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ELECTRODEPOSITION OF Ni/SiC COMPOSITE COATING ON ALUMINIUM

ELEKTROLITYCZNE WSPÓŁOSADZANIE POWŁOK KOMPOZYTOWYCH Ni/SiC NA ALUMINIUM

A hydrometallurgical method for production of Ni/SiC composite coating on aluminium was developed. The following consecutive stages were proposed: zincating of aluminium substrate for 5 min in alkaline zincate solution, electroless nickel deposition for 1 h by immersion in nickel-acetate solution with sodium hypophosphite as a reductant and, finally, electrodeposition of Ni/SiC composite from a chloride-sulphate bath for 6 h at current density of 1 A/dm². The stages were essential to achieve good adherence of the multilayer system to the aluminium surface. Microscopic observations showed uniform thickness of the individual layers over cross-sections of the sample. Microhardness of the composite was approx. 770 HV.

Keywords: Nickel; Composite; Electrodeposition; Aluminium

Opracowano hydrometalurgiczną metodę wytwarzania powłok kompozytowych Ni/SiC na aluminium. Proces obejmuje następujące główne etapy: nakładanie powłoki cynkowej na aluminium na drodze cementacji w roztworze alkalicznym przez okres 5 min; bezprądowe (autokatalityczne) osadzanie powłoki niklowej przez okres 1 godz. przy użyciu podfosforynu sodu jako reduktora; elektrolityczne współosadzanie powłok kompozytowych Ni/SiC z kąpeli chlorkowo-siarczanowej przez okres 6 godz. przy gęstości prądu 1 A/dm². Wymienione etapy pozwalają na uzyskanie układu wielowarstwowego o dobrej wzajemnej przyczepności poszczególnych warstw. Obserwacje mikroskopowe przekrojów poprzecznych próbek wykazały tworzenie się warstwek o równomiernej grubości. Mikrotwardość powłoki kompozytowej nałożonej na aluminium wynosiła ok. 770 HV.

1. Introduction

Aluminium and its alloys are widely used as constructional materials of special importance. They have been found to be well suited for applications that require corrosion resistance, high strength at low density (strength to density ratio higher than for steel), good electric and thermal conductivity. Industrial practice takes the advantage of the aluminium alloys, especially in automobile, aeronautical and aerospace, housing utensils or electronics [1]. However, aluminium base materials characterize usually poor surface properties, which restrict their applications in some fields. To improve the hardness and wear resistance, aluminium alloys are covered by protective layers. These are often nickel-base coatings deposited in electroless [2-4] or electrolysis processes [5]. In some cases, both methods are competitive for providing deposits with ceramic particles uniformly incorporated in the bulk of the layer [4, 6-9]. Highly efficient method for the composite deposi-

tion appears electroplating. It allows to produce a variety of particle-metal matrix combinations from aqueous solutions at high enough deposition rates and low-costs equipment. The most extensive studies were performed on nickel matrix composites that contain incorporated SiC particles. It was found [8, 9] that the presence of SiC particles can increase the hardness of the electroplated nickel coatings from 350-390 HV up to 550 HV.

Independently on the method used to plate aluminium, the process is accompanied by some difficulties due to the tenacious oxide layer present on the substrate surface. Hence, an appropriate pre-treatment stage is essential to provide good adhesion of the metallic coating directly to the metal substrate. The most satisfactory and practical way is zincating conducted in strong alkaline solutions [10]. It allows to dissolve alumina and produce thin uniform zinc layer on the aluminium metal. It protects aluminium surface from reoxidation before subsequent nickel electroless [2, 3] or electrolytic [5] deposition.

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Experiments described below were performed to develop a method for Ni-SiC composite deposition on aluminium substrate. This paper reports the consecutive stages of the hydrometallurgical route: zincating of aluminium, electroless nickel deposition and electrodeposition of Ni-SiC composites. Compositions and microstructures of as-plated layers are also presented.

