

Studies of the structure and properties of Ni-P and Ni-P/Si₃N₄ surface layers deposited on aluminum by the electroless method

M. Trzaska*

Faculty of Material Science and Engineering, Warsaw University of Technology,
ul. Wołoska 141, 02-5076 Warsaw, Poland

* Corresponding author: E-mail address: matr@inmat.pw.edu.pl

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Properties

ABSTRACT

Purpose: The paper presents the results of studies on the structure and properties of the nickel Ni-P surface layers and composite Ni-P/Si₃N₄ surface layers deposited on the surfaces of aluminum 1200 (A2) and its 7075 (PA9) alloy by the electroless method.

Design/methodology/approach: The aluminum substrate, the sample surfaces were treated by: degreasing, etching and zinking. The composite layers were produced from a disperse Si₃N₄ ceramic phase with an amorphous structure and nanometric size grains.

Findings: The structure of the ceramic disperse phase Si₃N₄ and the layer materials was determined. The topography and morphology of the layers were examined. The content of the Si₃N₄ phase in the layer material was determined. The microhardness of the Ni-P and Ni-P/Si₃N₄ layers and of the substrate material was examined. The adhesion of the nickel phosphorus and composite layers to the aluminum substrate was determined. The results of studies of the corrosion resistance of the layers are presented. The anodic polarization characteristics, corrosion current densities and corrosion potentials were determined. The results of measurements of the impedance characteristics and the counterpart results obtained by modeling with the use of equivalent electrical circuits are presented. Both the nickel Ni-P and composite Ni-P/Si₃N₄ layers ensure excellent properties of the aluminum products.

Practical implications: A good quality of final the nickel Ni-P surface layers and composite Ni-P/Si₃N₄ surface layers on the surfaces of aluminum are obtained. The surface layers are characterized by high hardness, frictional wear resistance and ensure excellent protection of the aluminum substrate against corrosion.

Originality/value: The produced nickel and composite surface layers have show high hardness as well as very good resistances not only to corrosion but also to mechanical wear.

Keywords: Electroless surface layers; Nickel layers; Composite layers; Layer structures

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1. Introduction

At the present, aluminum products are widely used in a variety of effective practical applications. They are made not only from pure aluminum but also from its various alloys. Because of the small mass density, very good electrical and thermal conductivities, very useful constructional properties and many other advantages when subjected to appropriate treatments during the fabrication and post-fabrication processes, aluminum and its alloys are the most popular materials (after steel alloys) used practically in all branches of the world industries. To meet the growing and urgent needs for such useful products it is vital to carry out research of many prospective problems such as e.g. the improvement of the surface resistance to corrosion and high temperatures. One of main tasks in this research is the development of efficient methods for depositing desired (polycrystalline, amorphous or composite) surface layers on aluminum substrates. Although certain additives to the alloy and its post-production thermal treatments improve the performance properties of aluminum products such as the mechanical strength and resistance to high temperatures, their disadvantages, such as e.g. the brittleness or low thermal stability threshold, limit the prospects for their practical use. One of possible solutions to obviate the drawbacks of aluminum-based products is to deposit very thin layers, composed of appropriate materials, on their surfaces. By selecting properly the layer material and forming adequately its structure it is possible to produce layers which fulfill all the exploitation demands. The surface layers of this type can improve significantly the reliability and the service life of ready-made aluminum products [1-6].

In order to produce mechanically rigid, non-porous protective surface layers on aluminum and its alloys we used a chemical method, developed in the Laboratory of Surface Engineering, Warsaw University of Technology. The basic idea underlying this method consists of an *a priori* special preparation of the aluminum substrate surface and then deposition of the surface layer in a bath composed of appropriate components [7].

Studies realized within the scope of the present research are focused on the surface nickel Ni-P layers and composite Ni-P/Si₃N₄ layers deposited on aluminum and its alloys by an electroless method. The nickel surface layers thus produced have esthetic appearance and show high hardness as well as very good resistances not only to corrosion but also to mechanical wear. By incorporating hard particles of the Si₃N₄ ceramic phase into the nickel-based Ni-P surface layers we can increase substantially the hardness and wear resistance of the surface layer material. The useful properties of the Ni-P/Si₃N₄ composite layers can be modified by choosing appropriately the content of the disperse phase and the degree of its dispersion in the layer material.

