ISSN1027-5495. Functional Materials, 32, No.1 (2025), p. 63-66
doi:http://dx.doi.org/10.15407/fm32.01.63 © 2025 — STC "Institute for Single Crystals"

Functional cobalt-vanadium coatings deposition via programmed electrolysis mode

M.D. Sakhnenko, Yu. A. Zhelavska, V.O. Proskurina, A.V. Dzheniuk, S.I. Rudneva

National Technical University "Kharkiv Polytechnic Institute",
2 Kyrpychova St., 61002 Kharkiv, Ukraine

Received October 15, 2014

The electrocatalytic activity of a cobalt-vanadium alloy coating in the hydrogen evolution reaction was investigated. The cobalt-vanadium coating is electrodeposited from a complex citrate electrolyte via pulse electrolysis modes. According to the results of the X-ray dispersive spectrometry, the resulting coating contains 0.2–1.0 mass % vanadium. It is found that on a cathode with a Co-V coating, the overvoltage in the hydrogen evolution reaction is 0.15-0.2 V lower, and the exchange current is higher than on a cobalt coated electrode. As the vanadium content in the alloy increases, the value of the hydrogen evolution overvoltage decreases. This indicates the electrocatalytic activity of the vanadium-containing materials in the hydrogen evolution reaction. The microhardness of the Co-V coating is higher, than that of the cobalt coating. Electrodes coated with Co-V can be recommended as cathodes for the electrochemical production of hydrogen, since the energy consumption of this process is reduced by 10-15 %.

Keywords: electrocatalytic activity, programmed electrolysis, Co-V coating, overpotential, microhardness.

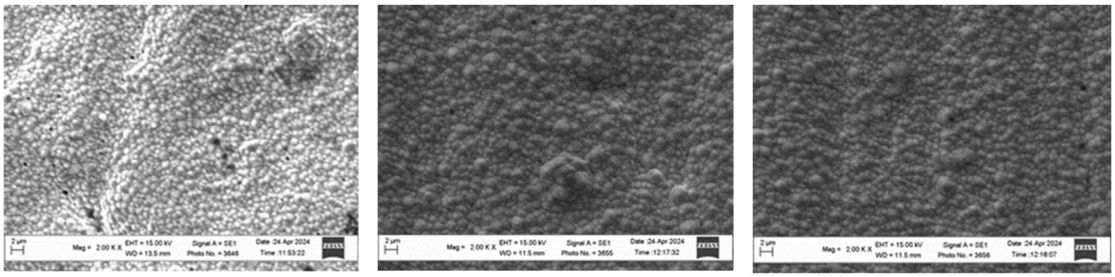
Осадження функціональних покриттів кобальт-ванадій програмованим електролізом. *M.D. Sakhnenko, Yu. A. Zhelavska, V.O. Proskurina, A.V. Dzheniuk, S.I. Rudneva*

Досліджено електрокаталітичну активність покриття сплавом кобальт-ванадій щодо реакції виділення водню. Покриття кобальт-ванадій осаджували з комплексного цитратного електроліту в режимі імпульсного електролізу. За результатами рентгенодисперсійної спектрометрії отримане покриття містить 0.2–1.0 мас.% ванадію. Встановлено, що перенапруга реакції виділення водню на катоді з Co-V покриттям на 0,15-0,2 В нижча, а значення струму обміну вище ніж на електроді з кобальтовим покриттям. Із збільшенням вмісту ванадію в сплаві величина перенапруги виділення водню зменшується. Це вказує на електрокаталітичну активність ванадійвмісних матеріалів у реакції виділення водню. Мікротвердість покриття Co-V також вища ніж кобальтового покриття. Електроди з покриттям Co-V можна рекомендувати як катоди для електрохімічного отримання водню, що дозволить знизити енерговитрати на проведення цього процесу на 10-15 %.

1. Introduction

The development of functional materials with predictable properties is one of the top priorities in modern research. For hydrogen energy production, specifically for the electrochemical release of hydrogen, it is important to obtain new materials that have catalytic properties for the hydrogen evolution reaction (HER) at the cathode. Such materials should also have a long service life, corrosion and wear resistance, low cost.

The analysis of the literature data allows us to predict the catalytic activity for the HER for materials containing molybdenum, tungsten, and vanadium. Electrodes coated with alloys of these metals with metals of iron subgroup should be considered promising for hydrogen energy [1, 2]. In addition, cobalt in such coat-



a b c

Fig. 1. Surface morphology of cobalt vanadium coating with different vanadium contents, mass %: 0.32 (a); 0.62 (b); 0.8 (c).

ings can give them strength and ductility, and vanadium, accordingly, density, absence of oxides and a fine-grained structure [3, 4].

Such coatings can be deposited in stationary or pulsed electrolysis modes using electrolytes containing complex or simple ions [5-7].

Concept of using the 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 [8]; this should lead to an increase in the content of vanadium in the cobalt-vanadium alloy and coating current efficiency.

2. Experimental

Cobalt-vanadium alloy coatings were deposited in a citrate electrolyte (mol·dm^{-3}): 0.4 $Na_3C_6H_5O_7 \cdot 2H_2O$, 0.1 $CoSO_4 \cdot 7H_2O$, and 0.1 V_2O_5. Electrodeposition was carried out from a cobalt anode at 35–40 °C and pH = 3–3.5 using unipolar pulsed current with amplitude of 5–7 A·dm^{-2}, the pulse and pause period duration was $5 \cdot 10^{-3}$–$5 \cdot 10^{-2}$s [8, 9]. The coating thickness was 9–12 μm. Before electrodeposition, the surface of steel electrodes with area of 1 cm^2 was polished and degreased.