2. Experimental

The substrates used in this study were aluminium plates with area of 12-15 cm². The procedure for the Ni-SiC composite electrodeposition was carried out in a few stages. Details are shown in Table 1. Samples were ground with abrasive papers, degreased in alkaline carbonate solution, etched in sodium hydroxide solution and then brightened in nitric acid. The substrates were thoroughly rinsed with distilled water after each stage. Zinc interlayer was produced in an alkaline sodium zincate solution at various times to determine optimal zincating conditions. Thickness of the zinc layer was determined with a thickness gauge (Ultrameter AB 400) at few points on the sample surface. Prior to the electroplating experiments, the sample was electrolessly covered with a Ni-P layer by immersion in an acidic nickel-hypophosphite bath. The process was activated by displacement of zinc with nickel. The deposited nickel nuclei were catalytic sites for further Ni-P deposition. The process was carried out at various sodium hypophosphite concentrations for 1 h and various times at 5 g/dm³ of sodium hypophosphite in the bath. In the course of the plating, hydrogen in the gaseous burette was collected. The mass of deposited Ni-P film was determined gravimetrically. The morphology of the deposit was observed with scanning electron microscopy (Hitachi), while the content of phosphorus (by-product in the autocatalytic deposition of nickel in the presence of hypophosphite ion as reductant) was determined by means of SEM-EDS analyzer (Noran). Electrodeposition of Ni-SiC composites was carried out in a chloride-sulphate solution. To keep uniform distribution of the SiC particles in the suspension, the solution was stirred using a combination of a magnetic stirrer (400 rpm) and circulation with a peristaltic pump (7.4 dm³/h). Before each experiment, the bath was intensively agitated with a mechanical stirrer (900 rpm) for 1h. The solution pH was continuously monitored and maintained at a constant level (4.4) throughout the plating by periodical addition of a few drops of acids mixture (HCl + H₂SO₄ with Cl⁻: SO₄²⁻ concentration ratio as in the bath). The potential of the cathode was recorded with respect to the saturated calomel electrode. Cathodic current efficiencies were determined by weight gain and the coulometric data. SiC volume fraction within

nickel matrix was determined by image analysis using the "Aphelion" software. Calculations were done on grey levels images of polished deposit surfaces observed with the use of the optical microscope (Neophot 32). Vickers hardness of the composites was measured with a microhardness method at the load of 2 g by means of Micro-Combi-Tester (CSEM).

TABLE 1

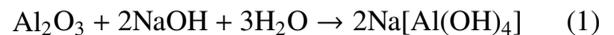
Procedure of the composite plating

Stage	Composition of solutions	Parameters
Grinding with abrasive papers		
↓		
Degreasing	NaOH 7.5 g/dm ³ Na ₂ CO ₃ 20 g/dm ³	T = 85 °C t = 120 s
↓		
Etching	NaOH 10 %	T = 55 °C t = 150 s
↓		
Brightening	HNO ₃ 30 %	T = 20 °C t = 20 s
↓		
Zincating	NaOH 95 g/dm ³ ZnO 8 g/dm ³	T = 20 °C t = 60 - 600 s
↓		
Electroless nickel deposition	NiSO ₄ ·7 H ₂ O 28 g/dm ³ NaH ₂ PO ₃ ·H ₂ O 5, 15, 30 g/dm ³ CH ₃ COOH 30 g/dm ³ pH 4, 4.5, 5	T = 80 °C t = 1, 2, 3 h
↓		
Ni-SiC composite electrodeposition	NiSO ₄ ·7 H ₂ O 25 g/dm ³ NiCl ₂ ·6 H ₂ O 180 g/dm ³ H ₃ BO ₃ 25 g/dm ³ Saccharin 1 g/dm ³ α-SiC (4.1 μm) 20 g/dm ³ pH 4.4	T = 20 °C t = 6 h i = 1 A/dm ²

3. Results and discussion

3.1. Zincating

The presence of oxide film on aluminium surface protects the metal against corrosion, however, it prevents to achieve good adhesion of coatings deposited. During the zincating carried out in alkaline solution aluminium oxide is first dissolved:



and then exposed metallic substrate is covered with zinc in displacement reaction:

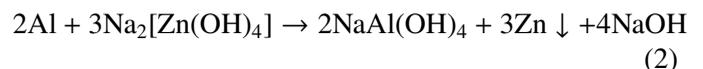


Fig.1 shows the morphology of aluminium surface polished and then covered with zinc. It was found that zinc leveled the substrate surface forming fine-grained layer. It confirms observations reported by Khan et al. [2].

