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ELECTRODEPOSITION OF CATALYTIC TERNARY COBALT BASED COATINGS

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The electrodeposition of Co−Mo−W and Co−Mo−Zr coatings from a polyligand citrate-pyrophosphate bath was investigated. The effects of both current density amplitude and pulse on/off time on the quality, composition and surface topography of the electrodeposited alloys were determined. It was established that the content of alloying components in Co−Mo−Zr coatings increases with an increase in the current density. The content of zirconium was shown to increase with the on-time. The content of molybdenum grows with the off-time. This is because the chemical reduction of their intermediate oxides by hydrogen ad-atoms. It was stated that the dependences of the refractory metals content in the Co−Mo−W coating upon both current density and on/off times have an extremal character; a maximum content of Mo and W corresponds to the current density range of 12 to 18 A□dm^2 and to the on-/off-times of 5 to 10 ms. The Co−Mo−W alloys exhibit a high catalytic activity towards the hydrogen evolution reaction in acidic media, this catalytic activity is comparable to that of a platinum electrode. The electrodeposited Co−Mo−Zr alloys with a zirconium content of 1.5 to 2.0% wt show a high catalytic activity towards the reaction of carbon oxide (II) oxidation. This confirms the efficiency of such materials as catalysts for the purification of gaseous wastes and allows us to recommend them as catalysts for hydrocarbons combustion.

Keywords: cobalt ternary alloy, citrate-pyrophosphate bath, catalytic properties, electrodeposition, hydrogen evolution reaction, pulse electrolysis

Energetic security of any country is based on the several factors, among which there are the network of national energy generating enterprises, developed industrial basis on the energy accumulating devices and energy sources production. Eco-friendly fuel cells (FC) are among the promising renewable energy sources, however, the high cost of the noble metal electrodes prevents their dissemination and widespread use [1]. Development of the flow battery at various red-ox systems (RFB) also needs to create effective catalytically active electrodes on the basis of transition metals [2]. Among the most important requirements to electrode materials of FC and RFB are: chemical stability of the surface and inactivity to technological environment components; wide window of polarization potentials, in which electrode stays inactive; high selectivity and catalytic activity toward main electrode reactions; significant specific surface area. Even brief review gives an impression that electrode materials that are being used in these electrochemical systems are not optimized [3]. For instance, one of the most widespread electrode material is a number of carbon modifications − graphite, carbon fibers, porous and pressed carbon,

carbon cloth, graphite with thermally or chemically modified surface, nickel foam, platinum or platinum titanium, platinides' oxides, etc [4]. It is worth mentioning that in scientific literature for the last years there are no publications on electrode materials on the basis of hi-tech materials, such as nano-structured and nanocrystallized materials based on the corrosion resistant amorphous metal alloys (metal glass), or nanostructured deposits by synergistic alloys [5]. The most efficient directions of catalytic materials synthesis by physic-inorganic chemistry methods are electrochemical technologies that provide the opportunity to very flexibly control the component content, the rate of deposition, the state of the surface, by varying the electrolyte composition and polarization mode (static or pulse, reverse current or decrease of the potential) [6]. Utilization of the electrochemical methods favors the interactions in the chain "process parameters − composition and structure of the material − properties − functions − application". Because of this it is possible to fabricate the deposits of varied qualitative and quantitative composition and with desirable functional properties (synergistic or additive), such as microhardness, wear-,

thermo-, chemical and corrosion resistance, catalytic activity, etc [7]. When synthesizing new and improving existing catalysts it is necessary to determine the factors influencing the catalytic activity and especially the nature of the catalyst, since electro-catalytic activity depends on chemical composition and state of the surface (amorphous, crystalline, grain size, etc.).

It has previously been shown prospects of electrolytic binary cobalt alloys with molybdenum or tungsten to produce hydrogen by alkali electrolysis [8,9] as well as to the oxidation of hydrocarbons [10]. However, it is of interest to create catalytic materials based on ternary synergistic cobalt alloys.

The aim of this work is to study the influence of the electrolysis conditions on the quality, composition, morphology and catalytic properties of ternary galvanic Co−Mo−W and Co−Mo−Zr covers.

