Leveling Power of Co-W and Fe-W Electrodeposited Coatings
Zhanna Bobanova1,a, Vladimir Petrenko1,b*, Natalia Tsyntsaru1,2,c, Aleksandr Dikusar1,d

1Institute of Applied Physics, Chisinau, Moldova
2Dept. of Physical Chemistry, Vilnius University, Vilnius, Lithuania
abobanova@phys.asm.md, bv_petrenko@phys.asm.md, cashra_nt@yahoo.com,
ddikusar@phys.asm.md

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Abstract. The leveling power of gluconate and citrate electrolytes used to obtain the Co-W and Fe-W alloys was studied. The leveling power parameter P was calculated according to the results of profilographic measurements of microprofile carried out before and after deposition of the coating on surface. It was shown that deposition of said alloys occurs with preferential coating thickness increase on microprofile peaks and low microlevelling power.

Introduction
The deposition of W and iron group metal is now actually of live interest [1]. Actual studies of microdistribution during electrodeposition of metals and alloys are associated with the ability to create coatings with desired functional properties that depend on the structural and chemical heterogeneity of alloys arising during the electrolysis process on the microrelief and thickness of the coatings. When applying protective and decorative coatings from conventional electrolytes, the cost of grinding and polishing make up 70-80% of the cost of the entire process. When precipitating from leveling electrolytes, the cathode surface roughness decreases, which makes it possible to completely eliminate finishing polishing operations of the coatings and to increase the economic advantages of the technological process as compared with electrolytes of another type. Earlier it was shown that a significant decrease in the roughness growth of said coatings (down to initial level of substrate roughness) on smooth samples is possible only with the use of special additives [2]. Much attention is paid to the achievement of uniform coating and smoothing of substrate defects, both in the theoretical description of the peculiarities of the process [3] and in practical research [4]. In this work, we studied the leveling properties of gluconate and citrate electrolytes used for induced codeposition of cobalt or iron with tungsten on samples with regular microrelief.

Technique
Microleveling is observed on the surface with irregularities when the influence of the ohmic current distribution is negligible. This occurs when the size of irregularities of the order of micrometers or several tens of micrometers. Of great importance is the microdistribution of potential and diffusion limitations. In some cases, such as when deposition occurs on a sawtooth profile or samples with slits, a geometric leveling takes place due to the closing of the layers growing on the adjacent slopes (walls) of the profile. In this case, the influence of the nature of the electrolyte is smeared.

The coating microdistribution on samples with a repetitive mildly sloping sinusoidal profile (peak height ~ 10 μm and spacing ~ 50 μm) was investigated in the present study. As the samples were used plates cut from a nickel matrix for forming gramophone records. This practice is often observed in similar studies.

The electrolyte levelling power P was determined according to the data of profilographical surface measurements with a Surtronic 25 (Taylor Hobson) profilograph as a change in the peak height of the surface microprofile with an increase in the average coating thickness. The effect of current density
under galvanostatic conditions and the citrate and gluconate electrolyte composition on the microdistribution of Co-W and Fe-W alloy coating was studied.

To study the dynamics of profile change with increasing coating thickness, deposition was carried out step by step forming of several layers on one sample with registration of microprofile after application of each layer. At the beginning of the experiment, the initial profile of the sample was fixed, then sample was degreased, cleaned, activated, and subjected to electrolysis. After applying the coating layer, measurements were made again. Then the sample preparation procedure was repeated. The next layer was applied and the measurements were repeated. This procedure allows you to reduce the experiment time and material costs. Comparative experiments with applying a layer of large final thickness did not show a significant difference. Using one sample allows you to eliminate errors due to the uneven profile height on different samples. A large number of repeated measurements of the profile at each stage dramatically reduces the determination errors due to the growth of dendrites or the imperfection of the deposition process.

The obtained profiles, the height of the peaks were analyzed using the TalyMap Gold 5.0 program and the parameter P was calculated for each stage. The evaluation of the electrolyte leveling power of P was carried out using the results of profilographic measurements and was calculated according the formula

\[ P = -\frac{a}{2\pi d_m} \ln \frac{H_t}{H_0}, \]

where \( a \) is length of profile wave, \( d_m \) is the average coating thickness, \( H_0 \) is the initial height of the protrusion (peak-valley height difference), \( H_t \) is the current peak height.

