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EFFECT OF VARIOUS ORGANIC ADDITIVES IN GALVANIC BATH ON PROPERTIES
OF Ni-SiC COMPOSITE COATINGS

The paper presents the results of the electrodeposition of nickel composite coatings reinforced with the ceramic SiC particles. A Watts type galvanic bath modified with various organic additives was used. These additives were: 2-sulfobenzoic acid imide (LSA), dioctyl sulfosuccinate sodium salt (DSS), sodium dodecyl sulfate (SDS), tris (hydroxymethyl) aminomethane (THAM) and hexamethyldisilizane (HMDS). The nickel composite coating was electrodeposited on a 2xxx aluminum alloy series substrate (EN-AW 2017) with zinc interlayer. Studies concerned the effect of the applied organic additives on properties of composite coatings such as: microstructure, microhardness, adhesion to the substrate, corrosion resistance and roughness. The structure of the coatings was assessed by scanning electron microscopy and light microscopy. Based on the studies of zeta potential it was found that the bath modification had a significant impact on the amount of the ceramic phase embedded in metal matrix. The tests conducted in a model 0.01 M KCl solution were not fully representative of the true behavior of particles in a Watts bath.

Keywords: organic additives, SiC, composite coatings, nickel coatings, zeta potential

1. Introduction

Composite coatings are materials which consist of at least two components (phases) of different characteristics, combined in such a way that improved or novel properties are obtained compared to the same materials used separately. An interesting group of materials is that of metal matrix composite coatings containing in their composition very fine and hard particles of carbides, oxides or nitrides. Coatings of this type are the most promising and growing group of materials, and enjoy great interest as an object of theoretical studies and practical applications.

Composite coatings are electrodeposited in various types of plating baths, usually of complex composition, reinforced with the additions of ceramic powders in the form of dispersed particles. The most commonly used dispersed particles are: oxides [1], sulfides, borides [2-3], nitrides [4], silicides [5] and carbides [6]. The choice of the compound depends on the type of matrix. The particles introduced into the matrix are characterized by the melting point and microhardness definitely higher than the melting point and microhardness of the matrix material. The addition of ceramic particles has also some impact on other properties of produced coatings, including their abrasion resistance and corrosion.

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 spe-

cific quantity of surfactants to the bath enables obtaining and maintaining a stable dispersion of the ceramic particles in this bath, 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 ceramic 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 microhardness).

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: 2-sulfobenzoic acid imide (LSA), dioctyl sulfosuccinate sodium salt (DSS), sodium dodecyl sulfate (SDS), tris (hydroxymethyl) aminomethane (THAM) and hexamethyldisilizane (HMDS) introduced in an amount of 2 g/l. The criteria for the selection of

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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 the technical literature [7-13]. In this study it was decided to use the particles of silicon carbide (SiC) with an average particle size of about 5 μm 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. 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 2 or 3 measurements were performed, depending on the consistency of the results obtained. 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. Measurements of corrosion potential were made after 60 minutes of stabilization of open circuit potential.

3. Results

When the plating bath with dispersed ceramic particles is prepared, the parameter important for its functional application is the zeta potential of ceramic particles. The value of this potential is a key indicator of the future stability of the suspension. When particles in the slurry have a high negative or positive zeta potential, they will tend to repel each other with no chance to flocculate. When the particles have a low zeta potential, there are no forces to prevent their approaching each other closely and flocculation 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 [14]. 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 silicon carbide used in the tests. The specific surface area and density of the SiC powder were determined and the particle size distribution
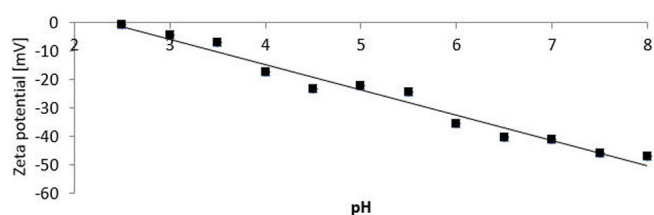

