



Full Length Article

Ternary cobalt-molybdenum-zirconium coatings for alternative energies

Gulmira Yar-Mukhamedova^{a,*}, Maryna Ved'^b, Nikolay Sakhnenko^b, Maryna Koziar^b^a Institute Experimental and Theoretical Physics of Al-Farabi Kazakh National University, Al-Farabi Ave., 71, 050040, Almaty, Kazakhstan^b National Technical University "Kharkov Polytechnic Institute", Kharkov, Ukraine

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ABSTRACT

Consistent patterns for electrodeposition of Co-Mo-Zr coatings from polyligand citrate-pyrophosphate bath were investigated. The effect of both current density amplitude and pulse on/off time on the quality, composition and surface morphology of the galvanic alloys were determined. It was established the coating Co-Mo-Zr enrichment by molybdenum with current density increasing up to 8 A dm^{-2} as well as the rising of pulse time and pause duration promotes the content of molybdenum because of subsequent chemical reduction of its intermediate oxides by hydrogen ad-atoms. It was found that the content of the alloying metals in the coating Co-Mo-Zr depends on the current density and on/off times extremely and maximum Mo and Zr content corresponds to the current density interval $4\text{--}6 \text{ A dm}^{-2}$, on-/off-time $2\text{--}10 \text{ ms}$. Chemical resistance of binary and ternary coatings based on cobalt is caused by the increased tendency to passivity and high resistance to pitting corrosion in the presence of molybdenum and zirconium, as well as the acid nature of their oxides. Binary coating with molybdenum content not less than 20 at.% and ternary ones with zirconium content in terms of corrosion deep index are in a group "very proof". It was shown that Co-Mo-Zr alloys exhibits the greatest level of catalytic properties as cathode material for hydrogen electrolytic production from acidic media which is not inferior a platinum electrode. The deposits Co-Mo-Zr with zirconium content 2–4 at.% demonstrate high catalytic properties in the carbon(II) oxide conversion. This confirms the efficiency of materials as catalysts for the gaseous wastes purification and gives the reason to recommend them as catalysts for red-ox processes activating by oxygen as well as electrode materials for red-ox batteries.

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1. Introduction

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), solar cells (SC) are among the promising renewable energy sources, however, the high cost of the noble metal electrodes prevents their dissemination and widespread use [1,2]. Development of FC, SC and various red-ox flow batteries (RFB) needs to create effective catalytically active electrodes on the basis of transition metals [3,4]. 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 [5,6]. For instance, one of the most widespread electrode material for FC and FRB 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, oxides of platinum group metals, etc [7–10]. It is worth mentioning that in scientific literature for the last years there are too few publications on electrode materials on the basis of hi-tech materials, such as nanostructured and nanocrystalline materials based on the corrosion resistant amorphous metal alloys (metal glass), or nanostructured deposits by synergistic alloys [11–13]. The most efficient directions of catalytic materials synthesis by physico-chemical methods are electrochemical technologies that provide the opportunity to flexibly control the component content, the rate of deposition, the state of the surface, by varying the electrolyte composition and polarization mode (static or

* Corresponding author.

E-mail address: shariph@list.ru (G. Yar-Mukhamedova).

pulse, reverse current or decrease of the potential) [14–18]. 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 [19–23]. 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.) [24–26].

Particular interest to cobalt alloys is due to their wide use in materials for advanced applications, such as super-alloys for aircraft turbine vanes and blades, alloys for powerful, high-coercive force magnets, hard metal alloys for cutting tool materials (Co-Cr-W-C, Co-Cr-W-Mo-Ni-Fe-C), and electrodeposited Ni-Co alloys for protective hard coatings. Cobalt is also used as a basic component in speciality materials, including alloys for dental and surgical implants or bone fracture fixation (Co-Cr-Mo-Si-C, Co-Cr-Ni-Ti-Mo), low thermal expansion alloys (Fe-Ni-Co, Co-Fe-Cr), magnetic recording thin film materials (Co-Ni, Co-Fe-Mg-C, Co-Mo-Zr-Nb), catalysts [27].

The combination of cobalt and molybdenum with zirconium can significantly extend the range of functional properties of materials, and electrodeposition of alloys allows implementing these properties in thin surface layers. Attention is drawn to number of promising publications on electrodeposition of binary and ternary cobalt and molybdenum alloys. Cobalt–molybdenum alloys with low coercivity and high saturation magnetization (molybdenum percentages 10%) were deposited from a sulfate-citrate solutions containing a fixed sodium citrate concentration (0.2 mol dm^{-3}) and variable concentrations of CoSO_4 and Na_2MoO_4 [28]. It was shown the electrolytic alloys presented a close-packed hexagonal structure when formed at low current densities and mixed crystalline + amorphous structure at higher cathodic polarization [29]. Adherent, compact and uniform Co and Co–Mo (with 1–8 wt.% Mo content) deposits were obtained onto copper substrates from various ionic liquids based on choline chloride (ChCl) – urea and ChCl–ethylene glycol eutectic mixtures at current density in the range of $7\text{--}25 \text{ mA cm}^{-2}$, at $90\text{--}100^\circ\text{C}$ [30]. Cobalt–molybdenum–boron amorphous electrolytic alloys (51% Co, 47% Mo and 2% B) with high hardness, corrosion resistance, wear resistance and also sufficient ductility were deposited from citrate-phosphate-ammonia electrolyte with cathode current efficiency 29–65% [31]. Cobalt–molybdenum–phosphorus (Co–Mo–P) alloy coatings containing 8% Mo, 20% P and Co balance were electrodeposited from citrate-phosphate electrolyte, and were recommended as barrier layer to replace nickel [32]. The amorphous Co–Mo–C alloy coatings were obtained through electrolytic deposition in the magnetic field of parallel orientation of forces lines towards the working electrode. The content of Mo in the deposited alloys ranged from 27.6 at.% to 34.2 at.% for alloys deposited in a magnetic field [33], and the last had low overvoltage of hydrogen evolution.

