



Beata Kucharska¹, Maria Trzaska^{2*}

¹ Warsaw University of Technology, Faculty of Materials Engineering, ul. Wołoska 141, 02-507 Warsaw, Poland

² Institute of Precision Mechanics, ul. Duchnicka 3, 01-796 Warsaw, Poland

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

Received (Otrzymano) 13.02.2012

THE STRUCTURE OF NANOCOMPOSITE LAYERS WITH Ni MATRIX AND DISPERSE PHASE Si₃N₄ AND PTFE

The surface nickel layers produced by the method of electrochemical reduction are used to protect the substrate material against abrasive wear and corrosion. The incorporation of dispersed phases such as lubricative polytetrafluoroethylene (PTFE) and hard silicon nitride (Si₃N₄) in a nickel matrix allows one to improve the tribological and corrosive properties. The aim of this work was a study of the influence of the deposition process parameters on the structure of the hybrid composite layers Ni/PTFE/Si₃N₄ produced by the electrochemical method. The examinations included composite layers of the nanocrystalline nickel (Ni) matrix with the disperse phases of polytetrafluoroethylene (PTFE) and silicon nitride (Si₃N₄). The layers were deposited in a Watts bath at a current density of 5 A/dm², constant stirring rate of 500 rpm and constant phase content of PTFE (50 g/dm³) and Si₃N₄ (10 g/dm³). The stability of the suspension of the disperse phase in the bath, and uniform incorporation of its particles in the nickel matrix was provided by a cationic surfactant. Nanocrystalline nickel layers and nanocomposite Ni/PTFE layers produced by the electrochemical method were also investigated for comparative purposes. The aqueous dispersion of PTFE particles of a size of 0.1÷0.3 μm and polydisperse Si₃N₄ powder with rather different particle sizes were used to produce the composite layers. The topography and morphology of the silicon nitride powder and the structures of the produced nickel and composite layers were studied using transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The structural analysis of the produced layers were performed and the crystallite sizes were determined with the X-ray diffraction method. The microhardness of HV 0.02 of the produced layers was determined using Zwick's tester. The completed examinations have shown that hybrid Ni/PTFE/Si₃N₄ composite layers are characterized by a cohesive texture and nanocrystalline structure of the nickel matrix.

Keywords: composite Ni/PTFE/Si₃N₄ coating, Si₃N₄, PTFE, electrochemical method, microhardness

STRUKTURA WARSTW NANOKOMPOZYTOWYCH Z OSNOWĄ Ni ORAZ DYSPERSYJNYMI FAZAMI Si₃N₄ I PTFE

Powierzchniowe warstwy niklowe wytwarzane metodą elektrochemiczną stosowane są do ochrony materiału podłoża przed zużyciem ściernym i korozją. Wbudowanie w warstwę niklową faz dyspersyjnych takich, jak samosmarny politetrafluoroetylen (PTFE) oraz twardy azotek krzemu (Si₃N₄), pozwala na uzyskanie lepszych właściwości tribologicznych i korozyjnych. Celem badań zrealizowanych w ramach niniejszej pracy było określenie wpływu parametrów procesu na strukturę hybrydowych warstw kompozytowych Ni/PTFE/Si₃N₄ wytwarzanych metodą elektrochemiczną. Badania obejmowały warstwy kompozytowe o nanokrystalicznej osnowie Ni z fazami dyspersyjnymi w postaci politetrafluoroetylen (PTFE) i azotku krzemu (Si₃N₄). Warstwy wytwarzano w kąpeli Wattsa przy gęstości prądu 5 A/dm², stałej szybkości mieszania mechanicznego wynoszącej 500 obr./min oraz zawartościach faz PTFE i Si₃N₄ w kąpeli wynoszących 50 g/dm³. Trwałość zawiesiny faz dyspersyjnych w kąpeli oraz równomierne wbudowywanie ich cząstek w osnowę niklową podczas procesu osadzania zapewniał kationowy środek powierzchniowo czynny. W celach porównawczych badano również nanokrystaliczne warstwy niklowe oraz warstwy nanokompozytowe Ni/PTFE wytwarzane metodą elektrochemiczną. Do wytwarzania warstw kompozytowych stosowano PTFE w postaci wodnej dyspersji o wymiarach cząstek 0,1÷0,3 μm oraz polidispersyjny proszek Si₃N₄ o dość zróżnicowanych wymiarach cząstek. Za pomocą mikroskopii transmisyjnej (TEM) oraz skaningowej (SEM) badano topografię i morfologię proszku azotku krzemu oraz strukturę wytworzonych warstw niklowych i kompozytowych. Metodą dyfrakcji rentgenowskiej przeprowadzono analizę strukturalną wytworzonych warstw i wyznaczono wielkości kryształitów. Metodą Vickersa wyznaczono mikrotwardość wytworzonych warstw za pomocą aparatu Zwicka. Zrealizowane badania wykazały, że hybrydowe warstwy kompozytowe Ni/PTFE/Si₃N₄ charakteryzują się zwartą budową i nanokrystaliczną strukturą osnowy niklowej.

