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Reflection and structural characteristics of semi-bright and mirror bright nickel coatings

NEBOJŠA D. NIKOLIĆ[1*#], ZLATKO RAKOČEVIĆ[2], DEJAN R. ĐUROVIĆ[2] and KONSTANTIN I. POPOV[3#]

[1]*ICTM – Institute of Electrochemistry, Njegoševa 12, P. O. Box 473, YU-11001 Belgrade,* [2]*Vinča Institute of Nuclear Sciences, P. O. Box 522, YU-11001 Belgrade, and* [3]*Faculty of Technology and Metallurgy, Karnegijeva 4, P. O. Box 3503, YU-11001 Belgrade, Yugoslavia*

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The reflection and structural characteristics of the nickel coatings obtained in the presence of a basic brightening addition agent only, and of both a basic and top brightening addition agent are examined. It is shown that the nickel coating obtained in the presence of both a basic and top brightening addition agent fulfilled the conditions to be characterized as a mirror bright metal surface. The nickel coating obtained in the presence of a basic brightening addition agent only is characterized as a semi-bright metal surface.

Keywords: bright nickel coatings, STM technique, X-ray diffraction analysis.

INTRODUCTION

Except for chromium coatings, smooth and bright metal coatings can only be obtained in the presence of leveling and brightening addition agents. Nickel is an especially interesting metal because bright nickel surfaces are deposited in the presence of two groups of brightening addition agents.

Class I brightening addition agents, which are also referred to as basic brighteners, are mostly aromatic or unsaturated, aliphatic sulfonic acid compounds, or compounds that contain divalent sulfur. These substances impart a microcrystalline structure and a limited brightness to a nickel deposit.[1]

Class II brightening addition agents, which are also referred to as top brighteners, are unsaturated compounds that are usually derived from acetylene or pyridine. These are the substances that are responsible for providing the leveling effect and the deposition of mirror bright nickel deposits.[1]

The reflection and structural criteria which must be fulfilled in order for a metal surface to exhibit mirror brightness were recently defined.[2,3] Then, it was shown by the com-

* Corresponding author. Fax: +381 11 337 03 87. E-mail address: kosta@elab.tmf.bg.ac.yu.
\# Serbian Chemical Society active member.

parison of reflection and structural characteristics of different copper surfaces with those of a silver mirror surface[2–4] that mirror brightness of metal surfaces is determined by: (a) flat and mutually parallel parts of a surface which are smooth on the atomic level, and (b) the distances between adjacent flat parts which are comparative with the distances between adjacent flat parts of a silver mirror surface as the reference standard. In the same investigation it was also shown that mirror brightness could not be associated directly with the preferred orientation of a surface.[2,3]

In this work, different nickel coatings were examined in order to establish the difference between the effects of basic and both basic and top brightening addition agents on the reflection and structural characteristics of nickel coatings. The nickel coating obtained in the presence of a basic brightening addition agent alone, and the nickel coating obtained in the presence of both basic and top brightening addition agents were examined by STM, X-ray diffraction (XRD) analysis and measurements of the reflection of light from their surfaces.

EXPERIMENTAL

Nickel was galvanostatically deposited from commercial plating baths (Protecta-Belgrade, Yugoslavia).

The solutions were Watt electrolytes with the corresponding addition agents for ductility (ZZM Ni-305), wetting agent (ZZM Ni-304), basic brightness (ZZM Ni-302) and top brightness (ZZM Ni-301). The compositions of plating baths for nickel electrodeposition are given in Table I.

TABLE I. The compositions of the plating baths for nickel electrodeposition

Watt electrolyte/g l^{-1}	Plating bath	
	I	II
$NiSO_4 \cdot 7H_2O$	275	275
$NiCl_2 \cdot 6H_2O$	50	50
H_3BO_3	45	45
Addition agents/ml l^{-1}		
ZZM Ni-301	–	1
ZZM Ni-302	5	5
ZZM Ni-305	8	8
ZZM Ni-304	6	6

The depositions were carried out galvanostatically, at a temperature of 55.0 ± 0.1 ºC, in an open cell, with a stirred electrolyte, on polycrystalline copper cathodes. The deposition current density was 60 mA cm^{-2}. The anode was pure nickel. The thicknesses of the nickel coatings were 20 μm.

The preparation of the copper cathodes consisted of alkaline degreasing at 70 ºC, followed by acid etching (20 % H_2SO_4) at 50 ºC. After each phase, the copper surfaces were rinsed with distilled water.

