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COMPOSITES THEORY AND PRACTICE

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THE STRUCTURE AND PROPERTIES OF NANOCRYSTALLINE Ni/Al_2O_3 LAYERS PRODUCED BY ELECTROCRYSTALLIZATION

The paper presents the study of nanocrystalline Ni/Al_2O_3 layers produced by the electrocrystallization method on a copper substrate. Two variants of Ni/Al_2O_3 layers with different contents (5 and 10 g/dm^3) of Al_2O_3 disperse phase in the nickel plating bath and, for comparison a nickel layer of nanocrystalline structure were tested. The Al_2O_3 powder and composite layers were characterized using the following research techniques: scanning electron microscopy (SEM), X-ray diffraction (XRD), optical microscopy, microhardness measurements, measurements of surface roughness parameter R_a and electrochemical corrosion resistance studied by the potentiodynamic method. The paper presents results of the studies of the Al_2O_3 powder, Ni and Ni/Al_2O_3 structure, and the results of microhardness and corrosion resistance in the environment of 0.5 M NaCl. The produced layers have a nanocrystalline structure, are compact and have uniform thickness. The Al_2O_3 powder particles embedded in the nickel matrix increase the degree of expansion of the surface layer and hardness of the layer material. There is no increase in the corrosion resistance of the Ni/Al_2O_3 composite layers compared with the nickel layer in the same test corrosive environment.

Keywords: nanocomposites, electrocrystallization, Ni layers, Al_2O_3 disperse phase

STRUKTURA I WŁAŚCIWOŚCI NANOKRYSTALICZNYCH WARSTW Ni/Al_2O_3 WYTWARZANYCH METODĄ ELEKTROKRYSTALIZACJI

Przedstawiono wyniki badań nanokrystalicznych warstw Ni/Al_2O_3 wytwarzanych metodą elektrokrystalizacji na podłożu miedzianym. Badano dwa warianty warstw kompozytowych Ni/Al_2O_3 o różnej zawartości (5 i 10 g/dm^3) fazy dyspersyjnej Al_2O_3 w kąpieli do niklowania oraz - w celach porównawczych - warstwę niklową o nanokrystalicznej strukturze. Proszek Al_2O_3 oraz warstwy kompozytowe badano z użyciem następujących technik badawczych: skaningowej mikroskopii elektronowej (SEM), dyfrakcji promieniowania rentgenowskiego (XRD), mikroskopii optycznej, pomiarów mikrotwardości, pomiarów parametru chropowatości R_a oraz elektrochemicznych badań odporności korozyjnej metodą potencjodynamiczną. Przedstawiono wyniki badań struktury proszku Al_2O_3, warstw Ni oraz Ni/Al_2O_3, a także wyniki mikrotwardości oraz odporności korozyjnej w środowisku 0,5 M NaCl. Wytworzone warstwy charakteryzują się nanokrystaliczną strukturą, zwartą budową i równomierną grubością. Wbudowanie cząstek proszku Al_2O_3 w niklową osnowę wpływa na zwiększenie stopnia rozwinięcia powierzchni oraz twardości materiału warstwy. Nie stwierdzono zwiększenia odporności korozyjnej warstw kompozytowych Ni/Al_2O_3 w porównaniu z warstwą niklową w badanym środowisku korozyjnym.

Słowa kluczowe: nanokompozyty, elektrokrystalizacja, warstwy Ni, Al_2O_3 faza dyspersyjna

INTRODUCTION

One of the basic techniques used in surface engineering to improve the useful properties of the final products is the deposition of suitable metal layers on the surface of the pre-final product. The surface layers may be deposited from various metals and by different methods. One of the main methods for producing metallic surface layers is electrocrystallization. By such a method, layers constituted of pure metals, metal alloys and composite materials can be prepared. Nickel is distinguished among metals deposited by the electrochemical technique due to its numerous beneficial properties and relatively simple technology. By appropriately controlling the electrodeposition process parameters, surface layers of a desired thickness and a micro to nanocrystallite structure can be easily prepared . In addition, the so-formed layer can be modified by the incorporation of other phase particles in the metal matrix. By choosing the disperse phase material it is possible to manufacture composite materials whose properties, created as a result of the combination of two different materials, take suitable forms [1-7].