Experimental

Coatings were deposited on steel substrates, pretreated with grinding, degreasing, rinsing and etching. Coatings cobalt+molybdenum+tungsten (zirconium) Co−Mo−W(Zr) were formed at a temperature of 25−30⁰C from a polyligand citrate-pyrophosphate bath. Electrolytes were prepared from analytically pure reagents: $CoSO_4 \cdot 7H_2O$, $Na_2MoO_4 \cdot 2H_2O$, $Na_2WO_4 \cdot 2H_2O$, $Zr(SO_4)_2$, $K_4P_2O_7$, $Na_3C_6H_5O_7 \cdot 3H_2O$ (Na_3Cit) dissolved in a small amount of distilled water following by solution mixture in a certain sequence, based on the ionic equilibrium study results. The coatings were formed in two modes:

1 − direct current (DC) with current density (i) of 2−8 A·dm⁻²;

2 − unipolar pulse current (PC) with amplitude 2−20 A·dm⁻² in the frequency (f) range of 19−910 Hz, pulse time t_{on} $2 \cdot 10^{-3}$−$2 \cdot 10^{-1}$ sec, pause − t_{off} $2 \cdot 10^{-2}$−$2 \cdot 10^{-1}$ sec; duty cycle was 2−20, both were supported by potentiostat PI 50-1.1 with programmer PR-8. Coplanar cobalt plates were used as soluble anodes. The electrode potentials were measured relative to an EVL-1M1 silver chloride reference electrode connected to the working cell via a salt bridge filled with saturated potassium chloride solution jellied with Ceylon gelatin. The potentials presented in the paper are given relative to the standard hydrogen electrode (SHE).

The electrodeposition effectiveness (current efficiency Ce) was determined gravimetrically using the electrochemical equivalent of the alloy. The thickness of the coatings was calculated from the actual mass increase of the samples during the electrolysis.

The chemical composition of the coatings 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. The surface morphology of the coatings was studied with a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were obtained by recording the backscattered electron emission (BSE) induced by the scanning electron beam, which made it possible to examine the topography with high resolving capacity and high contrast. The surface roughness was evaluated by the contact method on 10×10×2 mm samples with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2.0 and 0.2 nm, respectively; 1024×1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm). The phase composition of the coatings was studied by X-ray structural analysis using a DRON-2.0 in the emission of iron anode.

Electrocatalytic properties of covers were studied in model reaction of electrolytic hydrogen evolution from acidic and alkali media. The hydrogen current exchange current density i_H^0 is utilized as the criteria of electrochemical catalysis since this parameter is independent of the electrode potential. Experimentally i_H^0 was determined at the point of intersection of the linear portions of the polarization dependencies in Tafel coordinates within the range 200−300 mV from steady-state potential [11]. 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 dm³·min⁻¹. Reactor temperature was increased gradually from 20 to 420⁰C. Content of CO in the final mixture was analyzed using the indicator-analyzer «Dozor» [12].

Theoretic aspects

It was shown in previous papers [13,14] the necessity of using poly-ligand electrolyte for the co-deposition of cobalt with tungsten, molybdenum and zirconium because of the significant potential difference for alloying components. Citrate (Cit) and pyrophosphate (Pyro) ions that are indifferent to electrochemical oxidation and reduction and create coordination with many single and polyvalent ions are selected as ligands. The pH maintaining in the interval 8−10 is recommended for stable pyrophosphate ($pK[CoP_2O_7]^{2-}$=6.1) and citrate ($pK[CoCit]^-$=5.0) complexes since the strength of compounds depends on the ligands protonation. Moreover, in a weakly alkaline medium Mo (VI) and W (VI) are the mono-oxometalates MoO_4^{2-} [15] and zirconium predominantly is ZrO^{2+} which creates conditions for the formation of heteropolynuclear complexes, of which induced precipitation [16] of ternary coatings including zirconium occurs.