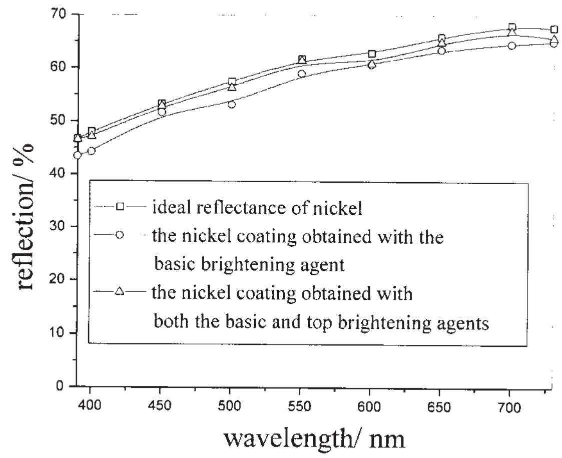
The reflection was determined using a Reflectance Spectrophotometer Beckman UV 5240, *i.e.,* the specimen was illuminated by a beam normal to the specimen [normal/total (abbreviation, 0/t): normal/diffuse (abbreviation, 0/d)]. The reflected flux was collected by means of an integrating sphere. This type of Reflectance Spectrophotometer gives the dependences of total reflection and diffuse reflection as a function of wavelength in the visible region. The difference between the total reflection and the diffuse reflection is the mirror reflection, which is a parameter for the estimation of the brightness of a metal surface.[5]

The topography of the surfaces were determined using a STM NanoScope III in air (the maximum scan size was (880×880) nm). The STM images were obtained in the constant current mode using a W tip which had been electrochemically sharpened in 1 M KOH solution. The bias voltage ranged from 18 to 22 mV and the tip current from 4.3 to 4.8 nA for nickel surfaces.

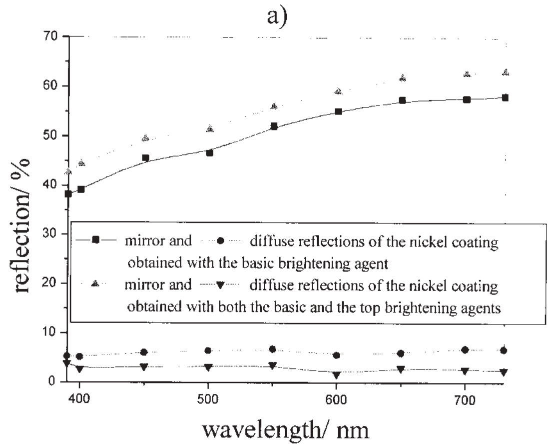
X-Ray diffraction (XRD) analysis was performed for the characterization of the nickel surfaces. A Siemens instrument (type D 500) with Ni filtered CuKα radiation (35 kV and 20 mA) was used at a continuous scan speed of 0.02° 2θ s^{-1}.

RESULTS AND DISCUSSION

The ideal reflectance of nickel[6] and the degrees of total reflection as a function of wavelength of visible light for the nickel coating electrodeposited in the presence of the basic brightening addition agent and the nickel coating electrodeposited in the presence of both the basic and the top brightening addition agents are shown in Fig. 1a. The degrees of mirror and diffuse reflections of the same nickel coatings as a function of wavelength are shown in Fig. 1b.



a)



b)

Fig. 1. The dependence of the degrees of reflection on the wavelength of visible light: a) the ideal reflectance of nickel (□) and the total reflections of the nickel coating electrodeposited in the presence of the basic brightening addition agent (○) and the nickel coating electrodeposited in the presence of both the basic and the top brightening addition agents (Δ); b) mirror (■) and diffuse (●) reflections of the nickel coating electrodeposited in the presence of the basic brightening addition agent alone; mirror (▲) and diffuse (▼) reflections of the nickel coating electrodeposited in the presence of both the basic and the top brightening addition agents.

It can be seen from Fig. 1b that the addition of the top brightening addition agent to the nickel plating bath containing the basic brightening additive led to an increase of the degree of mirror reflection and a decrease of the degree of diffuse reflection. The degree of mirror reflection of the nickel coating obtained in the presence of both the basic and the top brightening addition agents is approximately 3 – 6 % greater than the degree of mirror reflection of the nickel coating obtained in the presence of the basic brightening addition agent only, while the degree of diffuse reflection is smaller by up to 4 % than the degree of diffuse reflection of the nickel coating obtained in the presence of the basic brightening addition agent only. Also, it can be observed from Fig. 1 that the degree of mirror reflection of the nickel coating obtained in the presence of the basic and top brightening addition agents approaches very nearly the ideal reflectance of nickel. Although the degree of mirror reflection of the nickel coating obtained in the presence of the basic and top bitghtening addition agents was only 3 – 6 % greater and the degree of diffuse reflection was only 4 % smaller than the same degrees of the nickel coating obtained in the presence of the basic brightening addition agent alone, the visual difference between these nickel coatings was apparent.

