



Iron binary and ternary coatings with molybdenum and tungsten



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ABSTRACT

Electrodeposition of Fe-Mo-W and Fe-Mo layers from a citrate solution containing iron(III) on steel and iron substrates is compared. The utilization of iron(III) compounds significantly improved the electrolyte stability eliminating side anodic redox reactions. The influence of concentration ratios and electrodeposition mode on quality, chemical composition, and functional properties of the alloys is determined. It has been found that alloys deposited in pulse mode have more uniform surface morphology and chemical composition and contain less impurities. Improvement in physical and mechanical properties as well as corrosion resistance of Fe-Mo and Fe-Mo-W deposits when compared with main alloy forming metals is driven by alloying components chemical passivity as well as by alloys amorphous structure. Indicated deposits can be considered promising materials in surface hardening technologies and repair of worn out items.

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The development of technology and modernization of equipment in mechanical engineering and instrumentation as well as in the chemical industry places high requirements for physical and mechanical properties of functional metals and alloys. Intensive search for approaches to ensure high strength, wear and corrosion resistance for low cost materials must be paired with the principles of ecology compatibility and resource saving processes for their production.

The performance characteristics of materials can be effectively improved by the surface layer modification during electrodeposition [1–4]. Small amount of material, process simplicity, formation of multi-component metal deposits which are difficult to produce by metallurgical or chemical processes as well as wide variation of galvanic alloys properties depending on the components nature [5–7] ensure the possibility of their industrial application.

To harden the working surfaces of items electrolytic chromium based deposits characterized by high hardness and wear resistance are often utilized [8,9]. However, high aggressiveness and carcinogenicity of chromium (VI) electrolytes require additional measures to ensure the safety of personnel during the electrodeposition process as well as wastewater special treatment. Therefore, the actual alternative is development of the galvanic deposits with improved

physical and mechanical properties, the formation of which would correspond to the criteria of resource conservation, environment protection, and cost effectiveness.

Effective replacement of chromium deposits can be achieved by the electrodeposition of iron doped with various metals [10–12]. Electrolytic iron hardness is significantly higher compared with the smelt one; however, the presence of residual stresses and electrocrystalline structural defects leads to cracking and poor deposit adhesion to the substrate. Selection of components for electrolytic alloy formation is based on a wide experience in the alloyed steels utilization and their functionality dependence on the composition [13,14]. Introduction of molybdenum and tungsten into deposit predictably allows for minimizing the internal stresses inherent to the electrolytic iron and improving the physical and mechanical properties [15–18].

The goal of this work is to study the influence of both the electrolyte composition and electrolysis mode on the quality, composition, morphology, mechanical properties and corrosion behavior of electrolytic binary Fe-Mo and ternary Fe-Mo-W alloys as well as the impact of the third component on their functional properties.

1. Experimental

Alloys were deposited onto the substrates out of steel and the cast iron. Pretreatment of samples included grinding, degreasing in a solution of sodium carbonate at 50 °C, washing, etching in a

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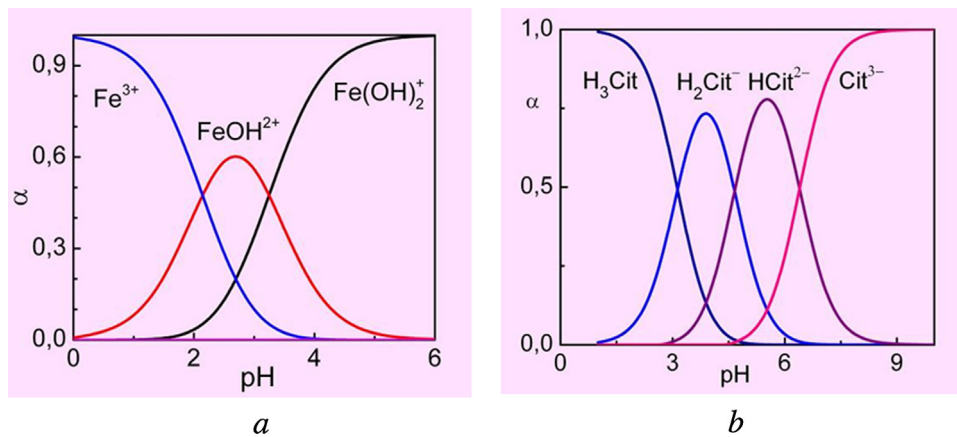


Fig. 1. Ionic equilibria in the systems Fe^{3+} – H_2O (a) and Cit^{3-} – H_2O (b).

mixture of hydrochloric acid and sulfuric acid at a temperature of 20°C and thoroughly washing in flowing water.

