 3 (2009).
- [5] P. Gyftou, M. Stroumbouli, E.A. Pavlatou, A. Asmidis, N. Spyrellis, Electrochimica Acta **50**, 4544-4550 (2004).
- [6] L. Burzyńska, E. Rudnik, J. Koza, Ł. Błaż, W. Szamański, Surface and Coatings Technology **202**, 2545-2556 (2007).
- [7] S.K. Kim, H.J. Yoo, Surface and Coatings Technology **108-109**, 564-569 (1998).
- [8] B. Szeptycka, Instytut Mechaniki Precyzyjnej, Warszawa, 2009.
- [9] Li Chen, Liping Wang, Zhixiang Zeng, Junyan Zhang, Materials Science & Engineering A **434**, 319-325 (2006).
- [10] Huynh Thi Ha, Cao Tuan Anh, Nguyen Thu, Ha, Dao Tran Cao, Conference Series **187**, 012083 (2009).
- [11] I. Garcia, J. Fransaer, J.-P. Celis, Surface and Coatings Technology **148**, 171-178 (2001).
- [12] M. Lekka, N. Kouloumbi, M. Gajo, P.L. Bonora, Electrochimica Acta **50**, 4551-4556 (2005).
- [13] Ping Wang, Ying-liang Cheng, Zhao Zhang, Journal of Coatings Technology and Research **8** (3), 409-417 (2011).
- [14] H.K. Lee, H.Y. Lee, J.M. Jeon, Surface and Coatings Technology **201**, 4711-4717 (2007).
- [15] C. Cai, X.B. Zhu, G.Q. Zheng, X.Q. Huang, F.H. Cao, J.F. Yang, Z. Zhang, Surface and Coatings Technology **205**, 3448-3454 (2011).