Peculiarities of deposition of thick coatings based on binary Co-W alloy

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Abstract. The present paper has represented the results of the research of electrochemical deposition of coatings based on Co-W alloy from the citrate electrolyte. Possibility to obtain large (more than 40 μm) thicknesses without cracking has been demonstrated. Peculiarities of the surface relief structure change after increase of the coating thickness have been researched. Possibility to control a concentration of tungsten in the coating alloy within the range 14 at.% – 21 at.% has been shown. Dependence of the coating microhardness on the thickness has been represented.

1. Introduction

At present, there is a constantly growing interest in theoretical and practical researches of the electrochemical deposition of alloys based on metals of the Fe-group with tungsten [1–3]. Among them Co-W alloy coatings are the most promising types of electrodeposited coatings. Area of its application is rather wide. Electrodeposited Co-W alloys represent a great potential as corrosion protective and wear-resistant coating coatings because of its hardness, wear resistance, corrosion resistance (resistance to acid and alkaline solutions) and thermal stability. Covering by the binary Co-W alloy is a perspective replacement for solid chrome coatings [4]. Technology for Co-W coating obtaining in contrast to solid chrome coatings is non-toxic and environmentally safe [5], and also it is less energy-consuming.

Main issues restricting the application of Co-W coating are coating defects of the form of cracks, as well as significant inhomogeneity and high roughness. These effects degrading the coating quality especially appear after increase of the tungsten concentration in the alloy and, correspondingly, hardness and also at large (several tens micrometers) thicknesses.

Publication [3] researched the process of electrochemical deposition and characteristics of the Co-W coating possessing the maximum thickness 20 μm. Mode of the steady-state electrolysis was used in the citrate electrolyte. There are known papers where thickness of the Co-W coating achieved 50 μm, however, data on the coating structure, defect (cracks, pores) presence, application uniformity etc. were not mentioned. Besides, publications researching the process of the surface relief structure change with growth of the coating thickness are not known. Special attention should be paid to thicknesses being more than 10 μm when influence of the substrate has practically no effect. Topical task is to develop methods to form the coating structure based on the Co-W alloy with high tungsten content providing a small number of coating defects.
The present paper has researched possibilities to obtain coatings based on the Co-W alloy of large thicknesses and also to control coatings composition and structure and, consequently, properties.

2. Experiment details

Citrate electrolyte of the following composition: CoSO₄·7H₂O – 56 g/l; Na₃WO₄·2H₂O – 99 g/l; C₆H₅O₂·7H₂O – 80 g/l; H₃BO₃ – 40 g/l; C₃H₅SO₄Na – 1 g/l has been used for deposition in the present paper. Deposition has been performed in the steady-state electrolysis mode at the 7.0-pH level. Cathodic current density has been varied within the range 0.5–1.5 A/dm². Standard two-electrode cell with the insoluble platinum anode having 4 cm² area has been used. Plates of Cu-DHP oxygen-free copper with 1×2 cm² dimensions and 1 mm thickness have been used as substrates. Substrates were mechanically polished by the felt disk without usage of the abrasive material and then they were degreased in the solution containing NaOH and Na₂CO₃ with 30 g/l concentration for each component at 70 °C temperature. Immediately prior to deposition, substrates were immersed into 15% HCl solution within 30 seconds and they were washed by bidistilled water. Temperature of the electrolyte was 60 °C for all experiments and electromagnetic heated stirrer C-MAG HS 7 digital equipped with the system of feedback through the temperature sensor PT 1000 maintained the temperature constant. Electrolyte agitation was not used. All samples of coatings had a metallic lustre and good adhesion to the substrate.

Morphology of the sample surfaces and chemical composition have been researched using the scanning electron microscope JSM-6610LV (JEOL, Japan) equipped with the X-ray fluorescence energy-dispersive detector INCA X-MAX (Oxford Instruments, England). Research of the coating sample microhardness has been performed using a hardness tester PMT – 3M (LOMO, Saint-Petersburg) according to the Vickers method (GOST 9450-76) under load 0.196 H.

