The effect of architecture of Cu/Ni–Cu multilayer coatings on their microhardness

A.A.Maizelis, B.I.Bairachniy, L.V.Trubnikova, B.A.Savitsky

National Technical University "Kharkiv Polytechnic of Institute",
21 Frunze Str., 61002 Kharkiv, Ukraine

The results of measuring of the microhardness of Cu/(Ni–Cu) multilayer coatings are reported. These coatings were deposited from the pyrophosphate-ammonium electrolyte. It is shown that the microhardness of the multilayer coatings strongly depends on their architecture, as long as coatings were formed from the layers under the identical optimal conditions. The microhardness reaches its maximum when the bilayer thickness is in the range of 40–60 nm and the Ni–Cu and Cu layers thicknesses ratio is in the range of 1.8–2.5. For each layer thickness ratio, the microhardness has the maximum at its own bilayer thickness range.

Приведены результаты определения микротвердости по Виккерсу мультислойных Cu/(Ni–Cu) покрытий, электроосажденных из пирофосфатно-аммонийного электролита. Показано, что микротвердость мультислойных покрытий, сформированных из слоев, полученных в идентичных оптимальных условиях, существенно зависит от их архитектуры. Микротвердость максимальна в диапазоне значений толщины бислоя от 40 до 60 нм и отношения толщин слоев сплава к меди от 1,8 до 2,5. При каждом соотношении толщин слоев микротвердость максимальна в своем диапазоне толщины бислоя.

1. Introduction

The multilayer coatings with simple architecture are used to improve the functional properties of the product surface. For the multilayer made of two types layers the architecture parameters are the number of layers, their thicknesses and the ratio of layer thicknesses in the bilayer [1–3]. Microhardness and wear resistance are among the most important functional properties of the contacting surfaces of various engineering materials. The relationship between surface hardness and wear resistance of coated parts in contact with another surface is not single-valued. However, it is obvious that study of the microhardness of coatings is an important step toward understanding and control of the wear resistance [4]. One of the ways to improve the surface mechanical properties is the electrodeposition of composition-modulated coating, particularly, Cu/Ni–Cu multilayer coating, which consists of the alternating layers of copper and nickel-copper alloy (in the paper we will refer it simply "alloy"). The significant elastic modulus and an increase of the hardness of multilayer coatings can be associated with a high density of boundary layers in a coating [5].

It is shown in [6] that the multilayer copper-nickel coating with high wear resistance exhibits high microhardness too. Wear resistence depends on a ratio of thickness of copper and nickel layers as well as on thickness of the bilayer. The authors of [6] found that copper-nickel multilayer coatings with a ratio of nickel and copper layers thicknesses of 1:2 demonstrate the highest wear resistance. For multilayer coatings obtained by magnetron sputtering the microhardness maximum was observed at a ratio of the thicknesses of nickel and copper layers of 3:1 [7] and the bilayer thickness of 20 nm [8]. In [9] it was studied the proper-

ties of Cu/Ni multilayer coatings electrode-posited using the programmed potential, with different bilayer thicknesses and ratios of the metal layers thicknesses. Multilayer coatings exhibit greater microhardness than the nickel-plated, with the increase in microhardness by up to 25 % for the thickness of the bilayer of about 10 nm.

The cited studies of microhardness of the multilayer coatings refer to the coatings formed by various physical and electrochemical methods on the substrates of different materials. In the most of studies of the electrodeposited miltilayer coatings microhardness, the sulfamate electrolyte was used [5, 9−11]. Meanwhile, microhardness largely depends on the type of electrolyte, which itself affects the composition and microstructure of the coatings. It is technically difficult to obtain thick multilayer coatings, so the small thicknesses of 3−8 μm were used and microhardness was measured by nanoindentor or microindentor with small load (0.2−10 g, the method of Knoop). Since the values of microhardness depend [12] on the method of the measurement, thickness of the coating and microhardness of the substrate, it is difficult to compare the published data with the values of Vickers microhardness for other metallic coatings.