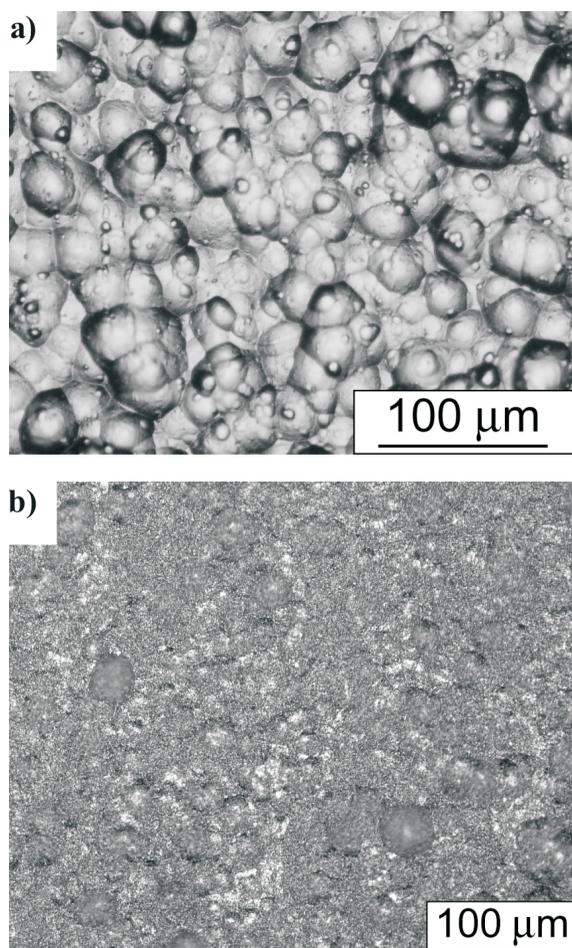


Fig. 1. Surface morphology: a) aluminium substrate, b) zinc layer

The zincating process was conducted at various times to determine the optimal conditions for complete coverage of the sample with a uniform zinc deposit. The reaction (2) can occur as long as metallic aluminium remains in the contact with the solution. It was observed

that the thickness of the zinc layer increased gradually from about 1.3 μm after 1 min up to 5.3 μm for deposition times of 5 min and longer (Fig.2). Hence, the zinc-plating time of 5 min was accepted as sufficient in further experiments.

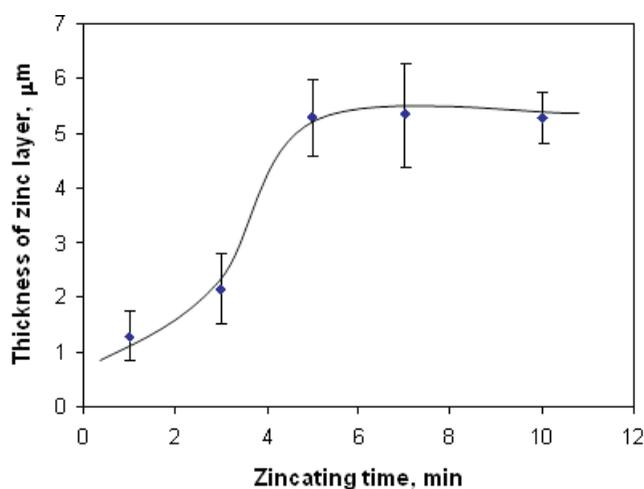
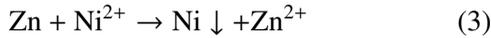


Fig. 2. Influence of time on thickness of zinc layers

3.2. Electroless nickel deposition

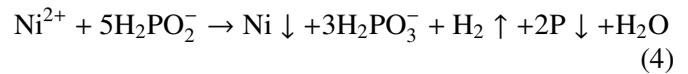
Zinc layer deposited directly on aluminium protects its surface against the oxide formation, but some troubles can arise, when the sample is immersed in the acidic solution used for nickel composite electrodeposition. In those conditions, zinc dissolution starts spontaneously with simultaneous deposition of porous layer of nickel:



This process is uncontrolled and changes the features of the sample surface before the beginning of the electrolysis. To avoid this phenomenon, additional interlayer of electrolessly deposited nickel was introduced.