3. Results and discussion

At the first stage, structure and morphology of the coating surface were researched. Deposition was performed under current 0.5 A/dm². A set of six samples with increasing coating thickness from 3 to 42 μm was obtained. Deposition time was changed within the range 40–600 minutes. Change of the surface relief structure with increasing coating thickness is shown on SEM-images (figure 1).

The present SEM-images represents several typically relief growth forms appearing during the process of film growth. Under considered conditions, a regular morphological type of the surface relief structure starts forming after 40 minutes of deposition (thickness 2–3 μm). Then the relief is almost unchanged up to thickness 8–10 μm. Structure of the coating relief obtained under the present conditions is rather homogeneous (figure 1(a)). Basis of the relief structure is V-shaped pyramidal formations which lateral dimensions are 0.5–1.5 μm. Figure 1(b) demonstrates a structure of the surface relief with the range of thickness 10–25 μm. Increase of separate structure with preservation of the shape and faceting can be seen. Principal change of the growth forms happened at thickness about 30 μm (figure 1(c)). Their smoothing happens simultaneously with following increase of separate relief elements and, correspondingly, decreases of their total number. Faceting disappeared. Increase of surface structure elements is observed up to thicknesses 38 μm. Lateral dimensions of separate globules are 10 and more micrometers in the present case. As figure 1(d) shows, globule boundaries start appearing. Coating surface roughness increases. Following increase of the deposition time leads to separation of globules from each other with extension of the space between them up to several tens of micrometers. Cracks and coating delamination appear.

Experiments under current 1 A/dm² have allowed revealing several peculiarities. Significant change of the growth form (transfer from the V-shaped pyramidal form to the more smoothed-globular one) already happens at thickness about 10 μm. Under considered conditions the maximum possible coating thickness is less than in the first case and it is about 34–36 μm. Increase of the cathodic current density up to 1.5 A/dm² reduces this value up to 20 μm.

Analysis of the elementary composition and microhardness of the obtained samples have been performed. Results of the study of the elementary composition of coatings based on Co-W alloy
correspond to the data of current researches [6] and show a possibility to control a tungsten concentration in the coating alloy within the range 14 at.% – 21 at.% by changing cathodic current density from 1 to 0.5 A/dm². The highest concentration of the tungsten was obtained at the minimal current density value.

Figure 1. SEM-images of typical parts of the coating sample surfaces based on the Co-W alloy with various thicknesses: (a) – 6 μm; (b) – 13 μm; (c) – 30 μm; (d) – 40 μm.

Results of the research of the coating thickness influence on its microhardness are shown on figure 2. Two deposition current modes have been considered: 0.5 A/dm² and 1 A/dm² influencing on the tungsten content in the alloy. As the figure 2 shows, microhardness of the coating deposited under the cathodic current density being equal to 1 A/dm² steadily increases from 370 HV to 550 HV with increase of the thickness. Microhardness of the coating obtained under current density 0.5 A/dm² is higher within the whole researched interval of the thickness change. It should be noted that in the present case significant increase of the microhardness happens after achievement of thickness 20 μm and it grows up to the maximum value 675 HV. Influence of the copper substrate with its small microhardness value (60–70 HV) significantly affects within the thickness range 6–20 μm in spite of enough high concentration of the tungsten in the alloy at 20 at.% that contributes to insignificant fluctuations of the microhardness within the range 395–430 HV.

4. Conclusions
So, during the performed researches the possibility of electrochemical deposition of coatings based on the Co-W alloy of larger thickness with high tungsten content within the range 21 at.% has been shown. Deposition method provides a uniform application of the rather smooth coating with the
homogeneous relief structure. Maximum values of the microhardness have been obtained for the galvanic coating of the present alloy without cracks at 690 HV level.

Figure 2. Dependence of the coating microhardness based on the Co-W alloy on the thickness.

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