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*M.D. Sakhnenko, Yu.A. Zhelavska, S.I. Zyubanova, N.V. Horokhivska, S.I. Rudneva***COBALT-VANADIUM COATING DEPOSITION VIA PROGRAMMED ELECTROLYSIS MODE****National Technical University «Kharkiv Polytechnic Institute», Kharkiv, Ukraine**

In the current work, the co-deposition of cobalt with vanadium from a complex citrate electrolyte via stationary and pulse electrolysis modes was investigated. The process was carried out at a current density of 1–15 A·dm⁻² in stationary electrolysis mode and 2–10 A·dm⁻² in pulse electrolysis mode, with variable ratio of pulse time to pause time at a temperature range of 35–40°C and pH 3.0–3.5. According to the results of X-ray fluorescence spectrometry, the maximum content of vanadium in the coating obtained via the programmed electrolysis mode is 1.20–1.45%, which is tens of times higher than in the coating deposited by the stationary electrolysis mode (vanadium content of 0.007–0.017%) under similar conditions. The obtained results may confirm the hypothesis of additional vanadium reduction from oxo-anions by adsorbed hydrogen atoms formed on the cathode surface during the pause period. Based on the results of the analysis of 3D graphs, the optimal parameters of the process for fabricating a cobalt-vanadium coating with the maximum vanadium content in the alloy and a coating current efficiency of 80% have been established.

Keywords: co-deposition, citrate electrolyte, programmed electrolysis, cobalt-vanadium coating, additional reduction.

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Introduction

The development of functional materials with predictable properties is one of the most important trends in modern materials science and applied electrochemistry. For hydrogen energy production [1], specifically for the electrochemical release of hydrogen, it is important to prepare new materials that show catalytic properties for the hydrogen evolution reaction (HER) at the cathode.

Analysis of the literature data allows stating that materials containing molybdenum, tungsten, and vanadium should exhibit an enhanced catalytic activity towards the HER. Electrodes coated with alloys of iron subgroup metals with molybdenum, tungsten, and vanadium should be considered promising for hydrogen energy.

Electrodeposition of such metals as vanadium, molybdenum and tungsten from their aqueous solutions is difficult due to their high negative potential values. However, these metals can be co-deposited from

aqueous solutions with metal-catalysts (iron, cobalt or nickel) through the formation of cluster intermetallic compounds with Me–V, Me–Mo, and Me–W bond adsorbed on the cathode surface.

Electrodeposition of such coatings can be carried out in stationary or pulsed electrolysis modes using electrolytes containing complex or simple ions.

The following mechanism of the deposition process was proposed when obtaining a nickel-tungsten coating from a pyrophosphate electrolyte [5]. First, a particle of NiOH_{ads} is formed, then it chemically interacts with WO₄²⁻ adsorbed on the surface to form a cluster heterometallic compound [WO₄(NiOH)]_{ads}²⁻ with a direct Ni–W bond. The [WO₄(NiOH)]_{ads}²⁻ complex is further reduced. The formation of [WO₄(Ni)]_{ads}²⁻ particle leads to a rearrangement and a sharp weakening of the tungsten-oxygen bond energy, which makes the entire particle unstable, capable of further easy recovery at the cathode. Tsyntsaru et al. [5] claimed that since the mechanism

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Cobalt-vanadium coating deposition via programmed electrolysis mode

is not connected to any specific type of electrolyte or specific metals, it can be used to describe the cathodic reduction of any refractory metal together with any co-depositing metal from any electrolyte with the appropriate correction on the nature of the formed particles.

Co-deposition of nickel with vanadium was studied in some publications [6,7]. It was established that high-quality nickel-vanadium alloy coatings can be fabricated from a nickel plating sulfate electrolyte with the vanadium content of 0.1–0.3 g·dm⁻³ (in terms of metal) as a vanadate ion VO³⁻. The content of vanadium in the coating is only 0.3–0.45%.

When comparing the processes of the cobalt-molybdenum alloy electrochemical production from an ammonia-citrate electrolyte, similar in composition to the electrolyte for the Ni-Mo alloy deposition [8], it was established that the cobalt-molybdenum alloy is formed at lower pH values (5.0–6.0), than the Ni-Mo alloy (7.0–9.0). The current efficiency of the studied alloys depended significantly on the electrolyte pH, while the chemical composition of deposits was practically independent of pH (in the pH range of 5.0–8.0 and current densities of 2.5–10.0 A·dm⁻²).