The research presented in this paper concerns Ni/Al_2O_3 layers produced by electrocrystallization with a nanocrystalline structure and different Al_2O_3 ceramic phase content. For comparative purposes, the studies were also performed for nanocrystalline nickel layers.

RESEARCH METHODOLOGY

Composite Ni/Al_2O_3 coatings were produced on a copper substrate by the electrocrystallization method. The deposition process was carried out in a bath containing: sulfate(VI) nickel(II), chloride nickel(II), boric acid, and organic compounds. As the dispersion phase was alumina powder with a content of 5 and 10 g/dm^3 in the bath, the electrochemical deposition process was carried out at a constant current density of 3 A/dm^2 in the bath at a temperature of 45°C for 45 minutes. During the process, the bath was stirred by a mechanical stirrer at the speed of 600 rpm. The topography and morphology of the produced layers were examined by using a scanning electron microscope (SEM) manufactured by ZEISS. The chemical composition of the produced composite coatings was tested by using SEM EDS. The structure of the Al_2O_3 powder and nickel layers was analyzed by X-ray diffraction using a Phillips X-ray diffractometer PW 1830. The thickness of the layers and their structures were assessed by analyzing metallographic specimens in sections perpendicular to the surface using an optical microscope Nikon ECLIPSE 150 LV. The microhardness of the layers was examined on cross-sections by the Vickers method at a load of 25 g (HV 0.025) by an INNOVATEST hardness tester. The studies of surface roughness were performed using a TR100 Surface Roughness Tester. The corrosion properties of the produced layers were carried out in an 0.5 M sodium chloride solution at 30°C by the potentiodynamic method. Measurements were carried out using a three-electrode system, applying as a reference electrode a silver chloride electrode, Ag/AgCl/KCl, with a potential of +222 mV with respect to the hydrogen electrode. The counter electrode was made of platinum. The polarization test was performed in the potential range from –400 to 400 mV by means of an ATLAS 98. The scanning speed was taken as 1.0 mVs^{-1}. The extrapolation tangent to polarization $E = f(j)$ curve from the cathode and anode areas was used to determine the corrosion current density (j_{cor}) and the corrosion potential (E_{cor}).

STUDY RESULTS

The polydispersed Al_2O_3 powder of a nanometric particle size was used to produce composite layers with a ceramic disperse phase. An image of the aluminum oxide powder is shown in Figure 1. The X-ray structural analysis results of the Al_2O_3 powder are shown in Figure 2.

The X-ray analysis showed that the polydispersed ceramic powder used in the manufacture of the composite layers is a variant of the allotropic α-Al_2O_3 form, known as corundum. This is a variation of the hexagonal crystal lattice which is characterized by very high hardness and a high melting point.

