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COMPOSITES THEORY AND PRACTICE

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MICROCRYSTALLINE AND NANOCRYSTALLINE NICKEL LAYERS REINFORCED BY Al_2O_3 PARTICLES

Nickel coatings produced by plating processes are mainly used for decorative purposes and as a material that protects the substrate from corrosion. The incorporation of a reinforcing phase of alumina in a ductile nickel matrix allows for improved tribological and corrosion properties. The aim of this study was to investigate the effect of the process parameters on the structure of Ni/Al_2O_3 composite layers produced by the electrochemical method. The study included composite layers of a microcrystalline and nanocrystalline Ni matrix and micrometric and nanometric particle size disperse phases of Al_2O_3. The layers were deposited in a Watts bath modified by a nickel grain growth inhibitor, at a current density of 5 A/dm^2. In order to ensure uniform co-embedding of the disperse phase particles with the nickel matrix and to produce a stable suspension, a cationic surfactant was also used. The completed studies have shown that addition of the nickel grain growth inhibitor significantly affects the reduction of the nickel crystallite size. The particle size of alumina affects its content and distribution in the Ni/Al_2O_3 composite layer. Both, the grain size of the nickel, as well as the amount and type of built-in phase affect the microhardness of the examined nickel and composite layers.

Keywords: **nickel coating, Al_2O_3 particles, electrochemical method, microhardness**

MIKROKRYSTALICZNE I NANOKRYSTALICZNE WARSTWY NIKLOWE WZMOCNIONE CZĄSTKAMI Al_2O_3

Powłoki niklowe wytwarzane w procesach galwanicznych stosowane są głównie w celach dekoracyjnych oraz jako materiał chroniący podłoże przed korozją. Wprowadzenie w plastyczną osnowę niklową fazy zbrojącej w postaci tlenku glinu pozwala na uzyskanie lepszych właściwości tribologicznych i korozyjnych. Celem niniejszej pracy było zbadanie wpływu parametrów procesu na strukturę warstw kompozytowych Ni/Al_2O_3 wytwarzanych metodą elektrochemiczną. Badania obejmowały warstwy kompozytowe o mikrokrystalicznej i nanokrystalicznej osnowie Ni oraz mikrometrycznych i nanometrycznych wymiarach cząstek faz dyspersyjnych Al_2O_3. Warstwy osadzano w kąpieli Wattsa modyfikowanej zawartością inhibitora wzrostu ziaren niklu przy gęstości prądu 5 A/dm^2. Aby zapewnić równomierne współosadzanie cząstek faz dyspersyjnych z osnową Ni oraz wytworzenie trwałej zawiesiny, stosowano również kationowy związek powierzchniowo czynny. Zrealizowane badania wykazały, że dodatek inhibitora wzrostu ziaren niklu wpływa znacząco na zmniejszenie wielkości krystalitów niklu. Wielkość cząstek tlenku glinu wpływa na jego zawartość i rozmieszczenie w warstwie kompozytowej Ni/Al_2O_3. Zarówno wielkość ziaren niklu, jak również ilość i rodzaj wbudowanej fazy mają wpływ na mikrotwardość badanych warstw niklowych i kompozytowych.

Słowa kluczowe: **powłoka niklowa, cząstki Al_2O_3, metoda elektrochemiczna, mikrotwardość**

INTRODUCTION

The increasing popularity of composite coatings is related to their advantage over metallic coatings, because they increase resistance to frictional wear and corrosion. One of the methods of producing such coatings is electrochemical deposition [1]. With the applicable match of current parameters, the use of an organic inhibitor, disperse phase content and the degree of its dispersion, the microstructure and consequently the properties of the produced materials can be controlled [2]. Ni/Al_2O_3 composite layers produced by the electrochemical reduction method are studied in the presented paper. Built-in hard ceramic particles of Al_2O_3 in a ductile nickel matrix assure increased hardness and frictional wear resistance of the material. The combination of these two materials allows mutual complementarity of their properties [3, 4]. The incorporation of Al_2O_3 particles in the nickel layer in an electrochemical process depends on many factors, such as current density, the content of powder in the bath, hydrodynamic conditions, bath composition, and, in particular, the presence of cationic surfactants. Surfactants bind the ceramic particles with a relevant charge, which forces incorporation of the ceramic particles with the nickel. Proper stirring, in turn, allows for the maintenance of a stable, uniformly dispersed suspension of alumina, and therefore uniform distribution of the particles in the coating [2-9].