To obtain desired nickel-based Ni-P and Ni-P/Si₃N₄ surface layers which are able to perform their functions under given conditions, many process parameters (factors, involved in the production process) must be taken into account since they affect both the deposition process itself and the properties of the final product. They all must be considered during the design of a given surface layer and then verified experimentally so that the final products perform properly their tasks under the specified conditions of exploitation [8-11].

2. Experimental

The nickel Ni-P and composite Ni-P/Si₃N₄ surface layers were deposited on aluminum 1200 (A2) and its 7075 (PA9) alloy substrates using a chemical method. To guarantee a high quality and sufficient adhesion of the layers to the substrate, the sample surfaces were treated according to the procedure:

- degreasing in an organic solvent with the aid of ultrasounds,
- etching in a base or acid solutions,
- zinking in a multi-component solution containing NaOH, ZnO and other buffering-complexing substances.

The surface layers were produced by electroless deposition in a plating bath composed of NiSO₄ salt, NaH₂PO₂ reducer, and substances that stabilized the pH reaction on a level of 4.3 ÷ 4.6. The bath temperature during the layer deposition processes was maintained at 353 K.

To produce composite layers a Si₃N₄ ceramic material in the form of a poly-disperse powder with nanometric grains was used. The composite layers were deposited in a bath added with 10 g/dm³ of the Si₃N₄ powder.

An analysis of the structure of the ceramic disperse phase Si₃N₄ and the layer materials was performed in a PHILIPS PW-1830 X-ray diffractometer. The morphology and topography of the surface of the layers and their internal structure were examined in SU70 and HITACHI S-3500 N scanning electron microscopes. The contents of the disperse phase Si₃N₄ in the composite material of the surface layers were determined by the quantitative metallographic methods and the computer image analysis. The adhesion of the layers to the substrate was examined in a CSM Instruments scratch tester using the technique of controlled cracks on the layer surface made with a diamond indenter under variable load. The microhardness of the material of the layers was determined by the Vickers method under a load of 20G HV(0.02).

Tribological investigations were performed by the three rollers-cone method using a T-04 tester equipped with a computer control and data processing system. In the wear measurements, the counter-sample was made of quick-cutting steel. The investigations were carried out in an oil environment at a load of 50 MPa. The wear depth was taken to be the criterion of the wear resistance [12].

Corrosion studies of the layers and of the substrate materials were conducted by the potentiodynamic method and electrochemical impedance spectroscopy with the use of an Autolab[®] potentiostat and an ATLAS apparatus, respectively, both computer-controlled. A neutral 0.5M NaCl solution at 297 K was taken to be the corrosive environment. The measurements were performed in a three-electrode system, and the reference electrode was a calomel Hg/Hg₂Cl₂/KCl electrode at a potential of + 244 mV with respect to the hydrogen electrode. A platinum plate served as the auxiliary electrode. The investigations conducted by the anodic polarization method were recorded within the range from - 600 mV to +500 mV for the layers and from -850 mV to +500 mV for the substrates. The potential was varied at a rate of 0.2 mV/s in the corrosion potential region and 0,4 mV/s in the anodic region. In the electrochemical impedance spectroscopy examinations the amplitude of the sinusoidal voltage signal was 10 mV and the frequency range was from 23 kHz to 6 mHz.

3. Results and discussion

The dispersive ceramic phase used for producing the Ni-P/Si₃N₄ composite surface layers on aluminum and aluminum alloy substrates was a Si₃N₄ powder with a nanometric grain size. The diffraction pattern obtained for the dispersive Si₃N₄ phase is shown in Fig. 1 and its morphology - in Fig. 2.

The silicon nitride powder had an amorphous structure and its grains were spherical in shape with grain size ranging from 30 to 40 nm.