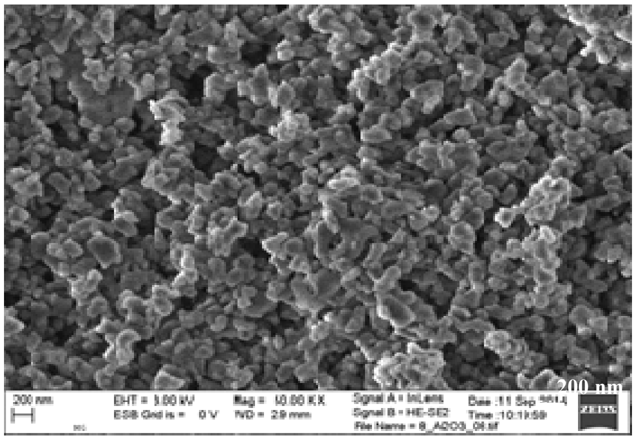

Fig. 1. Image of Al_2O_3 powder particles

Rys. 1. Obraz cząstek proszku Al_2O_3

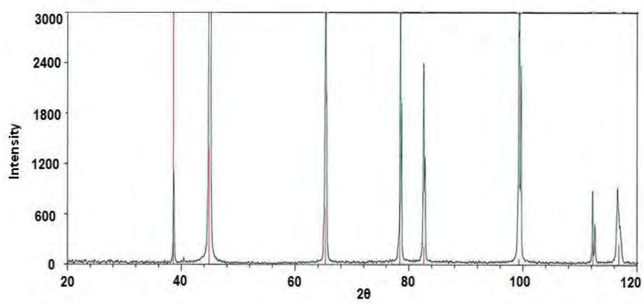

Fig. 2. X-ray diffraction pattern of Al_2O_3 powder

Rys. 2. Dyfraktogram proszku Al_2O_3

The X-ray structural analysis results of the nickel produced by electrocrystallization in the applied bath are shown in Figure 3.

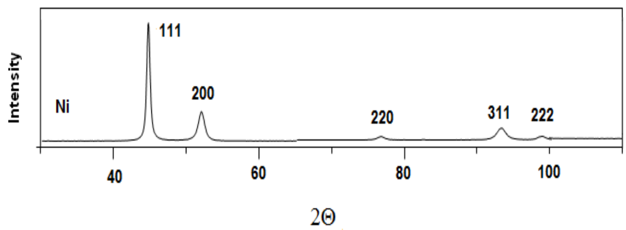

Fig. 3. X-ray diffraction pattern of nickel layer

Rys. 3. Dyfraktogram rentgenowski warstwy niklowej

In the diffraction pattern (Fig. 3), the X-ray reflections indicate the nanocrystalline structure of the nickel. Based on the assumption of the W.H. Hall and Scherer dependence, based on the broadening of X-ray reflections, the size of the nickel crystallites present in the produced layers was determined. They are of the order of 14 nm. Images of the surface layers of the nickel and composite material prepared in the bath containing different amounts of Al_2O_3 powder are shown in Figures 4-6.