This paper presents the results of the microstructure and microhardness of microcrystalline and nanocrystalline Ni/Al_2O_3 composite layers. The microcrystalline and nanocrystalline nickel layers without Al_2O_3 particles produced by the electrochemical method were also investigated for comparative purposes.

EXPERIMENTAL PROCEDURE

The electrodeposition process of nickel and Ni/Al_2O_3 composite layers was carried out in a Watts bath, modified by a cationic surfactant (for composite layers) and by the addition of benzoic sulfimide (saccharin) (for the preparation of nanocrystalline layers) (Table 1).

Two types of alumina were used as the ceramic material: a polydisperse powder of 2.7÷11.5 μm particle size and a powder of 50 nm particle size. The composite layers were produced in a bath of constant content of ceramic phase (10 g/dm^3) and stirring rate of 400 rpm. The process was carried out at a current density of 5 A/dm^2.

The microstructure of the nickel and Ni/Al_2O_3 composite layers was studied using a Hitachi SU-70 scanning electron microscope. The coatings thickness and distribution of ceramic phase particles in the composite layer was determined by the analysis of images of cross-sections of the Ni and Ni/Al_2O_3 layers. The microhardness of the produced layers was examined by the Vickers method at a load of 20 G (HV0.02).

TABLE 1. **Bath composition for producing nanocrystalline nickel**

TABELA 1. **Skład kąpieli do wytwarzania powłoki nanokrystalicznego niklu**

Component	Concentration $[g \cdot dm^{-3}]$
$NiSO_4 \cdot 6H_2O$	300
$NiCl_2 \cdot 6H_2O$	40
H_3BO_3	35
Saccharin	5

RESULTS

The microstructure of the layers produced in the bath without the addition of growth inhibitor is shown in Figure 1. All the layers produced in this bath are characterized by a microcrystalline structure. The uniformly distributed agglomerates of the ceramic phase built by the nickel are seen on the surface in the case of the composite layer with micrometric Al_2O_3 (Fig. 1b). A change of surface morphology of the composite layer in comparison with the nickel layer was also observed.

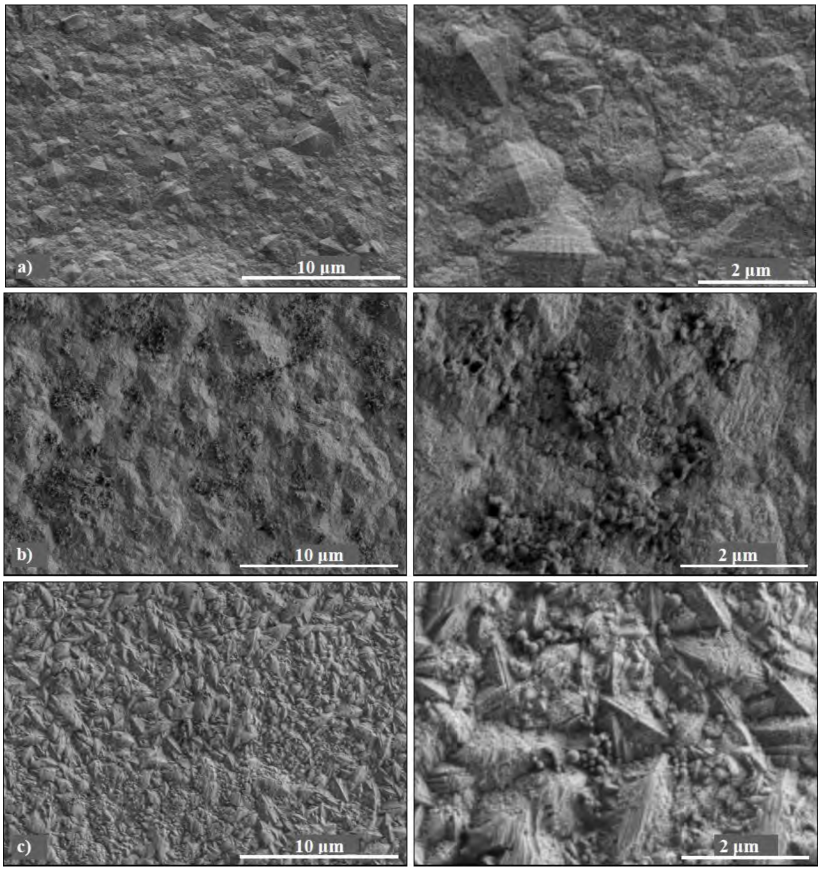

Fig. 1. Morphology of microcrystalline layers: a) nickel, b) composite with micrometric Al_2O_3, c) composite with nanometric Al_2O_3

