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NICKEL COMPOSITE COATINGS REINFORCED NANO SiC PARTICLES

The paper presents the results of the electrodeposition of nickel composite coatings reinforced with the nano size SiC ceramic particles. The type and size of the ceramic particles or organic additives used play a important role during electrodeposition processes. A Watts type galvanic bath with various organic additives was used. These additives were: 2-sulfobenzoic acid imide, dioctyl sulfosuccinate sodium salt (DSS), sodium dodecyl sulfate, tris (hydroxymethyl) aminomethane and hexamethyldisilizane. The nickel composite coating was electrodeposited on a 2xxx aluminum alloy series substrate (EN-AW 2017) with zinc interlayer. The work concerns the determination of the impact of the change in the zeta potential of SiC nanoceramic particles used on properties of composite coatings (wear resistance, corrosion, etc.). The paper characterized the composite nickel coatings on aluminum alloy using SEM techniques, wear resistance tests by TABER method and coating adhesion to the substrate using the "scratch test" method. The corrosion resistance of coatings was also tested using electrochemical methods. The research allowed to determine the effect of SiC nanoceramic particle size on the value of the zeta potential in the model KCl solution.

Keywords: nano particles**,** organic additives, SiC, composite coatings, nickel coatings, zeta potential

1. Introduction

Available literature data on the impact of dispersion particle size on their percentage share in composites published by various authors are different. In the Ni-ZrO_2, Ni-TiC and Ni-SiC systems [1], it has been observed that as the particle size increases, the proportion of the dispersion phase in the matrix decreases. For Fe-α-Al_2O_3 [1] and Ni-SiC [2] systems, their volume fraction in the composite increases as the particle size increases. However, in the case of Ni-SiC composite deposition, an increase of SiC dispersed phase in the composite was observed as the particle size increased. This relationship is interpreted by the authors [3] as follows: as the particle size increases, the number of Ni^{2+} ions adsorbed on their surface increases, which entails an increase in Coulomb interactions between the particle and the cathode surface, resulting in an increased proportion of dispersion particles in the composite. As a result of these interactions, a maximum is reached, beyond which the particles are too large and tend to sediment due to the high mass, which leads to a decrease in the proportion of dispersion particles in the composite.

In case of nickel matrix composites, they are deposited from Watts type baths ($NiSO_4$, $NiCl_2$, H_3BO_3) or from aminosulfonate baths (Ni $(SO_3NH_2)_2$, $NiCl_2$, H_3BO_3). Acid baths are used, whose pH ranges from 3 to 5. Addition of boric acid (H_3BO_3) in a limited range of general alkalizing of the electrolyte, which is combined by sharing and nickel on the cathode. Usually, additional substances appear for electrolytes in which composites are secreted. They are intentionally introduced to provide additional composite properties. They can be divided into three main groups. First – substances to be included in the matrix, monovalent ion sets to them, such as: Tl^+ [4], Cs^+ [5,6], NH^{4+}, and chemicals such as alanine, EDTA, polyamines, etc. [7] second – substances improving the surface quality of the composite, their addition in various ways to the content of dispersion components, their occurrence causes that they are used in the strengthening phase, and third – surfactants that facilitate electrolyte wetting of units, and also prevent the use of particle agglomerates in the bath [8].

It should be noted that uniform distribution of the ceramic phase in a composite coating requires the use of a number of organic additives that improve the quality of the plating bath and properties of produced coatings. The introduction of a specific quantity of surfactants to the bath enables obtaining and maintaining a stable dispersion of the ceramic particles in this bath,

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while modification of the zeta potential of particles facilitates their transport and deposition on the electrode. Organic compounds must be selected experimentally to correspond to the type of particles and chemical composition of the plating bath. This study is exploring the possibility of using selected organic compounds, such as: 2-sulfobenzoic acid imide (LSA), dioctyl sulfosuccinate sodium salt (DSS), sodium dodecyl sulfate (SDS), tris (hydroxymethyl) aminomethane (THAM) and hexamethyldisilizane (HMDS) to modify the zeta potential. The aim was to obtain deagglomeration of nanoceramic SiC particles in the plating bath and composite coating, and thereby produce coatings with improved properties (more uniform distribution of ceramic particles in metal matrix and higher microhardnessComposite coatings can be used as an alternative for hard anodic oxide coatings, which are insulator on aluminum (e.g. engine block), or replacement for chrome coatings.