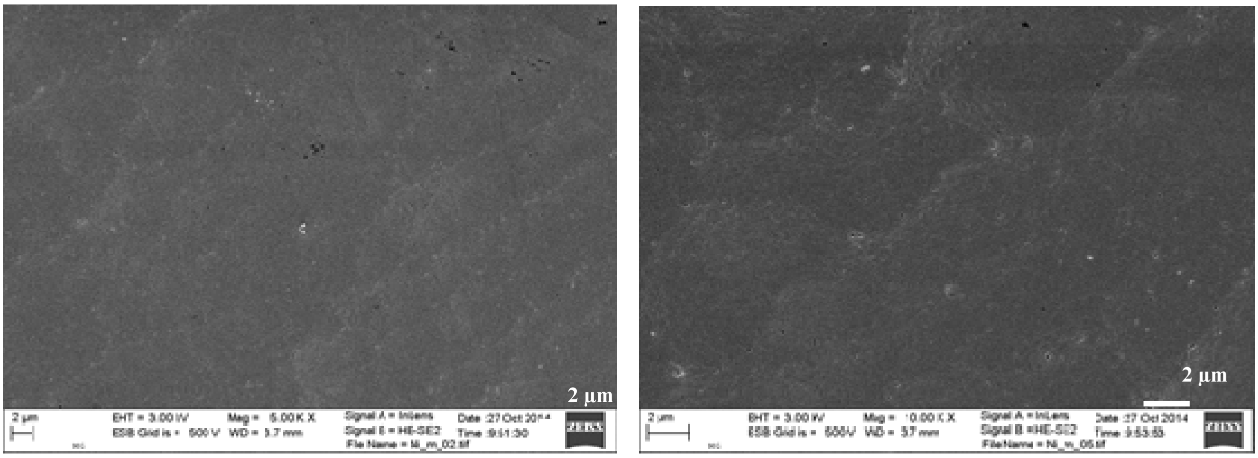

Fig. 4. Images of nickel layer surface with nanocrystalline structure

Rys. 4. Obrazy powierzchni warstwy niklowej o nanokrystalicznej strukturze

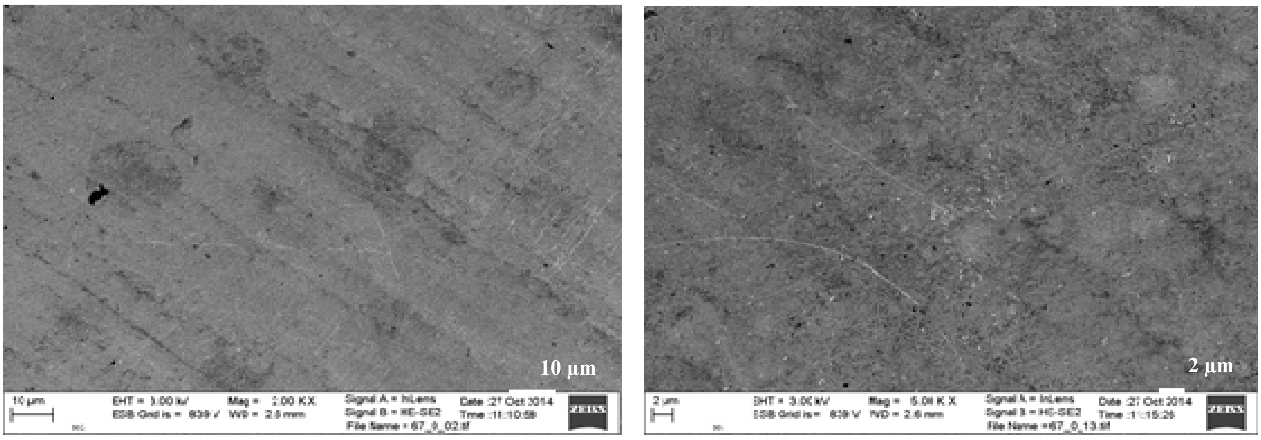

Fig. 5. Images of Ni/Al_2O_3 composite layer surface (5 g/dm^3)

Rys. 5. Obrazy powierzchni warstwy kompozytowej Ni/Al_2O_3 (5 g/dm^3)

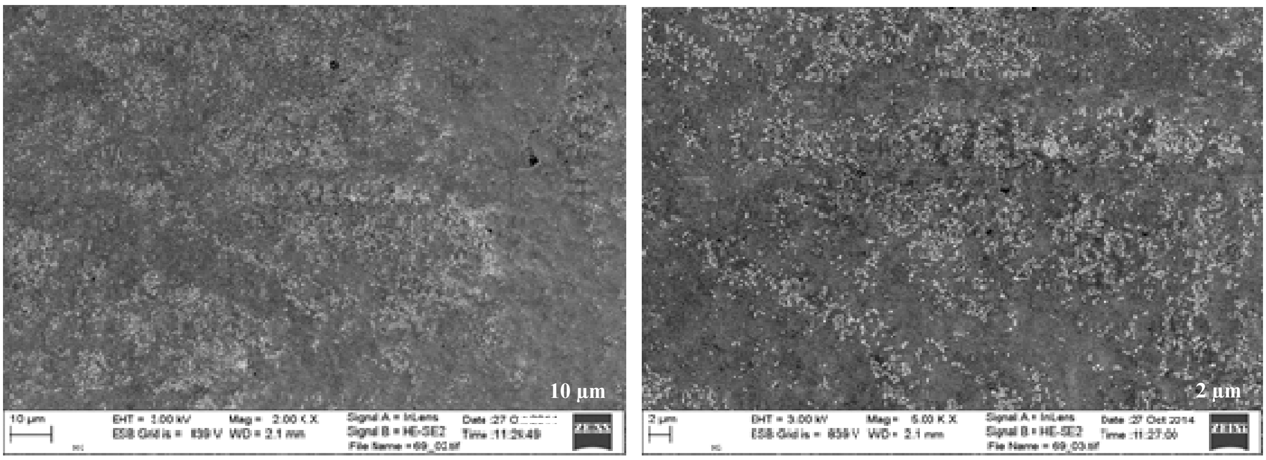

Fig. 6. Images of Ni/Al_2O_3 composite layer surface (10 g/dm^3)