Rys. 1. Morfologia mikrokrystalicznych warstw: a) niklowych, b) kompozytowych wytworzonych przy udziale mikrometrycznego Al_2O_3, c) kompozytowych wytworzonych przy udziale nanometrycznego Al_2O_3

The nanometric alumina (in comparison with micrometric alumina) is incorporated in the nickel matrix in a less uniform way, mainly at the “foot” of the nickel grains, which are a shaped like “rice grains” (Fig. 1c)

Figure 2 presents the surface morphology of the nickel and composite layers produced in the bath modified by the addition of saccharin. This substance blocks the growth of nickel grains by adsorbing on the surface of the cathode, resulting in a nanometric dimension of crystallites, clearly visible in the figures below. In the case of a composite layer with micrometric alumina, deeply incorporated agglomerates of the ceramic phase were observed. On the surface of the layer produced with nanometric alumina, a uniformly dispersed ceramic phase was observed, but not deeply incorporated in the nickel matrix.

The structural studies of the nickel and composite layers were complemented by microstructure analysis performed on a metallographic cross-section (Fig. 3).

The largest number of disperse phase particles and the most uniform distribution in the layer was observed in the case of micrometric Al_2O_3 co-embedded from a bath without the growth inhibitor (Fig. 3b). In the case of the composite layer produced with the same ceramic particles, but in the presence of the inhibitor, a smaller number of incorporated disperse phase particles and a lower tendency of the particles to agglomeration has been observed (Fig. 3e).

Nanometric Al_2O_3 very poorly and ununiformly incorporated in the layer of the microcrystalline structure, while in the case of the nanocrystalline layers the presence of such particles was not observed. This may be due to the presence of the inhibitor which, by adsorbing on the surface of the cathode, may also cause blocking of the incorporation of nanometric alumina. The incorporation of such small particles may also require a much greater stirring rate than 400 rpm. Moreover, observation of the nanometric ceramic phase incorporated in the nanocrystalline nickel under a microscope can not give a complete picture of the structure.

