

UDC 621.35

CORROSION-ELECTROCHEMICAL PROPERTIES OF COBALT-MOLYBDENUM-ZIRCONIUM DEPOSITS

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Galvanic alloy coatings of cobalt–molybdenum and cobalt–molybdenum–zirconium were deposited on substrates steel 3 from a poly-ligand citrate-pyrophosphate bath at a temperature of 25–30°C. The acidity of the electrolyte was maintained in the range pH 8–9. The coatings were deposited using a pulsed electrolysis with current amplitude 2–20 A×dm⁻² in the frequency range of 19–910 Hz, pulse time 2×10⁻³–2×10⁻¹ sec, pause durability 2×10⁻²–2×10⁻¹ sec; duty cycle was 2–20. The electrolysis parameters influence on cobalt–molybdenum–zirconium alloy deposition peculiarities, composition and surface morphology has been revealed. The elevating in current density leads to a decrease in the zirconium content and cracking of deposits due to the growth of internal stresses. The effect of cobalt–molybdenum–zirconium alloys composition and topography on their corrosion resistance in acid, neutral and chloride-containing media was investigated. It was established the cobalt–molybdenum–zirconium functional alloys have a high chemical resistance in aggressive media due to the both molybdenum and zirconium trend to passivity especially for local corrosion.

In our time, the rapid development of new trends in energetics, microelectronics, creating compact equipments and appliances is impossible without using of new materials with a wide range of functional properties. One way their creating is forming of thin layers of electrolytic coatings with high corrosion resistance, hardness, heat resistance and catalytic activity on the surface of traditional structural materials [1, 2].

For expansion possibilities use of electrolytic coating alloys with two or more components are used in addition to pure metal. In recent years becomes relevant research cobalt alloys with refractory metals (molybdenum, tungsten) [3–5]. This choice is primarily due to their high acceptor capacity, their ability to passivity and create multivalent oxides that causes their functional properties. Considering the growing interest in coatings with high resistance to local types of corrosion, which is provided by alloying components, special attention was paid to the alloy Co-Mo-Zr. It's known that zirconium can't be deposited from aqueous

solutions because they have negative standard potential $-1,21$ V. However, as shown in [6], we obtained electrolytic deposits Co–Mo from poly-ligand electrolyte, which contain up to 4 wt. % zirconium.

The goal of this study is to investigate the composition, morphology, and composition of the electrolytic cobalt–molybdenum–zirconium alloy coatings and to determine their corrosion resistance in various aggressive environments.

Research Methodology

The coatings were deposited on substrates of steel 3, surface pretreatment of which was performed by standard technique.

Coatings Co–Mo–Zr were deposited from a poly-ligand citrate-pyrophosphate bath at a temperature of $25\text{--}30^\circ\text{C}$. The acidity of the electrolyte was maintained in the range pH 8–9. Electrolyte was prepared of the certified reactive "pure grade" mark on the distilled water.

The coatings were obtained in unipolar pulse current with amplitude $2\text{--}20\text{ A}\cdot\text{dm}^{-2}$ in the frequency f range of 19–910 Hz, pulse time $t_{\text{on}} 2\times 10^{-3}\text{--}2\times 10^{-1}$ sec, pause durability $t_{\text{off}} 2\times 10^{-2}\text{--}2\times 10^{-1}$ sec; duty cycle was 2–20. As soluble anodes were used coplanar cobalt plates with anode to cathode area ratio as 5 : 1. Electrolysis mode (t_{on} , t_{off} , current density) set by potentiostat PI-50-1.1 with programmer PR-8 [7].

The chemical composition of the coatings was examined with X-ray photoelectron spectroscopy using energy dispersive spectrometer INCA Energy 350 and with X-ray fluorescence method using a portable spectrometer "SPRUT", the absolute error of components did not exceed 1 wt.%. The surface morphology was evaluated from the images obtained using a scanning electron microscope (SEM) ZEISS EVO 40XVP registering secondary electrons (BSE) during scanning the patterns by electron beam. Corrosion tests were carried out in model medium of different pH: 3 % sodium chloride solution (pH 7) and 1 M solution of sodium sulfate at pH 3 and 11. The corrosion rate of coatings was determined by polarization resistance technique analyzing cathodic and anodic polarization dependences in semilogarithmic coordinates [8].

Results and Discussion

Results of studies showed the possibility of deposition of ternary Co–Mo–Zr alloy using pulsed electrolysis, which can not be obtained in the direct current dc mode [6]. The composition and surface topography of coatings depend on the energy parameters of electrolysis that allowing to flexibly managing the quality and properties of materials.