2. Experimental

Nickel composite coatings were prepared in a Watts type bath containing 150 g/l $NiSO_4 \cdot 7H_2O$, 30 g/l $NiCl_2 \cdot 6H_2O$, 30 g/l H_3BO_3 modified with additions of organic compounds, such as: LSA, DSS, SDS, THAM and HMDS in an amount of 2 g/l. The criteria for the selection of organic compounds were based on the beneficial effect of these compounds on the properties of composite coatings when used with other types of the ceramic particles described in [9]. In this study it was decided to use the particles of silicon carbide (SiC) with an average particle size of about 50 nm as hard dispersed particles incorporated into the coating. SiC was introduced to the bath in an amount of 20 g/l. To produce the substrate with a well-developed surface and improved adhesion of coating deposited on the EN AW-2017 aluminum alloy, zinc interlayers were used. The intermediate layer of zinc was obtained by electroless method in a solution containing: 50 g/l ZnO, 200-300 g/l NaOH, 2 g/l $FeCl_3$ and 20 g/l $C_4H_4KNaO_6$. The nickel composite coatings were electrodeposited for 30 minutes using the cathode current density of 4 A/dm^2 in a bath of pH 4 at 40°C. The bath was stirred with a magnetic stirrer and peristaltic pump. The aim of the stirring was to maintain the homogeneity of the slurry and break the agglomerates formed.

The specific surface area of the silicon carbide powder was measured with a Gemini 2360 apparatus from Micromeritics. The density of the silicon carbide powder was measured with an AccuPyc 1330 helium pycnometer. To determine the distribution of particle size, a Nanotec device was used. The electrokinetic potential (zeta potential) of the ceramic particles was measured with a ZETASIZER NANO ZS90 apparatus made by Malvern Instruments Ltd. Studies of the zeta potential were carried out in a model solution of KCl at concentration of 0.01 M with the addition of an organic additives (1 g/l) and SiC particles (0.2 g/l). The applied temperature was 40°C (the operating temperature of the plating bath used for the preparation of composite coatings). Tests were carried out in solutions with the pH value changing every 0.5 unit in a range of 2.5-8.

The microstructure of electrodeposited composite coatings was examined using a Philips XL30 SEM microscope. SEM images (not included in the article) were also used to calculate the volume participation of SiC particles in composite coatings. Ceramic particle content was measured using computer image analysis. The thickness and continuity of coatings were measured on the metallographic cross-sections using a Olympus GX71 light microscope. The microhardness of coatings was measured using a Micromet 5103 microhardness tester. The coating adhesion test was made on a CSM REVETEST Scratch Tester using a Rockwell type indenter in the form of a rounded diamond cone with 2 mm fillet radius. The measurements consisted in making a linear scratch under the gradually increasing indenter downforce. The force was applied in the range of 1-100 N at a rate of 49.5 N/min to produce a scratch of 10 mm length. For each sample 3 measurements were performed. Abrasion tests were performed after 24 h sample acclimatisation under the following environmental conditions: temperature 23 ± 2°C, humidity 50 ± 5%, using a Taber Abraser model 5155 apparatus. The CS-10 abrasive wheels, load of 500 g (4,9 N) and 10 000 abrasive cycles were used.

The roughness of coatings was measured using a Hommel Etamic W10 profilometer made by JENOPTIC. Potentiodynamic characteristics were taken using an AUTOLAB PGSTAT 302 device. The working electrode was nickel electrode with an area of 2 cm^2, the reference electrode was Ag/AgCl 3M KCl electrode, and the auxiliary electrode was platinum electrode. Polarization measurements were performed in a glass cell at 25°C using a naturally aerated 3.5% NaCl solution. The applied polarization rate was 0.01 V/s.

3. Results

The magnitude of the zeta potential indicates the potential stability of the colloidal system (ceramic parts in the galvanic bath). When particles, in the galvanic, bath have a high negative or positive zeta potential, they will tend to repel each other with no chance to agglomerate. When the particles have a low zeta potential, there are no forces to prevent their approaching each other closely and agglomeration occurs. Generally, the potential of + 30 mV or -30 mV is a line marking the division between stable and unstable suspensions. Particles with an absolute value of the zeta potential higher than 30 mV are considered to be stable. Figures 1-5 illustrate the change of the zeta potential of SiC particles with the pH of the solution with different additives.

