

- Название:** Electrodeposition of iron–molybdenum–tungsten coatings from citrate electrolytes
- Другие названия:** Электроосаждение покрытий железо–молибден–вольфрам из цитратных электролитов
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- Реферат:** Specific features of the electrodeposition of iron–molybdenum–tungsten coatings from citrate electrolytes based on iron(III) sulfate in the dc mode and with a unipolar pulsed current were studied. It was shown that varying the relative concentrations of salts of alloy-forming metals and the solution pH makes it possible to obtain lustrous compact coatings with low porosity and various contents of high-melting components. The effect of temperature on the coating composition and current efficiency was examined. The current density ranges providing high electrolysis efficiency were found and it was demonstrated that using a pulsed current favors formation of more compositionally homogeneous surface layers at a smaller amount of adsorbed nonmetallic impurities in the coatings. The iron–molybdenum–tungsten coatings are X-ray-amorphous and have better physicomechanical properties and corrosion resistance as compared with the base, which makes it possible to recommend these coatings for application in techniques for surface reinforcement and restoration of worn-out articles.
- Исследованы особенности электроосаждения покрытий железо–молибден–вольфрам из цитратных электролитов на основе сульфата железа(III) на постоянном и униполярном импульсном токе. Показано, что

варьирование соотношения концентраций солей сплавообразующих металлов и pH раствора позволяет получать блестящие компактные покрытия с низкой пористостью и различным содержанием тугоплавких компонентов. Исследовано влияние температуры на состав покрытий и выход по току. Установлены интервалы плотности тока, обеспечивающие высокую эффективность электролиза, и показано, что применение импульсного тока способствует формированию более равномерных по составу поверхностных слоев при снижении количества адсорбированных неметаллических примесей в покрытиях. Покрытия железо–молибден–вольфрам являются рентгеноаморфными, обладают более высокими по сравнению с основой физико-механическими свойствами и коррозионной стойкостью, что позволяет рекомендовать их для использования в технологиях поверхностного упрочнения и восстановления изношенных деталей.

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#### VARIOUS TECHNOLOGICAL PROCESSES

### Electrodeposition of Iron–Molybdenum–Tungsten Coatings from Citrate Electrolytes

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**Abstract**—Specific features of the electrodeposition of iron–molybdenum–tungsten coatings from citrate electrolytes based on iron(II) sulfate in the dc mode and with a unipolar pulsed current were studied. It was shown that varying the relative concentrations of salts of alloy-forming metals and the solution pH makes it possible to obtain lustrous compact coatings with low porosity and various contents of high-melting components. The effect of temperature on the coating composition and current efficiency was examined. The current density ranges providing high electrolysis efficiency were found and it was demonstrated that using a pulsed current favors formation of more compositionally homogeneous surface layers at a smaller amount of adsorbed nonmetallic impurities in the coatings. The iron–molybdenum–tungsten coatings are X-ray amorphous and have better physicochemical properties and corrosion resistance as compared with the base, which makes it possible to recommend these coatings for application in techniques for surface reinforcement and restoration of worn-out articles.

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The development of technology and modernization of equipment in numerous industries (machine-building, chemical, oil-refining) impose strict requirements on the physicochemical properties of the construction materials being used and on the existence of modern repairing techniques providing fast and full restoration of performance at minimum maintenance duration and high quality of executed services. At present, techniques of surface reinforcement and repair by galvanicochemical restoration of work surface via deposition of coatings of Cr, Fe, Ni, Cu, Zn, and other metals [1]. The application of electroplated coatings for reinforcement of new articles and restore worn-out surfaces has the following advantages: minimum thermal treatment of the material of an article because such treatment may cause undesirable changes in the structure and properties of the metal; formation of coatings with prescribed thickness, with the minimum allowance for machining, and enhanced functional properties; small expenditure of a material for performing the operation; possible automation of the process and simultaneous processing of a large number of articles, which substantially reduces the cost of the technological process [2].

The electrolytic iron plating occupies a particular place among the known processes for deposition of galvanic coatings. This technique is distinguished by high output capacity, technological simplicity, comparatively low cost, possible deposition of coatings with various thicknesses, and prospects for deposition of not only pure iron, but also alloys on its basis. Owing to a combination of valuable characteristics of individual metals, multicomponent coatings impart to article surface various functional properties that occasionally cannot be obtained by the conventional metallurgical method [3]. The most preferable alloying components of electrolytic iron alloys, which relieve internal stresses and improve their physicochemical and tribological properties, are, in our opinion, high-melting metals (in particular, molybdenum and tungsten). In this context, a topical research area consists in studying the processes of electrochemical formation of coatings composed of iron alloys with molybdenum and tungsten on substrates of the most widely occurring construction material, low-alloyed steel, which will make it possible to obtain materials with unique functional properties as an alternative to stainless steel in numerous industries.