Electroplated cobalt-molybdenum alloy contained a larger amount of refractory metal than nickel-molybdenum electrodeposits, which is consistent with the adsorption-film hypothesis, according to which the release of refractory metal occurs due to the formation of an adsorption complex between hydroxo-compounds of the co-deposited metal formed during electrochemical reduction of its ions, and refractory metal atoms that are part of oxo-anions. The adsorption capacity of cobalt hydroxo-compounds is somewhat higher, which accounts for the higher content of molybdenum in cobalt-molybdenum deposits compared to nickel-molybdenum coatings.

The deposition of cobalt-vanadium alloy coatings from a citrate electrolyte via stationary and pulse modes was investigated in this work. Concept of using a pulse mode is based on the hypothesis that during the pause period there is an additional chemical reduction of vanadium from oxo-ions by adsorbed hydrogen atoms, which were formed in the electrochemical process during the pulse period, which should lead to an increase in the content of vanadium in the cobalt-vanadium alloy and coating current efficiency.

Experimental

Cobalt-vanadium alloy coatings were deposited in a citrate electrolyte containing (mol·dm⁻³): 0.4 Na₃C₆H₅O₇·2H₂O, 0.1 CoSO₄·7H₂O, and 0.1 V₂O₅. Electrodeposition was carried out at 35–40°C and pH 3–3.5 with a cobalt anode using the galvanostatic mode with the current density of 1–15 A·dm⁻² and unipolar pulsed current with the amplitude of

2–10 A·dm⁻², the pulse and pause period duration being 5·10⁻³...5·10⁻² s. The coating thickness was about 6–9 μm. Before electrodeposition, the surface of copper electrodes with area of 2 cm² was polished and degreased. The vanadium content in the coating was determined by X-ray fluorescence (XRF) spectrometry.

Electrolysis in galvanostatic mode was performed using stabilized DC power supply B5-47, in pulse mode using a pulse potentiostat PI-50-1.1 with PR-8 programmer.

The experimental data were processed in the form of 3D graphs using the Microsoft Excel program.

Results and discussion

Some studies [9,10] have been devoted to clarifying the forms of the vanadium state in aqueous solutions, but this issue is still far from being fully resolved. The peculiarity of the vanadium (V) chemistry is that its state in aqueous solutions depends on the environment pH, concentration and potential in the system. The variety of vanadium ionic forms in solutions leads to the formation of a large number of compounds with different ratios of metals and vanadium, as well as complex compounds with inorganic and organic ligands.

According to ref. [11], the state of vanadium (V) ions depends on their concentration and pH. In acidic solutions, vanadium (V) exists in the form of a mononuclear oxo-cation, while it exists as a mononuclear oxo-anion in a neutral and weakly acidic environments. An increase in the vanadium concentration leads to the formation of polynuclear anionic particles with a maximum degree of polymerization equal to 10.

Organic acids reduce pentavalent vanadium to trivalent and tetravalent vanadium with the formation of vanadyl-ions [12]. Vanadyl complexes of tartaric, lactic malic and citric acids were synthesized to study the spectral properties [13]. Adding vanadium oxide (V) to a solution of sodium citrate results in formation of a yellow solution containing vanadate ions, which includes pentavalent vanadium. Over time, the color changed to green and then to dark blue, which may indicate the reduction of vanadium (V) compounds to vanadium (III) with the formation of vanadium (III) complex ions [V(C₆H₅O₇)₂]³⁻. This solution of mentioned vanadium (III) complex ion oxidizes by air to form oxovanadium (IV) citrate complexes [VO(C₆H₅O₇)₂]⁴⁻ [12,14]. Treatment of the resulting solution with cobalt sulfate leads to the electrolyte containing both cobalt and oxovanadium (IV) citrate complexes.

Taking into account the electrochemical (k_s) and chemical reactions (k_f) rates, the ionic product of water (k_w), the formation of ad-atoms (ads) or atoms of crystalline lattice (cr), the course of partial reactions

The current efficiency of cobalt-vanadium coating more than 50% can be obtained at a current density of 5–7 A·dm⁻², and the maximum current efficiency of 80% can be reached at a current density of 7 A·dm⁻² (Fig. 4) with a maximum value of the pause period of 5·10⁻² s, which also indicates additional chemical reduction of vanadium from vanadyl-anions by adsorbed hydrogen atoms, which were formed in the electrochemical process during the pulse period.