Usually, electroless (autocatalytic) process involves activation of plated surface by formation of palladium catalyst in SnCl_2 - PdCl_2 system [11] or by galvanic couple [6], as examples. In this experimental study, the Ni-P nucleation was associated with some dissolution of zinc

according to equation (3). The deposited nickel nuclei became then catalytic sites for further spontaneous reaction:



Electroless deposition of Ni-P was carried out in the solution with pH similar to the value for the electrolytic bath. It prevented any unfavorable reactions, which could appear during transfer the sample from alkaline to acidic solution. Fig. 3 shows the influence of pH on the composition, deposition rate and plating efficiency. It was observed that increasing of the solution pH from 4 to 5 was accompanied by decreasing phosphorus content in the deposit (from 13.5 wt% to 5.1 wt%) and deposition rate (from 46 mg/h to 30 mg/h), while the plating efficiency was increased. The observed relationships are in accordance with published data [11-12].

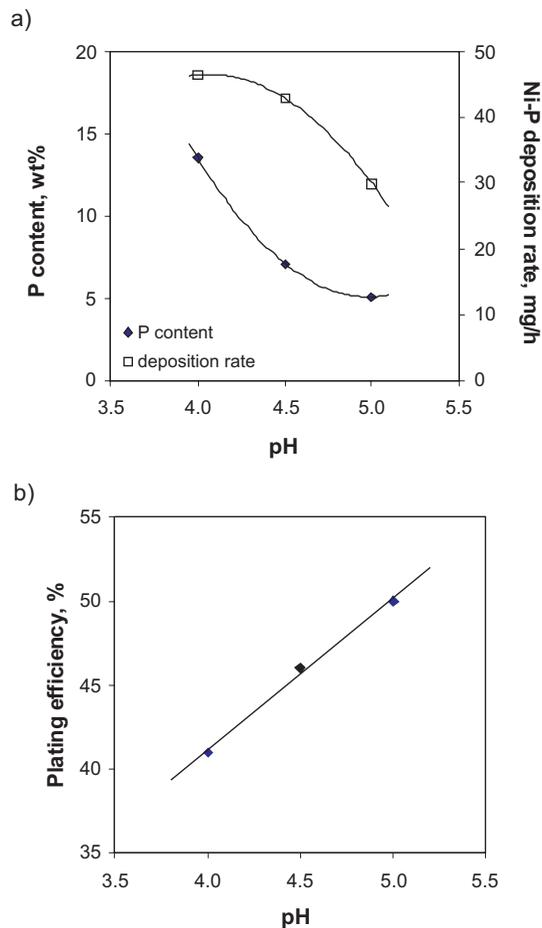


Fig. 3. Influence of solution pH on electroless Ni-P deposition (1h, $5 \text{ g/dm}^3 \text{ NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$): (a) P content and deposition rate; (b) plating efficiency

The plating efficiency was calculated according to method described elsewhere [13] and adopted for nickel. The process of Ni-P electroless deposition described



According to the electrochemical mechanism, the electroless process occurs via local cells on the metal surface. Therefore, the rate of the process (5) expressed as current intensity is the sum of the rates of the processes (6)-(8):

$$I_A = I_{\text{Ni}} + I_P + I_H \quad (9)$$

where: I_A , I_{Ni} , I_P , I_H – the rates of the processes (5)-(8), respectively.

It can be assumed that the efficiency of the electroless plating η is determined by the ratio of the amount of reductant consumed for the reduction of metal ions in the reaction (6) $n_{\text{H}_2\text{PO}_2^-/\text{Ni}}$ to the total amount of hypophosphite $n_{\text{H}_2\text{PO}_2^-}$ consumed in the process (4):

$$\eta = \frac{n_{\text{H}_2\text{PO}_2^-/\text{Ni}}}{n_{\text{H}_2\text{PO}_2^-}} \cdot 100\% \quad (10)$$

H_2PO_2^- ions are utilized in the reaction (5) to course the cathodic processes; they also are substrates in the reaction (7). Hence:

$$\eta = \frac{n_{\text{H}_2\text{PO}_2^-/\text{Ni}}}{(n_{\text{H}_2\text{PO}_2^-/\text{Ni}} + n_{\text{H}_2\text{PO}_2^-/\text{P}} + n_{\text{H}_2\text{PO}_2^-/\text{H}_2})} \cdot 100\% \quad (11)$$

