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FUNCTIONAL COATINGS BY TERNARY COBALT BASED ALLOYS FOR THE AUTUMOBILE INDUSTRY

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Abstract. *The environmentally friendly and resource-saving technologies for producing multifunctional coatings based on cobalt and silver alloys with refractory metals are proposed. The catalytic activity testing results of binary and ternary alloys based on cobalt in the carbon monoxide oxidation reaction in carbon dioxide were analyzed. It was revealed that there is on improvement of functional properties of galvanic alloys when the content of tungsten and molybdenum is within the range of 10–30 wt. %.*

Key words: *citrate-pyrophosphate electrolyte, cobalt-molybdenum-tungsten (silver) alloy, corrosion resistance, catalytic activity, electrolysis.*

ФУНКЦИОНАЛЬНЫЕ ПОКРЫТИЯ ТЕРНАРНЫМИ СПЛАВАМИ КОБАЛЬТА ДЛЯ АВТОМОБИЛЬНОЙ ПРОМЫШЛЕННОСТИ

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Аннотация. *Предложены коррозионно стойкие и каталитически активные электролитические покрытия сплавами. Обсуждаются результаты исследования гальванохимических процессов синтеза тернарных сплавов кобальта из нетоксичных электролитов. Проанализировано влияние условий осаждения на состав и морфологию покрытий, а также их физико-механические свойства.*

Ключевые слова: *цитратно-пирофосфатный электролит, сплав кобальт–молибден–вольфрам (серебро), коррозионная стойкость, каталитическая активность, электролиз.*

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Анотація. *Запропоновано корозійно стійкі й каталітично активні електролітичні покриття сплавами. Обговорюються результати дослідження гальванохімічних процесів синтезу тернарних сплавів кобальту з нетоксичних електролітів. Проаналізовано вплив умов осадження на склад і морфологію покриттів, а також їх фізико-механічні властивості.*

Ключові слова: *цитратно-пірофосфатний електроліт, сплав кобальт–молібден–вольфрам (срібло), корозійна стійкість, каталітична активність, електроліз.*

Introduction

The automotive industry is still one of the major customers for electroplating industry and surface treatment, as well as the initiator of many research's and developments. In [1, 2] a wide range of functional galvanic coatings application in automobile production is described, namely:

1. To restore the worn surfaces of the parts. After the restoration the geometry of the threadbare surface with creating galvanic layer is increased in size from a few microns to 1–2 mm. (iron, chrome, zinc plating and so on).

2. To protect the machined surfaces of parts from the environment, aggressive media, temperature, increased wear, etc. (zinc and chrome plating).

3. To form on the surface a layer the physical and mechanical properties of which differ from ones of the main material details (copper – for improving electrical conductivity, chrome – to rise the microhardness, zinc – for corrosion protection, and so on).

4. For decorative purposes mainly chromium and nickel electroplating is used. Such coatings have luster and uniform surface. In addition, precious metals (silver, gold, platinum) can be applied by plating.

5. In order to achieve one or more objectives together. Usually plating performs multiple tasks simultaneously. For example, the zinc plating to protect against corrosion and has excellent anti-vibration properties, chrome plating is restoring the worn surfaces and at the same time increasing the microhardness of processed surface (when applied to a substrate of a softer metal).

Analysis of publications

Considerable attention in modern studies [3–5] is given to cobalt based alloys: binary (Ag-Co, Co-Mo, Co-Ni, Co-Cr, and others) and triple or ternary (Fe-Co-Ni, Co-Mo- P, Co-Mo-W, Ni-Co-B et al.), properties and industrial applications of which are significantly different. Of particular interest are alloys of metals, which are almost impossible to deposit from the aqueous solutions in pure form – tungsten, molybdenum, zirconium, niobium, et al. It was shown [6] the possibility of their co-deposition with cobalt (nickel, iron) under certain conditions. Cobalt alloys with refractory metals due to physic-chemical and physic-mechanical properties can serve firstly as an alternative to hard chromium [7, 8] deposited out of Cr (VI) based electro-

lytes. The last are classified as environmentally hazardous galvanic production class 1 because of the high toxicity [9]. Secondly, Co alloys are efficient to substitute the catalytic materials based on platinum group metals, since the deficit, high cost, and the irrevocable loss during operation, make the problem of their complete or partial replacement in catalytic systems increasingly urgent [10, 11].