Taking into account the considerable difference of alloying components' redox potentials (tab. 1) and their step reduction conjugated as shown in [17]

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Equilibrium potentials for alloying component step reduction

Reaction	Equilibrium potential E, V
$Co^{2+}+2e^-=Co^0$	$-0,277+0,0295lg[Co^{2+}]$
$MoO_4^{2-}+2H_2O+2e^-=MoO_2+4OH^-$	$0,606-0,1182pH+0,0295lg\left[MoO_4^{2-}\right]$
$MoO_2+2H_2O+4e^-=Mo+4OH^-$	$-0,072-0,0591pH$
$WO_4^{2-}+2H_2O+2e^-=WO_2+4OH^-$	$0,386-0,1182pH+0,0295lg\left[WO_4^{2-}\right]$
$WO_2+2H_2O+4e^-=W+4OH^-$	$-0,119-0,0591pH$
$ZrO^{2+}+H_2O+4e^-=Zr+2OH^-$	$-1,570-0,0295pH+0,0148lg[ZrO^{2+}]$

with chemical reaction preference is given to forming ternary coatings using pulse electrolysis mode.

Thus, we can to obtain and control the composition of ternary Co−Mo−W and especially Co−Mo−Zr galvanic alloys by changing the concentration ratio of alloying metal salts, electrolyte pH and electrolysis mode. It should be taken into account the fact that the formation of heteronuclear complexes of molybdenum, tungsten and zirconium and their subsequent reduction in the alloy may be competing.

Results and discussion

The galvanic Co−Mo−Zr alloys were deposited at steel substrates from polyligand bath of components composition, mole▫dm⁻³: Na_3Cit − 0.2, $CoSO_4$ − 0.1, Na_2MoO_4 − 0.02, $Zr(SO_4)_2$ − 0.05, $K_4P_2O_7$ − 0.2, Na_2SO_4 − 0.5 [18] under varying both energetic and time parameters of pulse electrolysis. Increase the current density amplitude (i) of 5 to 12 A▫dm⁻² rises the rare elements content in the alloy up to ω(Mo)=16.2 wt.% and ω(Zr)=2.1 wt.% (Fig. 1,a). Coating enrichment by alloying components with increasing current density is entirely predictable since the reduction of these metals is at least a two-step process and requires a greater polarization for zirconium and is accompanied by chemical reduction of intermediate molybdenum oxides with Hydrogen ad-atoms H_{ad}. Experimental established interval of deposition potentials for cobalt-molybdenum-

zirconium alloy is −(2.0−2.8) V (Fig. 1,b). Thus with increasing current density electrode potential shifts in the negative direction that increases the partial rate of zirconium ions reduction as a most active component as well as the chemical step of molybdenum oxides reduction by H_{ad}.

Dependence of alloy current efficiency *Ce vs* the current density has extreme character (Fig. 1,b): *Ce* increases by 20% and reaches 63% with rising current density from 5 to 8 A▫dm⁻²; however further increase in (i) reduces the current efficiency up to 47%. Such behavior may be attributed with more significant cathodic potential fluctuations and shift at higher current amplitude which promote the hydrogen evolution site reaction.

Time parameters of pulsed electrolysis (duration of pulse t_{on} and pause t_{off}) strongly affect for the composition and current efficiency of coating alloy Co−Mo−Zr. Thus, the minimum value t_{on} should be sufficient to achieve the potential of metals co-deposition in the alloy, and the maximum − to ensure quality coatings and efficiency of electrolysis.

It was found that with increasing pulse time of 0.5 to 5.0 msec at a constant current density (i= =8 A▫dm⁻²) and pause duration t_{off} 10 msec molybdenum content in the Co−Mo−Zr coating reduces from 15.9 to 13.7 wt.%, and zirconium, by contrast, is growing from 0.8 to 1.5 wt.% (Fig. 2,a). This is due to an increase in active current at the
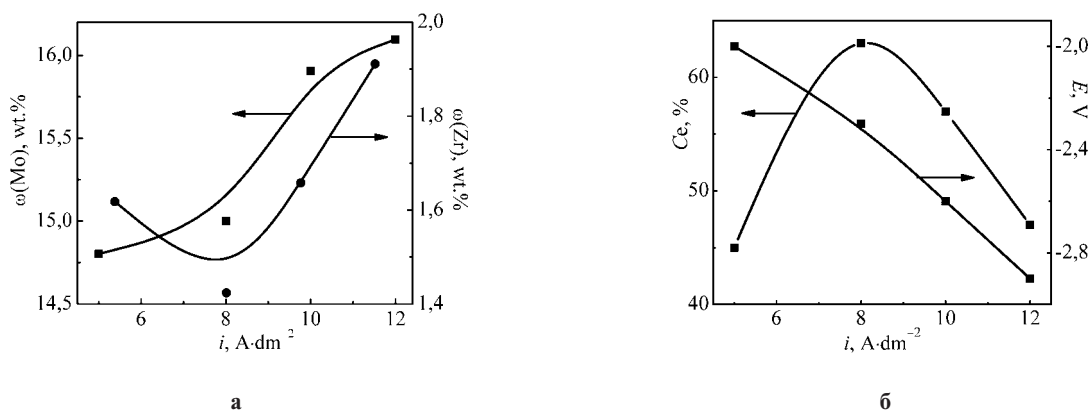