The purpose of the current study is to determine the effect of architecture of the multilayer coatings deposited from pyrophosphate-ammonium polyligand electrolyte on the coating microhardness.

2. Experimental

Cu/Ni–Cu multilayer coatings were deposited on copper samples from pyrophosphate-ammonium electrolyte [13] by single-bath technique, using a current regime programmed by the programmer PR-8 and potentiostat PI-50.1. A saturated silver chloride electrode was used as a reference electrode.

Thicknesses of the copper and alloy layers h, nm, were calculated from the value of current and time of deposition of each layer, according to Faraday's law,

$$h = \frac{k \cdot J \cdot t \cdot E_C}{36\rho},\qquad(1)$$

where k is the electrochemical equivalent of copper or the alloy, $g \cdot A^{-1} \cdot h^{-1}$; J is the current density during deposition of copper or the alloy layer, $mA \cdot cm^{-2}$; t is the time of copper or the alloy deposition, s; E_C is the

current efficiency of copper or the alloy deposition, %; ρ is the density of copper or the alloy, $g \cdot cm^{-3}$.

The electrochemical equivalent of the alloy k is

$$k = \frac{k_{Cu} \cdot k_{Ni}}{k_{Cu} \cdot n_{Ni} + k_{Ni} \cdot n_{Cu}},\qquad(2)$$

where k_{Cu} and k_{Ni} are the electrochemical equivalents of copper and nickel, respectively; n_{Cu} and n_{Ni} are the mass fractions of copper and nickel in the alloy.

The density ρ of the alloy is

$$\rho = \frac{\rho_{Cu} \cdot \rho_{Ni}}{\rho_{Cu} \cdot n_{Ni} + \rho_{Ni} \cdot n_{Cu}},\qquad(3)$$

where d_{Cu}, d_{Ni} are the densities of copper and nickel, respectively.

The current efficiencies of copper and the alloy deposition, as well as the mass fractions of copper and nickel in the alloy, were determined by the anodic stripping voltammetry, when the individual copper and the alloy layers on platinum electrode were dissolved in ammonia-glycinate solution [14]. The current efficiency E_C of the alloy is

$$E_C = \frac{Q_{Cu} + Q_{Ni}}{Q},\qquad(4)$$

where Q_{Cu} and Q_{Ni} are charges calculated from the peak areas of the anodic polarization curve, corresponding to dissolution of copper and nickel, respectively; Q is charge during the cathodic deposition of the alloy layer.

The current efficiency of copper allocation is determined by Eq.(4) with $Q_{Ni} = 0$.

The mass fraction of copper in the alloy is

$$n_{Cu} = \frac{k_{Cu} Q_{Cu}}{k_{Cu} \cdot Q_{Cu} + k_{Ni} \cdot Q_{Ni}}.\qquad(5)$$

The relative error in determining of the layers thickness was less than 5 %.

The surface morphology was observed using a scanning electron microscope REMMA-101A at an accelerating voltage of 20 kV.

Vickers microhardness of the coating with thickness of 28−33 μm was studied using microhardness tester PMT-3. The load on the diamond pyramid was 20 g. Each microhardness value was the average one of the 5−8 measurements.

Table 1. The parameters of the multilayer coatings and their Vickers microhardness