With consideration for specific features of the electrochemical behavior of oxo anions of the above high-melting metals and for the impossibility of their individual deposition onto a cathode from aqueous electrolyte solutions, of particular scientific interest is a study of the fundamental aspects of alloying of galvanic iron alloys with simultaneously two components, molybdenum and tungsten, and examination of the functional properties of the resulting coatings.

A rather large number of electrolytes from which multicomponent galvanic alloys of iron with molybdenum and tungsten can be formed have been developed by researchers [4-6]. In most cases, these are based on the known iron-plating electrolytes with addition of high-melting metal ions and ligands (nitric acid, ammonia, etc.). Because  $Fe^{3+}$  ions have rather long been considered a detrimental impurity in iron-plating electrolytes, most of electrolytes intended to form iron coatings with high-melting components are based just on  $Fe(II)$  salts.

It has been shown previously that it is advisable to use complex citrate electrolytes based just on  $Fe(II)$  salts to form iron-molybdenum electrolytic coatings [7]. The suggested electrolyte is stable and provides a high output capacity because the following factors were taken into account in its development: standard potentials of alloy-forming metals and electrode reactions involving these metals; possible competing reactions of hydrolysis and complexation in aqueous solutions; thermodynamic stability and the degree of protonation and polymerization of oxo anions; and cathodic stability of a ligand used. A similar approach was used when the composition of the electrolytes for deposition of Fe-Mo-W alloy coatings was developed.

The goal of our study was to examine factors affecting the current efficiency, composition, morphology, and functional properties of iron-molybdenum-tungsten electrolytic coatings.

#### EXPERIMENTAL

Iron-molybdenum-tungsten alloy coatings were deposited at a temperature of 18–40°C from a complex electrolyte of composition (mol dm<sup>-3</sup>): iron(II) sulfate 0.1–0.5, sodium molybdate 0.06–0.08, sodium tungstate 0.04–0.06, sodium citrate 0.2–0.3, and boric acid 0.1. The pH value was adjusted in the range 3.0–4.5 by addition of concentrated sulfuric acid or sodium hydroxide. Solutions were prepared from certified reagents of chemically pure grade and distilled water.

The coatings were formed in two modes: galvanostatic, with current density varied within the range 2.5–6.5 A dm<sup>-2</sup>, and with unipolar pulsed current with amplitude of 2.5–8.5 A dm<sup>-2</sup> at a pulse width  $t_{on} = 10$  ms and pulse duration  $t_{pulse} = 20$  ms. As anodes served 12Kh18N10T steel plates (GOST (State Standard) 5949) with the cathode to anode area ratio  $S_c/S_a$  being 1–10. The galvanostatic polarization was performed with a BS-49 stabilized dc power source. The pulsed electrolysis was performed and the corrosion behavior of the coatings was determined by using a PI-50-11 potentiostat with a PR-8 programming unit. The electrode potentials were measured with an EVM-1M1 reference electrode connected to the working cell via an electrolytic bridge filled with jelly agar-agar with a saturated KCl solution. All the potentials are given in the communication relative to the standard hydrogen electrode.

The coatings were formed on S1.3 steel (GOST 380) substrates. The preliminary preparation of a substrate included the grinding, degreasing, washing, and etching procedures. The current efficiency by the alloys was determined with consideration for the electrochemical equivalent of an alloy [7]. The throwing power of the electrolytes was determined by the standard procedure with a classical Hall cell with angular dismountable cathode containing seven sections [8].

The surface chemical composition of the coatings was examined with an FNCA Energy 350 energy-dispersive spectrometer. The composition of the coatings (wt %) is given in terms of the metallic components of the alloy; the surface topography is assessed with consideration for the content of nonmetallic adsorbed impurities (oxygens). The surface morphology of the coatings was examined with a Zeiss EVO 40XVP microscope. The surface roughness of the deposits was evaluated with an AFM NT-206 scanning probe microscope (CSG-37 probe, B cantilever). The quality of adherence of the coatings to the substrate material was examined by the method of polishing with pastes based on chromium oxide, bending at an angle of 90°, and heating to 150–200°C with the subsequent cooling in air. The microhardness of the coatings was determined with a PMT-3 microhardness meter under a load of 50–100 g. The tribotechnical properties of the coatings on gray cast iron (GOST 1412) were evaluated by the friction coefficient  $f_0$ . In addition, the wear-resistance parameters were determined on a commercial 2070 SMT-1 friction machine under gradual loading of mated samples from