Słowa kluczowe: warstwa kompozytowa Ni/PTFE/Si₃N₄, Si₃N₄, PTFE, metoda elektrochemiczna, mikrotwardość

INTRODUCTION

The implementation of new industrial technologies is mainly aimed at improving the performance charac-

teristics, and above all, improving the corrosion resistance and wear characteristics of materials. The tri-

biological and corrosion properties of machines and equipment can be improved by producing composite coatings on product surfaces. That modification of the surface layer assures good performance properties of the products and adapts them to the desired needs [1, 2].

In the case of composite materials, more than other materials, their properties can be designed and controlled during their production processes to meet user requirements. The specific properties of composite materials that meet a variety functions in technology are shaped by the proper selection of their components and the creation of a specific structure of the material [3-6].

The subject of research presented in this study is aimed at hybrid Ni/PTFE/Si₃N₄ composite layers produced by electrochemical reduction. A ductile nickel matrix provides many favorable mechanical properties, while the built-in hard ceramic particles provide increased hardness and wear resistance to friction. In addition, the self-lubricative and chemical resistant fluoropolymer embedded in the nickel matrix improves wear and corrosion resistance in comparison to nickel coatings. A combination of these three such different materials allows the mutual complementarities of their properties, and interactions between such different phases to induce modification of these properties. By controlling the structure of the material matrix and content of the ceramic and polymer phases in the composite material and their degree of dispersion, advantageous performance properties of the composite material can be achieved [5-8].

The incorporation of Si₃N₄ particles and a hydrophobic polymer PTFE in the nickel layer during the electrochemical process requires proper preparation of the galvanic bath and conducting of the process in accordance with the selected optimal experimental parameters. It is essential to maintain a stable, evenly dispersed suspension of PTFE and Si₃N₄ phases and give their particles the appropriate charge to force co-deposition of the ceramic and polymer particles with the nickel. This is achieved by using surfactants and mechanical stirring [1-3].

Preparation of the nanocrystalline nickel layer on the surface of the metal substrate, additionally containing lubricative polytetrafluoroethylene particles and hard silicon nitride particles, allows one to produce a material with more favorable tribological and corrosion properties [5-6]. The aim of the study carried out in this work was to produce by the electrochemical reduction method hybrid Ni/PTFE/Si₃N₄ nanocomposite layers and characterize their structures. Nanocrystalline nickel and nanocrystalline composite Ni/PTFE layers produced by the electrochemical method have also been investigated for comparative purposes.

EXPERIMENTAL PROCEDURE

Composite layers with a nickel matrix and disperse ceramic and polymer phases were produced by the elec-

trochemical reduction method in a Watts bath, modified with the addition of benzoic sulfimide (saccharin) and a cationic surfactant (Table 1).

TABLE 1. Bath composition
TABELA 1. Skład kąpielii podstawowej

Component	Concentration [g·dm ⁻³]
NiSO ₄ ·6 H ₂ O	300
NiCl ₂ ·6 H ₂ O	40
H ₃ BO ₃	35
Saccharin	5

In the deposition of the composite layers, the ceramic material Si₃N₄ was used in the form of a poly-disperse powder and PTFE polymer phase in the form of an aqueous dispersion. The applied dispersion contained a nonionic surfactant that allows uniform dispersion of the hydrophobic polymer in the Watts bath. The composite layers were deposited in solutions with a constant content of polymer (50 g/dm³) and ceramic (10 g/dm³) phases. The process was carried out at the current density of 5 A/dm² and stirring rate of 500 rpm. Nickel Ni, composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers were deposited on an aluminum A2 substrate. Granulometric analysis of the silicon nitride powder was performed using a Laser Diffraction Particle Size Distribution Analyzer, LA-950 Horiba, and scanning electron microscopy methods. The structures of the disperse ceramic Si₃N₄ phase and produced nickel and composite layers were analyzed by a Philips PW1830 X-ray diffractometer. The characteristics of the structure of the nickel, composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers were analysed using transmission electron microscopy (TEM) JEOL JEM 1200 EX.