When the current density increases to 10 A·dm⁻², the vanadium content in the alloy decreases (Fig. 3) and the coating quality significantly deteriorates due to the intensification of hydrogen release.

Thus, a current density of 5–7 A·dm⁻² with a

pulse and pause duration of 1·10⁻²...5·10⁻² should be considered optimal for electrolysis to obtain a coating with the maximum vanadium content and current efficiency.

Conclusions

1. Electrodeposition of a cobalt-vanadium alloy coating was studied from a citrate electrolyte in stationary and pulsed modes under similar conditions. According to the results of X-ray fluorescence analysis, the resulting cobalt-vanadium alloy coating prepared in the stationary mode contains 0.017% of vanadium and shows a current yield no more than 19%.

2. It was established that the cobalt-vanadium alloy coating fabricated by using the pulse mode

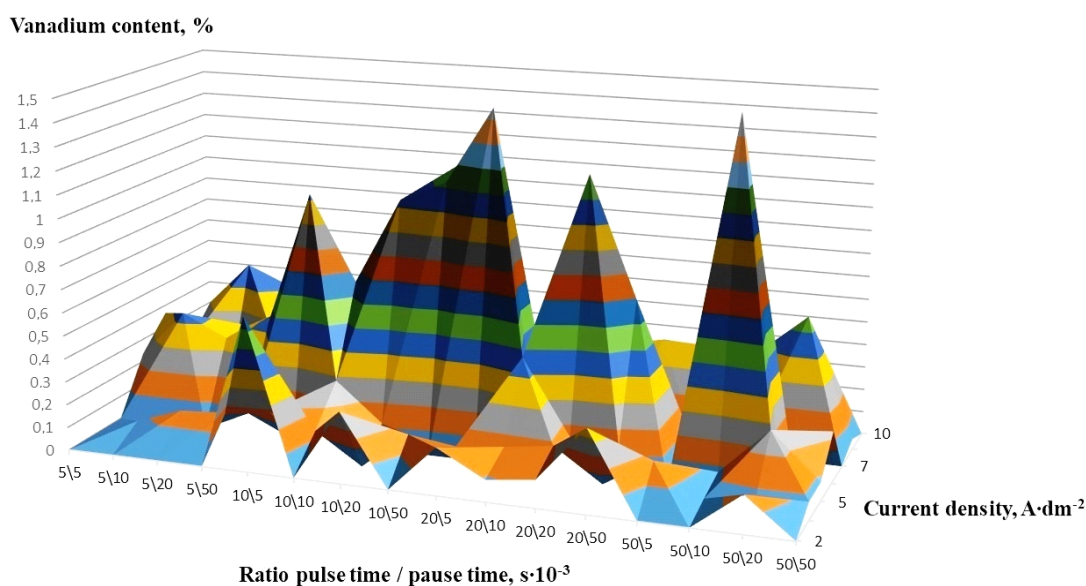


Fig. 3. Dependence of the vanadium content in the alloys on the current density and the ratio pulse time/pause time