The material of the nickel layers and of the matrix of the composite layers produced by the electroless method was an amorphous solid solution of phosphorus (7 wt%) in nickel (Ni-P) (Fig. 3).

The morphology and topography of the surfaces of the nickel and composite layers are shown in Fig. 4.

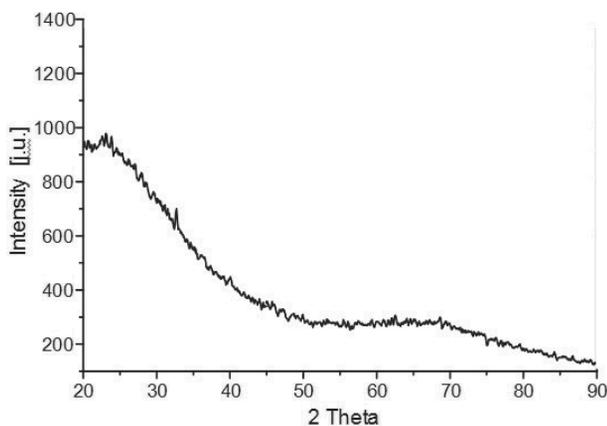


Fig. 1. Diffractogram of the Si₃N₄ ceramic phase

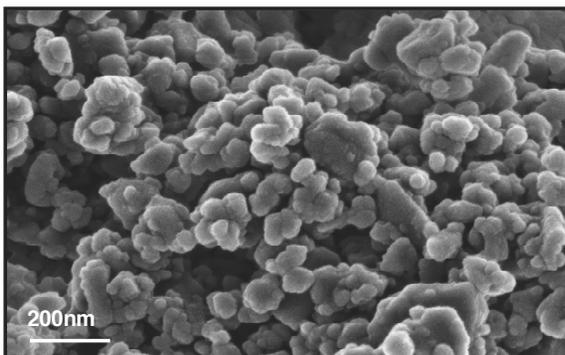


Fig. 2. Morphology of the Si₃N₄ disperse ceramic phase

The nickel-phosphorous layer has naturally a smooth brilliant surface, but the incorporation of the Si₃N₄ powder particles results in its surface becoming lusterless. The agglomerates of the ceramic phase which have not been fully built into the matrix material are visible on the surface of the composite layer. The structures and properties of the composite layers thus produced depend on both the structure of the matrix material and the number of the disperse phase ceramic particles contained in the layer volume