Purpose and tasks

Purpose of the work is to develop the electrochemical mode of functional coatings by silver and cobalt alloys with refractory metals deposition from polyligand electrolytes to produce the layers with high corrosion resistance, catalytic activity, microhardness. To achieve the aim it is necessary to solve the following tasks:
– to develop the electrolytes for above mentioned coatings co-deposition;
– to define the parameters of synthesis regims;
– to determine the effect of electrolysis parameters on the composition, morphology and properties of galvanic alloys.

Primary Section

Materials and methods. The deposition of cobalt ternary alloys with refractory metals (Co-Mo-W, and Co-Mo-Ag) was carried out from citrate-pyrophosphate bath using both direct current (DC) mode with current density j of 2–8 A·dm^{-2} and a unipolar pulse current of amplitude 2-27,5 A·dm^{-2} in the frequency f range of 19-910 Hz, pulse time was varied τ_{on} $2\cdot10^{-3}$–$2\cdot10^{-1}$ s, pause – τ_{off} $2\cdot10^{-2}$-$2\cdot10^{-1}$ s; duty cycle was 2-20. The electrolysis modes were supported by potentiostat PI 50-1.1 with programmer PR-8. Coplanar cobalt plates were utilized as soluble anodes.

Solutions for alloys Co-Mo-W (Ag) deposition were prepared from analytically pure reagents: $CoSO_4\cdot7H_2O$, $Na_2MoO_4\cdot2H_2O$, $Na_2WO_4\cdot2H_2O$, Ag_2SO_4, $K_4P_2O_7$, $Na_3C_6H_5O_7\cdot3H_2O$ dissolved in a small amount of distilled water following by solution mixture in a certain sequence, based on the ionic equilibrium study results.

Ternary alloy coatings were applied to a substrate made of copper and steel Ст3. Pretreatment of the samples was carried out by the standard technique according to the testing material [12, 13]. To eliminate external defects and reduce the surface roughness the substrates were

mechanically treated with sandpaper before coating deposition. In order to completely remove grease traces of different nature and improve the wetting the substrate surface was degreased in an alkali solution (Na_2CO_3). Finishing operations were pickling and rinsing in distilled water. The chemical composition of the coatings was determined by X-ray fluorescence method using a portable spectrometer "SPRUT". In the addition the coating surface was analyzed by X-ray photoelectron spectroscopy with an INCA Energy 350 energy-dispersive spectrometer; the X-rays were excited by exposure of the samples to a beam of 15 keV electrons. Measurement error of component content was ± 1 wt. %. The morphology of the surface was studied with a scanning electron microscope (SEM) ZEISS EVO 40XVP. Images were obtained by registering the secondary electrons by scanning the electron beam, which allowed investigating the topography with high resolution and contrast.

Corrosion resistance of synthesized coatings was established using the polarization and gravimetric tests. Corrosion current density j_{cor} was determined by extrapolation of partial anodic and cathodic linear plots in Tafel coordinates lg$j$-ΔE at corrosion potential E_{cor}.

The corrosion depth indicator k_h was calculated using j_{cor} from the equation

$$k_h = \frac{8,76 k_e j_{cor}}{\rho}, \qquad (1)$$

where k_e – electrochemical equivalent of a metal or alloy kg/C; j_{cor} – corrosion current density, $A \cdot m^{-2}$; ρ – density of the metal or alloy, $kg \cdot m^{-3}$.

The tests of catalytic activity of galvanic alloys cobalt-molybdenum-tungsten (silver) of different composition was performed in model hydrogen evolution reaction. The hydrogen exchange current density j_H^0 was utilized as the criteria of electrochemical catalysis since this parameter is independent of the electrode potential. Experimentally j_H^0 was determined by extrapolation of the polarization dependences linear plot in Tafel coordinates within the range 200-300 mV from steady-state potential.

The testing of catalytic properties was also carried out by the carbon (II) oxide oxidation in a tubular flow reactor fabricated from quartz glass with the coaxially situated heating element. Initial mixture of CO (1 vol. %) and air was supplied to the reactor inlet at a rate of 0,025 $dm^3 \cdot min^{-1}$. Reactor temperature was increased gradually from 20 to 420 °C. Content of CO in the final mixture was analyzed using the indicator-analyzer «Dozor» [14].

Results and discussion. Results of studies have confirmed the earlier assumptions about the possibility of refractory metals co-deposition with cobalt from citrate-pyrophosphate electrolytes. The kinetic parameters of the cathodic reaction obtained from the polarization dependencies analysis [13] indicate the mechanism tungsten and molybdenum reduction from the complexes $[CoCitWO_4]^{3-}$ and $[CoCitMoO_4]^{3-}$. It is noted that when a concentration ratio $MoO_4^{2-} : WO_4^{2-}$ in electrolyte is 1:2 alloy is enriched with molybdenum [6].