The 3D (three-dimensional) STM images (880×880) nm of these nickel coatings are shown in Fig. 2. It can be seen from Fig. 2 that the addition of the top brightening addition agent to the plating bath containing only the basic brightening addition agent led to a decrease of the roughness of the nickel coating.

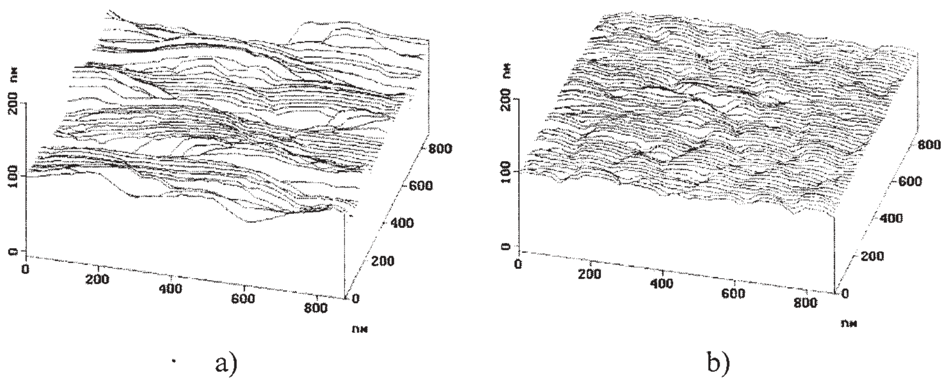
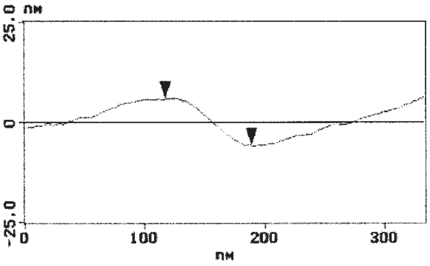
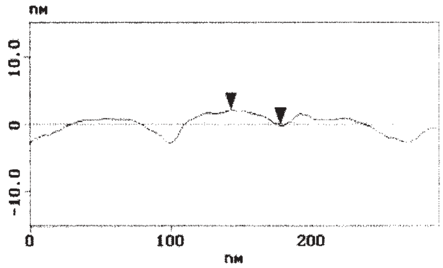


Fig. 2. 3D STM images of the nickel coatings electrodeposited with: a) basic brightening addition agent, b) both basic and top brightening addition agents. Scan size: (880 × 880) nm.

The line sections analysis of portions of the nickel surfaces shown in Fig. 2 are shown in Fig. 3. Relatively flat parts of the surface can be observed both for the nickel coating obtained in the presence of the basic brightening addition agent only and the nickel coating obtained in the presence of both the basic and top brightening addition agents. From Fig. 3b it can be seen that the nickel coating obtained in the presence of both the basic and top brightening addition agents consisted of flat and mutually parallel parts of the surface. It was shown by the STM software that the distances between adjacent flat parts of the nickel coating obtained in the presence of the basic brightening addition agent only are several times greater than the same distances of the nickel coating obtained in the presence of both the basic and the top brightening addition agents.



a)



b)

Fig. 3. The line sections analysis from the portion of the STM surfaces shown in Fig. 2: a) the nickel coating obtained in the presence of the basic brightening addition agent, b) the nickel coating obtained in the presence of both the basic and the top brightening addition agents. The distances between the markers represent: a) 11.650 nm; b) 2.335 nm.

The distance between adjacent flat parts of the nickel coating obtained in the presence of both the basic and the top brightening addition agents is several atomic diameters of nickel.[7] The same distance for the nickel coating obtained in the presence of the basic brightening addition agent only is approximately 40 atomic diameters of nickel.

The line section analysis of the flat part of the nickel coating obtained in the presence of both the basic and the top brightening addition agents is shown in Fig. 4. The roughness of this flat part of the surface is very small and less than the atomic diameter of nickel. For this reason, it can be said that the flat parts of the surface are smooth on the atomic level.

