NICKEL COATINGS WITH SUBMICROMETRIC HARD CERAMIC PARTICLES ON ALUMINUM ALLOYS

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Abstract

This paper present the results of electrolytic nickel composite coatings manufacture. The process was conducted in Watts-type solutions with the addition of finely dispersed hard ceramic particles of alumina (Al_2O_3) in concentrations of 50 and 100 g/l. The coatings were produced on aluminum alloys 2xxx and 5xxx series. Morphology, structure and microhardness of the obtained composite coatings were examined. The corrosion resistance of coatings was investigated in the neutral salt spray test (NSS) and by electrochemical methods. The results of Taber abrasion resistance test were also given. Based on the overall results of studies, a varying effect of nickel sulfate and Al_2O_3 concentration in bath on the properties of composite coatings deposited on aluminum alloys was stated.

Introduction

Electroplated nickel coatings are widely used in various industries. Attractive appearance of coatings, high corrosion resistance, and good mechanical properties allow to use such coatings for decorative, protective and technical purposes. Even better properties of the coatings can be achieved when they are made as composite systems. Composites are materials with new properties that differ from their homogeneous and single-phase counterparts. They consist of at least two components, the properties of which are improved or new as compared to the individual components applied separately. In the case of nickel coatings, as a reinforcing phase are used, among others, the ceramic particles of Al_2O_3 or SiC [1-4]. The size and amount of the introduced reinforcing phase decide about the properties of the newly formed nickel composite coatings.

Forming a composite layer of hitherto unattainable properties is a process that relies not only on the selection of optimum components of this layer, but also on the possibility of producing a specific structure in the composite material.

One of the primary purposes of the fabrication of nickel composite coatings on machine parts and equipment is the improvement of performance characteristics. With the ever increasing needs of industrial practice, traditional coating materials are no longer sufficient. This has resulted in the rapid development of production of various types of composite materials.

For the manufacture of nickel composite coatings, a plurality of baths with different chemical compositions are used. The most extensive industrial use have found Watts-type baths based on three basic components: nickel sulfate, nickel chloride and boric acid. The thickness of nickel coatings deposited on aluminum and its alloys is 3÷40 μm; the thickness of technical coatings exceeds 50 μm.

The purpose of this study was to investigate the effect of the concentration of nickel sulfate and Al_2O_3 in bath on the properties of coatings, their abrasion resistance in particular. Coatings of this type are used, among others, as a protection from wear on exposed to abrasion parts made of aluminum alloys. Abrasion resistance does not depend on microhardness only, but is also related with the type of coating. In contrast to hard anodic oxidation coatings with thermal insulation properties, nickel coatings are characterized by good thermal conductivity, and as such can be used on parts made of aluminum alloys which should offer high heat dissipation rate, to mention as an example cylinder blocks in I.C. engines.

Making proper coating requires adequate pre-treatment of the surface. In the case of aluminum alloys, electrolytic nickel coatings are generally deposited on surfaces on which intermediate layers have been produced previously.

Characteristics of material and research methodology

For studies of nickel composite coatings with dispersed Al_2O_3 particles the following alloys were selected:

- wrought alloys 2xxx series with Cu additions – specifically the EN-AW-2017A (AlCu4MgSi (A)) alloy, which in the entire high-strength 2xxx series is the one most commonly used. Its main applications are for the machinery parts exposed to wear during operation, including worm gears and pulley drives. The copper content in the alloy is from 3.5 to 4.5%,
- wrought alloys without the addition of Cu - specifically the EN-AW-5754 (AlMg3) alloy, which in this series is the one most commonly used for parts of machines and equipment exposed to wear such as pulley wheels.

Nickel composite coatings were produced on aluminum alloys in the Watts-type baths. The production process was preceded by cleaning of the surface (surface pretreatment) and producing an intermediate zinc coating in zincate solutions.

Surface pretreatment carried out on samples of aluminum alloys included grinding with emery cloth, degreasing, and etching. The digestion was carried out in a 100 g/l solution of NaOH at ambient temperature, time: 3-5 minutes. Brightening was carried out in a 200 g/l solution of HNO_3 at ambient temperature, time: 1-5 minutes.

On elements with properly cleaned surface, an intermediate layer was produced to improve the composite coating adhesion to the substrate. The intermediate zinc layer was produced in a solution of the following chemical composition: 50 g/l ZnO, 200-300 g/l NaOH, 2 g/l $FeCl_3$, 20 g/l $KNaC_4H_4O_6 \cdot 4H_2O$. After production of intermediate zinc layer, nickel composite coatings were produced on those elements.