Deposition of Co-W and Fe-W alloys was carried out at cathodic current densities of 1, 2, and 5 A/dm² in the galvanostatic mode with various compositions of citrate and gluconate electrolytes. Concentration of precursors (Co and W – components of depositing alloys) varied from 0.05 M (as in commonly used electrolyte [6] to 0.25 M – at 5 times. As a reference, nickel from the Watts electrolyte was also deposited onto the samples with the same profile. The morphology and the average chemical composition of the coating on different parts of the microprofile were studied using Hitachi TM 3000 Scanning Electron Microscope with the integrated EDX module.

Results and Discussion

The study of the electrolyte leveling properties in the case of cobalt and iron with tungsten codeposition is a necessary condition for obtaining high-quality electroplated coatings. The high leveling power of electrolytes is the ability to form deposit smoothed by microprofile. When alloys are depositing from citrate and gluconate electrolytes with the formation of complex compounds (with a high molecular weight [5]) under diffusional restrictions, combinative types of microdistribution are realized, unlike the pure nickel deposition.

The calculation of the leveling power \( P \) based on profilographic studies has shown that in most cases of Co/Fe with W alloys codeposition from these electrolytes the height of the profile peak increases, for them basically \( P < 0 \), which indicates that electrolytes do not have leveling properties or have weak alignment. Only some leveling occurs when sufficiently thick coating is plated. \( P \) in such electrolytes ranges from -0.13 to 0.06.

It was determined that in the process of electrodeposition of Co-W coatings from dilute gluconate electrolytes, the nature of the micro distribution of the alloy changes; in the evolution of the microprofile, positive (\( P > 0 \)) and negative alignment (\( P < 0 \)) effects appear on different areas of the cathode surface; anti-leveling and at the same time fixed areas of uniform distribution of the content of the components of the alloy Co-W in the micro grooves and microprotrusions. When \( P > 0 \), there is a predominant increase of the deposit thickness in the groove compared to the microprotrusion. Negative values of the leveling parameter are characteristic for dilute and concentrated gluconate electrolytes for the deposition of Co-W and Fe-W alloys.

Changes in electrolysis conditions by increasing the concentration of metal components in electrolyte and current density affect the leveling power of gluconate electrolytes. With an increase in the concentration of deposited metal salts 0.05 M to 0.25 M, Co-W alloys coatings are characterized
by a uniform chemical composition by microprofile, and an increase in current density to 5 A/dm² contributes to the fact that the electrodeposition of both components of the alloy of Co-W alloys occurs predominantly on the places of profile valley, which indicates the better electrolyte leveling properties. They are primarily associated with preferential deposition on profile hollow. The calculated leveling power $P$ increases from -0.006 to -0.1 with increasing coating thickness. For comparison, nickel coatings obtained from the Watts electrolyte have $P$ values 0.001 up to 0.35, that is, microroughness is smoothed out even at the coating thickness 30 microns and less.

The dynamics of changes in the profile of samples with coatings of nickel and cobalt-tungsten alloys shows that when nickel is deposited, the height of the protrusions stably and rapidly decreases (Fig. 1a), which is reflected in the value of $P$ (Fig. 2). In contrast, during the deposition of alloys, a significant increase in the profile height occurs at the beginning (Fig. 1) and only with sufficiently thick coatings the height of the protrusions decreases. The $P$ value decreases accordingly (Fig. 3).

When comparing microleveling power of different electrolytes, it can be seen that gluconate electrolytes have better leveling properties than citrate ones (Fig. 3). However, in all cases, the profile evolution passes through a stage of a sharp increase in the profile height that result in negative value of $P$ (compare Fig. 1 and 3). In contrast, nickel plating occurs with successive smoothing of the profile (compare Fig. 1 and 2). An increase in the deposition current density leads to an increase in smoothing (Fig. 4).

| 1 | 2 |
|---|---|
| 3 | 4 |

**Fig. 1.** Dynamics of profile height change during deposition of nickel (a) and Co-W (b).
1. Sample profile; 2. First layer (20 µm thick); 3. Second layer (total thickness 40 µm); 4. Third layer (total thickness 60 µm)
The process of Fe-W deposition from citrate electrolytes is inhibited, practically does not occur, the coating thickness varies from 4 to 5 µm for each layer and slightly increases only on profile protrusions, the calculated leveling power varies from -0.13 to 0.001. This is probably due to the formation of a phase film on the cathode consisting of hydroxide metal compounds formed during alkalization of the near-electrode layer during electrolysis.