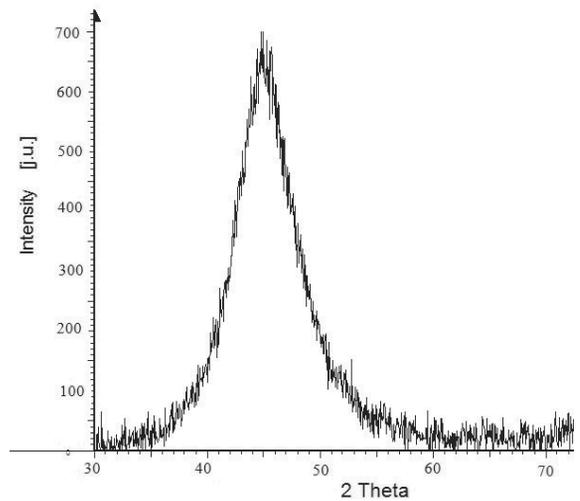


Fig. 3. Diffractogram of the nickel Ni-P

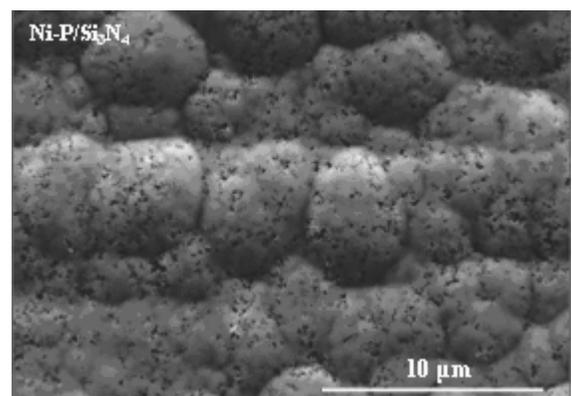
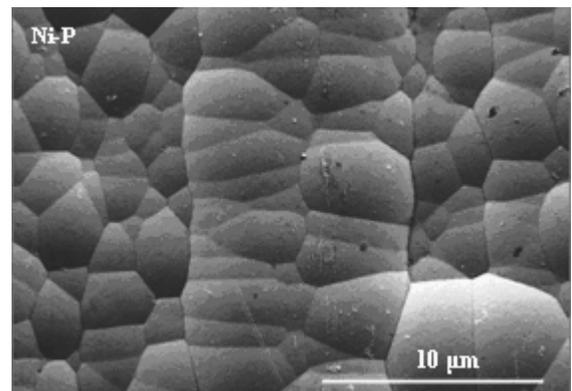


Fig. 4. Morphology of the surface of Ni-P and Ni-P-Si₃N₄ layers

Fig. 5 shows the structures of the Ni-P and Ni-P/Si₃N₄ layers as seen on their cross-sections.

Both the nickel and composite layers have compact structures and their thickness is similar on the entire covered surface of the substrate. The Si₃N₄ particles constitute 11 wt% of the composite layer material and are distributed uniformly throughout its volume.

One of the basic criteria in the estimation of the quality of surface layers is their adhesion to the substrate. The evaluation of the adhesion of the nickel and composite layers to the aluminum substrate was based on the results of the scratch tests. The damages of the layer were identified and analyzed using the diagrams of the acoustic emission, measured during the scratch tests, and the microscopic images of the scratches.

The results of the scratch tests of the Ni-P and Ni-P/Si₃N₄ layers produced on aluminum substrates are shown in Figs. 6 and 7.

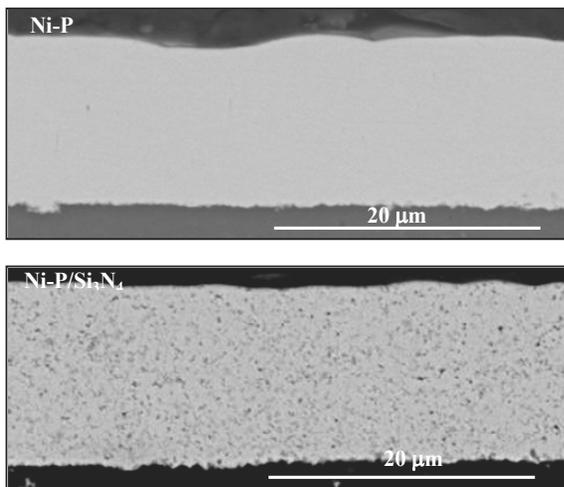


Fig. 5. Structures observed on cross-sections of the Ni-P and Ni-P/Si₃N₄ layers

The results of the scratch tests of the Ni-P and Ni-P/Si₃N₄ layers produced on aluminum substrates are shown in Figs. 6 and 7.

Both the acoustic emission diagrams and the scratch images show that the layers adhere perfectly well to the aluminum substrate. No layer chipping, de-cohesion or characteristic acoustic signals were observed during the scratch tests. The differences occurring in the scratch images of the layer surfaces indicate that, during the scratch test, the nickel Ni-P and composite Ni-P/Si₃N₄ materials differ in their behaviour and the way of deformation.

Because the deposition of the nickel and composite layers on the cutting-edge products made of aluminum is chiefly aimed at improving their exploitation properties, in particular their hardness and wear resistance, our study was concerned with examining just these properties. The results of microhardness measurements of the substrate and surface layers are given in Table 1.

Table 1.
Microhardness HV0.02 of the layers and substrates

Material	A2	PA9	Ni-P	Ni-P/Si ₃ N ₄
HV0.02	49	196	480	524

Although the hardness of the nickel-based Ni-P layers produced by the electroless method is significantly higher than that of aluminum 1200 (A2) and also of its 7075 alloy (PA9), the Ni-P/Si₃N₄ ceramic phase particles introduced into the Ni-P layer matrix yet increase the hardness of the composite layers. The material of the surface layers produced by the proposed method has a heterogeneous structure and contains the hard disperse ceramic phase embedded in the soft (plastic) matrix.