Nickel composite coatings were deposited under galvanostatic conditions. The following parameters were observed: current density of 6 A/dm^2, time of 60 minutes and temperature of 60°C. The main bath components included nickel sulfate ($NiSO_4 \cdot 7H_2O$)

- 100-250 g/l, nickel chloride ($NiCl_2 \cdot 6H_2O$) - 30 g/l and boric acid (H_3BO_3) - 30 g/l. The addition of an organic matter was also introduced; it was saccharin in an amount of 2.0 g/l. The bath before the formation of the composite coating was purified using activated carbon and overworked with current of 0.2-0.3 A/dm^2. The bath pH value was kept constant at a level of 3.8 ± 0.2 adding a mixture of HCl-H_2SO_4 (1: 1) or NaOH [5-6].

The bath was enriched with the Al_2O_3 ceramic particles of submicrometric size (average particle size was 0.8 μm) added in an amount of 50 and 100 g/l. As anode, nickel plates with a purity of 99.9% were used, cathode was made of 2017A and 5754 aluminum alloys.

The fabricated nickel composite coatings were subjected to detailed examinations. Their thickness was measured by a coulometric method with a CULOSCOPE CMS-STEP device, and by optical microscopy on the cross-section of samples using an OLYMPUS GX71 optical microscope. Structure was examined under a Philips XL30 scanning electron microscope. The microhardness of coatings was measured with a Buehler Micromet 5103 microhardness tester. Abrasion resistance tests were performed on the composite coatings using a TABER test device model 5155. The test parameters were as follows: load of 1000 g, number of cycles: 1000, abrasive wheels of CS-17 type, temperature of 23±2°C, humidity of 50±5%. Before testing, samples were acclimatized for 24 hours under the specified conditions of temperature and humidity. Corrosion testing in artificial atmosphere was conducted in accordance with the PN-EN ISO 9227: 2012 standard using a DURA HKT1000 salt spray chamber. Basic test parameters were as follows: the corrosive solution of 50 g/l NaCl, pH of the solution - 7.05, pH of the collected solution - 7.2, the volume of collected solution - 1.71 ml/h, the density of the collected solution - 1.035 g/cm^3, test time - 144 h. Electrochemical measurements were performed using an "Autolab" set, which comprised a potentiostat/galvanostat made by EcoChemie BV with a GPES software ver. 4.9 for the experiment control, data collection and analysis of results. The examined electrodes were aluminum samples with the nickel composite coating formed on them, the auxiliary electrode was a stainless steel electrode in the form of a 2 mm diameter wire, while the reference electrode was an Ag/AgCl 3M KCl electrode. As a corrosive solution, 3,5% NaCl was used. The adhesion of the nickel coating to the substrate was determined by the thermal shock method according to the PN-EN ISO 2819 Standard. Samples were heated in a furnace to a temperature of 220°C and then cooled in water at 25°C.

Results

Studies of coating structure by SEM and optical microscopy

Microscopic examinations showed the continuous structure of coatings and good adhesion to the substrate. In nickel coatings, the presence of an evenly distributed Al_2O_3 ceramic phase was observed (Fig. 1). Microscopic examinations also revealed that particles contained in the coating tended to form large clusters (agglomerates) – a phenomenon obviously undesirable. This phenomenon was more pronounced in coatings made in the solutions with a lower content of nickel sulfate (Fig. 2). Microscopic observations of the cross-sections of composite coatings showed that the highest degree of refinement of the hard ceramic particles was obtained in nickel coatings with the nickel sulfate concentration of 250 g/l. At lower concentrations of the nickel sulfate, regardless of the content of Al_2O_3, the single agglomerates formed in the coating were much more numerous.

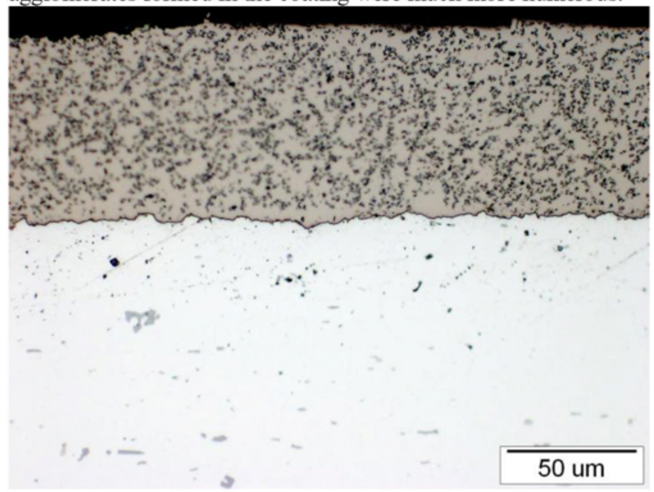

Fig.1. The structure of nickel composite coating produced on 2017A alloy with 250 g/l $NiSO_4 \cdot 7H_2O$ and 50 g/l Al_2O_3