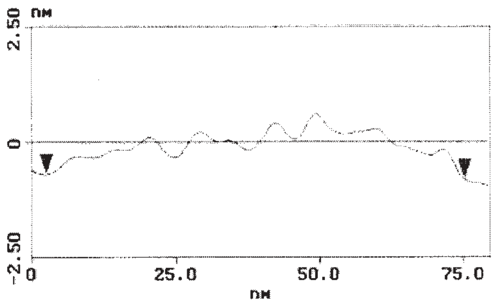
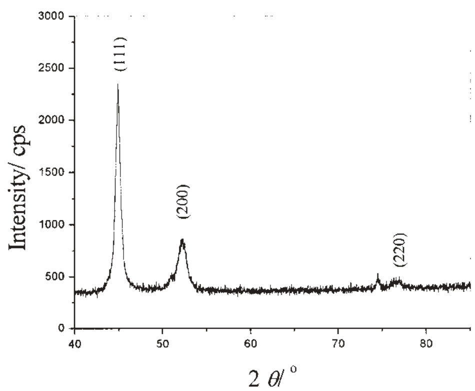


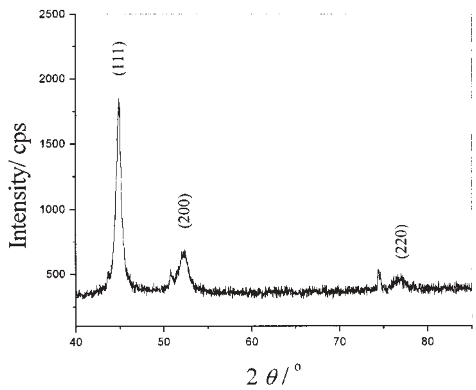
Fig. 4. The line section analysis of the flat part of the nickel coating obtained in the presence of both the basic and the top brightening addition agents. The roughness of the observed surface was 0.220 nm.

X-Ray diffraction (XRD) analysis of the nickel coating obtained in the presence of the basic brightening addition agent only, and the nickel coating obtained in the presence of both the basic and the top brightening addition agents are shown in Fig. 5. The preferred orientation of these nickel surfaces was determined according to the ASTM standard for nickel powder.[8] Both nickel coatings showed the preference for the (111) orientation.

Hence, reflection analysis of the nickel coating obtained in the presence of both the basic and the top brightening addition agents showed that the degree of mirror reflection of this coating approaches very near to the ideal reflectance of nickel. The structural details which enabled this degree of mirror reflection are: flat parts of the surface which are smooth on the atomic level and distances between adjacent flat parts which are several atomic diameters of nickel and which are comparative with the same distances of a silver



a)



b)

Fig. 5. XRD Patterns of: a) the nickel coating obtained in the presence of the basic brightening addition agent, b) the nickel coating obtained in the presence of both the basic and the top brightening addition agents.

mirror surface. On the basis of these facts, it can be concluded that this nickel coating fulfilled the reflection and structural criteria to be considered a mirror bright metal surface.

The difference in the degrees of mirror reflection between the examined nickel coatings (up to 6 %) probably arose from the larger distances between the adjacent flat parts of the nickel surface obtained in the presence of the basic brightening addition agent only compared to the same distances of the nickel surface obtained in the presence of both the basic and the top brightening addition agents. On the basis of this fact, the nickel coating obtained in the presence of the basic brightening addition agent only can be considered as a semi-bright metal surface.

Hence, reflection and structural analysis of these nickel surfaces showed a clear difference between the effects of the basic brightening addition agent only and the combined basic/top brightening addition agents mixture on the characteristics of the obtained nickel coatings.

Also, the fact that the preferred orientation of these nickel coatings which exhibited different reflection and structural characteristics was the same pointed clearly to the fact that the mirror brightness of metal coatings cannot be associated directly with the preferred orientation of the metal surface.

И З В О Д

РЕФЛЕКСИОНЕ И СТРУКТУРНЕ КАРАКТЕРИСТИКЕ ПОЛУСЈАЈНИХ И ОГЛЕДАЛСКИ СЈАЈНИХ ПРЕВЛАКА НИКЛА

НЕБОЈША Д. НИКОЛИЋ[1], ЗЛАТКО РАКОЧЕВИЋ[2], ДЕЈАН Р. ЂУРОВИЋ[2] и КОНСТАНТИН И. ПОПОВ[3]

[1]*ИХТМ – Центар за електрохемију, Његошева 12, п. пр. 473, 11001 Београд,* [2]*Институт за нуклеарне науке Винча, п. пр. 522, 11001 Београд и* [3]*Технолошко-металуршки факултет, Универзитет у Београду, Карнегијева 4, п. пр. 3503, 11001 Београд*

Испитане су рефлексионе и структурне карактеристике превлака никла добијених са основним, и са основним и врхунским додацима за сјај. Показано је да је превлака никла добијена са основним и врхунским додацима за сјај испунила услове да буде окарактерисана као огледалски сјајна површина. Превлака никла добијена само са основним додатком за сјај је окарактерисана као полусјајна метална површина.

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