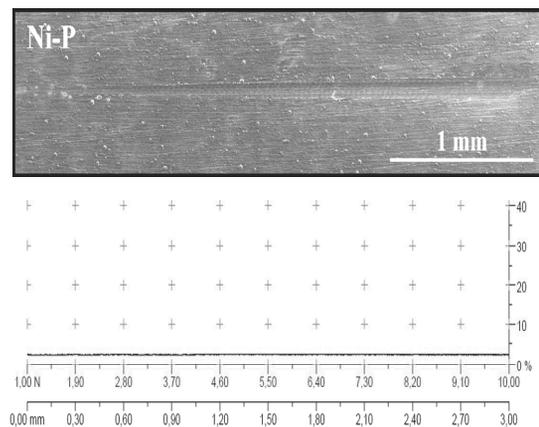


Fig. 6. Results of the scratch tests of the Ni-P layer

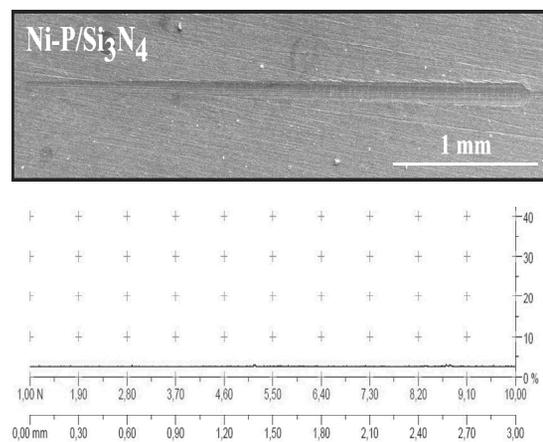


Fig. 7. Results of the scratch tests of the Ni-P/Si₃N₄ layer

The resulting hardness of the material of this type depends on both the share of the ceramic phase in the layer material and on its dispersion. The hardness of the composite layer depends not only on the hardness of the ceramic material itself, but also on the way in which its dispersed particles strengthen the material. The advantageous effect of the powder with nanometric particle size results from the dispersive strengthening of the material due to hampering the dislocation movements [13].

The wear damage of the Ni-P and Ni-P/Si₃N₄ surface layers and of the substrate 7075(PA9) material as a function of time, determined during the wear experiments, is shown in Fig. 8.

Both the nickel and composite layers exhibit increased resistance to frictional wear compared to that of the 7075 (PA9) substrate material. The image of the surface of the samples covered with Ni-P/Si₃N₄ layers and of the PA9 substrate after the frictional wear tests is shown in Fig. 9

One of the basic roles which must be realized by the surface layers during the exploitation of aluminum products is the protection against corrosion. In our study, examinations of the layers in this respect by the potentiodynamic method included determining the polarization curves $j=f(E)$ (Fig. 10), the densities j_{cor} of the corrosion current, and the corrosion potential E_{cor} of the Ni-P and Ni-P/Si₃N₄ layers and of the 1200 (A2) substrate material (Table 2).