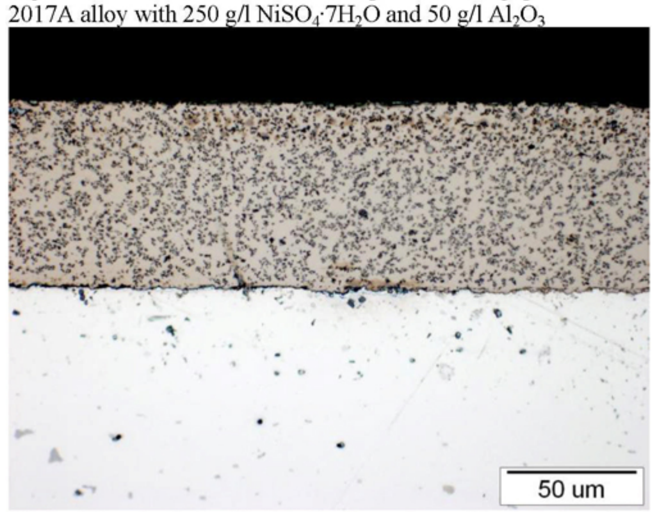

Fig.2. The structure of nickel composite coating produced on 2017A alloy with 150 g/l $NiSO_4 \cdot 7H_2O$ and 100 g/l Al_2O_3

Abrasion resistance test

The results of abrasion resistance test were evaluated by gravimetric method. The method consists in weighing a sample before and after the abrasion test. This type of test is used, among others, for metallic materials coated with either metallic coatings (nickel, chromium) or conversion coatings (anodic oxide coatings). Weighing was performed on an analytical balance with an accuracy of readings of 0.1 milligram. The results of abrasion resistance test were expressed as a calculated value of TWI (Taber Wear Index), which in this case corresponded to the loss of weight in the samples tested.

$$TWI = \frac{W_b - W_a}{N} \times 1000$$

where: W_b – sample weight in mg before the test, W_a – sample weight in mg after the test, N - number of cycles.

The results of abrasion resistance test are summarized in Figures 3-4. In the case of 2017 alloy, the best result (the highest abrasion wear resistance) was obtained for the coating produced in a solution containing 150 g/l of nickel sulfate and 50 g/l of alumina. For coatings produced at twice the alumina content, almost twofold decrease in the abrasion wear resistance was observed. Increasing alumina content in the coating resulted in the formation of large clusters of the ceramic phase (agglomerates). In this particular case those were the alumina clusters and they were falling out of the coating during tribological tests. At the nickel sulfate concentrations of 100, 200 and 250 g/l, somewhat inferior characteristics of the abrasion wear resistance were observed for coatings containing in their composition 50 g/l of alumina. In the case of 5754 alloy, in contrast to the 2017 alloy, the alumina content of 50 and 100 g/l, combined with the nickel sulfate concentration of 150 g/l, gave the lowest abrasion wear resistance. For this alloy, the best parameters of the abrasion wear resistance were obtained when the coating was produced in a solution containing 200 g/l of nickel sulfate and 100 g/l of alumina.