Equations (5)-(8) show that 1 mole of hypophosphite is consumed in the anodic reaction to produce 1 mole of metallic nickel or 1 mole of gaseous hydrogen, while 1.5 moles of reductant is needed to obtain 1 mole of elemental phosphorus. Therefore, the expression for the plating efficiency can be written as:

$$\eta = \frac{n_{\text{Ni}}}{n_{\text{Ni}} + n_{\text{H}_2} + 1.5n_{\text{P}}} \cdot 100\% \quad (12)$$

where: n_{Ni} , n_{H_2} , n_{P} – the amounts of the moles of nickel, hydrogen and phosphorus produced in the electroless (autocatalytic) process.

In each experiment, the total amounts of nickel, phosphorus and hydrogen were determined and counted over the number of moles. Using equation (12), the efficiencies of the process were calculated. It was estimated that only 41-50 % of the reductant was consumed

with reaction (4) can be resolved in four electrochemical half processes:

in nickel deposition. It is confirmed by some literature data [12], which reported that stoichiometric utilization of hypophosphite for metal deposition was always below 50%. However, the authors did not present any mathematical equations for calculating the efficiency.

Fig. 4 shows the influence of deposition time on the phosphorus content and thickness of the Ni-P deposits. It was observed that at constant values of pH and reductant concentration the composition of the coatings does not changes considerably (13-14 wt% P). The deposition rate was also constant (about 3.5 mg/cm²·h) and the thickness of the layer increased linearly with the time. The efficiency of the process was maintained at the same level and was 40±1%.

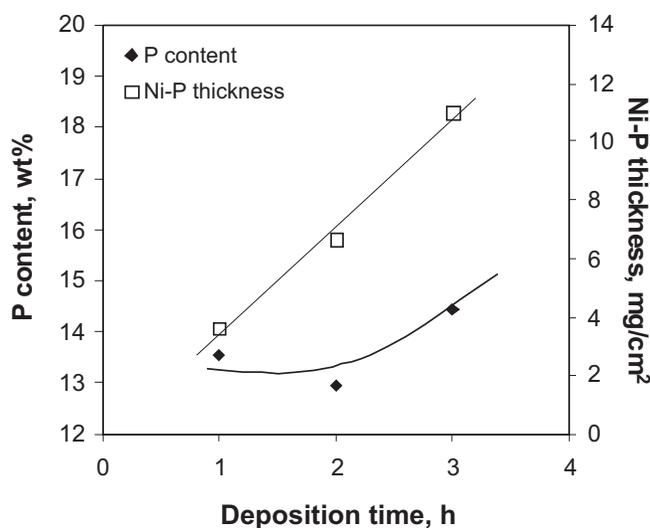


Fig. 4. Influence of electroless deposition time on P content and thickness of Ni-P layers (pH = 4; 5 g/dm³ NaH₂PO₂·H₂O)

The changes of the reductant concentration on the Ni-P deposition was also studied (Fig.5). It was found that the composition and thickness of the deposits changed with a similar way during 1 hour process. At higher hypophosphite contents in the bath the phosphorus contents and the thickness reached constant values 15.5-16 wt% and 6 mg/cm², respectively. However, the

plating efficiency decreased from 41 % to 30 % with increased reductant concentration.