Analysis of the surface topography and the diversity of morphology, as well as the internal structure of the produced layers, were realized using a Hitachi SU-70 scanning electron microscope. Based on the analysis of metallographic cross sections of images of the Ni, Ni/PTFE and Ni/PTFE/Si₃N₄ layers, the internal structure and distribution of the ceramic and polymer phases in the volume of the composite material were determined. The microhardness of the produced layers was determined by the Vickers method at a load of 20 G (HV0.02) using Zwick's microhardness tester.

RESULTS

In the production of hybrid Ni/PTFE/Si₃N₄ composite layers as a dispersion ceramic phase, polydisperse silicon nitride Si₃N₄ powder containing α and β crystalline varieties of a hexagonal structure was used. The structure of the ceramic used as a dispersive phase was characterized by the diffraction pattern shown in Figure 1. The morphology and differentiation of the shape and size of the powder particles of the Si₃N₄ ceramic phase are illustrated in Figures 2 and 3.

The wide variation in the determined particle size is due to the tendency of the ceramic disperse phase to agglomeration in both dry and aquatic environments.

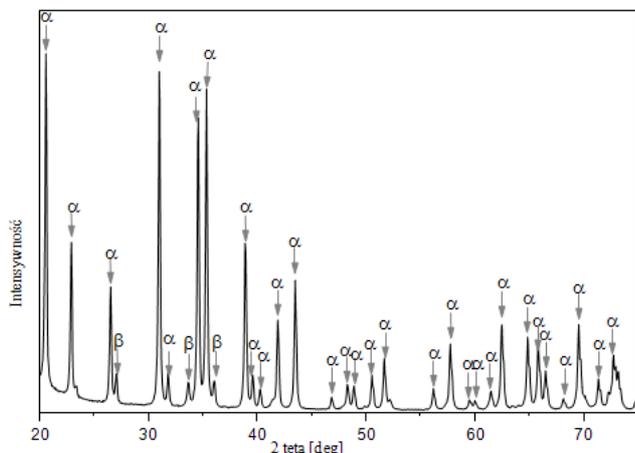


Fig. 1. Diffraction patterns of polycrystalline Si₃N₄ powder

Rys.1. Dyfraktogramy polikrystalicznego proszku Si₃N₄

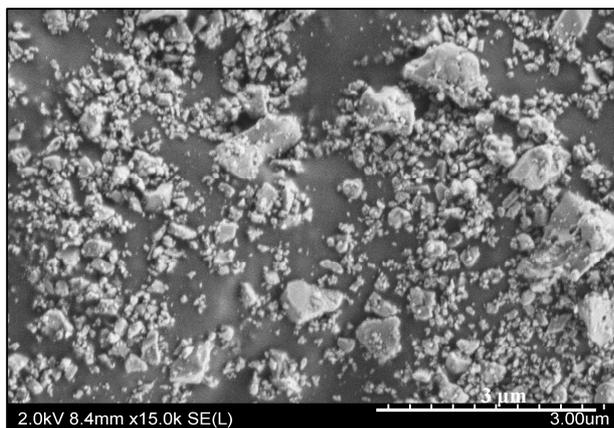


Fig. 2. Morphology of Si₃N₄ powder used to deposit Ni/PTFE/Si₃N₄ composite layers

Rys. 2. Morfologia proszku Si₃N₄ stosowanego do wytworzenia warstw kompozytowych Ni/PTFE/Si₃N₄