Sample	Fig.	Curve	d_{Cu}, nm	d_{Ni-Cu}, nm	d, nm	d_{Ni-Cu}/d_{Cu}	HV, kgF·mm^{-2}
1	1a	1	40	33	73	0,83	600
2	1a	2	50	33	83	0,66	552
3	–		14	23	37	1.64	500
4	–		9	23	32	2.56	656
5	1b	1	20	33	53	1.65	650
2	1b	2	40	33	73	0.83	600
6	2a		31	17	48	0.55	500
7	2b		31	51	82	1.65	463
8	2c		31	60	91	1.94	428
9	4	1	20	33	53	1.65	650
5	4	2	20	6	26	0.30	464
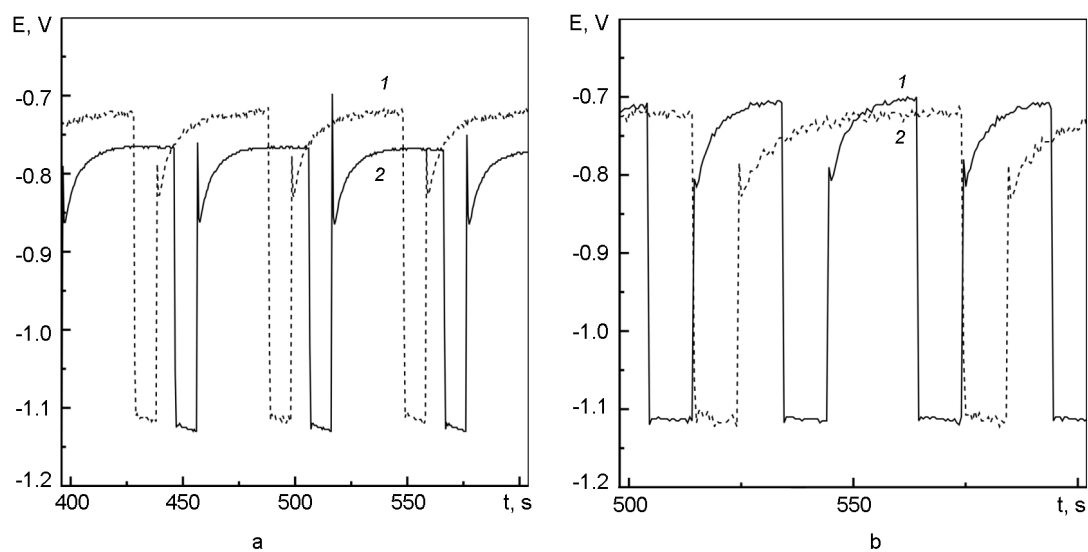
Fig. 1. $E-t$ — curves of electrodeposition of the multilayer coatings with different copper layer thickness using different current densities (a) and different time of electrolysis (b).

3. Results and discussion

In order to determine the effect of the multilayer coatings architecture on their microhardness the set of coatings was formed in the pyrophosphate-ammonium electrolyte. We varied the bilayer thickness and thickness of each layer by: (1) changing the chronogram of electrolysis, i.e. duration of the pulses of copper layer and the alloy layer deposition; (2) changing the rate of the layer electrodeposition, using the corresponding current density in the pulse.

The Table 1 shows the architecture parameters of the deposited multilayer coating, i.e. bilayer thickness d and the thicknesses ratio d_{Ni-Cu}/d_{Cu} of copper d_{Cu} and alloy d_{Ni-Cu} layers in the bilayer; the values of Vickers microhardness HV; the refer-

ences to the Figs. that show $E-t$ — curves (changing of electrode potential with time) of its obtaining. The $E-t$ — curves reflect the electrolysis chronograms and the potentials corresponding to the programmed current density in the period. Copper layers were deposited in the range of potentials from −0.7 V to −0.9 V, and the range of potentials of the alloy layers electrodeposition is from −1.1 V to −1.15 V. For comparison we obtained the value of microhardness $HV_{Cu} = 154$ kgF·mm^{-2} for copper coating that was deposited from copper pyrophosphate-ammonia electrolyte and did not contain nickel ions. Respectively, the value of microhardness of nickel coating $HV_{Ni} = 360$ kgF·mm^{-2} was found for the coating electrodeposited from nickel pyro-

phosphate-ammonium electrolyte in the absence of copper ions.

Fig. 1a shows the formation process for the two multilayer coatings with different copper layer thicknesses. Deposition durations of copper and the alloy layers for this two samples are the same, and an increase of copper layer thickness was achieved by increasing of the current density resulting in the shift of deposition potential to the negative side (curve *2*) and a decrease of the coating microhardness value (samples 1 and 2, Table).