Table 1 shows the characteristics of the nanosize silicon carbide used in the tests. The specific surface area and density of the SiC powder were determined and the particle size distribution was calculated. The term d_{50} 1.83 means that 50% of the powder particles were smaller than 1.83 mm. The obtained results may indicate a strong tendency to agglomerate of nano SiC powder used. Figure 6 shows the SEM image of the SiC nanoparticles.

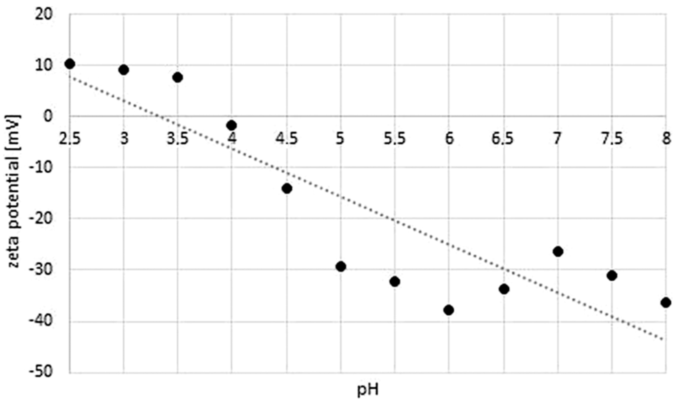

Fig. 1. Zeta potential of SiC particles in 0.01 M KCl with LSA addition

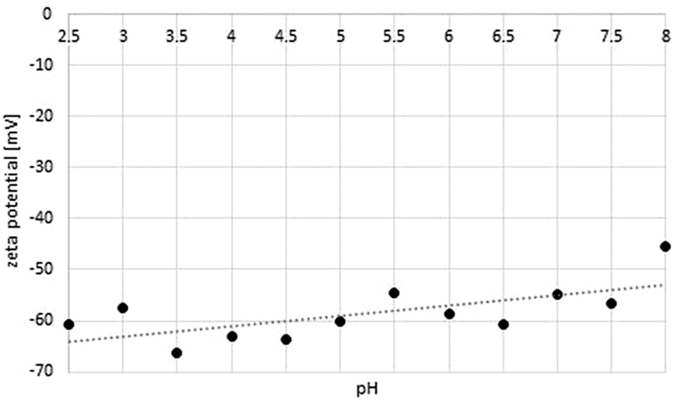

Fig. 2. Zeta potential of SiC particles in 0.01 M KCl with LSA+DSS additions

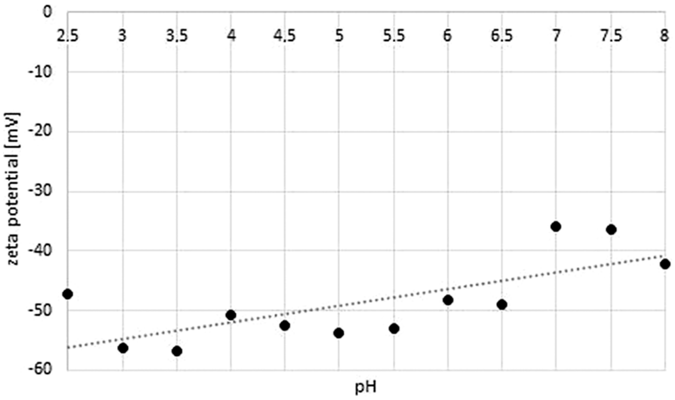

Fig. 3. Zeta potential of SiC particles in 0.01 M KCl with LSA+SDS additions

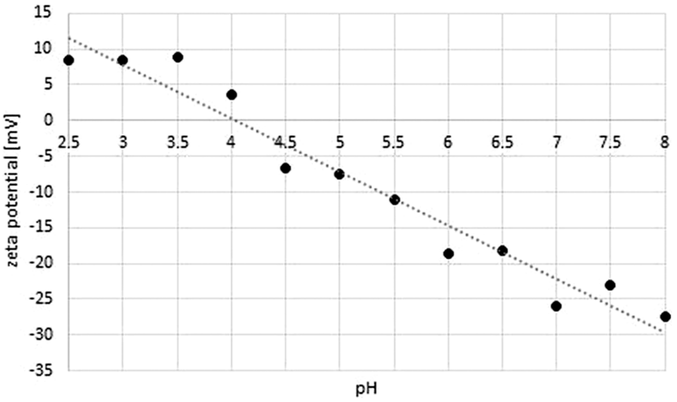

Fig. 4. Zeta potential of SiC particles in 0.01 M KCl with LSA+THAM additions

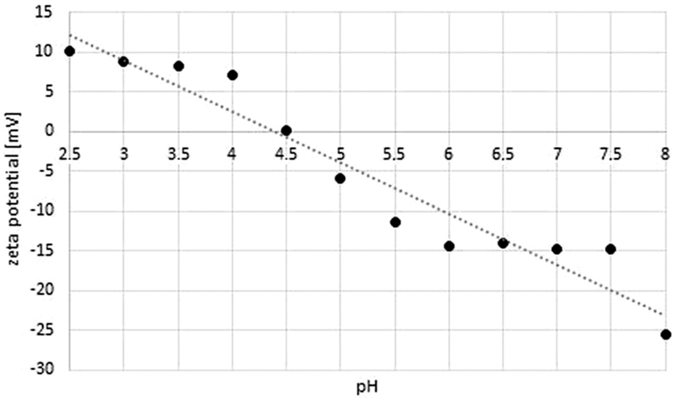

Fig. 5. Zeta potential of SiC particles in 0.01 M KCl with LSA+HMDS additions

TABLE 1

Silicon carbide characteristics

Specific surface area [m^2/g]	**Density [g/cm^3]**	**Grain size distribution d$_{50}$ [μm]**
28.8	3.01	1.83

Figures 7-11 show the results of SEM examinations of the plan view of electrodeposited composite coatings. SEM images (not included in the article) were also used to calculate the volume participation of SiC particles in composite coatings. Ceramic particle content was measured using computer image analysis. The following percentage by volume of ceramic particles in composite coatings was found: LSA 0.14%, LSA+DSS 0.04%, LSA+SDS 0.08%, LSA+THAM 0.9%, LSA+HMDS 0.53%.

The results of coating microhardness measurements are shown in Table 2.

TABLE 2

Microhardness of composite coatings

Type of organic additives	**Microhardness, [HV 0.5]**
—	276±8
LSA	472±8
LSA+DSS	472±10
LSA+SDS	452±7
LSA+THAM	476±12
LSA+HMDS	495±9

Coatings with additions: LSA, LSA+DSS and LSA+THAM have approaching microhardness. The highest microhardness has the LSA+HMDS coating and the lowest LSA+SDS coating. The results of abrasion resistance tests (table 3) showed that the best abrasion resistance has the nickel coating with additions of LSA+HMDS (mass loss 12.2 mg) and LSA (12.6 mg).