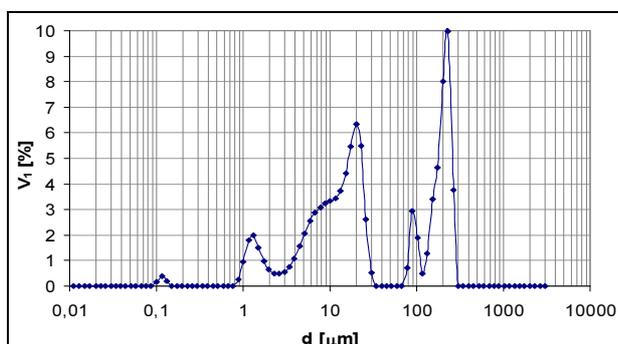


Fig. 3. Grain size distribution of Si₃N₄ particles

Rys. 3. Rozkład wielkości cząstek Si₃N₄

For the deposition of the composite layers, polytetrafluoroethylene in the dispersion form containing 55% PTFE, with a particle size within the limits of 0.1÷0.3 μm was used.

All the produced layers (Ni, Ni/PTFE, Ni/PTFE/Si₃N₄) have nanocrystalline nickel structures. This is revealed by both the X-ray diffraction patterns (Fig. 4), as well as images of the microstructure and diffraction patterns obtained by transmission microscopy (Fig. 7).

The diffraction line profiles (Fig. 4) indicate that the composite Ni/PTFE layers are characterized by a smaller dimension of crystallites (increased width of the reflections) as compared to nanocrystalline nickel produced in the same basic bath but without the addition of a disperse phase. The crystallite sizes were determined from the Scherrer relation and they are 27 nm for the Ni layers, 14 nm for the Ni/PTFE layers and 19 nm for the Ni/PTFE/Si₃N₄ layers.

The privileged direction of growth of nickel crystallites in the produced layers is the direction <111>.

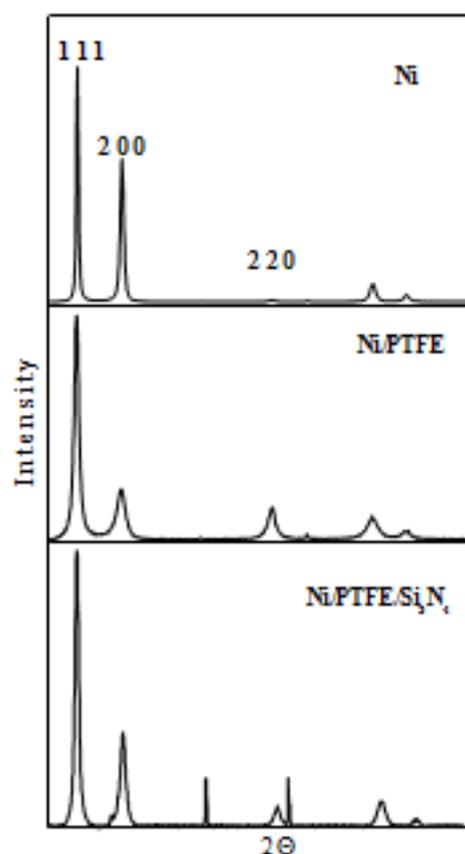


Fig. 4. Diffraction pattern of nickel and Ni/PTFE composite layers produced in Watts bath with saccharine additives

Rys. 4. Dyfraktogramy rentgenowskie warstw niklowych i kompozytowych Ni/PTFE wytworzonych w kąpielii Wattsa z dodatkiem sacharyny

The particles of the polymer PTFE and ceramic Si₃N₄ phases embedded in the nickel layer cause a significant alteration in the morphology of the surface. The images of the surface layers of nickel and composite materials are shown in Figure 5. In the case of the Ni/PTFE layers, the fluoropolymer is evenly dispersed in the nickel matrix (Fig. 5). The hybrid layers contain both embedded polymer particles as well as large particles of the silicon nitride phase.