The decrease of the microhardness with the increase of the current density of copper layer deposition is observed, if an agitation is used or for thinner layers of the bilayer (samples 3 and 4 in Table).

Using traditional pulsed electrolysis a deposition of copper layer occurs via the contact displacement mechanism during the current pause. Thickness of the layer is limited by kinetics of the contact displacement in this method. As opposed to the pulse electrolysis using the programming current or potential method does not impose any limits on copper layer thickness. However, this only applies to copper coatings obtained under the optimal conditions of electrolysis. If the current density is exceeded, which corresponds to more negative potentials at $E-t$ — curve, copper layers become less dense, which obviously is the reason for the coating microhardness decrease (samples 2 and 3).

Reduction of the thickness of copper layer, which was deposited under optimal conditions (Fig. 1b), leads to increasing of the microhardness of the multilayer structure (samples 1 and 5, Table).

Fig. 2 shows $E-t$ — curves of the multilayer coatings obtained with the same electrolysis parameters for copper layer deposition, and different amounts of charge for the alloy layer deposition (samples 6, 7, 8). Despite the increase of nickel fraction (which is harder than copper) in the coating the increase of the alloy layer thickness does dot lead to the increase of the microhardness of the whole multilayer coating. This is due to the inevitable codeposition of copper during nickel deposition. In any electrolyte for copper-nickel multilayer deposition when the polarization is very significant for electropositive copper, the concentration of copper ions in the region of near-electrode surface decreases. This leads to copper deposition with the rate limited by the diffusion of copper ions to the electrode surface. The coating quality deterio-
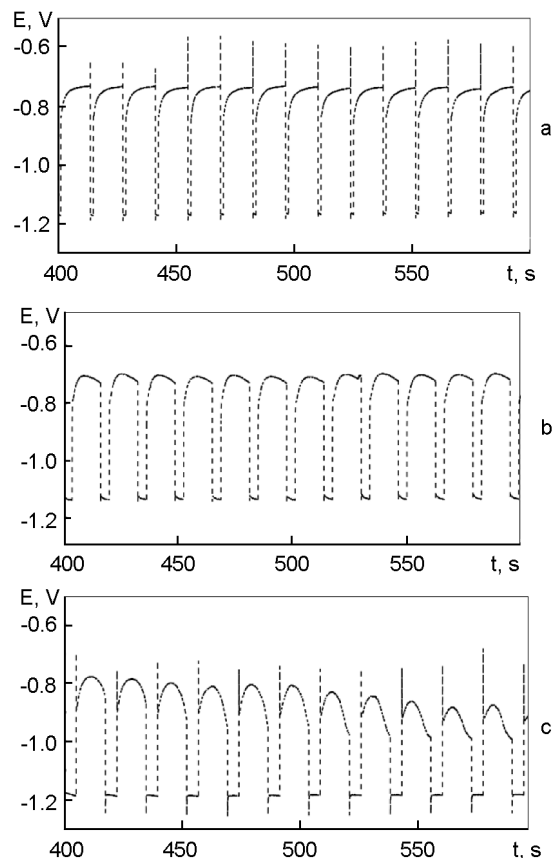

Fig. 2. $E-t$ — curves of electrodeposition of the multilayer coatings with different alloy layer thicknesses, using different charges.

rates with the increase of electrolysis time and the concentration of copper ions in the electrolyte. Character and degree of quality deterioration of the coatings depends on the electrolyte: at the limiting current the coating becomes either less compact or dendrites and outgrowths grow on the surface, it is polluted with hydroxides inclusions and its surface becomes dark and rough.

The feature of polyligand pyrophosphate-ammonium electrolyte is that a nature of the limiting current for copper deposition is not purely diffusive, but it is also associated with the previous stage of chemical dissociation of the complexes [15]. This allows deposition of compact coatings by nickel-copper alloy of greater thickness and greater concentration of copper ions in the electrolyte, which in its turn, can increase the thickness of a compact layer of the alloy, copper content in the alloy and rate of copper layer deposition.