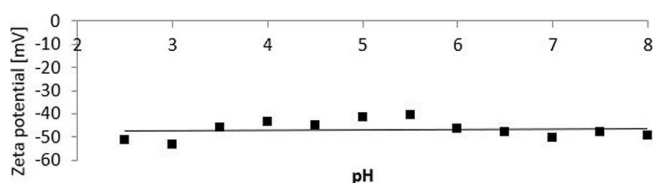Fig. 1. Zeta potential of SiC particles in 0.01 M KCl with LSA addition

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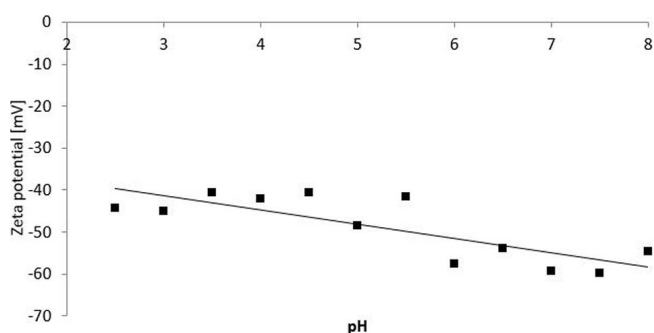

Fig. 3. Zeta potential of SiC particles in 0.01 M KCl with LSA+SDS additions
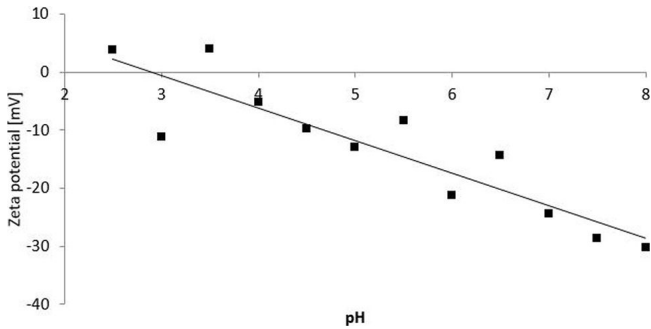
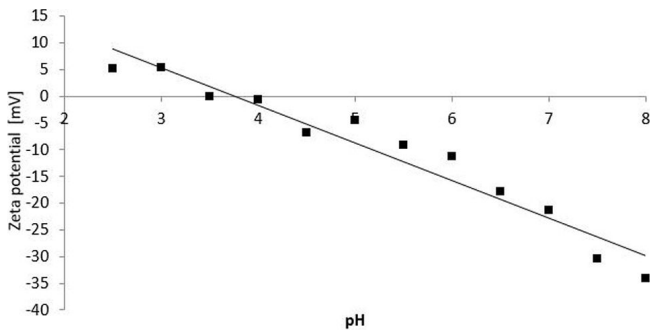Fig. 4. Zeta potential of SiC particles in 0.01 M KCl with LSA+THAM additions

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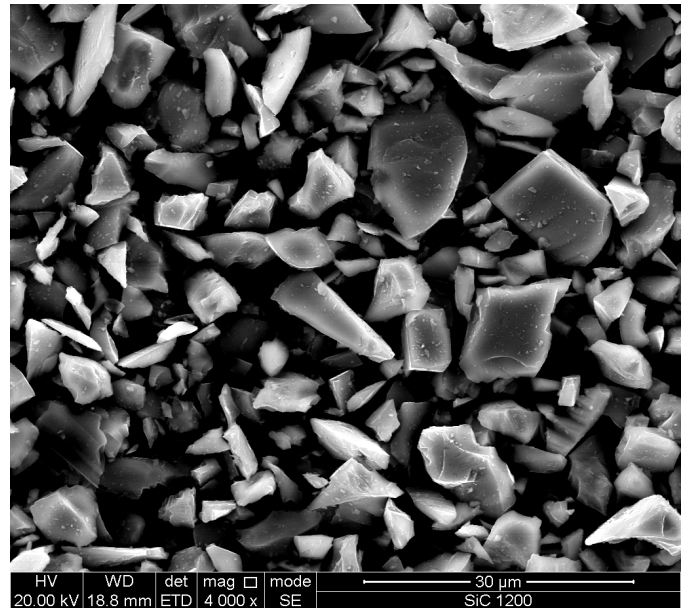