Rys. 6. Obrazy powierzchni warstwy kompozytowej Ni/Al_2O_3 (10 g/dm^3)

The surface of the nickel layer is smooth and the layer structure is homogeneous. In the case of the composite layers, not fully enclosed Al_2O_3 powder particles are visible on their surfaces. The EDS analysis results of the chemical composition of the Ni/Al_2O_3 composite layer prepared in the bath containing 10 g/dm^3 Al_2O_3 powder (Fig. 7) show the Al_2O_3 disperse phase embedded in the nickel layer.

The structure of the Ni and Ni/Al_2O_3 in the cross-section perpendicular to the surface is shown in Figure 8. Both the nickel layer and the composite layers are compact and of uniform thickness over the entire coated surface. In the composite layers embedded Al_2O_3 ceramic phase particles are visible in the entire volume of the material.

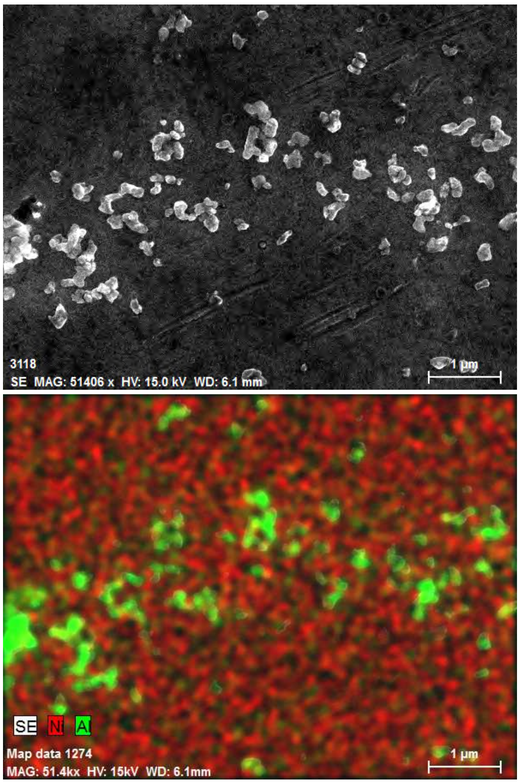

Fig. 7. EDS analysis of chemical distribution in Ni/Al_2O_3 composite layer (10 g/dm^3)

Rys. 7. Analiza EDS składu chemicznego warstwy kompozytowej Ni/Al_2O_3 (10 g/dm^3)

The results of the microhardness and roughness measurements of the nickel and the composite layers with different Al_2O_3 particle content are presented in Table 1. The lowest hardness of the layers is demonstrated by the nanocrystalline nickel layer. The Al_2O_3 ceramic particles embedded in the nickel matrix increase the microhardness of the material layer. Simultaneously, the embedded Al_2O_3 particle phase increases the degree of expansion of the surface layer.

TABLE 1. **Microhardness and surface roughness of Ni and Ni/Al_2O_3 layers**

TABELA 1. **Mikrotwardość oraz chropowatość powierzchni warstw Ni oraz Ni/Al_2O_3**

Layer	Microhardness HV 0.025 G	Roughness parameter Ra [µm]
Ni	466	0.076
Ni/Al_2O_3 (5 g/dm^3)	585	0.118
Ni/Al_2O_3 (10 g/dm^3)	611	0.138

The electrochemical corrosion test results of the Ni and Ni/Al_2O_3 layers are presented as potentiodynamic polarization curves, $j = f(E)$, in Figure 9. The parameters characterizing the corrosion properties of the layers, i.e. corrosion potential E_{cor} and corrosion current density j_{cor}, are presented in Table 2.