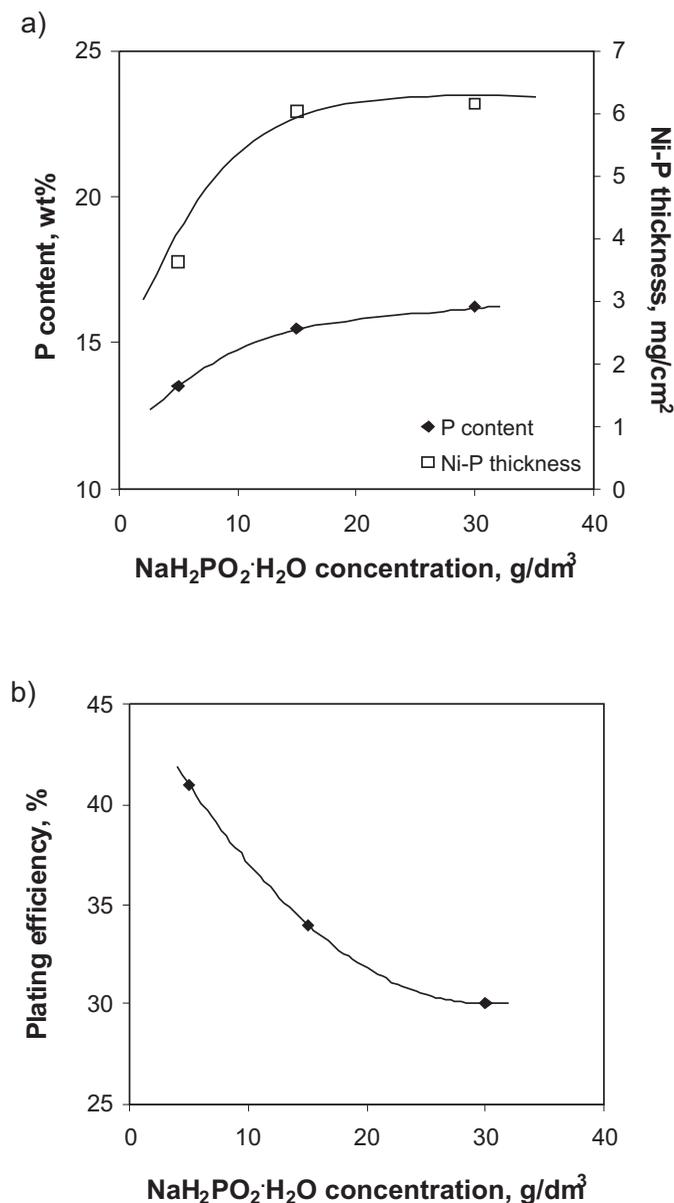


Fig. 5. Influence of reductant concentration on electroless Ni-P deposition (1h, pH = 4): a) P content and layer thickness; b) plating efficiency

All Ni-P deposits were compact and characterized by smooth gray-mat surfaces. The surface of the nickel-coated substrates was examined with a scanning electron microscope. It was observed that the deposits were characterized with dense nodular structure (Fig. 6). The size of spherical growths was dependent on the plating conditions. They slightly increased with increased hypophosphite concentration in the solution (from 1-5 μm to 7-9 μm) and deposition time (from 1-5 μm to 10-15 μm), while no clear changes were found with the solution pH. No deep pits were observed on the coating surface.

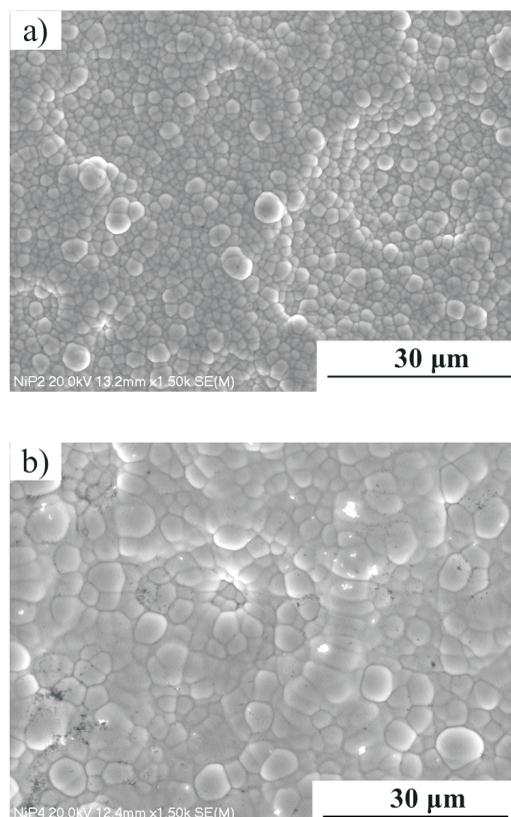


Fig. 6. Surface morphology of Ni-P deposits (pH = 4) at various NaH₂PO₂·H₂O concentrations: a) 5 g/dm³; b) 15 g/dm³

The application of the scanning microscope with EDS analyzer enabled qualitative as well as quantitative studies of the deposits. The mapping analysis showed uniform distribution of phosphorus on the surface of deposits.