It was established the change in the alloys composition as well as in surface morphology with current density increasing (Fig. 1). The internal stresses increase with the rising tungsten content when coatings are deposited under higher current density as evidenced by their cracking.
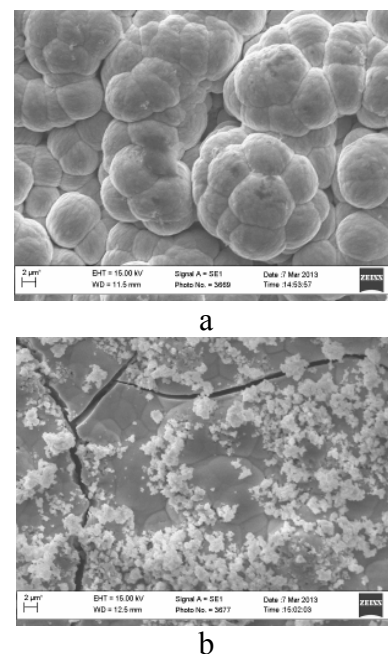

a

b

Fig. 1. Photo (x 2000) of Co-Mo-W alloy, deposited in the pulsed mode at a current density, $A \cdot dm^{-2}$: 4 (a); 10 (b)

Analysis of the Ag-Co-Mo coatings morphology was carried out on samples with different content of alloying components. It should be noted that the Co-Mo-Ag and a Co-Mo-W galvanic

alloys morphology is significantly changed if varying the pulse electrolysis energy parameter − current density. The coatings Co-Mo-Ag deposited at $j = 2$ A·dm^{-2} are bright, without cracking or other visible defects and the content of Mo is 9 wt. % and ω(Ag) 11 wt.%.

However, the coatings surface is heterogeneous: one can see large associates as well as individual grains of smaller sizes (Fig. 2, a). Increasing the current density up to 5A·dm^{-2} we can rise molybdenum content in the coating up to 12 wt. %. and simultaneous reduce silver to 7 wt.% (Fig. 2, b). Such a change in the chemical composition facilitates formation of a more uniform alloy structure and significantly increases the number of associates and reduces – grains.
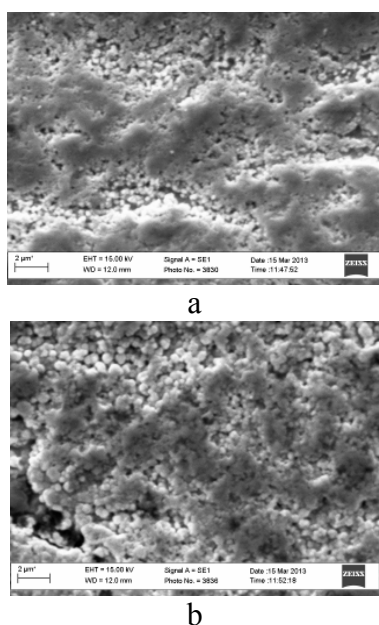

a

b

Fig. 2. Morphology of Co-Mo-Ag alloy ($\times$ 5000) deposited by pulsed mode at τ_{on}/τ_{off} = 2/20 ms, the current density A·dm^{-2}: 2 (a); 5 (b). Alloying components content, wt. %: a − Ag – 11, Mo – 9; b − Ag – 7, Mo – 12

Thus, the crystalline size is decreased with the silver content increasing in the alloy coatings, and the molybdenum presence promotes formation of globular smoothed surface structure. Obviously, the structurally dependent properties of coatings such as corrosion resistance, catalytic activity, microhardness et al. should be changed accordingly.