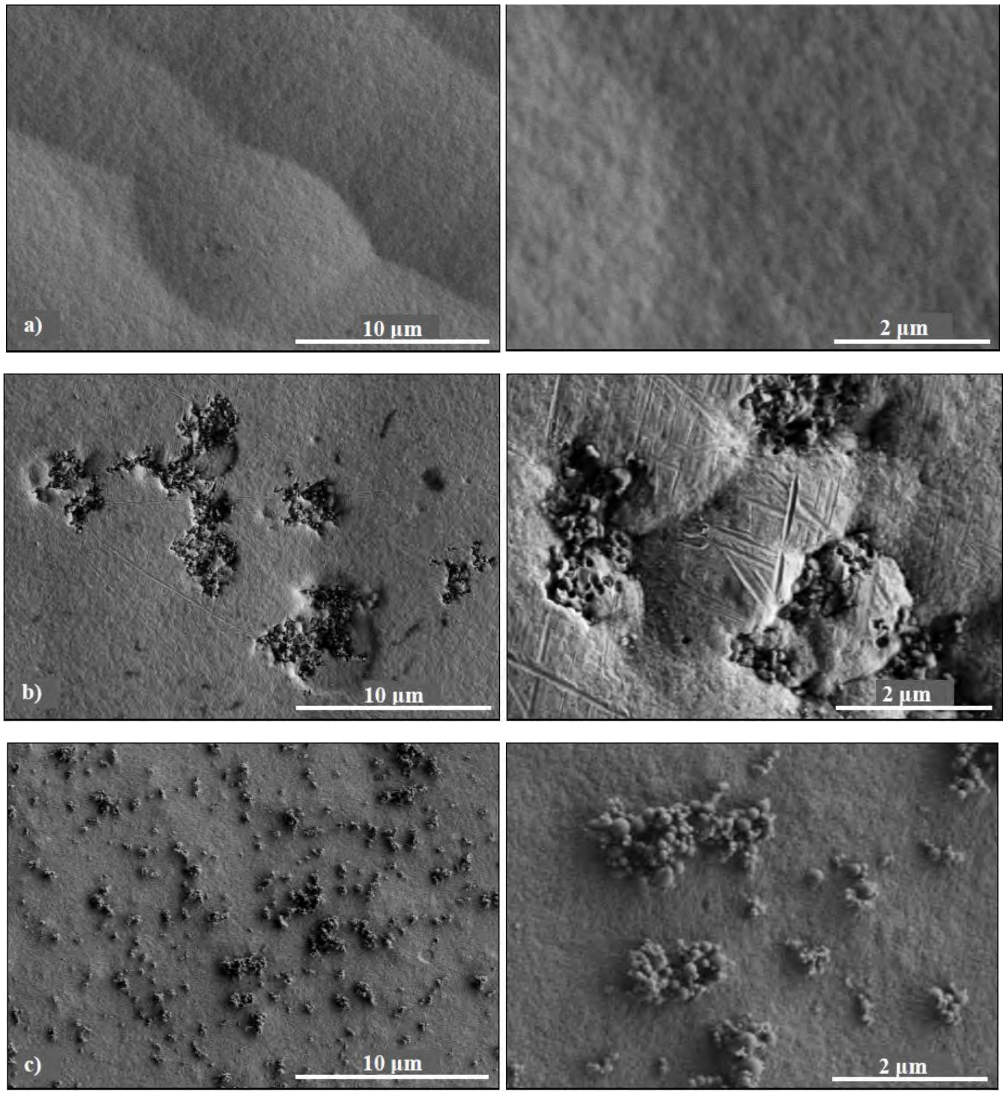

Fig. 2. Morphology of nanocrystalline layers: a) nickel, b) composite with micrometric Al_2O_3, c) composite with nanometric Al_2O_3

Rys. 2. Morfologia nanokrystalicznych warstw: a) niklowych, b) kompozytowych wytworzonych przy udziale mikrometrycznego Al_2O_3, c) kompozytowych wytworzonych przy udziale nanometrycznego Al_2O_3