Fig. 6. Silicon carbide particles morphology

TABLE 1

Silicon carbide characteristics

Specific surface area [m²/g]	Density [g/cm³]	Grain size distribution d_{50} [μm]
1.18	3.19	4.9

was calculated. The term d_{50} 4.9 means that 50% of the powder particles were smaller than 4.9 mm. Figure 6 shows the SEM image of the SiC particles with different morphology and size. Based on microscopic observations it was found that particles of SiC powder had different distributions of individual grain sizes and sharp-edged morphology.

Figures 7-11 shows the results of SEM examinations of the plan view of electrodeposited composite coatings and the results of examinations of sample cross sections done by light microscopy (7b-11b).

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

TABLE 2

Microhardness of the composite coatings

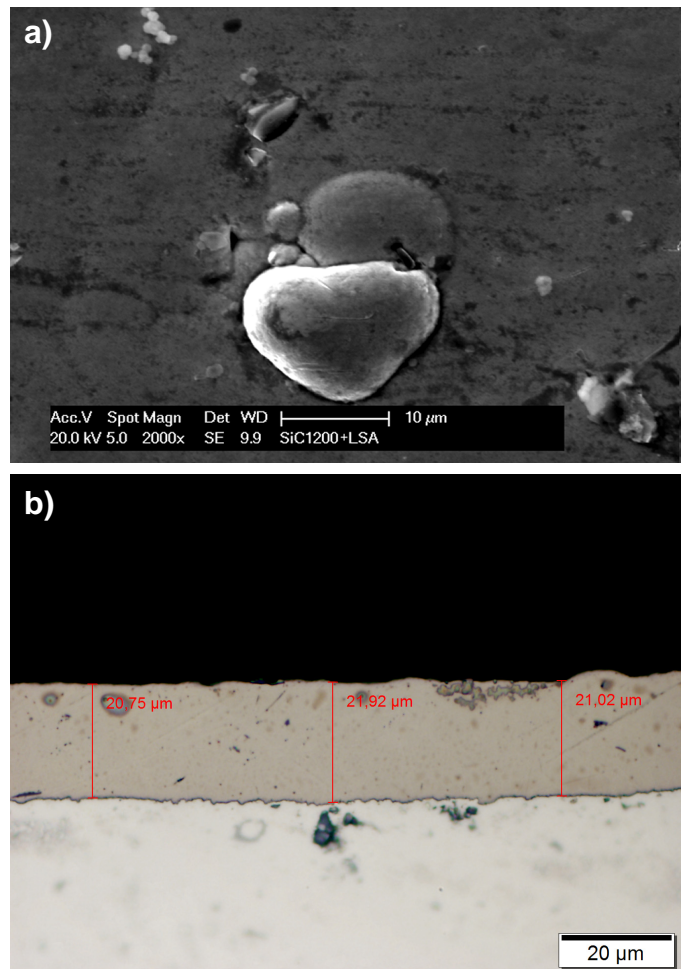| Type of organic additive	Microhardness [HV 0.5]
LSA	459±6
LSA+DSS	433±8
LSA+SDS	415±12
LSA+THAM	536±5
LSA+HMDS	464±5

Fig. 7. Surface images of composite coating with LSA addition a) plan view, b) cross section cross section