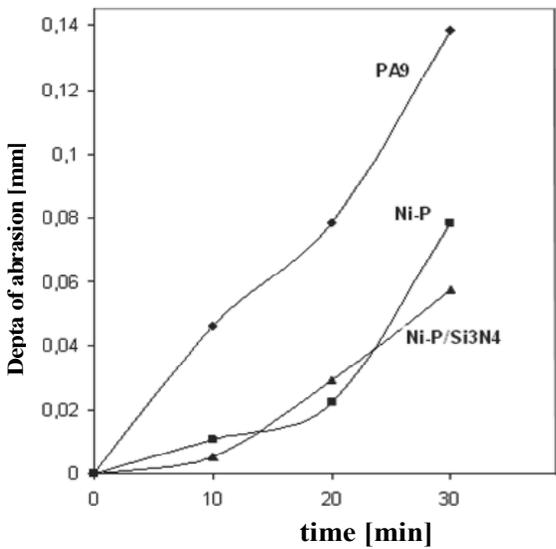
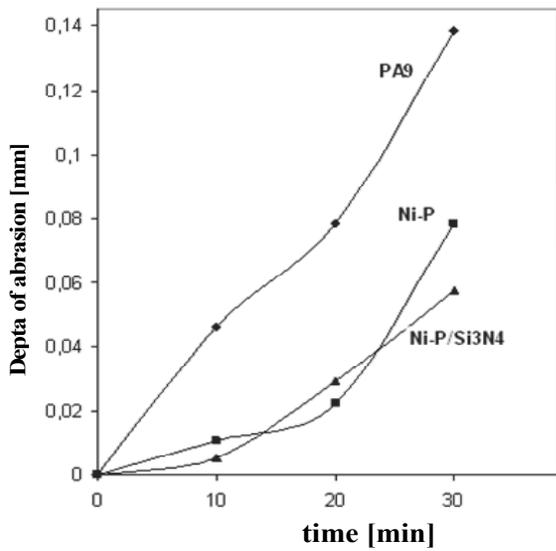


Fig. 8. The abrasion wear of the aluminium alloy PA9 and surface layers Ni-P and Ni-P/Si₃N₄

Table 2. Corrosion data obtained from potentiodynamic polarizations

Material	E_{cor} [mV]	J_{cor} [μAcm^{-2}]
Al	-790	5
Ni-P	-390	4.5
Ni-P/Si ₃ N ₄	-310	1.5

The shapes of the potentiodynamic curves (Fig. 10) and the measured corrosion parameters indicate that both the Ni-P layers and the Ni-P/Si₃N₄ layers guarantee excellent protection of the aluminum substrates against corrosion.

In order to gain more information about the layer resistance to corrosion processes, the layers were in addition examined by electrochemical impedance spectroscopy (EIS). The results, presented in the form of the Nyquist (Fig. 11) and Bode (Fig. 12) diagrams.

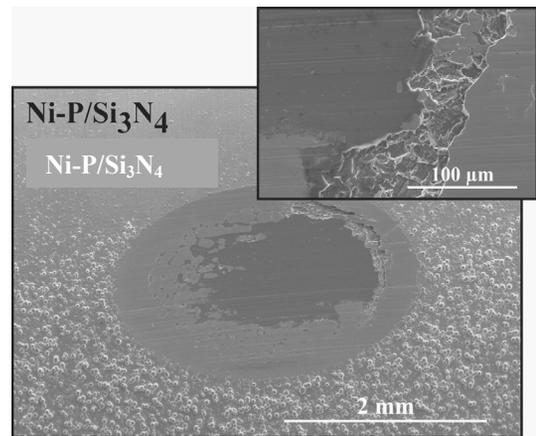
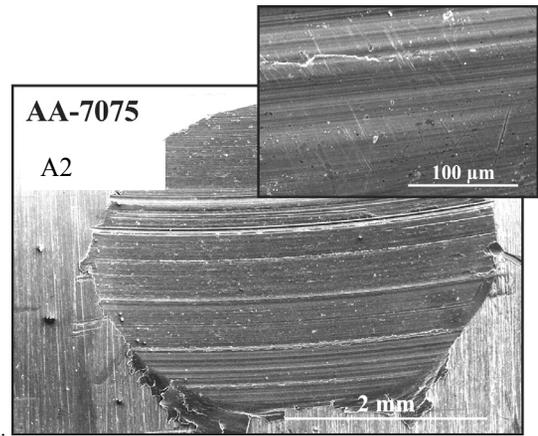