Up on experiments described above, the optimal conditions for the electroless deposition of the Ni-P inter-layer were chosen. These were: 5 g/dm³ NaH₂PO₂·H₂O, pH = 4.5 and deposition time 1 h.

3.3. Ni/SiC composite electrodeposition

The aluminium sample covered with double inter-layer was plated with a Ni-SiC composite coating. The process was carried out galvanostatically, but the cathode potential stabilized at constant value of approx. -0.670 V (vs NHE) during the electrolysis. Polished surface of the obtained composites were observed by means an optical microscope. It was found that SiC particles were quite uniformly distributed within the nickel matrix (Fig.7). The image analysis such micrographs showed 6.3 ± 0.1 vol% of SiC in the material. It is worth to note that the conditions of the composite codeposition allowed to obtain highly reproducible results. The current efficiency was also high and it was 96.7 ± 0.1 %. Thickness of the composite coatings was about 65 ± 8 m.

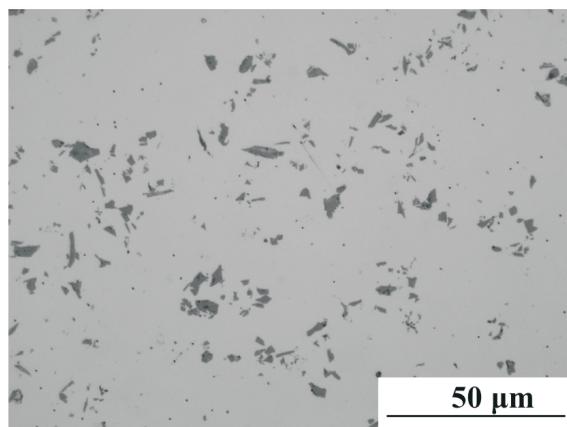


Fig. 7. Polished section of Ni/SiC composite surface

Fig. 8 shows the cross-sections of the sample coated with the multilayer. It was observed that zinc and Ni-P layers were uniform and comparable thicknesses. All layers were tightly adhered to each other, any pores were not between them. They represented very thin system in comparison to the composite coating. Hence, the microhardness measured on the outer layer characterized solely the composite material. The hardness was 766 ± 22 HV.

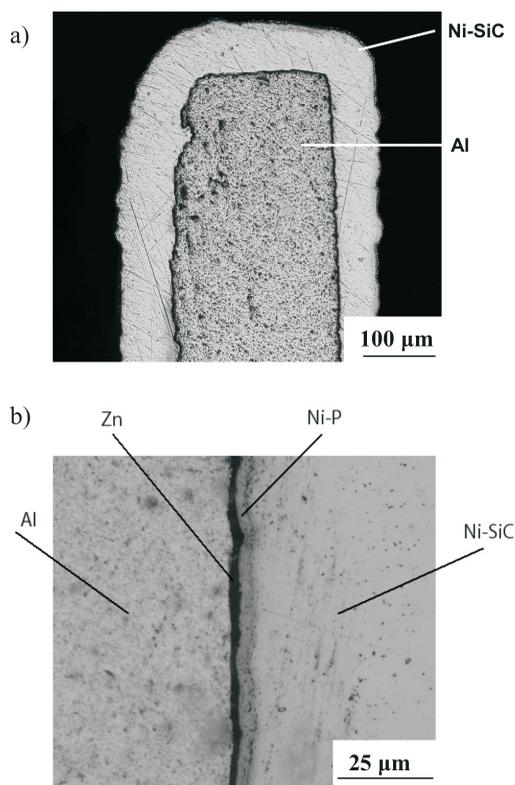


Fig. 8. Cross-section of aluminium sample covered with Zn/Ni-P/Ni-SiC multilayer: a) macrograph; b) micrograph

4. Conclusions

A hydrometallurgical method for production of Ni-SiC composite coating on aluminium was developed. It was found that treatment of the substrate in zincate solution and subsequent electroless deposition of nickel and nickel-phosphorus layers are essential steps to achieve good adherence of the electrodeposited composite to the aluminium surface. Microscopic observations showed uniform composition and thickness of the individual layers.

Acknowledgements

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