An increase of the alloy layer deposition time leads to greater decrease of the concentration of copper ions in the electrolyte be-
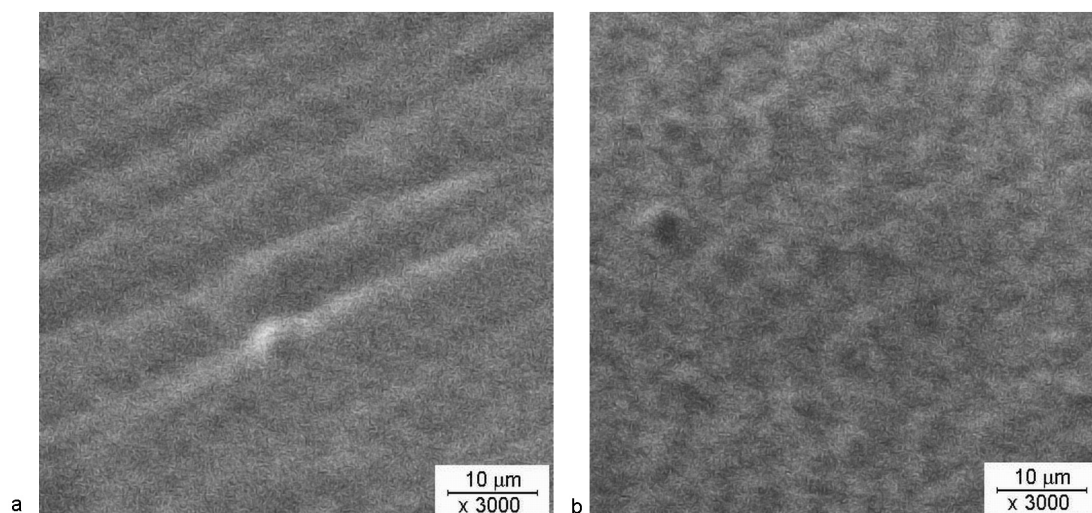
Fig. 3. Surface morphology of the samples 6 (a) and 8 (b) from Table.

side an electrode, so the value of its limiting current decreases. If it decreases to the value of the operating current density for copper layer deposition the deposition potential shifts to the negative side. In the case of sample 8, the potential shifts by 200 mV (Fig. 2c) during 10 cycles. This results in deposition of copper under the limiting current not only during its codeposition with nickel, but also during copper layer formation. The multilayer coating becomes less dense and its microhardness decreases.

Fig. 3 shows SEM images of the surface of the samples 6 and 8. The images reflect a small grain size of the coating, that is comparable with those given in [16, 17] for the nanostructured multilayer coatings. It also can be seen, that the surface of the sample 6 (Fig. 3a) is more compact than for the sample 8 (Fig. 3b).

An increase in the alloy layer thickness leads to decreasing of the coating microhardness due to decrease of its density. But this dependence has a maximum, when decreasing of the alloy layer thickness leads to increasing of the microhardness first, and then it decreases. The examples of this can be the samples 5 and 9 (Table), which differ by the time of the alloy layer electrodeposition. The decrease of the microhardness with the decrease of the layer thickness is obviously caused by weakening of the strength of a thin layer, and then by loss of the layer continuity and incomplete overlap with the previous layer. The minimal thickness of the continual layer decreases with an increase of the number of nuclei formed during the layer electrodeposition, and in-
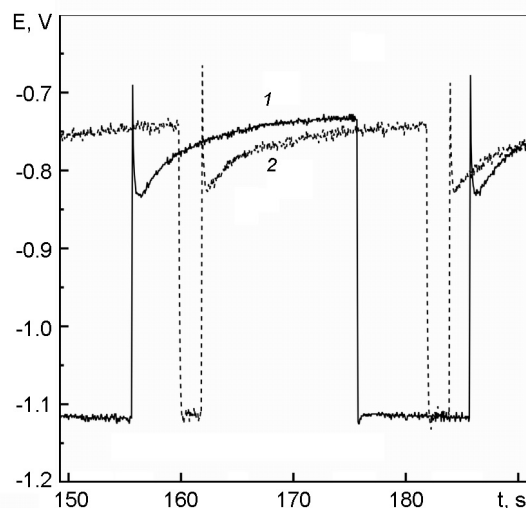