а **б**

Fig. 1. Pulse current density influence on the composition (a) and current efficiency (b) for Co−Mo−Zr coatings; t_{on}/t_{off} 2/10 msec; T 20−25⁰C; pH 8; plated time 20 min
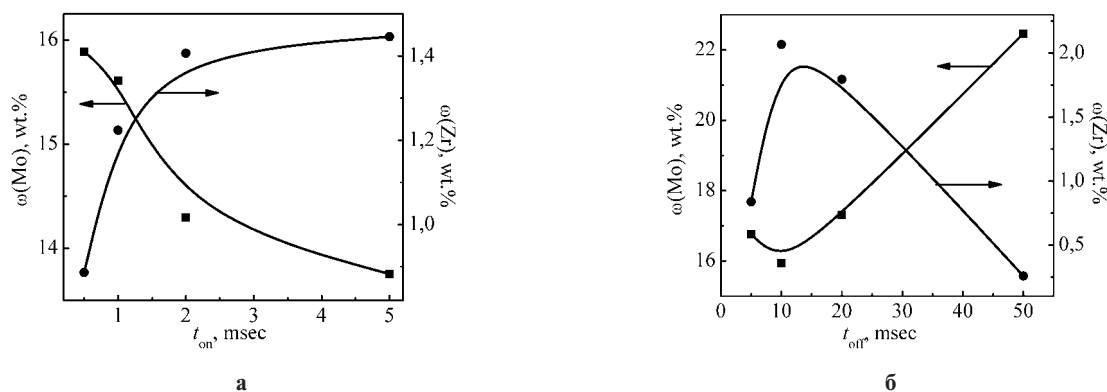
a

б

Fig. 2. Dependence of Co−Mo−Zr coating composition on the time of pulse t_{on} (a) (t_{off} 10 msec) and pause t_{off} (b) (t_{on} 2 msec); I=8 A·dm^{-2}; T=20−25^{0}C; pH 8; plated time 20 min

expense of a full signal handling, thereby achieving potential of zirconium reduction in alloy. It also shows the different mechanism of zirconium and molybdenum deposition in the ternary coating under studied conditions.

Prolong pause of 5 to 10 msec at a constant current density and pulse duration (t_{on} 2 msec) provides growth zirconium content in the alloy from 0.8 to 2.1 wt.% which is followed by decreasing of w(Zr) at larger current interruption (Fig. 2,b). So the maximum concentration of zirconium in the alloy is reached under the ratio t_{on}/t_{off} 2/10 msec. At the same time the content of molybdenum in the alloy regularly increases from 16.0 to 22 wt.% with the duration of the pause due to more complete chemical reaction of intermediate oxides reduction by H_{ad} (Fig. 2,b). Current efficiency logically decreases from 60 to 36% with increasing pulse time due to increasing the rate of the partial hydrogen evolution reaction at a higher polarization. Prolong the pause positively influences the current efficiency of cobalt-molybdenum-zirconium alloy as more fully realized subsequent chemical reactions accompanying the alloying metals discharge. Thus current efficiency reaches 78% when t_{off} 50 msec and t_{on} 2 msec.