The composition and the current efficiency of the Co-Mo-Ag galvanic alloy both depend on the amplitude of the pulse current density. Increasing in the energy parameter from 0,5 to 9,0 A·dm^{-2} rises the content of molybdenum and cobalt in the coatings and decreases the noble alloy component concentration (Fig. 3).
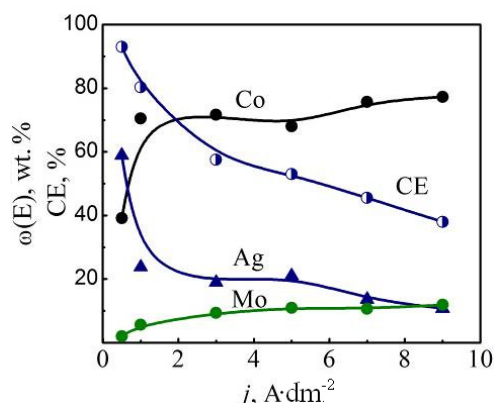

Fig. 3. Effect of current density on the composition and the current efficiency of the Co-Mo-Ag alloy, at τ_{on} / τ_{off} = 2/20 ms

The maximum amount of silver (58 wt.%) is achieved under $j = 0,5$ A·dm^{-2}. The content of other alloying components is changed for Co from 40 to 78 wt.% and for Mo is raised for about 10 wt.% when increasing the current density. At the same time the alloy deposition rate increases from 6,5 to 37 μm/h (Table 1).

Table 1 The deposition parameters of Co-Mo-W alloy

Current density, A·dm^{-2}	Deposition rate, μm·h^{-1}	Deposition potential, V
0,5	6,5	−0,5
1	9,0	−0,6
3	19,6	−0,8
5	28,0	−1,0
7	35,0	−1,2
9	37,0	−1,5

The observed dependencies of components content *vs j* can be explained taking into account the shift of cathode potential towards more negative values from −0,5 V to −1,5 V during a current density rising. Consequently, the rate of cobalt (as more active alloy component) deposition increases at such potentials leading to coating enrichment with Co. In addition the reduction of the refractory metal in the alloy is the result of the discharge conjugation reactions of the hetero-nuclear complexes with cobalt. However, the molybdenum content in the coating changes symbiotically the cobalt concentration. The decrease in the current efficiency from 98 to 40 % with an increase of the current density occurs due to intensification of hydrogen evolution

reaction. Such behavior gives reason to predict high catalytic activity of alloy coatings Ag-Co-Mo in electrochemical reactions involving protic particles.

The corrosion protective properties of cobalt alloys with silver were discussed in[14]. Corrosion resistance of the Co-Mo-W galvanic alloy was evaluated using the corrosion depth indicator. Table 2 shows that the corrosion rate is reduced in an acidic medium with increasing total content of refractory components. This is due to the capability of tungsten and molybdenum to form protective acidic oxides with high chemical stability in acidic and neutral media. In turn, the forming cobalt oxide has alkali nature, and therefore exhibits passivity in alkaline and neutral media.

Table 2 Corrosive characteristics of Co-Mo-W alloys

Content of refractory components ω, wt. %	Corrosion rate $k_h \cdot 10^3$, mm/year		
	pH 3	pH 7	pH 11
Mo 10,6 W 15,1	2,00	1,00	7,00
Mo 16,1 W 13,8	1,00	2,00	8,00
Mo 18,8 W 12,9	0,8	4,00	8,10

The corrosion resistance of the alloys in neutral and alkaline media decreases as well as corrosion potential shifts to negative side if increasing the refractory components content in the alloy. This can be explained by the fact that the tungsten and molybdenum oxides are dissolved in an alkali conditions occurring both in the appropriative media and in neutral ones as a result of local alkalization during hydrogen evolution reaction.

Testing coatings of different composition shows that dependence k_h from the total tungsten (12,9–15,1 wt.%) and molybdenum (10,6–8,8 wt.%) content differs for alkaline and acidic media. Thus, for example, the corrosion resistance at pH 3 rise with increasing ω(Mo) from 10,6 to 18,8 wt. %. The deep corrosion rate indicator allows to divide coating into groups: a rack (pH 3) and highly resistant (pH 7, 11), which allows their further use in aggressive environments.

The catalytic activity of the ternary alloys we have compared with the kinetic parameters of the hydrogen evolution reaction (Table 3) at individual metals and binary alloys.

Table 3 Kinetic parameters of the hydrogen evolution reaction

Metal	$-\lg j_H^0$, [A·cm^{-2}]	
	Acidic medium	Alkaline medium
Pt	3,3	3,1
Co	4,33	4,29
Mo	8,25	4,79
W	5,75	–
Fe	5,83	6,9
Ag$_9$Co$_{91}$	2,3	–