Doping cobalt by molybdenum and zirconium promotes the formation of globular amorphous surface. The elevating in current density leads to cracking of deposits due to the growth of internal stresses (Fig. 1).

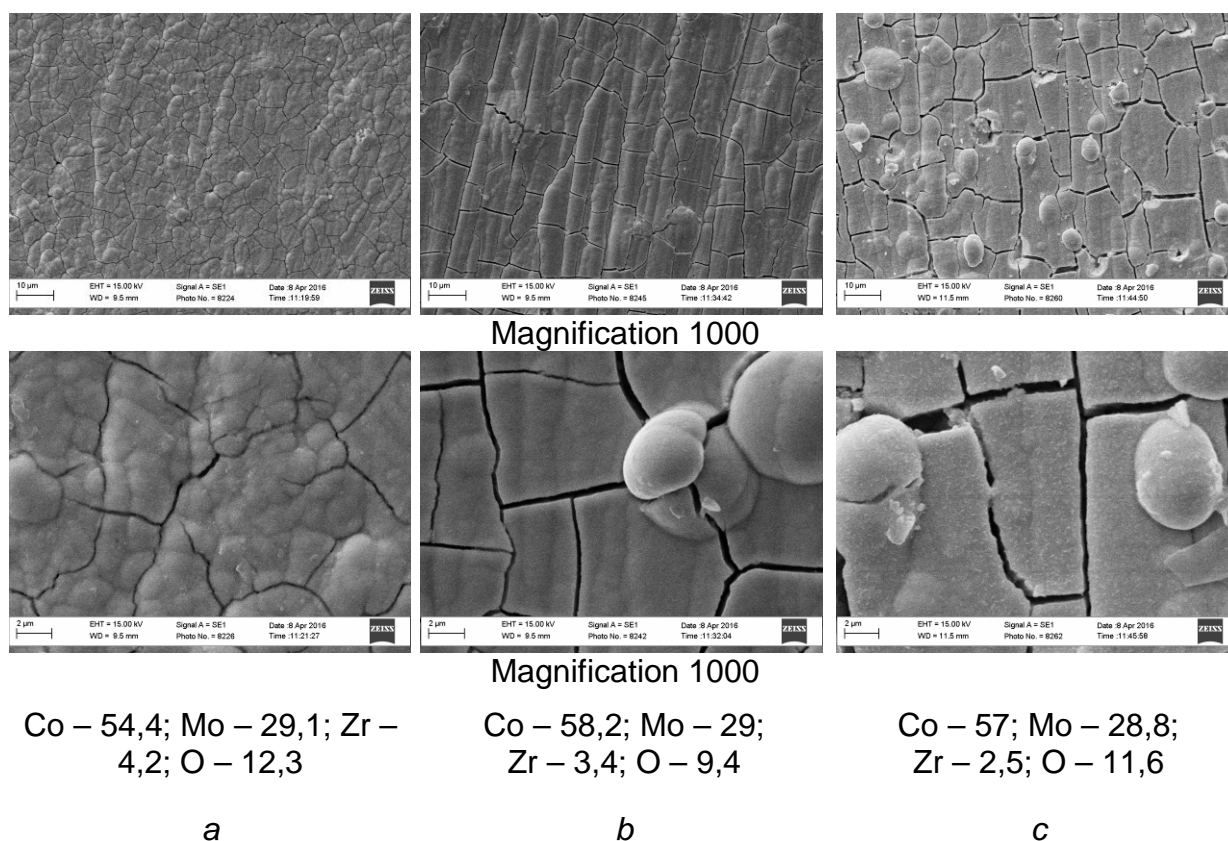


Figure 1. Morphology and composition (wt. %) of Co–Mo–Zr coatings deposited in pulse mode at current density, $A \cdot dm^{-2}$: 4 (a); 6 (b) and 8 (c); $t_{on}/t_{off} = 2 / 10$ msec; $T = 20\text{--}25$ °C; pH 8; plated time 30 min.

Composition analysis of ternary coatings revealed that content of zirconium decreases with an increase in current density. Also they contain some oxygen. This can be explained by including not completely recovered molybdenum oxides and partially hydrolyzed oxo-zirconate ions in the surface layers. It should be noted that with rising current density grid of cracks on the surface of precipitates becomes denser and branched due to increased internal stresses in the coating.