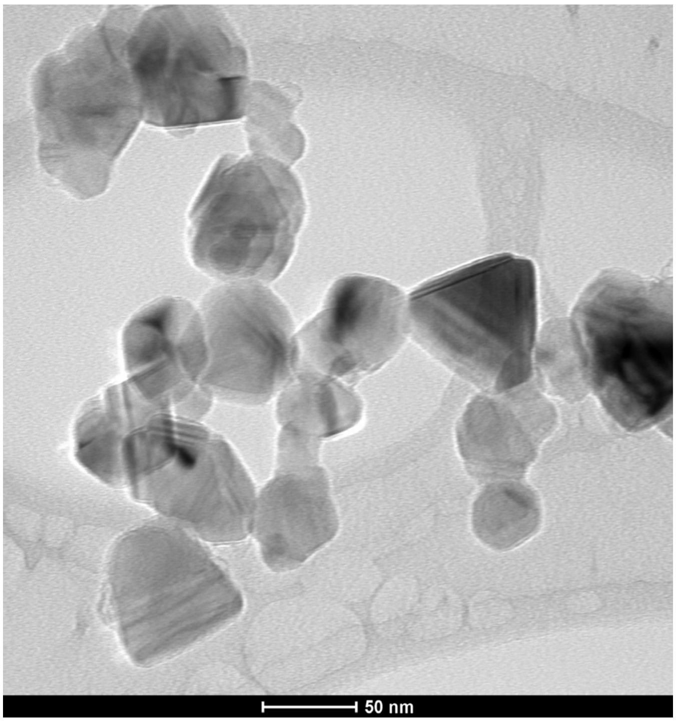

Fig. 6. Silicon carbide nanoparticles morphology

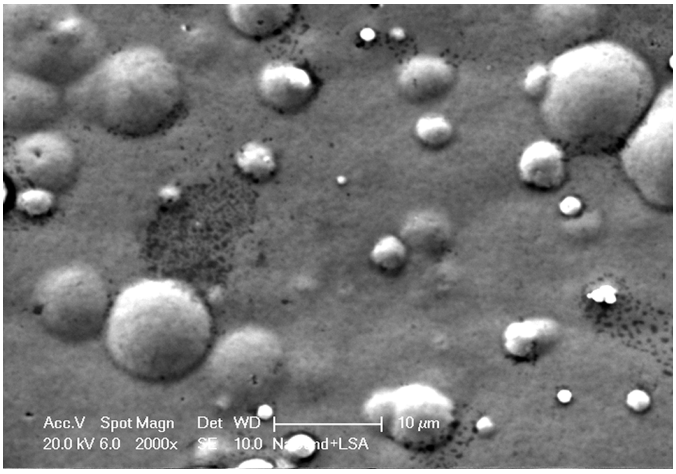

Fig. 7. Surface images of composite coating with LSA addition

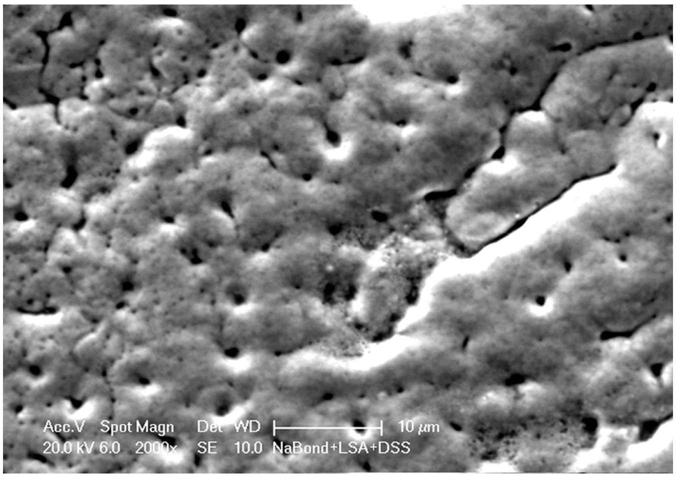

Fig. 8. Surface images of composite coating with LSA+DSS additions

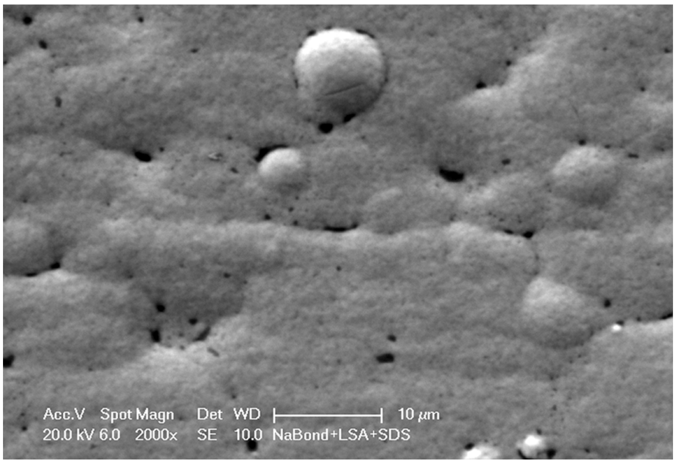

Fig. 9. Surface images of composite coating with LSA+SDS additions

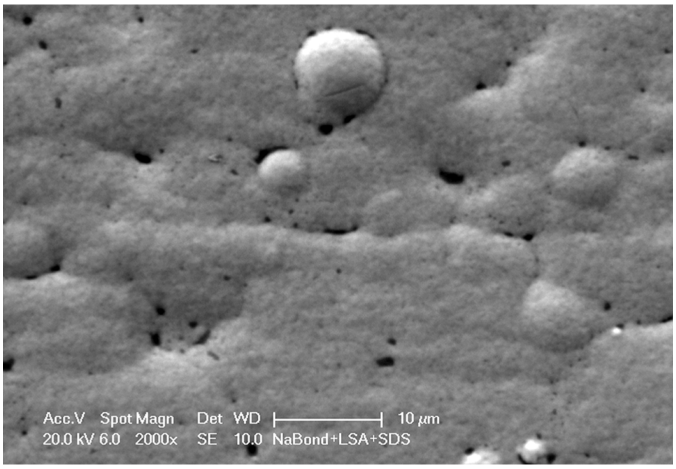

Fig. 10. Surface images of composite coating with LSA+THAM additions

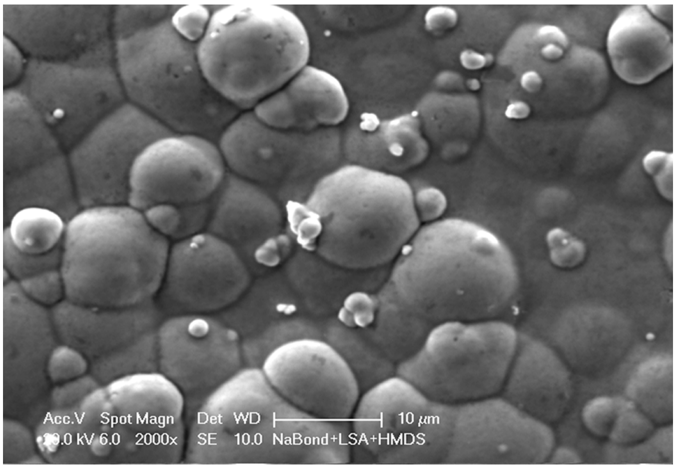

Fig. 11. Surface images of composite coating with LSA+HMDS additions

Table 4 gives the results of scratch resistance test. The only coating characterized by a smooth crack surface and no cracks is the LSA + HMDS coating (Fig. 12). The remaining ones have cracks perpendicular to the force applied, indicating the cohesive nature of the cracks.

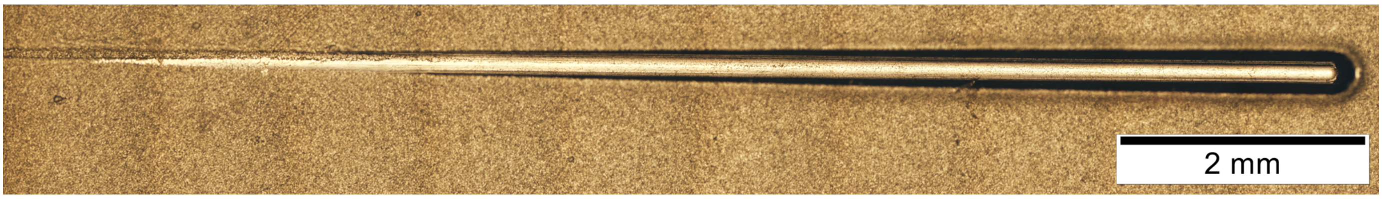

Fig. 12. Scratch test result for the LSA + HMDS coating

TABLE 3

Abrasion resistance of composite coatings by TABER method

Type of organic additives	Mass loss, [mg]
LSA	12.6±0.4
LSA+DSS	20.1±1.0
LSA+SDS	15.6±1.9
LSA+THAM	15.1±0.9
LSA+HMDS	12.2±0.6

TABLE 4

Scratch test results