Increasing the amplitude of the current enriches coating with zirconium and molybdenum, but this changes the surface topography and amplified internal stress that leads to fracture grid (Fig. 3). The Fig. 3 shows the surface becomes less smooth and more globular, and the crystallite sizes increase exactly due to the higher content of alloying metals. It should be emphasized sufficiently uniform distribution of the coating components on uneven relief, which may be attributed to a good hiding power of the electrolyte.

Increasing the temperature to 50^{0}C contributes to the content of cobalt and zirconium in the coating while molybdenum concentration is significantly reduced (Fig. 4). Apparently therefore both stress and fracture of coatings reduce and one can observe some smoothing of the relief as well as the grain size decreasing.
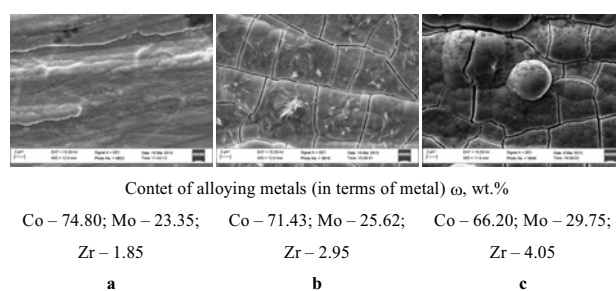

Contet of alloying metals (in terms of metal) ω, wt.%

Co – 74.80; Mo – 23.35;	Co – 71.43; Mo – 25.62;	Co – 66.20; Mo – 29.75;
Zr – 1.85	Zr – 2.95	Zr – 4.05
a	**b**	**c**

Fig. 3. Morphology (×3000) and composition Co−Mo−Zr coatings deposited in pulse mode at current density, A·dm^{-2}: 3 (a); 5 (b) and 8 (c); t_{on}/t_{off}=2/10 msec; T=20−25^{0}C; pH 8; plated time 20 min
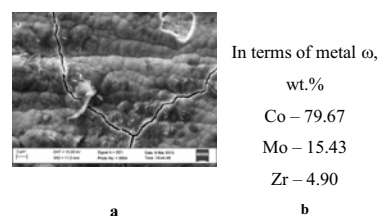

In terms of metal ω, wt.%

Co – 79.67

Mo – 15.43

Zr – 4.90

a   **b**

Fig. 4. Morphology (×3000) (a) and composition (b) Co−Mo−Zr coatings deposited in pulse mode at current density 8 A·dm^{-2}; t_{on}/t_{off}=2/10 msec; T=50^{0}C; pH 8; plated time 20 min

The galvanic Co−Mo−W alloys were deposited at copper substrates from polyligand bath of components composition, mole·dm^{-3}: Na$_3$Cit − 0.2, CoSO$_4$ − 0.2, Na$_2$MoO$_4$ − 0.08, Na$_2$WO$_4$ − 0.16, K$_4$P$_2$O$_7$ − 0.4.

Unlike the galvanic alloy Co−Mo−W the dependence of both alloying metal content in the coating Co−Mo−Zr on the current density has a maximum at interval 17−20 A·dm^{-2} wherein the above components' concentration in an alloy vary symbatically (Fig. 5). The current efficiency decreases with rinsing current density and this behavior is explained by the intensification of the side reaction of hydrogen evolution.
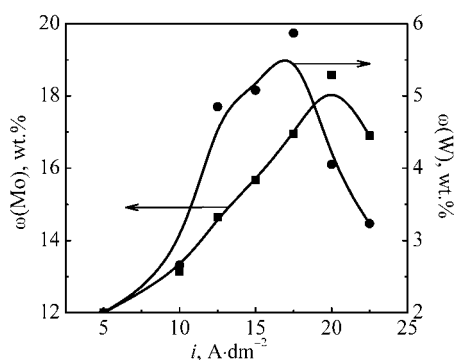
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Fig. 5. Pulse current density influence on the composition
Co−Mo−W coatings; t_{on}/t_{off} 2/10 msec; T 50^0C; pH 8;
plated time 20 min

dependencies of refractory metals content in the alloy on the energy and time parameters of electrolysis, as well as taking into account the ratio of the molybdate and tungstate concentrations in a solution the formation of heteronuclear complexes, and their discharge at the cathode are competing reactions.