The results of abrasion resistance tests (Table 3) showed that the best abrasion resistance has the nickel coating with additions of LSA+THAM.
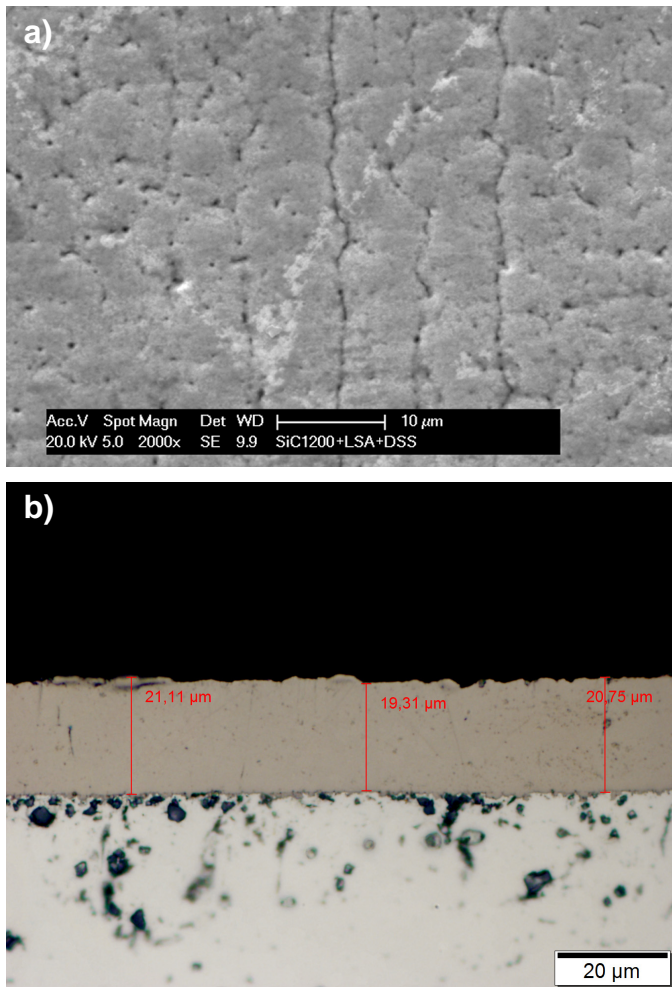
Fig. 8. Surface images of composite coating with LSA+DSS additions a) plan view, b) cross section
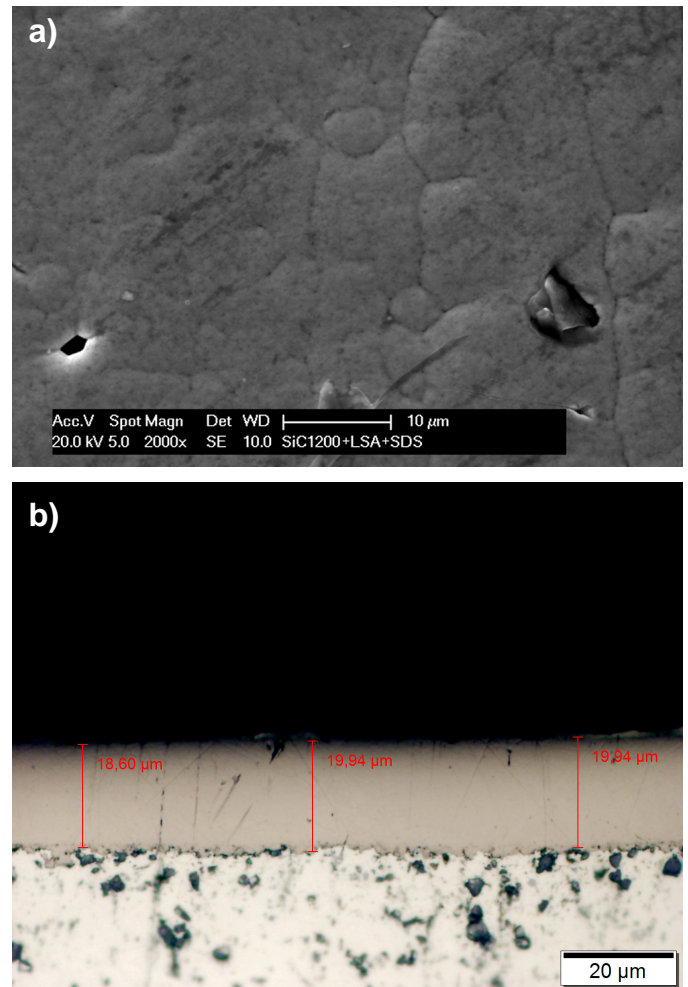