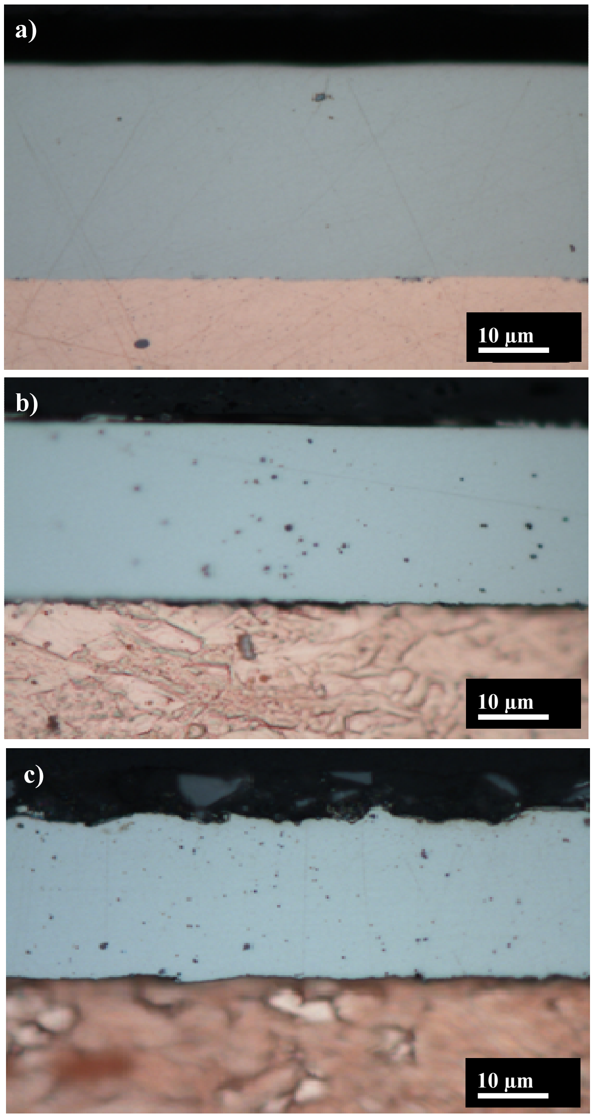

Fig. 8. Cross section of deposited layers: a) Ni, b) Ni/Al_2O_3 (5 g/dm^3), c) Ni/Al_2O_3 (10 g/dm^3)

Rys. 8. Przekroje warstw: a) Ni, b) Ni/Al_2O_3 (5 g/dm^3), c) Ni/Al_2O_3 (10 g/dm^3)

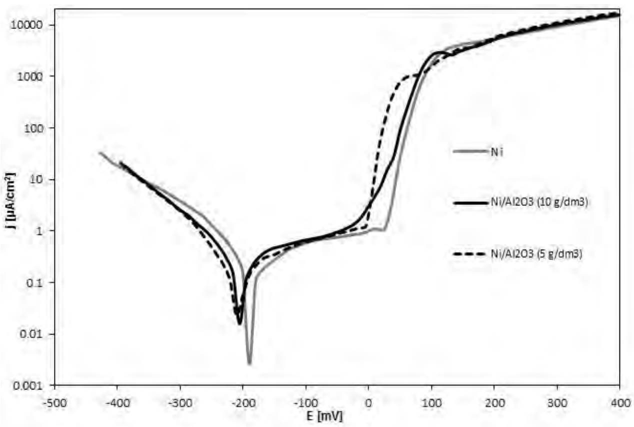

Fig. 9. Potentiodynamic polarization curves of Ni and Ni/Al_2O_3 layers in 0.5 M NaCl

Rys. 9. Krzywe potencjodynamicznej polaryzacji wytworzonych warstw w środowisku 0,5 M NaCl

TABLE 2. **Corrosion potential and corrosion current density j_{cor} of Ni and Ni/Al_2O_3 layers**