Fig. 4. E–t — curves of electrodeposition of the multilayer coatings with different alloy layer thicknesses using different electrolysis times.

crease of the tangential growth rate [18]. We found that both 2D instantaneous and 3D progressive nucleation take place during electrodeposition of copper and nickel layers from the ammonium-pyrophosphate electrolyte [19]. Also it is known that the coatings that were deposited from pyrophosphate electrolyte have small grain size [20, 21]. So we can suggest the possibility of electrodeposition from polyligand electrolyte of the continuous layers with the lower thickness than, for example, from acid solutions.

The samples layers thickness in Figs. 1 and 3 is the same, but the microhardnesses of the coatings differ due to the different potential of the electrodeposition. So, we used the electrodeposition time variation
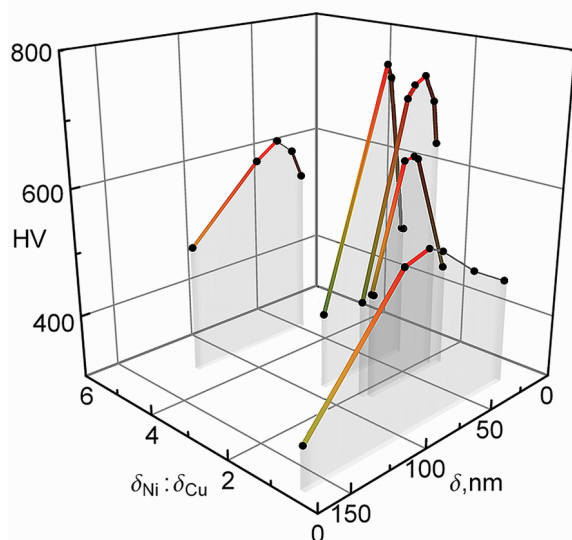
Fig. 5. Dependence of microhardness of multilayer coatings on the bilayer thickness d and thickness ratio d_{Ni-Cu}/d_{Cu} of copper and alloy layers in the bilayer.

for formation of the layers with different thickness. Also, thickness of the layers was limited by the formation of the compact layers of copper and alloy. Pyrophosphate-ammonium electrolyte allows reducing the lower boundary of the thickness of copper and the alloy layers due to more uniform thickness and fine-grained coatings overlaying the previous layer. Also, this electrolyte allows raising the upper limit of the thickness of compact alloy layers due to the mixed nature of the limiting current of copper electrodeposition [22]. We electrodeposited the coatings with Vickers microhardness in the range of $300-800$ kgF·mm^{-2}.

Dependence of microhardness on the bilayer thickness and ratio of the layer thickness in the bilayer is shown in Fig. 5. All of the dependences have a maximum, which shifts from the bilayer thickness of 80 nm, when thickness ratio of alloy and copper layers is 0.5, to the bilayer thickness of 40 nm, at a ratio of $1.8-2.5$. With the further increase of the ratio, the dependence maximum shifts to the greater bilayer thicknesses again.

4. Conclusions

Microhardness of the multilayer coatings formed under identical optimum conditions extremely depends on their architecture. The microhardness of the coatings elec-

trodeposited from pyrophosphate-ammonium polyligand electrolyte has the maximum in the range of the bilayer thickness of 40 to 60 nm and the thicknesses ratio of copper and the alloy layers from 1.8 to 2.5. Each dependence of the microhardness on the bilayer thickness has a maximum different for each layer thickness ratio.