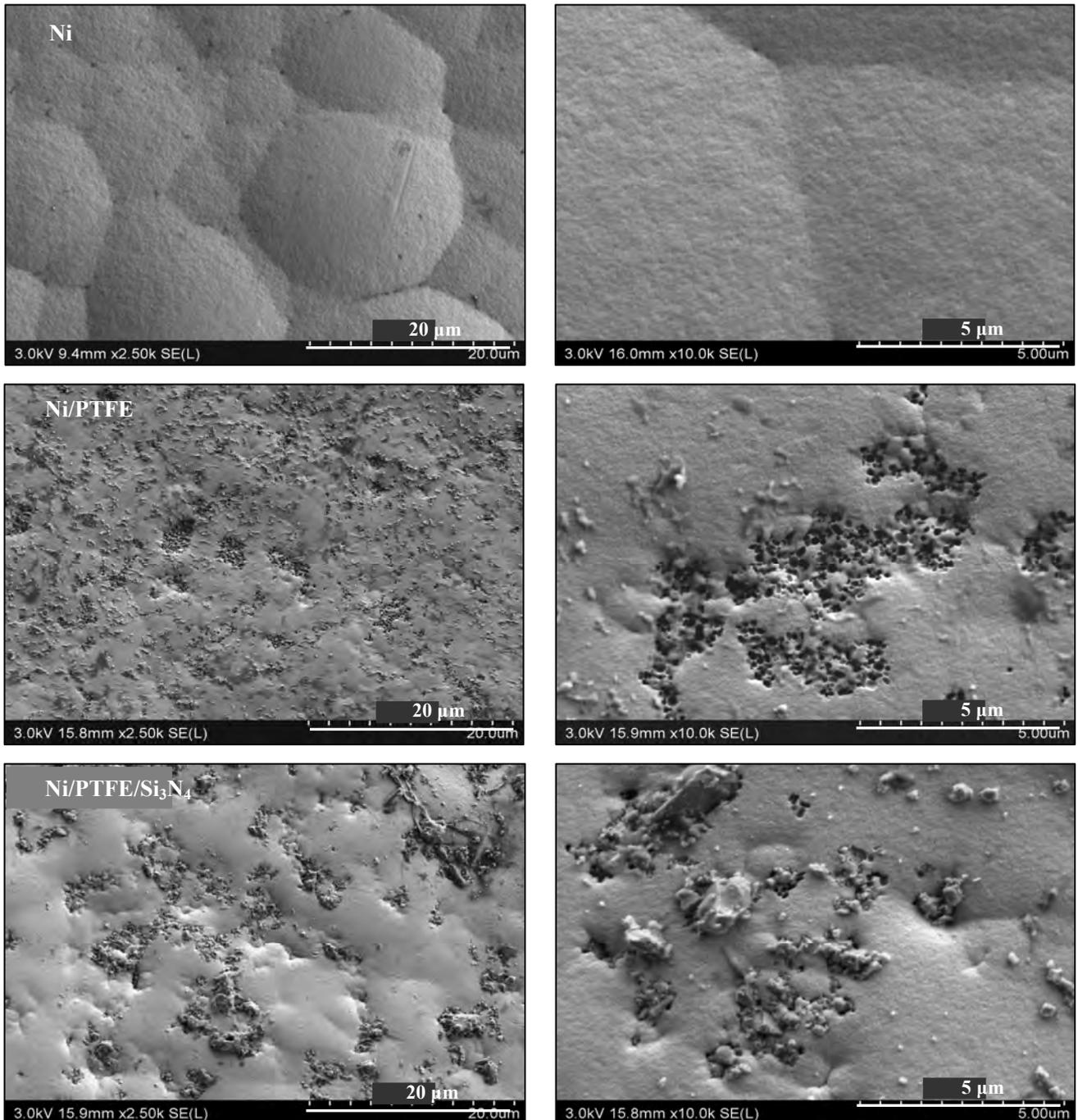


Fig. 5. Morphology of nickel and composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers

Rys. 5. Morfologia warstw niklowych i kompozytowych Ni/PTFE oraz Ni/PTFE/Si₃N₄

The preparation of a good composite with a metal matrix and ceramic and polymer dispersion phases requires both proper selection of the components as well as formation of a specific structure which ensures proper interaction of the materials forming the components of the composite. The surface material in the produced composite Ni/PTFE and Ni/PTFE/Si₃N₄ coatings is characterized by a heterogeneous internal structure and consists of a hard dispersion ceramic phase and a soft polymer phase embedded in a ductile nickel matrix. The structure of the composite material of such layers is defined to a large extent by the content and

distribution of the ceramic and polymer particles of the disperse phase in the whole volume of the material.