TABELA 2. **Potencjał korozyjny E_{cor} oraz gęstość prądu korozji j_{cor} warstw Ni oraz Ni/Al_2O_3**

Layer	E_{cor} [mV]	j_{cor} [μA/cm^2]
Ni	–187	0.348
Ni/Al_2O_3 (5 g/dm^3)	–210	0.271
Ni/Al_2O_3 (10 g/dm^3)	–203	0.322

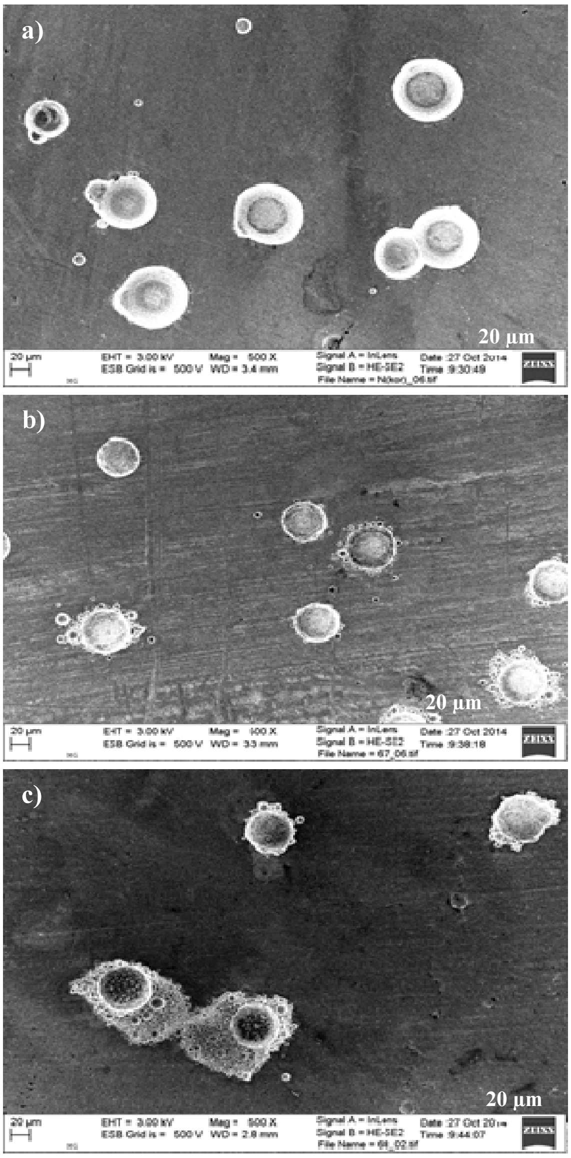

Fig. 10. Images of surface layers after corrosion tests in 0.5 M NaCl: a) Ni, b) Ni/Al_2O_3 (5 g/dm^3), c) Ni/Al_2O_3 (10 g/dm^3)

Rys. 10. Obrazy powierzchni warstw po badaniach korozyjnych w środowisku 0,5 M NaCl: a) Ni, b) Ni/Al_2O_3 (5 g/dm^3), c) Ni/Al_2O_3 (10 g/dm^3)

The composite Ni/Al_2O_3 layers have a slightly lower corrosion resistance as compared with the nickel layer of. The images of the of Ni and Ni/Al_2O_3 layer surfaces after corrosion tests are shown in Figure 10.

Both the nickel layer and the Ni/Al_2O_3 layers in an 0.5 M NaCl solution were destroyed by local corrosion.

CONCLUSIONS

The electrocrystallization method was used to produce nickel and Ni/Al_2O_3 layers which have nanocrystalline structures and compact as well as uniform thickness. The embedded hard particles of the ceramic α-Al_2O_3 phase in the nickel matrix significantly increase the hardness of the material layer. The composite layers are characterized by a higher degree of expansion of the surface and similar corrosion resistance in an 0.5 M NaCl corrosive environment as compared to the nickel layer.

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