It was established the change in the alloys composition as well as in surface morphology with polarization mode and current density increasing (Fig. 7). The coatings deposited under galvanostatic mode are fine-grained bright and shiny bluish-gray but contain a very small amount of tungsten (Fig. 7,a). The coatings produced in pulsed mode are different by smooth surface, but there is a grid of cracks due to the internal stresses which increase with the rising refractory metals content when coatings are deposited under higher current amplitude (Fig. 7,b−7,c).

Increasing the pulse duration in the range of 2−5 msec at fixed pause 20 msec promotes content both refractory components in the coating but more significantly for tungsten (Fig. 6,a). Rising the polarization time of more than 10 msec is impractical due to lack of any significant concentration dependence. Optimal in terms of alloying metals content the pause time for 2 msec pulse is in the range 5−10 msec (Fig. 6,b). Thus, we can conclude that the pulse/pause ratio that provides the maximum content of molybdenum and tungsten is 1/(2.5−5.0). It should be noted that, based on the obtained similar

Electroplated Co−Mo−W alloys have a developed surface as evidenced by the 3D-, 2D-map and cross section results of the scanning atomic force microscopy AFM (Fig. 8). Coatings Co−Mo−W are characterized by a smooth surface with the spherical grain agglomerates of 50−250 nm crystalline sizes (Fig. 8,c) which depend on a current density and consequent total content of molybdenum and tungsten. Obviously, the structurally dependent properties of coatings such as catalytic activity, microhardness et al. should be changed accordingly.
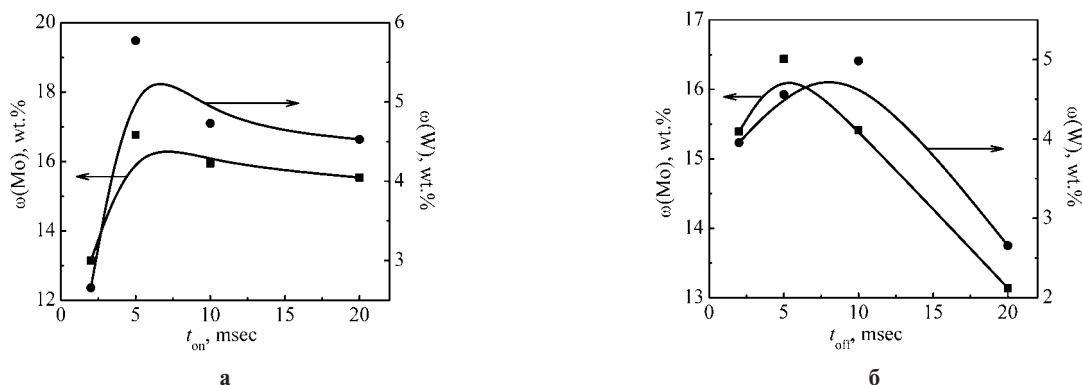

a

б

Fig. 6. Dependence of Co−Mo−W coating composition on the time of pulse t_{on} (a) (t_{off} 20 msec) and pause t_{off} (b) (t_{on} 2 msec);
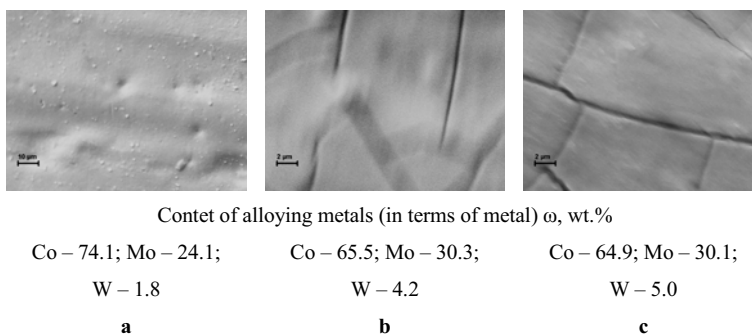i=10 A·dm^{-2}; T=50^0C; pH 8; plated time 20 min

Contet of alloying metals (in terms of metal) ω, wt.%

Co – 74.1; Mo – 24.1;	Co – 65.5; Mo – 30.3;	Co – 64.9; Mo – 30.1;
W – 1.8	W – 4.2	W – 5.0
a	b	c