Fig. 9. Surface images of composite coating with LSA+SDS additions a) plan view, b) cross section

TABLE 3

Abrasion resistance of composite coatings by TABER method

Type of organic additive	Mass loss [mg]
LSA	7.8±1.9
LSA+DSS	17.1±0.9
LSA+SDS	14.3±0.4
LSA+THAM	5.3±0.3
LSA+HMDS	11.9±0.9

Table 4 gives the results of scratch resistance test.

TABLE 4

Scratch test results

Type of organic additive	Force [N]
LSA	17.5
LSA+DSS	21
LSA+SDS	28
LSA+THAM	18
LSA+HMDS	20

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 additive	R_a [μm]	R_z [μm]	R_{max} [μm]
LSA	0.3	2.8	4.1
LSA+DSS	0.4	4.1	5.8
LSA+SDS	0.3	2.1	4.4
LSA+THAM	0.6	4.4	5.2
LSA+HMDS	0.8	5.4	6.7

The potentiodynamic measurements were performed in a 3.5% NaCl solution. Polarization started after one hour stabilization of the potential under open circuit conditions. Based on the polarization curves, the corrosion current density (i_{corr}) and
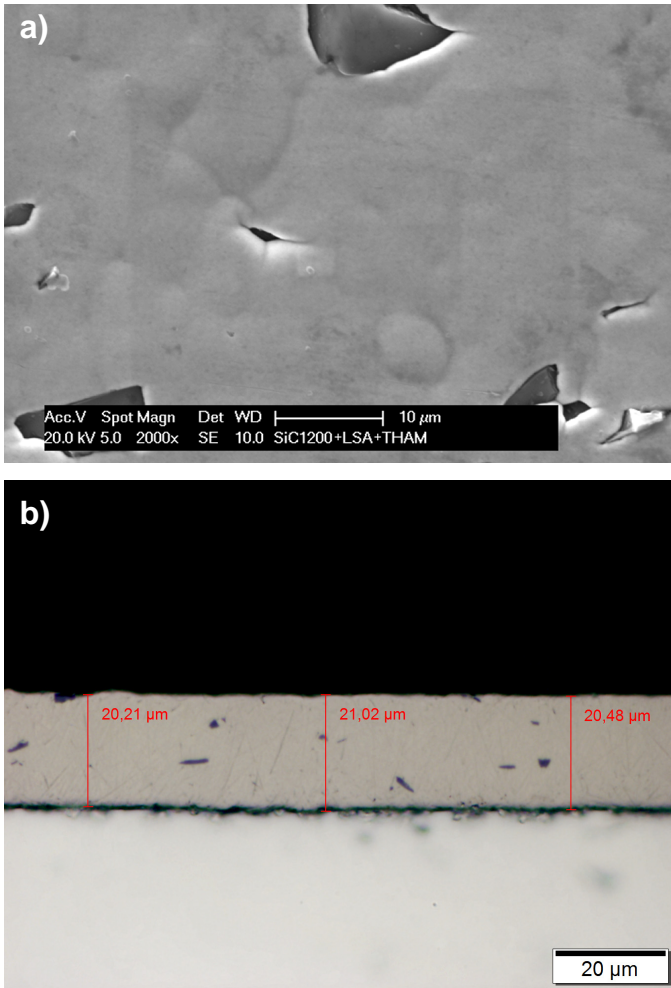
Fig. 10. Surface images of composite coating with LSA+THAM additions a) plan view, b) cross section
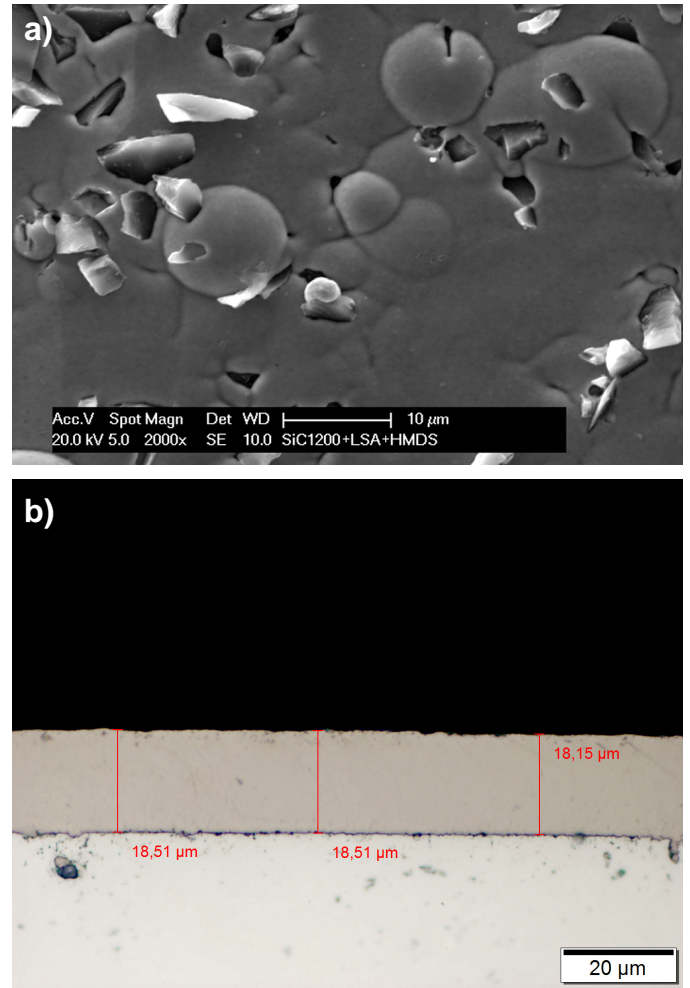