The doping of cobalt by molybdenum as it was shown in [8] leads to increased resistance to local types of corrosion – pitting and intergranular. In this study the corrosion resistance of ternary electrodeposited alloys was compared with corrosion resistance of binary Co–Mo systems [8]. The shift of the corrosion potential of coated samples in NaCl solution up to the negative region as compared to the same parameter in acidic solution as well as the character of anodic polarization dependences (Fig. 2, 3) testifies the cathodic control of corrosion process. The rise in corrosion potential simultaneously with the appearance of a plateau on the anode branches of voltammograms (Fig. 3) in alkali solution indicates an anode control of corrosion process, which can be explained by trend to passivity of the surface due to the formation of the oxide film [9].

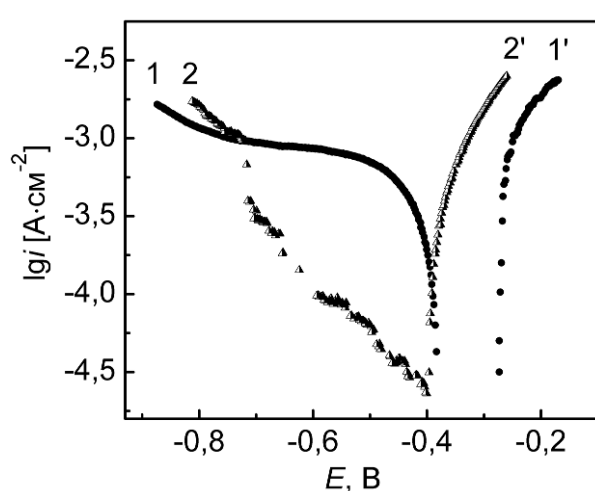


Figure 2. Corrosion diagrams for coatings Co–Mo (1) and Co–Mo–Zr (2) in 1 M Na₂SO₄ pH 3: cathodic plots (1, 2); anodic plots (1', 2)

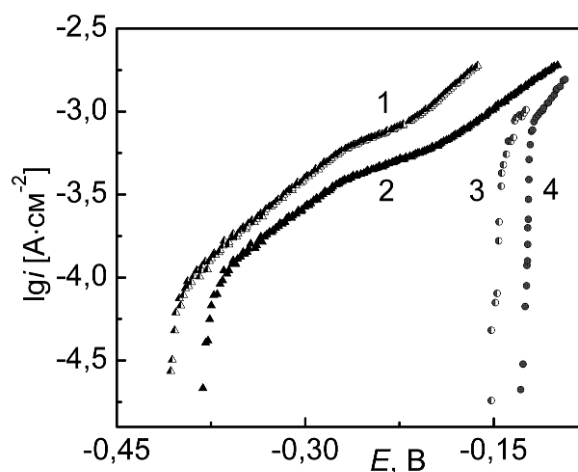


Figure 3. Anodic polarization dependences for coatings Co–Mo–Zr (1, 2) and Co–Mo (3, 4) in solutions: 1 M Na₂SO₄ with pH 11 (1, 3); 3 % NaCl pH 7 (2, 4)

Corrosion resistance of ternary alloys with zirconium content of 3–4 wt.% and molybdenum up to 25–30 wt. % proceeding from corrosion depth index in acid ($k_h = 3,1 \cdot 10^{-4}$ mm/year) and neutral chloride-containing media ($k_h = 2,2 \cdot 10^{-4}$ mm/year) increases practically an order of magnitude compared with a binary ones ($k_h = 2,3 \cdot 10^{-3}$ mm/year, $k_h = 2,9 \cdot 10^{-3}$ mm/year respectively). Corrosion resistance in an alkaline medium increases by three times – $k_h(\text{Co–Mo–Zr}) = 3,1 \cdot 10^{-4}$ mm/year, $k_h(\text{Co–Mo}) = 9,3 \cdot 10^{-4}$ mm/year.

Binary coatings with a molybdenum content not less than 10 at. % and ternary zirconium containing galvanic alloys belong to the group "very resistant" by the depth of corrosion index.

Conclusions

1. The surface Co–Mo–Zr electrodeposits obtained from polyligand citrate-pyrophosphate electrolyte is uniform, bright, brilliant, but is covered by a grid of cracks. It was found that an increase in current density leads to an increase of internal stresses in the coating. Thus, it is advisable process to conduct the electrodeposition at lower current densities ($4 - 6 \text{ A} \times \text{dm}^{-2}$).

2. Chemical stability of the electrolytic ternary coatings causes by increase tendency to passivity and resistance to pitting corrosion in the presence of molybdenum and zirconium. Ternary coatings by the corrosion depth index belong to the group "very resistant", and can be recommended as safety when working in aggressive media.

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