Fig. 7. Morphologyand composition Co−Mo−W coatings deposited in stationary i 4 A·dm^{-2} (×1000) (a) and pulse mode (×5000)
at current density, A·dm^{-2}: 5 (b) and 10 (c); t_{on}/t_{off}=2/20 msec; T=50^0C; pH 8; plated time 20 min
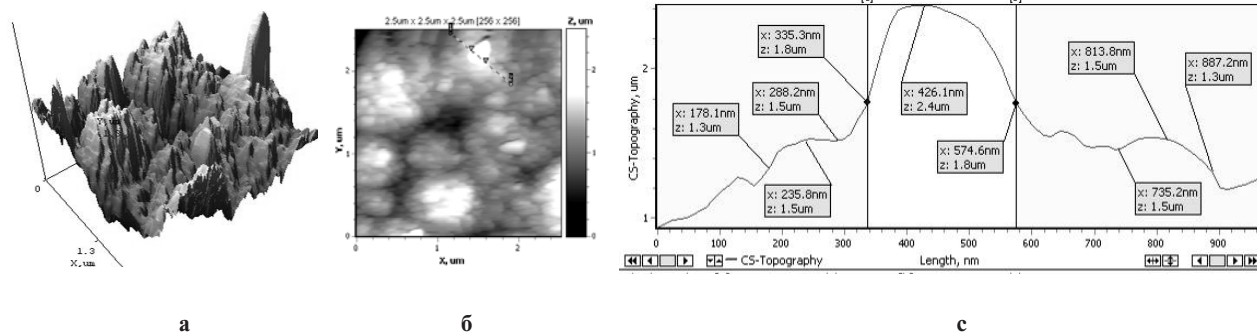
Fig. 8. 3D- (a), 2D-map (b) and cross section 1−2 (c) of the surface Co−Mo−W (Mo − 30.3 wt.%, W − 4.2 wt.%) deposited in pulse mode at current density 5 A·dm⁻²; t_{on}/t_{off}=2/10 msec; T=50⁰C; pH 8; plated time 20 min. Scan area AFM 2.5×2.5 мм

It should be noted that the Co−Mo−W coatings differ from the Co−Mo−Zr by uneven distribution of components on the surface topography. Thus, the projections are enriched with tungsten and depressions − with molybdenum and cobalt; moreover, they adsorb a significant amount of carbon (IV) oxide under environmental conditions.

Results of Co−Mo−W catalytic activity tests as cathodic material in a model electrochemical reaction of hydrogen evolution from acidic and alkali media (Tab. 2) demonstrate the synergetic nature of galvanic alloy. The hydrogen current exchange density on ternary coatings in acidic media is greater than for individual metal components and not inferior characteristics of platinum. Proceeding from data obtained coatings can be recommended as the active layer of the cathode in the electrolytic production of hydrogen.

Table 2

Hydrogen current exchange density lgi⁰_H for metals and Co−Mo−W alloy in different media

Catalyst composition, wt.%	$-lgi^0_H$, [A·cm⁻²]	
	Acidic medium	Alkali medium
Pt₁₀₀ [19]	3.3	3.1
Co₁₀₀ [19]	4.33	4.29
Mo₁₀₀ [19]	8.25	4.79
W₁₀₀ [19]	5.75	−
Fe₁₀₀ [19]	5.83	6.9
Co₇₀Mo₁₆W₁₄	3.05	4.5
Co₆₈Mo₁₉W₁₃	3.1	4.1

Testing of the catalytic activity of the synthesized Co−Mo−Zr coatings was performed in the model reaction of carbon oxide (II) oxidation to carbon (IV) oxide. Quantitative characteristics of the oxidation are the carbon oxide (II) conversion degree X(CO) and ignition temperature T_i. The catalytic properties of galvanic alloys were compared to platinum which is the most effective catalyst. As one can see from the temperature dependencies (Fig. 9,1) at the platinum catalyst plate with ω(Pt)=100 wt.% the oxidation of CO gas begins at