The structure, content and distribution of the dispersed phase in the volume of the composite coatings produced in baths containing PTFE and Si₃N₄ phases are illustrated by the cross sections shown in Figure 6.

All the investigated layers were characterized by a cohesive texture and did not show any discontinuity. In the case of the composite layers, the dispersed phase particles (PTFE, Si₃N₄) are evenly distributed throughout the volume of material (Fig. 6).

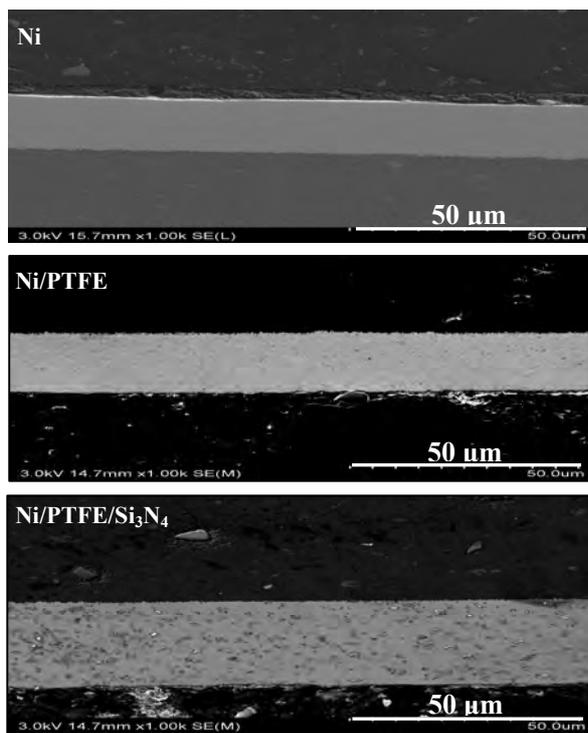


Fig. 6. Structures in cross sections of nickel and composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers

Rys. 6. Struktury w przekroju poprzecznym warstw niklowych i kompozytowych Ni/PTFE oraz Ni/PTFE/Si₃N₄

The internal structures of the layers of materials of Ni, Ni/PTFE, and Ni/PTFE/Si₃N₄ are presented in Figure 7. In the case of the nickel layer produced in the base bath, fragmentation of the nickel particles is visible. This is confirmed by TEM analysis and X-ray diffraction. The nanocrystalline nickel matrix structure is also visible in the composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers.

The nickel layer and nanocrystalline composite structure layers produced by the electrochemical method exhibit different properties. The nanocrystalline nickel layers (Ni nm) produced by the electrochemical method show a much higher hardness compared to the microcrystalline nickel layers (Ni µm) (Table 2). Incorporation of the polymer PTFE and ceramic Si₃N₄ dispersion phases into the nanocrystalline nickel layer increases the microhardness of the material layers. The hybrid layer (Table 2) is characterized by the highest hardness.

TABLE 2. Microhardness HV0.02
TABELA 2. Mikrotwardości HV0,02

Layer	Concentration PTFE in bath [g·dm ⁻³]	Concentration Si ₃ N ₄ in bath [g·dm ⁻³]	HV 0.02
Ni µm	-	-	182
Ni nm	-	-	327
Ni/PTFE	50	-	336
Ni/PTFE/Si ₃ N ₄	50	10	402