The catalytic activity of Co-Mo-W galvanic alloys was tested in the reaction of hydrogen evolution in acidic, neutral and alkaline media (Fig. 4).
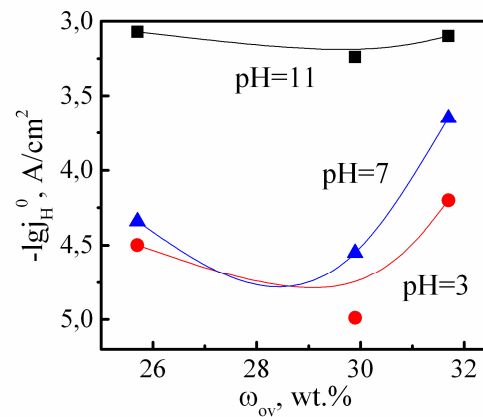

Fig. 4. The influence of the refractory components total content in the alloy on the hydrogen current exchange density in the solution 1 M Na$_2$SO$_4$

Experimentally derived constants *a* and *b* give the opportunity to analyze empirical equations of hydrogen evolution overvoltage (Table 4).

Table 4 Empirical equations of hydrogen evolution overvoltage in alkaline medium

Composition of alloy, wt.%			Empirical equations of hydrogen evolution overvoltage
Co	Mo	W	
74,3	10,6	15,1	$\eta = 0,609 + 0,167 \lg j$
70,1	16,1	13,8	$\eta = 0,682 + 0,15 \lg j$
68,3	18,8	12,9	$\eta = 0,691 + 0,159 \lg j$

The lowest overvoltage of hydrogen evolution is realized on a steel electrode coated with an Co-Mo-W alloy of composition, wt.%: Co – 74,3; Mo – 10,6; W – 15,1 (during the electrolysis at $j = 1$ A·cm^{-2}).

Testing of the catalytic activity of the synthesized cobalt-molybdenum-silver coatings was

performed in the model reaction of carbon oxide (II) oxidation to carbon (IV) oxide in a pilot plant as described in [13]. Quantitative characteristics of the oxidation are the carbon monoxide (II) conversion degree $X(CO)$ and ignition temperature t.

The catalytic properties of galvanic alloys were compared to platinum which is the most effective in catalyst, As one can see from the temperature dependencies (Fig. 5. place 1) at the platinum catalyst plate with $\omega(Pt) = 100$ wt,% the oxidation of CO gas begins at 190 ° C, while 100 % conversion degree is achieved at 250 °C, The galvanic alloy $Ag_{24}Co_{70}Mo_6$ exhibits the highest catalytic activity among the synthesized coatings: the ignition temperature for it is 200 °C (Fig. 5).
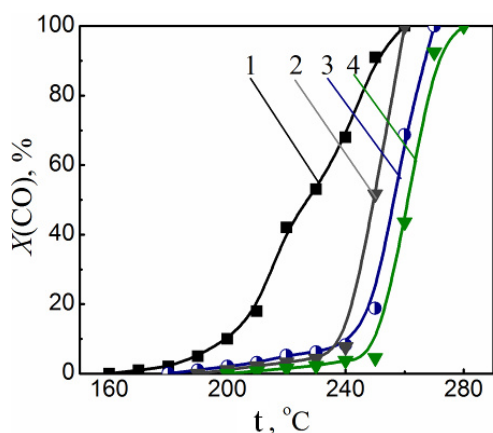

Fig.5. Thermogramms of CO conversion degree on different materials: Pt (1) and galvanic alloys Ag-Co-Mo of composition, wt ,%: 2 – Ag 23,8, Mo 5 6; 3 – Ag 10,8; Mo 11,9; 4 – ω Ag 13,6, Mo 10,6, Up to 100 wt.% – Co

It should be noted that increasing the content of noble and refractory metals in the alloy leads to a decrease in cobalt content, which adversely affects the catalytic activity of the material, to recommend them as catalysts for hydrocarbon combustion.

Conclusions

Compact multifunctional galvanic coatings by cobalt alloys with refractory metals were deposited from citrate-pyrophosphate bath both under steady and pulse electrolysis modes.

Galvanic alloys are shown to exhibit a high corrosion resistance in media with different pH compared to the substrate; thus they can be utilized for the purposes of corrosion protection.
The electro-catalytic activity of the alloys comparing to individual metals exhibits their synergetic nature. The greatest level of catalytic properties was obtained on synthesized alloys in acidic media for which the hydrogen exchange current density do not differ from the parameter for a platinum electrode.

The galvanic alloy $Ag_{23}Co_{71}Mo_6$High exhibits catalytic properties in the carbon oxide (II) oxidation analogical for platinum. This confirms the efficiency of materials as catalysts for the gaseous wastes purification and gives the reason.

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