Type of organic additives	Force, [N]
LSA	26
LSA+DSS	21
LSA+SDS	23
LSA+THAM	17
LSA+HMDS	15

Table 5 shows the results of coating roughness measurements and standard deviations from the values obtained. The final result is an average of five measurements. The following indicators were used: R_a – the arithmetic mean of the deviation of the roughness profile from the mean line, R_z – the height of the roughness profile in a 10 point scale, and $R_{\max}$ – the maximum height of the roughness profile.

TABLE 5

The results of roughness measurements

Type of organic additives	R_a [μm]	R_z [μm]	$R_{\max}$ [μm]
LSA	0.5	4.3	6.7
LSA+DSS	0.4	2.9	4.7
LSA+SDS	0.5	4.1	6.6
LSA+THAM	0.7	5.6	8.7
LSA+HMDS	0.5	4.7	7.2

TABLE 6

The results of the electrochemical test

Type of organic additives	i_{corr} [μA/cm^2]	E_{corr} [V]
LSA	0.03	-0.24
LSA+DSS	0.07	-0.20
LSA+SDS	0.23	-0.20
LSA+THAM	0.07	-0.21
LSA+HMDS	0.54	-0.24

The potentiodynamic measurements were performed in a 3.5% NaCl solution. Based on the polarization curves, the corrosion current density (i_{corr}) and corrosion potential (E_{corr}) were calculated. The obtained results of electrochemical measurements made by the potentiodynamic method are summarized in Table 6.