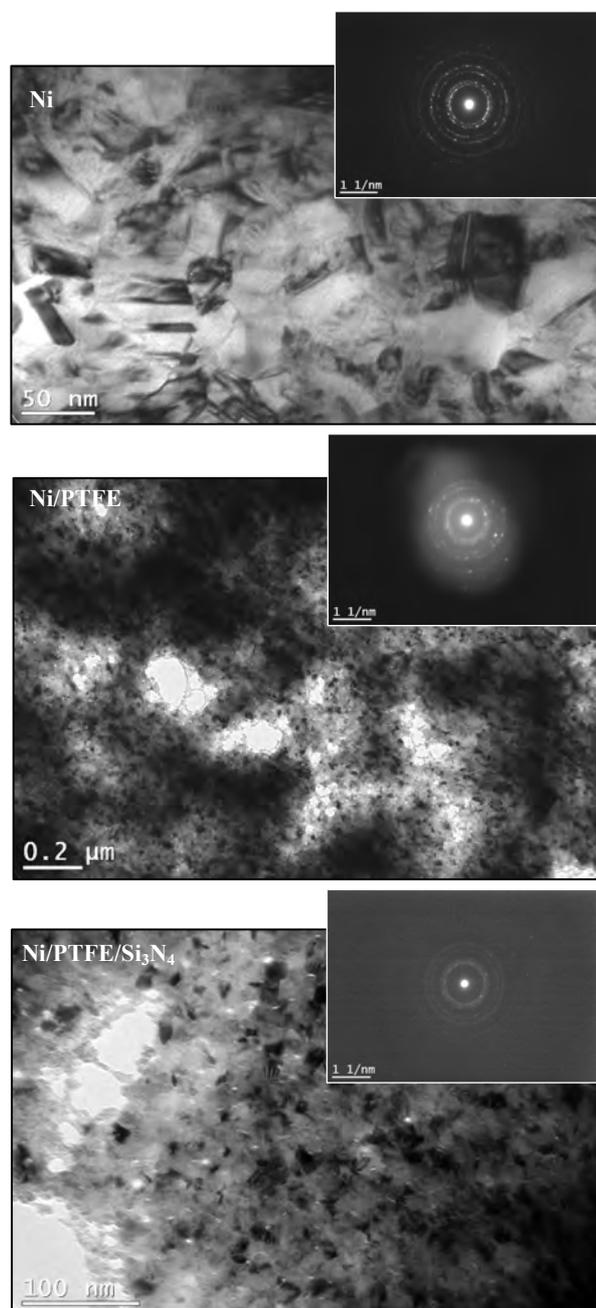


Fig. 7. Microstructure of nickel and composite Ni/PTFE and Ni/PTFE/Si₃N₄ layers

Rys. 7. Mikrostruktura (TEM) warstw: niklowej oraz kompozytowych Ni/PTFE i Ni/PTFE/Si₃N₄

CONCLUSIONS

All the investigated layers (Ni, Ni/PTFE, Ni/PTFE/Si₃N₄) produced by the electrochemical method in the modified Watts bath are characterized by a cohesive texture and structure of nanocrystalline nickel. The nanocrystalline nickel layers produced by the electrochemical method show a much higher hardness in relation to the microcrystalline nickel layer. The composite layers are characterized by an even distribution of polymer PTFE and ceramic Si₃N₄ dispersion phases in the volume of the composite material. The incorporation of PTFE and Si₃N₄ dispersion phases

in the nickel layer increases the hardness of the material layer.

All the produced layers are characterized by a cohesive and homogeneous structure and good adhesion to the aluminum substrates.

REFERENCES

- [1] Trzaska M., Kucharska B., Influence of current density and bath composition on properties of Ni/PTFE composite coatings, *Kompozyty (Composites)* 2008, 8, 77-81.
- [2] Trzaska M., Kucharska B., Surface properties of Ni/PTFE composite layers, *Kompozyty (Composites)* 2009, 9, 363-368.
- [3] Szeptycka B., Gajewska-Midziątek A., Badanie odporności na zużycie kompozytowych powłok Ni/PTFE, *Inżynieria Materiałowa* 2005, 5, 589-591.
- [4] Trzaska M., Odporność korozyjna nakompozytowych warstw nikiel/nanorurki węglowe (Ni/CNTs) wytworzonych metodą elektrochemiczną, *Ochrona przed Korozją* 2011, 2, 48-51.
- [5] Unal H., Mimaroglu A., Kadioglu U., Ekiz H., Sliding friction and wear behaviour of polytetrafluoroethylene and its composites under dry conditions, *Materials and Design* 2004, 25, 239-245.
- [6] Kowalewska M., Trzaska M., Właściwości tribologiczne warstw Ni/Si₃N₄, *Kompozyty (Composites)* 2006, 6, 32-37.
- [7] Zhao-Zhu Z., Qun-Ji X., Wei-Min L., Wei-Chang S., Friction and wear properties of metal powder filled PTFE composites under oil lubricated conditions, *Wear* 1997, 210, 151-156.
- [8] Kucharska B., Trzaska M., Struktura i właściwości tribologiczne warstw kompozytowych Ni-P/MoS₂, *Inżynieria Materiałowa* 2011, 4.