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COMPOSITE COATINGS OF Co-W(WO_2)-TiO_2 TO PRODUCTION OF ELECTROLYTIC HYDROGEN

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Abstract. The influence of electrolysis regimes and deposition conditions on the composition and morphology of composite coatings Co-W(WO_x)-TiO_2 was studied. It is shown that the application of a current density of 1.5-2.5 A/dm^2, a temperature of 45 – 50 °C and slow mixing of the working solution (up to 100 rpm) creates the conditions for the incorporation of titanium dioxide into the metal matrix of the coating, and tungsten in the form of oxides of variable valence. The use of an ultrasonic disperser allows increasing the tungsten content in the coating to 10 at. %; the content of the dispersed phase is preserved. Using scanning electron and atomic force microscopy, the influence of the nature and content of tungsten and titanium dioxide on the morphology and topography of the coatings was established.

Keywords: electrolytic hydrogen, electrolysis, composite coatings, titanium oxides, tungsten

Introduction. One of the promising areas of development of eco-technologies is the use of electrolytic hydrogen in low-temperature fuel cells, which is confirmed by the positive experience of foreign manufacturers of mobile modular alkaline electrolysis systems (Teledyne Technologies (USA) Hydrogenics (Belgium)). Electrolytic hydrogen is also used as an energy carrier for energy conversion and storage, and as a carrier gas in gas chromatography.

In addition, the latest experimental and clinical studies of leading scientists of many countries of the world have proven the preventive and therapeutic effect of using molecular hydrogen, which led to the development and implementation of non-medicinal methods of detoxification, rehabilitation and re-establishment of the psychophysical state of a person using hydrogen in intentional breathing and drinking mixtures.

The most effective and safe technology for obtaining molecular hydrogen is electrolysis, as it ensures the absence of impurities and high quality water saturated with hydrogen [1-4].

The main problem of the production of electrolytic hydrogen remains the high cost of existing electrolyzes associated with the use of expensive platinum electrodes and high energy consumption. The main way to reduce the cost of electrolytic hydrogen is the development of low-cost and efficient catalytically active systems as alternative materials to replace expensive platinum electrodes. Galvanic alloys of metals, which are located on different branches of the extreme dependence of the current density of the hydrogen evolution reaction on the energy of the "hydrogen-metal" bond demonstrated by Parsons and Gerisher, are considered promising [5].

Long-term research by scientists has proven the feasibility of using multi-component electrolytic alloys based on metals of the iron family with d^4-elements (Mo, W, Re), which make it possible to realize a complex of properties in thin layers: high catalytic activity, thermal and corrosion resistance [6-8]. Composite coatings doped with titanium/zirconium oxides, which have increased physical and mechanical properties and are characterized by higher indicators of electrocatalytic activity, compared to binary alloys, deserve special attention.

Experimental. Co-W(WO_2)-TiO_2 composite coatings were deposited from the basic citrate electrolyte of coating cobalt-tungsten alloys with the content, mol/dm^3: cobalt sulfate 0.2; sodium tungstate 0.06; sodium citrate 0.4; sodium sulfate 0.15 and boric acid 0.1; into which titanium dioxide powder was introduced in the form of a mixture of crystalline phases of anatase and rutile in varying amounts of $c(TiO_2) = 5.0 \div 20.0$ g/dm^3; pH 7.7 – 7.8. The basic composition of electrolytes was chosen on the basis of previous studies of the kinetics of the process of co-reduction of metals of the iron subgroup with refractory elements (molybdenum and tungsten), taking into account the mutual influence of thermodynamic and crystal-chemical characteristics of alloying elements and kinetic parameters of electrode reactions [9]. Coatings were deposited on substrates made of mild steel in the galvanostatic mode of electrolysis with varying cathode current density $i = 1.5 \div 4.0$ A/dm^2.

To prevent the settling of TiO_2 particles and to preserve the state of the electrolyte suspension, the deposition was carried out in two ways: 1) the electrolyte was stirred at 200 rpm for 3 hours, after which the coating was deposited at a stirring speed of 100 rpm; 2) electrolysis was performed using an ultrasonic disperser with an operating radiation frequency of 22 kHz.

Research results. Dense uniform coatings weighing 6 – 7 mg/cm^2 are deposited at a current density of 1.5 – 2.0 A/dm^2. The efficiency of the process significantly decreases when the current density increases to 4 A/dm^2. At the same time, the mass of the deposited coating is decreases to 3 mg/cm^2. This is explained by the fact that, firstly, increases in the current density causes a natural shift of the deposition potentials towards more negative values, which leads to an increase in the contribution of the parallel reaction of hydrogen evolution to the general cathodic process. Secondly, at more negative potentials, conditions are created for the deposition of a larger amount of the refractory component in the alloy, which may indicate the formation of a catalytically active surface, which will also cause the intensification of the hydrogen release reaction.

An increase in temperature from 25 °C to 50 °C predictably accelerates the cathodic process.

Surface morphology of Co-W-TiO_2 coatings is fine-grained and characterized by uniform distribution of elements on the surface. However, on the hills of the surface, it is possible to distinguish areas with clearly defined spheroid formations where the tungsten content is greater than other areas, which is associated with the realization of a higher current density on the hills than in the valley's. It should be noted the high content of oxygen both in the valley's and on the hills, which indicates the inclusion in the metal matrix of the alloy the particles of titanium dioxide and tungsten oxides, and the formation of composite coatings of the composition Co-$W(WO_x)$-TiO_2.

Conclusions. According to the results of studies, composite coatings of Co-W-TiO_2 with a tungsten content of up to 5 at. % was deposited from citrate electrolytes and titanium up to 5.5 at. % (in terms of metal). It is shown that at a current density of 1.5 – 2.5 A/dm^2, a temperature of 45 – 50 °C and slow stirring of the electrolyte (up to 100 rpm), conditions are created for the incorporation of titanium dioxide into the metal coating matrix and tungsten into in the form of oxides of variable valence.

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