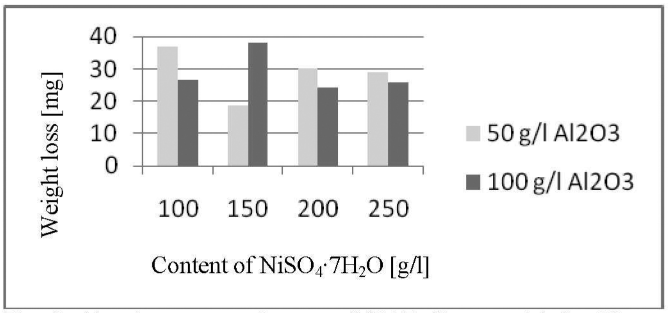

Fig. 3. Abrasion wear resistance of 2017 alloy vs nickel sulfate concentration

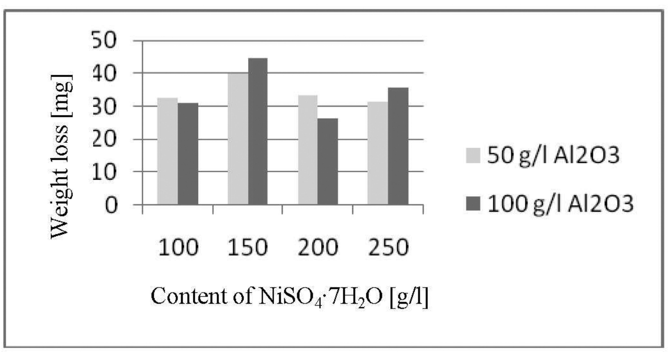

Fig. 4. Abrasion wear resistance of 5754 alloy vs nickel sulfate concentration

Corrosion resistance testing

The progress of corrosion was determined gravimetrically measuring the weight loss in selected samples and using the results of macroscopic observations. The results of gravimetric tests are compared in Table 1.

The weight gain observed in samples marked (+) was the result of penetration of the corrosive solution under the surface of coating produced on the samples tested. The result was subsurface corrosion. Penetrated under the coating, the sodium chloride was difficult to remove with other corrosion products, resulting in the sample gain of weight.

The smallest weight loss was observed in coating produced on the 5754 alloy in the solution containing nickel sulfate in an amount of 250 g/l with the addition of 100 g/l of dispersed alumina particles.

Table. 1 The results of gravimetric tests conducted on the investigated alloys

Sample designation (alloy/$NiSO_4 \cdot 7H_2O$ content/Al_2O_3 content)	Weight loss [g]	Weight loss [g/m^2]	Weight loss [%]
5754/100/50	0.027	48.754	0.5
5754/100/100	+0.055	-	-
5754/150/50	0.026	49.811	0.5
5754/150/100	0.018	33.208	0.4
5754/200/50	0.027	50.001	0.5
5754/200/100	+0.06	-	-
5754/250/50	+0.058	-	-
5754/250/100	0.01	4.925	0.1
2017/100/50	0.042	17.321	0.2
2017/100/100	+0.052	-	-
2017/150/50	0.031	14.233	0.1
2017/150/100	+0.045	-	-
2017/200/50	0.063	51.610	0.4
2017/200/100	0.064	51.614	0.4
2017/250/50	0.062	50.569	0.4
2017/250/100	0.064	51.613	0.4

Figure 5 below shows polarization curves of the examined composite coatings compared to the coating without the addition of ceramic particles. Tests conducted in neutral salt spray did not confirm the effect of nickel sulfate content in bath on the corrosion resistance of nickel composite coatings, but electrochemical studies clearly indicated the superior corrosion resistance of composite coatings compared to coatings without the addition of a ceramic phase. Coatings with the addition of alumina were characterized by the corrosion potential shifted towards the cathode, and the resulting current density values were lower as compared to the metallic coatings that did not contain in their composition a reinforcing phase of Al_2O_3.

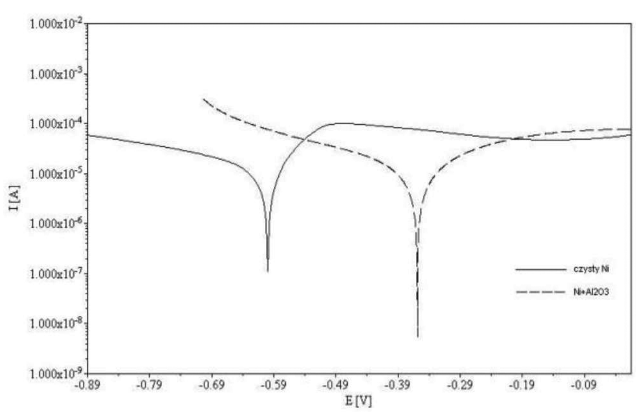

Fig. 5. Polarization curves for Ni and Ni/Al_2O_3 system

The results of electrochemical studies do not confirm with the results obtained in the salt mists. Electrochemical test results are summarized in Table 2. 5754/250/100 sample having the lowest weight loss after salt spray test is characterized by the lowest value of the polarization resistance.