References

1. S.Hassani, J.Klembergsapieha, M.Bielawski et al., *Wear*, **265**, 879 (2008).
2. A.Srivastava, V.Joshia, R.Shivpuria et al., *Surf. Coat. Technol.*, **163−164**, 631 (2003).
3. A.A.Voevodin, S.D.Walck, J.S.Zabinski, *Wear*, **203−204**, 516 (1997).
4. J.R.Tuck, A.M.Korsunsky, R.I.Davidson et al., *Surf. Coat. Technol.*, **127**, 1 (2000).
5. R.C.Cammarata, *Thin Solid Films*, **240**, 82 (1994).
6. Wei Zhang, Qunji Xue, Zhang, *Thin Solid Films*, **305**, 292 (1997).
7. H.C.Barshilia, K.S.Rajam, *Surf. Coat. Technol.*, **155**, 195 (2002).
8. Xiaohua Zhang, Daoxin Liu, Guohua Liu et al., *Tribol. Int.*, **44**, 1488 (2011).
9. A.Tokarz, T.Fraczek, Z.Balaga et al., *Rev. Adv. Mater. Sci.*, **15**, 247 (2007).
10. R.R.Oberle, R.C.Cammarata, *Scripta Metall. Mater.*, **32**, 4 (1995).
11. T.Hattori, Y.Kaneko, S.Hashimoto, *Mater. Sci. Forum*, **561−565**, 2451 (2007).
12. C.C.Useinov et al. in: Nauchnaja Sessija MIFI-2010, Moscow, Russia (2010), v.2, p.233.
13. Patent Ukraine 92430, (2010).
14. Patent Ukraine 63867, (2011).
15. A.A.Maizelis, B.I.Bairachniy, L.V.Trubnikova, *Vopr. Khim. i Khim. Tekh.*, **4**, 42 (2011).
16. S.K.Ghosh, A.K.Grover, G.K.Dey, M.K.Totlani, *Surf. Coat. Tech.*, **126**, 48 (2000).
17. I.Baskaran, T.S.N.Sankara Narayanan, A.Stephen, *Mater. Lett.*, **60**, 1990 (2006).
18. I.M.Kovenskij, V.V.Povetkin, Metallovedenie Pokrytij: Uchebnik Dlja Vuzov, SP Intermet Inzhiniring, Moscow (1999) [in Russian].
19. L.V.Trubnikova, B.I.Bayrachny, A.A.Maizelis, in: 9th Int. Frumkin Symposium: Electrochem. Technologies and Materials for 21st century, Moscow, Russia (2010), p.172.
20. V.V.Orehova, Poliligandnye Jelektrolity v Gal'vanotehnike, Vischa Shkola, Kharkov, (1979) [in Russian].
21. B.A.Purin, Jelektroosazhdenie Metallov iz Pirofosfatnyh Jelektrolitov, Zinatne, Riga (1975) [in Russian].
22. A.A.Maizelis, B.I.Bairachniy, L.V.Trubnikova in: XIX Mendeleev Congress on General and Applied Chemistry, Moscow, Russia (2011), v.4, p.172.

Вплив архітектури мультишарових покрить Cu/(Ni–Cu) на їх мікротвердість

А.О.Майзеліс, Б.І.Байрачний, Л.В.Трубнікова, Б.А.Савицький

Наведено результати визначення мікротвердості за Вікерсом мультишарових Cu/(Ni–Cu) покриттів, що електроосаджені з пірофосфатно-амонійного електроліту. Доведено, що мікротвердість мультишарових покриттів, що формовані з шарів, отриманих в ідентичних оптимальних умовах, суттєво залежить від їх архітектури. Мікротвердість максимальна в діапазоні значень товщин бішару від 40 до 60 нм і відношення товщин шарів сплаву до міді від 1,8 до 2,5. При кожному співвідношенні товщин шарів мікротвердість максимальна в своєму діапазоні товщин бішару.