190⁰C, while 100% conversion degree is achieved at 250⁰C. Unlike platinum two segments with different angular coefficients are observed on thermograms for electroplating alloys indicating the change of the oxidation reaction mechanism. On the first section up to a conversion of 50% thermogram slope is identical with platinum and further oxidation rate is decreased the more the smaller a content of zirconium is in the catalyst layer (Fig. 9,2−9,4). Thus, despite the fact that the ignition temperature on the galvanic alloy Co₈₃,₃Mo₁₅,₈Zr₀,₉ is 180⁰C systems with zirconium content 1.5−2.0 wt.% for which the temperature of both 50% and 100% conversion is in the range 375−380⁰C (Tab. 3) should be considered as more promising for CO oxidation.
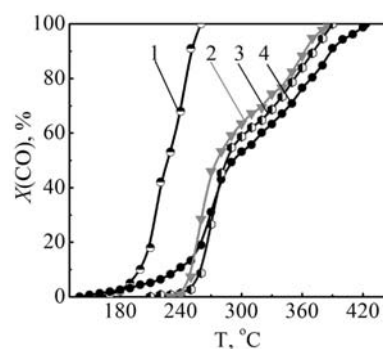

Fig. 9. Thermograms of CO conversion degree on Pt (1) and galvanic alloys Co−Mo−Zr of composition, wt.%: Co − 82.1, Mo − 16.0, Zr − 1.9 (2); Co − 83.0, Mo − 15.6, Zr − 1.4 (3); Co − 83.3, Mo − 15.8, Zr − 0.9 (4)

The above results are conclusive evidence not only of high catalytic activity but gives every reason to replace platinum catalysts at a cheaper galvanic alloys cobalt-molybdenum-zirconium an added benefit of which is a metallic substrate.

Conclusions

1. Uniform ternary coatings Co−Mo−Zr and Co−Mo−W of different composition can be produced in a pulsed mode from the polyligand citrate-pyrophosphate bath by varying the energetic and time electrolysis parameters.

2. The electro-catalytic activity of the

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Parameters of CO oxidation model reaction on different catalytic materials

Catalyst composition, wt.%	Ignition temperature, T_i, ^0C	Temperature for 50% conversion degree	Temperature for 100% conversion degree
Pt_{100}	190	220	250
$Co_{82,1}Mo_{16}Zr_{1,9}$	240	270	370
$Co_{83}Mo_{15,6}Zr_{1,4}$	245	280	375
$Co_{83,3}Mo_{15,8}Zr_{0,9}$	180	290	420

Co−Mo−W alloys comparing with 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.

3. The galvanic alloys Co−Mo−Zr with zirconia content 1.5−2.0 wt.% exhibit high catalytic properties in the carbon oxide (II) oxidation. This confirms the efficiency of materials as catalysts for the gaseous wastes purification and gives the reason to recommend them as catalysts for hydrocarbon combustion.

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ELECTRODEPOSITION OF CATALYTIC TERNARY COBALT BASED COATINGS

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The electrodeposition of Co−Mo−W and Co−Mo−Zr coatings from a polyligand citrate-pyrophosphate bath was investigated. The effects of both current density amplitude and pulse on/off time on the quality, composition and surface topography of the electrodeposited alloys were determined. It was established that the content of alloying components in Co−Mo−Zr coatings increases with an increase in the current density. The content of zirconium was shown to increase with the on-time. The content of molybdenum grows with the off-time. This is because the chemical reduction of their intermediate oxides by hydrogen ad-atoms. It was stated that the dependences of the refractory metals content in the Co−Mo−W coating upon both current density and on/off times have an extremal character; a maximum content of Mo and W corresponds to the current density range of 12 to 18 A⊡dm°² and to the on/off-times of 5 to 10 ms. The Co−Mo−W alloys exhibit a high catalytic activity towards the hydrogen evolution reaction in acidic media, this catalytic activity is comparable to that of a platinum electrode. The electrodeposited Co−Mo−Zr alloys with a zirconium content of 1.5 to 2.0% wt show a high catalytic activity towards the reaction of carbon oxide (II) oxidation. This confirms the efficiency of such materials as catalysts for the purification of gaseous wastes and allows us to recommend them as catalysts for hydrocarbons combustion.

Keywords: cobalt ternary alloy; citrate-pyrophosphate bath; catalytic properties; electrodeposition; hydrogen evolution reaction; pulse electrolysis.

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