Table. 2 The results of potentiodynamic measurement taken on the investigated alloys in 3,5% NaCl

Sample designation (alloy/$NiSO_4 \cdot 7H_2O$ content/Al_2O_3 content)	I_{corr} [A/cm^2]	R_p [Ω]	E_{corr} [mV]
5754/100/50	$2.73 \cdot 10^{-7}$	$1.11 \cdot 10^{3}$	-287
5754/100/100	$1.31 \cdot 10^{-7}$	$2.89 \cdot 10^{3}$	-305
5754/150/50	$2.49 \cdot 10^{-7}$	$7.22 \cdot 10^{2}$	-331
5754/150/100	$1.32 \cdot 10^{-7}$	$2.42 \cdot 10^{3}$	-285
5754/200/50	$1.83 \cdot 10^{-7}$	$1.37 \cdot 10^{3}$	-277
5754/200/100	$2.35 \cdot 10^{-7}$	$1.63 \cdot 10^{3}$	-292
5754/250/50	$2.90 \cdot 10^{-7}$	$1.36 \cdot 10^{3}$	-279
5754/250/100	$1.45 \cdot 10^{-7}$	$9.85 \cdot 10^{2}$	-279
2017/100/50	$8.33 \cdot 10^{-7}$	$1.60 \cdot 10^{3}$	-299
2017/100/100	$1.77 \cdot 10^{-7}$	$2.89 \cdot 10^{3}$	-320
2017/150/50	$3.00 \cdot 10^{-7}$	$9.89 \cdot 10^{3}$	-331
2017/150/100	$3.16 \cdot 10^{-7}$	$1.17 \cdot 10^{3}$	-277
2017/200/50	$1.17 \cdot 10^{-7}$	$2.67 \cdot 10^{3}$	-266
2017/200/100	$2.93 \cdot 10^{-7}$	$1.23 \cdot 10^{3}$	-289
2017/250/50	$5.77 \cdot 10^{-8}$	$6.87 \cdot 10^{3}$	-257
2017/250/100	$1.13 \cdot 10^{-7}$	$3.45 \cdot 10^{3}$	-266

Microhardness measurements

The results of microhardness measurements taken on the nickel composite coatings are compared in Table 3. The results are an average of five measurements. Based on these results it could be concluded that the highest value of microhardness had the composite coatings produced on the 2017A alloy with 50 g/l of Al_2O_3 and nickel sulfate concentration of 100 and 150 g/l. The situation was similar in the case of 5754 alloy; also here the highest microhardness values were recorded for the nickel sulfate concentration of 100 and 150 g/l and alumina addition in an amount of 50 g/l. In all cases, except for the 5754 alloy and nickel sulfate content of 200 g/l, microhardness values were observed to decrease after increasing the alumina content from 50 to 100 g/l. Increasing the nickel sulfate concentration in plating bath had no favorable effect on the obtained values of microhardness.

Table. 3. Microhardness HV 0.05 of composite coatings as a function of nickel sulfate concentration, Al_2O_3 content and aluminum alloy grade

$NiSO_4 \cdot 7H_2O$ content [g/l]	Alloy grade			
	2017A		5754	
	Al_2O_3 content [g/l]			
	50	100	50	100
100	572	336	432	289
150	519	225	485	225
200	275	258	249	258
250	246	241	264	245

Studies of coating adhesion by the method of thermal shock

The adhesion of metallic coatings, including nickel composite coatings, can be determined by heating and rapid cooling of the examined sample. The method uses difference in the coefficients of expansion of the coating and the substrate. The test result is considered positive when on the sample surface there are no signs of the coating detaching from the substrate, such as blistering, flaking or delamination.

Produced as part of this study program, composite coatings reinforced with Al_2O_3 ceramic phase were characterized by very good adhesion to the metal substrate.

Summary and conclusions

In the test fabrication of nickel composite coatings reinforced with hard dispersed particles of Al_2O_3, deposited on the examined 2xxx and 5xxx series aluminum alloys, continuous gray-color coatings were obtained with a thickness of about 75 μm.

Based on the conducted studies of the properties of the manufactured nickel composite coatings, it was found that:

a) the coatings were characterized by good adhesion to the substrate, were continuous and of a uniform thickness,
b) the highest degree of refinement of the hard ceramic particles in the coating was obtained with the nickel sulfate concentration of 250 g/l,
c) depending on the nickel sulfate and alumina concentration, the microhardness of composite coatings reached the level from 225 to 572 HV 0.05. The values of microhardness were decreasing (with one exception) after increasing the alumina concentration to 100 g/l,
d) Taber measurements of abrasion wear resistance depended on the nickel sulfate concentration and on the content of hard particles in the plating bath,
e) Coatings showed varying corrosion resistance in a neutral salt spray environment.

Acknowledgments

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