4. Discussion

Studies of the zeta potential in a model solution of KCl (Figs. 1-5) have proved that the stable dispersion of the ceramic particles in a plating bath was obtained only in solutions containing the mixtures of LSA+DSS and LSA+SDS. Similar results were also obtained in previous studies using micrometer SiC particles for both types of organic additives [9]. The zeta potential after the addition of LSA + DSS and LSA + SDS has assumed the values ranging from –30 to –60 mV. In the case of other organic compounds, except LSA at the pH values ranging from 3.5 to 4.5 (the operating range of pH values in the Watts bath), the isoelectric point has been reached. It means that the dispersion was unstable and particles formed agglomerates. Moreover, the zeta potential value was low enough to hinder the formation of a stable bath capable of producing composite coatings with a high content of the ceramic particles embedded in metal matrix. However, the results of examinations of the coatings cross sections did not fully support these findings due to very small particle sizes. Malfatti et al. [10] in work on the deposition of NiP-SiC coatings with the addition of SDS observed a decreasing number of the ceramic particles in coating relative to coating without the addition of organic compounds. They tried to explain this phenomenon in terms of the reduced surface tension and change in the properties of particles now converting into a hydrophobic system. Our studies using the Ni-SiC system have not confirmed the aforementioned effect of the SDS addition, both in this work and in the early ones using SiC with a micrometer size. A different situation was observed in the case of the LSA + THAM and LSA + HMDS systems. In both cases, the zeta potential measured in the solution of KCl at a pH of 3.5-4.5 has indicated a value close to zero (the isoelectric point). Composite coatings containing LSA (Fig. 7), LSA+SDS (Fig. 9), LSA+THAM (Fig. 10) and LSA+HMDS (Fig. 11) additions showed the presence of "nodular build-ups" on the surface. The organic additives LSA+DSS, conferred to those coatings an excellent surface finish. It was observed on plan-view images (Fig. 8) and confirmed by the results of roughness measurements (Table 5).

All additives of organic compounds had a beneficial effect on the microhardness of the produced coatings compared to a coating without organic additives. The microhardness increase to 495 HV0.05 for the LSA+HMDS and above 470 HV0.05 for the LSA, LSA+DSS and LSA+THAM proves a significant improvement in the microhardness of the resulting coatings. Based on the results of the scratch resistance test, it can be concluded that all coatings are characterized by a sufficiently strong adhesion to the substrate. Studies have shown total absence of partial (local) or total delamination of coatings. Figure 12 shows an example of scratch test result for the LSA + HMDS coating. The observed destructive mechanism has involved the formation of cohesive cracks progressing towards the outside area of the scratch path and cracks forming in the next step within the field of friction as a result of coating deformation made by the indenter. The values of forces observed in individual coatings are summarized in Table 3. The lowest value of the force necessary to wipe the coating off was observed in the case of the LSA+HMDS addition and it amounted to 15 N. For the LSA addition, this force has increased to 26 N. In the case of the LSA + DSS and LSA + SDS additions, the forces were similar and amounted to 21 N and 23 N, respectively.

The results of roughness measurements (Table 5) were consistent with the SEM examinations of coating microstructure. The highest value of roughness (R_a parameter) was observed in the coating with the additions of LSA+THAM (R_a 0.7 μm), while the lowest value was obtained in the coatings containing the additions of LSA+DSS (R_a 0.4 μm). LSA and LSA+SDS additives gave values of R_a 0.5 mm.

Based on the the values of corrosion current density (i_{corr}) obtained in the studies of corrosion resistance carried out by the electrochemical method (Table 6), it was concluded that the use of organic additives: LSA, LSA+DSS and LSA+THAM are characterized by a low value of corrosion current density which indicates a higher corrosion resistance in relation to the coatings such as: LSA+SDS and LSA+HMDS. The value of corrosion potential for all coating systems is similar and equal –0.20 to –0.24 mV

5. Conclusions

1. Nanometric sizes SiC particles are harder to deposit in nickel coatings than their micrometer equivalent. The percentage of particles determined by the SEM technique does not exceed 1%.
2. The coatings with the highest microhardness and resistance to abrasive wear was obtained with the additions of LSA + HMDS.
3. The highest volume content of SiC particles in the coating does not guarantee the highest parameters of microhardness and resistance to abrasive wear.

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