It has previously been shown prospects of electrolytic binary cobalt alloys with molybdenum or tungsten to produce hydrogen by alkali electrolysis [34,35] as well as to the oxidation of hydrocarbons [36,37]. However, it is of interest to create catalytic materials based on ternary synergistic cobalt alloys with metals of differing affinity to oxygen and hydrogen and high corrosion resistance for use as catalysts, and electrode materials for fuel and flow batteries.

The aim of this work is to study the influence of the electrolysis parameters on the quality, composition, morphology, catalytic properties and corrosion resistance of ternary Co–Mo–Zr coatings.

2. Experimental

Coatings were deposited onto the substrates out of steel. Pre-treatment of samples included grinding, degreasing in a solution of sodium carbonate at 50°C , and washing, etching in a mixture of hydrochloric acid and sulfuric acid at a temperature of 20°C , and thoroughly washing in flowing water.

Deposits of cobalt with molybdenum and tungsten or zirconium were formed at temperatures of $25\text{--}50^\circ\text{C}$ from a complex polyligand citrate-diphosphate bath. The coatings Co–Mo–Zr were deposited from electrolyte composition (M): cobalt sulfate 0.15, sodium molybdate 0.06, zirconium(IV) sulfate 0.05, sodium citrate 0.2, and potassium diphosphate 0.1. The pH value of electrolytes was adjusted within the range 8–9 by sodium hydroxide. Electrolytes were prepared from analytically pure reagents: $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{K}_4\text{P}_2\text{O}_7$, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ dissolved in a small amount of distilled water following by solution mixture in a certain sequence, based on the ionic equilibrium study results [38].

The deposits were formed in pulsed mode with unipolar pulse current of amplitude $2\text{--}15 \text{ A} \times \text{dm}^{-2}$ in the frequency f range of $19\text{--}910 \text{ Hz}$ at a pulse duration $t_{\text{on}} = 2\text{--}50 \text{ ms}$ and pause time $t_{\text{off}} = 5\text{--}50 \text{ ms}$, duty factor $q = (t_{\text{on}} + t_{\text{off}})/t_{\text{on}}$ was $2\text{--}26$. Coplanar cobalt plates were used as anodes. The cathode-to-anode area ratio was kept at 1:5. The pulse electrolysis was performed using pulse current supply unit (ZY-100 ± 12). 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 current efficiency C_e (%) was determined from the weight and chemical composition of the deposited alloys and the charge passed using the electrochemical equivalent of the alloy. The thickness of the deposits was calculated from a sample actual weight increase after the electrolysis.

The chemical composition of the coatings was determined by energy dispersive X-ray spectroscopy (EDS) on an Oxford INCA Energy 350 electron probe microanalysis integrated into the system of the SEM. The X-rays were excited by exposure of the samples to a beam of 15 keV electrons. The surface morphology of the deposits was studied with a Zeiss EVO 40XVP scanning electron microscope (SEM). Images were recorded by the registration of secondary electrons (SEs) via scanning with an electron beam; this mode made it possible to study the topography with a high resolution and contrast ratio. The surface roughness was evaluated by the contact method on $10 \times 10 \times 2 \text{ mm}$ samples with an NT-206 scanning probe AFM microscope (lateral and vertical resolutions 2 and 0.2 nm, respectively; 1024×1024 scanning matrix, CSC cantilever B as probe, probe tip radius 10 nm).

The structure of the deposits was examined by X-ray diffraction analysis using a diffractometer (DRON-2.0) in the emission of iron anode and $\text{CuK}\alpha$ radiation. Diffractograms were recorded in discrete mode with a step $2\theta = 0.1^\circ$ with the exposure at each point for 20 s; operating voltage was 35 kV, and current 20 mA.

Corrosion tests of the deposits were carried out in a model media 1 M sodium sulfate with the addition of sulfuric acid to pH 3 or potassium hydroxide to pH 11 and in 3% potassium chloride (pH 7). The corrosion current was determined by the polarization resistance technique using digital analysis of anodic and cathodic plots in Tafel coordinates within the range $200\text{--}300 \text{ mV}$ from open circuit potential [39,40]. The potentiostat IPC-Pro controlled by PC was used for voltammetry measurements with scan rate 1 mV s^{-1} . Cor-

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