Fig. 9. The abrasion wear of the aluminum A2 and surface layers Ni-P/Si₃N₄

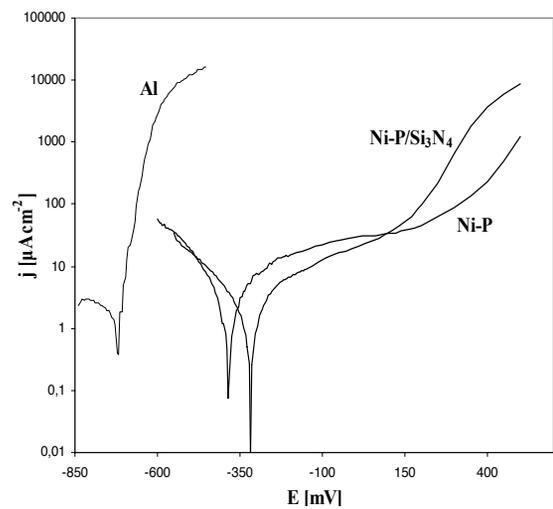


Fig. 10. The diagrams of the anode polarisation of the substrate (Al), and Ni-P coatings and of Ni-P/Si₃N₄ composite coatings

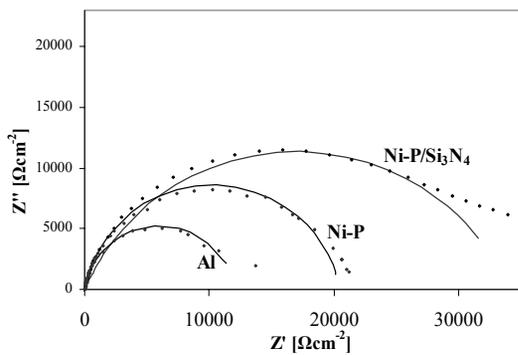


Fig. 11. Nyquist diagrams of Ni-P, Ni-P/Si₃N₄ layers and substrate

The semi-circles clearly visible in the Nyquist diagrams indicate that the corrosion processes which proceed in the material are actively controlled. A detailed analysis of the impedance spectra confirms the results obtained by the potentiodynamic method.

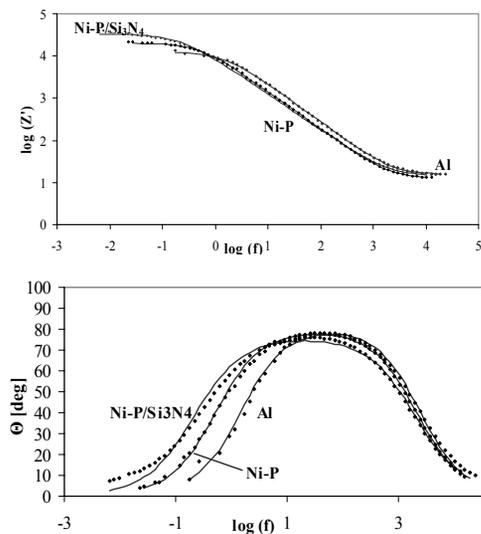


Fig. 12. Bode diagrams of the Ni-P, Ni-P/Si₃N₄ layers and aluminum substrate

The high values of the impedance moduli obtained for the substrates covered with the Ni-P and Ni-P/Si₃N₄ surface layers indicate that the layers ensure excellent protection of the aluminium substrate against corrosion [14, 15].

The equivalent electrical circuits shown in Fig. 13 were designed to interpret better the results of the EIS measurements. The impedance of the circuit is described by the relationship:

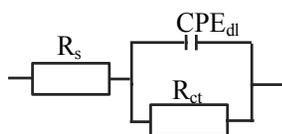


Fig. 13. Scheme of the equivalent electric circuit for studied corrosion systems

The adopted equivalent circuit represents the processes that proceed in the corrosion systems examined and permit determining the characteristic corrosion parameters. The coincidence between the impedance characteristics obtained experimentally (dotted lines) and those approximated with the use of the electric circuit models (continuous lines) can be seen in Figs. 11 and 12.