**Morphology.** Studies of the morphology of the applied coatings show that micro irregularities appear on the surface during the deposition of the studied alloys: structural imperfections, dislocation distortions that form crystalline roughness and crystalline structures of various types. Because of this,
there is a predominant increase in deposit thickness on the protrusions, a narrowing of the depression and an overall increase in the height of the profile peak (Fig. 5). During the deposition process the coating thickness increases (without taking into account the influence of the uneven distribution of the potential and the diffusion rate over the surface) in direction perpendicular to the base and the low parts overgrow with time. This alignment is typical for slots with steep sides. This phenomenon is called geometric levelling. The type of formations depends on the deposition current density.

In this case of the alloy deposition the profile evolution depending on the mean coating thickness increase leads to preferential peaks growth. This type of coating formation can be associated with different rates of diffusion processes on peaks and valleys.

In the case of the presence of complex compounds with a large mass, the diffusion rates at different sites may differ significantly, which affects the deposition rates with a predominant increase at the peaks. The negative leveling with P < 0 has been observed in the study (Fig. 3-5).

Local chemical composition. The chemical composition of alloys along microprofile is determined, depending on the nature of metal ions, current density, concentration of metal salts. It has been shown that the alloys under study have mainly non-uniform chemical composition by microprofile. The local chemical composition on peaks and in valleys differs from the average composition over the surface, which can affect the chemical and structural heterogeneity of alloys on the coating microrelief.

Co-W alloys obtained from dilute gluconate electrolyte show a difference in the chemical composition on the protrusions and hollows of the microprofile compared with the average surface chemical composition. Increasing the concentrations of cobalt salts to 0.25 M in gluconate contributes to the constancy of the chemical composition in all areas of the microprofile. The deposition of Co-W and Fe-W alloys from citrate electrolytes is characterized by a small degree of difference in the local alloy composition along microprofile (Table 1).

Uneven microdistribution is due on the one hand to the diffusion irregularity along the microprofile and, on the other hand, to the presence of diffusion limitations on the rate of alloy deposition, which causes the partial velocities of the components to vary along the microprofile in unequal degrees. Diffusion limitations can have a place as for the metal to be deposited, so for any other solution components, the diffusion rate of which to the cathode may affect the kinetics of the electrodeposition process.

In case of deposition of pure nickel coatings from the Watts electrolyte, the distribution over the microprofile is more uniform and homogeneous compared to the electrodeposition Co-W and Fe-W alloys from gluconate and citrate electrolytes. The P value reaches 0.3 and more, i.e. there is a smoothing of peaks even when the thickness of the coating is just only ~ 30 microns, that characterizes the good leveling properties of the nickel electrolyte.
Table 1. The distribution of Co-W and Fe-W alloys composition on peaks and valleys of the coating surface (1 A/dm²)

| Coating | Electrolyte                          | Alloy composition (average), [wt.%] | Alloy composition (peak/valley), [wt.%] |
|---------|--------------------------------------|------------------------------------|-----------------------------------------|
|         |                                      | W  | Co | Fe | W  | Co | Fe |
| Co-W    | Gluconate, diluted (0.05 M)           | Co-57, W-43 | 45/49 | 56/51 | 49/24 | 52/76 |
|         | Gluconate, concentrated (0.10 M)      | Co-85, W-15 | 38/23 | 62/41 |
|         | Gluconate, concentrated (0.25 M)      | Co-71, W-29 | 26/25 | 74/75 |
|         | citrate                              | Co-75, W-25 | 32/31 | 68/69 |
|         |                                      |       | 32/37 | 68/63 |
|         |                                      |       | 33/37 | 67/63 |
| Fe-W    | Gluconate, diluted (0.05 M)           | Fe-51, W-49 | 48/51 | 52/47 |
|         | Citrate                              | Fe-51, W-49 | 50/49 | 50/51 |
|         |                                      | Fe-66, W-34 | 41/32 | 59/68 |

Summary

1. The significant increase in the profile height occurs during the Co-W and Fe-W alloys deposition, and the profile leveling is observed only when sufficiently thick coatings are obtained. Much better the profile microleveling is observed in the case of nickel deposition.

2. In the case of induced cobalt-tungsten codeposition the electrolyte microleveling power can be improved only by using special additives.

3. The alloy components distribution on the deposited surface is irregular and is not associated with particular parts of the profile. This issue requires separate study.

4. It is shown that the method of surface profilogram registration for determination of microleveling power can significantly reduce the efforts to obtain information on the profile evolution (as opposed to the method of cross-section investigation) and makes it possible to obtain large statistical data sets.

5. The obtained data on the electrolyte leveling power are necessary to predict the “geometric alignment” effect of the microprofile. These data should be considered in the case of dimensional electrodeposition.

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