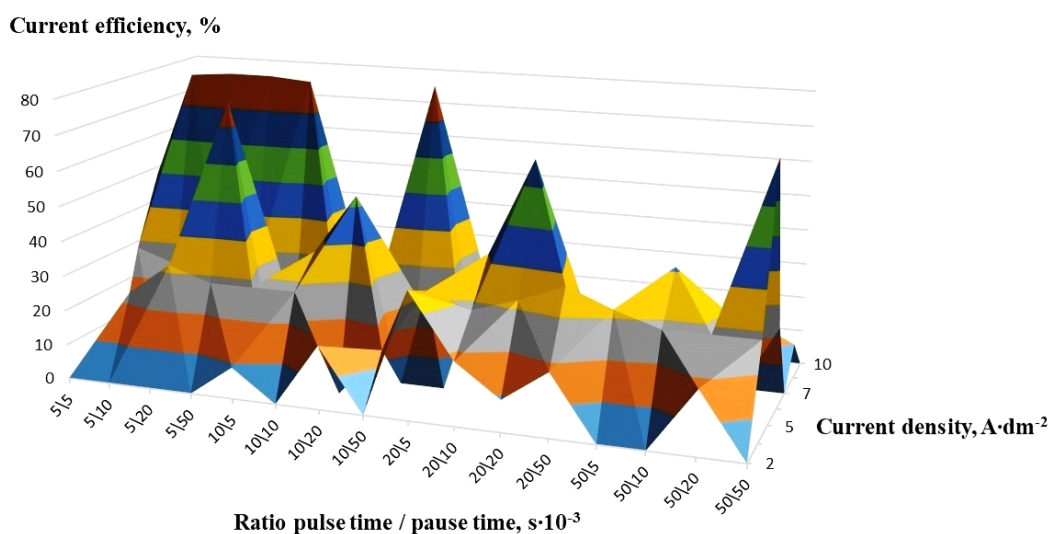


Fig. 4. Dependence of the coating current efficiency on the current density and the ratio pulse time/pause time

contains 1.0–1.5% of vanadium, which is ten times more than in the coating obtained via the stationary mode. The current efficiency here was more than 50%. The obtained data confirmed the assumption that during the pause period there was a chemical additional reduction of vanadium from complex vanadyl-anions by adsorbed hydrogen atoms, which were formed in the electrochemical process during the pulse period.

3. It was proved that the maximum vanadium content in the alloy is 1.45–1.5% and the current efficiency of 80% can be reached at a current density of 5–7 A·dm⁻² and a pulse and pause duration of 1·10⁻²...5·10⁻² s.

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ОСАДЖЕННЯ ПОКРИВІВ КОБАЛЬТ-ВАНАДІЙ ПРОГРАМОВАНИМ ЕЛЕКТРОЛІЗОМ

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В роботі досліджено співосадження кобальту з ванадієм з комплексного цитратного електроліту у стаціонарному та імпульсному режимах. Процес проводили в інтервалі густин струму 1–15 А/дм² в стаціонарному режимі та 2–10 А/дм² в імпульсному режимі, при варіюваному співвідношенні часу імпульсу до часу паузи, в температурному інтервалі 35–40°C та рН 3–3,5. За результатами рентгенофлуоресцентного аналізу, максимальний вміст ванадію в покритті, одержаному в режимі програмованого електролізу, становить 1,20–1,45%, що у десятки разів більше ніж у покритті, осадженому у стаціонарному режимі (вміст ванадію 0,007–0,017%) в аналогічних умовах, що може бути підтвердженням гіпотези про додаткове відновлення ванадію з оксо-аніонів адсорбованими атомами водню, які утворилися на поверхні катода в період імпульсу. За результатами аналізу 3D графіків, встановлені оптимальні параметри проведення процесу для одержання покриття кобальт-ванадій з максимальним вмістом ванадію у сплаві та виходом за струмом покриття 80%.

Ключові слова: співосадження, цитратний електроліт, програмований електроліз, покриття кобальт-ванадій, додаткове відновлення.

COBALT-VANADIUM COATING DEPOSITION VIA PROGRAMMED ELECTROLYSIS MODE

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In the current work, the co-deposition of cobalt with vanadium from a complex citrate electrolyte via stationary and pulse electrolysis modes was investigated. The process was carried out at a current density of 1–15 A·dm⁻² in stationary electrolysis mode and 2–10 A·dm⁻² in pulse electrolysis mode, with variable ratio of pulse time to pause time at a temperature range of 35–40°C and pH 3.0–3.5. According to the results of X-ray fluorescence spectrometry, the maximum content of vanadium in the coating obtained via the programmed electrolysis mode is 1.20–1.45%, which is tens of times higher than in the coating deposited by the stationary electrolysis mode (vanadium content of 0.007–0.017%) under similar conditions. The obtained results may confirm the hypothesis of additional vanadium reduction from oxo-anions by adsorbed hydrogen atoms formed on the cathode surface during the pause period. Based on the results of the analysis of 3D graphs, the optimal parameters of the process for fabricating a cobalt-vanadium coating with the maximum vanadium content in the alloy and a coating current efficiency of 80% have been established.

Keywords: co-deposition; citrate electrolyte; programmed electrolysis; cobalt-vanadium coating; additional reduction.

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