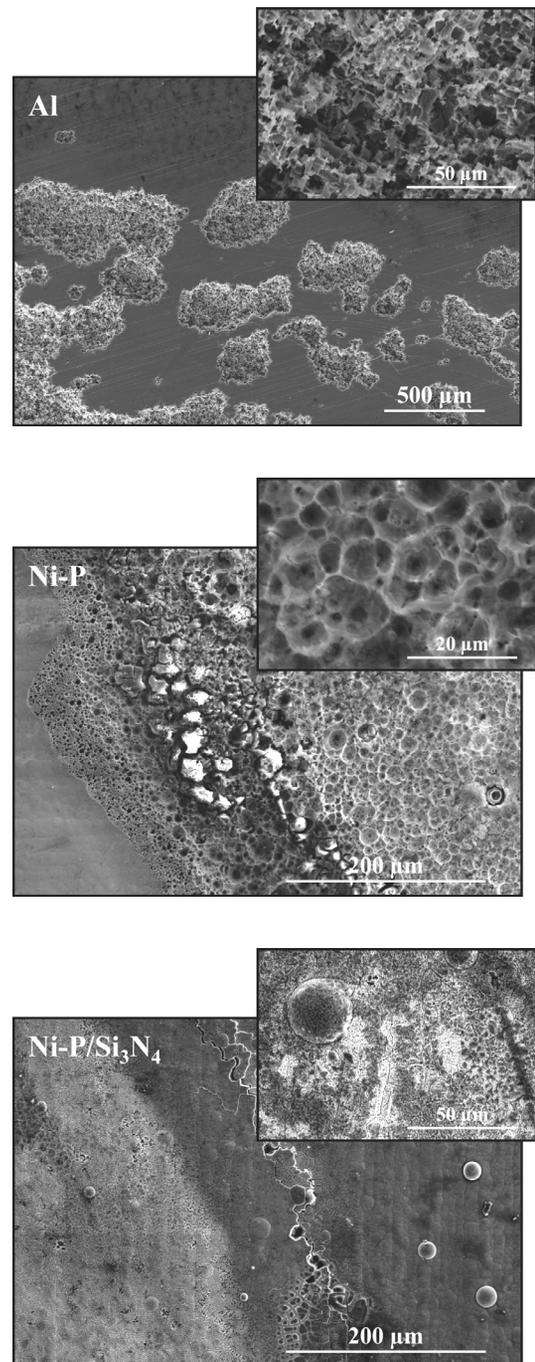


Fig. 14. Microstructures of aluminum surface, Ni-P coating surface and Ni-P-Si₃N₄ coating surface after corrosion examinations

The element R_s of the circuit model represents the resistance of the electrolyte which, in the present experiments, has been taken to be the corrosive environment. The element R_{ct} represents the rate of the corrosion processes, whereas the element CPE_{dl} represents the properties of the double electrochemical layer formed at the metal/electrolyte interface. The measured values of the equivalent circuit parameters are given in Table 3.

Table 3.
Electric parameters of corrosion systems

Material	R_s [Ωcm^2]	CPE_{dl}		R_{ct} [$\text{k}\Omega\text{cm}^2$]
		Y_{dl} [$\mu\text{F}\text{s}^{n-1}/\text{cm}^2$]	n_{dl}	
Al	15.68	10	0.9	12.0
Ni-P	12.45	17	0.9	20.43
Ni-P/Si ₃ N ₄	14	23	0.85	33.40

An analysis of the surfaces of the Ni-P and Ni-P/Si₃N₄ samples after the corrosion examinations (Fig. 14) shows that the whole exposed surface has been etched uniformly, whereas on the aluminum surface the corrosion damage has a local character.

4. Conclusions

The Ni-P and Ni-P/Si₃N₄ surface layers produced by the electroless method have compact structures and uniform thickness on the whole surface of the coated aluminum substrate. The grains of the ceramic disperse phase incorporated in the composite material appear to be perfectly built in the nickel matrix and uniformly distributed within the whole volume of the layer material.

The layers produced on aluminum 1200 (A2) and on its 7075 (PA9) alloy exhibit excellent adhesion to the substrate.

The Ni-P and Ni-P/Si₃N₄ surface layers are characterized by high hardness. The incorporation of the nanometric silicon nitride particles into the nickel-phosphorus matrix results in a substantial increase of the hardness and frictional wear resistance of the layers.

Both the nickel Ni-P and composite Ni-P/Si₃N₄ layers ensure excellent protection of the aluminum substrate against corrosion.

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