Deposits of iron with molybdenum were formed at a temperature of 25 – 30°C from a complex citrate electrolyte of composition (M): iron(III) sulfate 0.1 – 0.15 , sodium molybdate 0.06 – 0.08 , sodium citrate 0.3 – 0.4 , and boric acid 0.1 . The pH value was adjusted within the range 3 – 4 by sulfuric acid or sodium hydroxide [19]. Iron - molybdenum - tungsten deposits were deposited from the described electrolyte also containing 0.04 – 0.06 M of sodium tungstate.

The deposits were formed in two modes: (i) galvanostatic with the current density i 3 – 6 A/dm^{-2} and (ii) pulsed with unipolar pulse current of amplitude i 3.5 – 9.0 A/dm^{-2} at a pulse duration $t_{\text{on}} = 5$ – 10 ms and pause time $t_{\text{off}} = 10$ – 20 ms. Plates of AISI 304 steel were used as anode. The cathode-to-anode area ratio was kept at $1:10$. Both the galvanostatic and pulse electrolysis were performed using dc and pulse current supply unit (ZY-100 \pm 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 [20]. The thickness of the deposits was calculated from a sample actual weight increase after the electrolysis.

The chemical composition of deposits 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 deposits 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 $10 \times 10 \times 2$ 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.

Physical-mechanical properties of the deposits were evaluated according to metallographic studies of sections. The quality of adhesion to the substrate is tested by using a polishing paste based on chromium (III) oxide, by bending under angle of 90° and heat-

ing to a temperature of 150 – 200°C , followed by cooling in air. Microhardness H_μ was measured using a PMT-3 device with a diamond pyramid under a load of 50 g and 100 g; diagonal of imprint was measured by ocular micrometer MOB-1-15 (magnification of a microscope – 500).

Corrosion tests of the deposits were carried out in a model media with 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 [21]. The potentiostat IPC-Pro controlled by PC was used for voltammetry measurements with scan rate 1 $\text{mV}/\text{sec}^{-1}$. Corrosion depth index k_h (mm per year) was converted from corrosion current:

$$k_h = 8,76/k_e/i_{\text{cor}}/\rho,$$

where k_e – the electrochemical equivalent of alloy, kg/C^{-1} ;

i_{cor} – corrosion current density, A/m^{-2} ;

ρ – density of the alloy, kg/m^{-3} .

Electrochemical equivalent k_e and density ρ of the alloys were determined considering their quantitative composition [22].

2. Theoretic aspects

The advantages using an iron (III)-based electrolytes for deposition of iron alloys with refractory metals compared with currently used iron (II) ones are explained not only by preventing oxidation of Fe^{2+} by oxygen or anodic polarization. Oxometalates as strong oxidizing agents may also oxidize Fe^{2+} ions by reaction:



where M – Molybdenum or Tungsten.

Thus, we have increased the content of molybdenum in the Fe-Mo deposit and process current efficiency [19] by eliminating the side reactions, including (1) compared to the electrolytes based on iron(II).

The competing reactions of Fe^{3+} ion hydrolysis and complexing in aqueous solutions [23,24] as well as thermodynamic stability, the protonation and polymerization degree of oxometalates [25] significantly affect the stability and performance of electrolytes. In addition, on the basis of such equilibria it is possible determine the composition of the particles, which are discharged on the cathode.

It should be noted that the actual concentrations of complexing agent (Fe^{3+}) and the ligand (Cit^{3-}) as well as the composition of the resulting complex particles depend on the degree of Fe^{3+} hydrolysis and Cit^{3-} protonation [19], and therefore inseparably connected with solution pH (Fig. 1). As can be seen from Fig. 1, in the range

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