Fig. 11. Surface images of composite coating with LSA+HMDS additions a) plan view, b) cross section
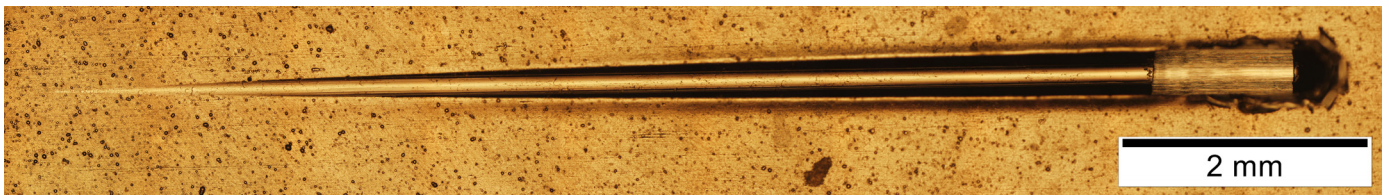

Fig. 12. Scratch test result for the LSA + SDS coating

corrosion potential (E_{corr}) were calculated. The obtained results of electrochemical measurements made by the potentiodynamic method are summarized in Table 6 and in Figure 13.

TABLE 6

The results of the electrochemical test

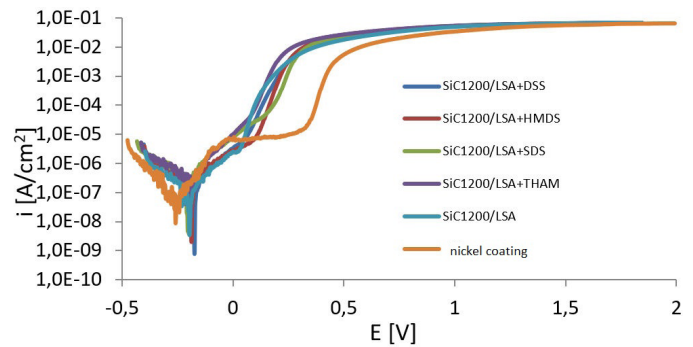| Type of organic additive	i_{corr} [A/dm^2]	E_{corr} [V]
LSA	$7.31 \cdot 10^{-8}$	-0.20
LSA+DSS	$5.59 \cdot 10^{-8}$	-0.18
LSA+SDS	$1.93 \cdot 10^{-7}$	-0.20
LSA+THAM	$2.26 \cdot 10^{-7}$	-0.19
LSA+HMDS	$8.92 \cdot 10^{-8}$	-0.20

Fig. 13. Polarization curves in 3.5% NaCl for nickel and composite coatings

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. 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, 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. In the case of LSA + DSS and LSA + SDS, the obtained values of zeta potential may explain the greater number of ceramic particles embedded in a metal matrix, when compared with the sole addition of LSA. Malfatti et al. [13] 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. 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), although the amount of the ceramic particles in these coatings was definitely higher than in the coatings without the aforementioned additives. The probable explanation of this situation is to be sought in the different behavior of the ceramic particles in a model system and in the true Watts type bath.

Composite coatings containing LSA additions showed the presence of "nodular build-ups" on the surface (Fig. 7a). The organic additives used in a double configuration of LSA+SDS, LSA+DSS, LSA+THAM and LSA+HMDS conferred to those coatings an excellent surface finish. It was observed on plan-view images (Fig. 8a-11a) and confirmed by the results of roughness measurements (Table 5). Microscopic examinations have confirmed also the continuous nature of the obtained composite coatings. The coatings thickness measured on the cross sections was 18-21 mm.

All additives of organic compounds had a beneficial effect on the microhardness of the produced coatings, but the most efficient seemed to be the LSA + HMDS mixture. The microhardness increase from 459 HV0.05 for the LSA to 536 HV0.05 for the LSA + THAM proves a significant improvement in the microhardness of the resulting coatings. The microhardness increase is due to a higher content of the ceramic particles of silicon carbide in the composite coating. 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. Nickel composite coatings differed from each other mainly in the value of forces necessary to break the coating continuity, but this was probably due to a difference in the coating thickness. 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 addition and it amounted to 17.5 N. For the LSA + THAM addition, this force has increased to 18 N. In the case of the LSA + HMDS and LSA + DSS additions, the forces were similar and amounted to 20 N and 21 N, respectively. The greatest force to wipe the coating off was necessary in the case of the LSA + SDS system (28 N).

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+HMDS (R_a 0.8 μm), while the lowest value was obtained in the coatings containing the additions of LSA and LSA+SDS (R_a 0.3 μm). Other additives gave values of R_a in terms of 0.4-0.6 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 such as: LSA + DSS, LSA + SDS and LSA + THAM has increased the corrosion current values, thus indicating the corrosion resistance inferior to the single addition of LSA. Compared to the three aforementioned additives, the addition of LSA + HMDS gave a lower corrosion current density of $8.92 \cdot 10^{-8}$ A/dm^2, but this value was still higher than the value obtained in a coating containing the single addition of LSA. A drop in the value of polarization resistance proving the deterioration of corrosion resistance was found in all cases of the use of double additives.

5. Conclusions

1. Preparation of a stable dispersion of silicon carbide ceramic particles in a galvanic bath by modifying the value of the zeta potential does not guarantee obtaining a composite with uniformly distributed particles and the lack of their agglomeration in a nickel matrix.
2. The coating with the highest microhardness and resistance to abrasive wear was obtained with the additions of LSA + THAM.

3. All used organic additives introduced to the plating bath allows obtaining continuous composite coatings strongly adhered to the aluminum substrate.

4. All analyzed composite coatings have a similar corrosion resistance.

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