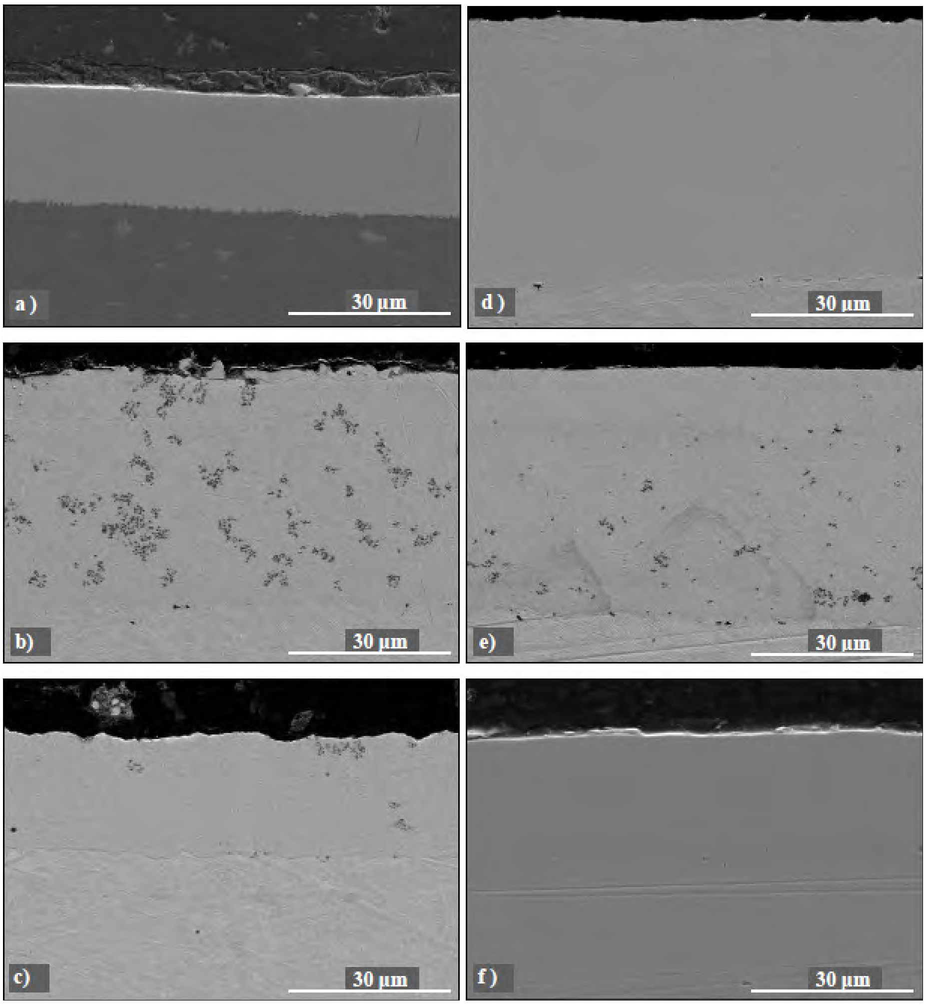

Fig. 3. Structures in cross sections of layers: a) microcrystalline nickel, b) microcrystalline composite with micrometric Al_2O_3, c) microcrystalline composite with nanometric Al_2O_3, d) nanocrystalline nickel, e) nanocrystalline composite with micrometric Al_2O_3, f) nanocrystalline composite with nanometric Al_2O_3

Rys. 3. Struktury w przekroju poprzecznym warstw: a) mikrokrystalicznych niklowych, b) mikrokrystalicznych kompozytowych wytworzonych przy udziale mikrometrycznego Al_2O_3, c) mikrokrystalicznych kompozytowych wytworzonych przy udziale nanometrycznego Al_2O_3, d) niklowych, e) nanokrystalicznych kompozytowych wytworzonych przy udziale mikrometrycznego Al_2O_3, f) nanokrystalicznych kompozytowych wytworzonych przy udziale nanometrycznego Al_2O_3

The amount of incorporated alumina and crystallite size of the nickel affect the properties of such layers. Microhardness is important from the usage point of view. The composite layers produced in the bath, respectively without and with a growth inhibitor, have greater microhardness in relation to the nickel layers. The nanocrystalline composite layer produced with the participation of micrometric Al_2O_3 has the highest microhardness (Table 2).

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

Layer	Concentration of Al_2O_3 in bath [g·dm^{-3}]	HV 0.02 (±2.2%)
$Ni_{\mu m}$	-	182
$Ni_{\mu m}/Al_2O_3$ (micrometric)	10	379
$Ni_{\mu m}/Al_2O_3$ (nanometric)	10	288
Ni_{nm}	-	327
Ni_{nm}/Al_2O_3 (micrometric)	10	530
$Ni_{\mu m}/Al_2O_3$ (nanometric)	10	466

The effect of reducing the nickel crystallite size on microhardness is also visible - in each examined case the nanocrystalline layers have greater microhardness in relation to the microcrystalline layers.

SUMMARY

The layers produced by the electrochemical method in a Watts bath modified by the addition of saccharin are characterized by a nanocrystalline nickel structure and higher microhardness in comparison with layers formed in the bath without the addition of an inhibitor (which are characterized by a microcrystalline nickel structure).

At the stirring rate of 400 rpm and current density of 5 A/dm^2, the micrometric Al_2O_3 are best incorporated in the nickel matrix. In the case of the microcrystalline layers a particularly high concentration of micrometric alumina which was uniformly distributed in the whole volume of the composite material was observed. The high concentration and uniformity also increases the microhardness of these layers in comparison with the nickel and composite layers with nanometric Al_2O_3.

Nanometric Al_2O_3 particles poorly incorporate into the nickel layer or applied research techniques do not detect them in an unambiguous way. The deficit of incorporation can be explained by the presence of the inhibitor, a too low stirring rate or inappropriate current density. The microhardness of these layers is greater than the corresponding nickel layers and less than the corresponding composite layers with micrometric Al_2O_3.

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