The chemical composition of the coatings was determined by energy dispersive X-ray spectroscopy using an Oxford INCA Energy 350 microanalyzer integrated into the scanning electron microscope system (SEM).

Electrolysis in pulse mode was performed using a pulse potentiostat PI-50-1.1 with a PR-8 programmer. Polarization dependences of hydrogen evolution on the cathode were obtained using an MTech PGP-550M potentiostat. Platinum was used as a counter electrode. The saturated silver/silver chloride electrode was used as a reference electrode. The values of electrode potentials were recalculated relative to the standard hydrogen electrode.

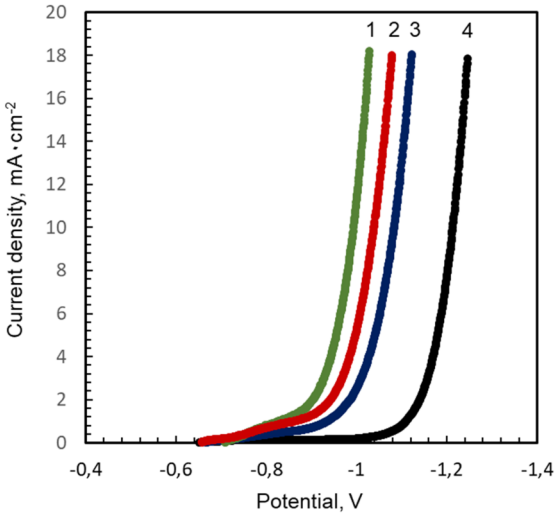


Fig. 2. Cathodic polarization curves of hydrogen evolution in 2.5M NaOH solution for electrodes with different coatings: 1 – Co-V coating (0.8–1.0 mass % V); 2 – Co-V coating (0.5–0.7 mass % V); 3 – Co-V coating (0.2–0.4 mass % V); 4 – Co coatin

Microhardness was determined using the Vickers method by indenting a diamond pyramid with a square base and an angle at the top of 136°, using a hardness tester PMT-3.

3. Results and discussion

The resulting electrodeposited coatings have a satisfactory quality: uniform, microcrystalline, light-gray, semi-shiny, rough (Fig 1). The vanadium content in coatings is in the range of 0.2–1.0 mass %.

Electrocatalytic properties of the obtained Co-V coatings for HER were determined in a solution of 2.5 M NaOH used for the industrial electrochemical production of hydrogen [5, 10].

Cathodic polarization curves of hydrogen evolution on the electrodes made of steel 20 with the Co coating and with the Co-V coating are shown in Fig. 2. According to the magnitude of electrode polarization, the studied materials

Table 1. Kinetic parameters of the HER on the cathodes studied

Electrode materials	Vanadium content, mass %	a, V	b, V	$-\lg j_0$, A·cm^{-2}
Pt	-	-0,31	-0,1	3.1
Steel 20 with Co coating	-	–0.61	–0.100	6.12
Steel 20 with Co-V coating	0.2–0.4	–0.56	–0.139	4.03
	0.5–0.7	–0.51	–0.139	3.67
	0.8–1.0	–0.46	–0.132	3.48

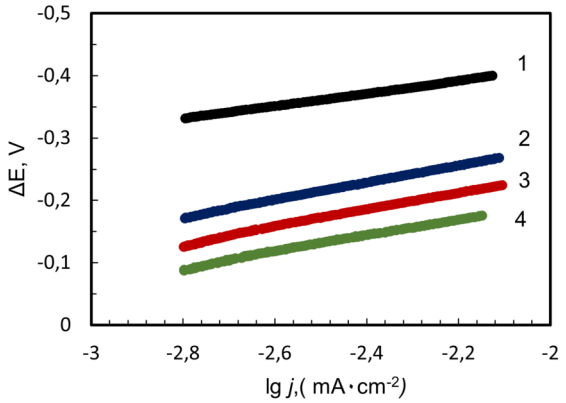


Fig. 3. Overvoltage dependence on the logarithm of current density in 2.5M NaOH solution for electrodes with different coatings: 1 – Co coating; 2 – Co-V coating (0.2–0.4 mass % V); 3 – Co–V coating (0.5–0.7 % V); 4 – Co-V coating (0.8–1.0 mass % V)

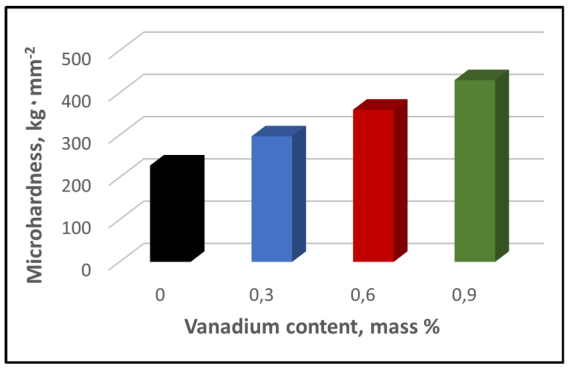


Fig. 4. Dependence of Co-V coating microhardness on vanadium content, mass %

are arranged in the following row: Co coating – Co-V coating (0.2-0.4 % V) – Co-V coating (0.5-0.7 % V) – Co-V coating (0.8-1.0 % V). Hydrogen evolution begins at a potential of –0.88 ÷–0.95 V on the Co-V coated electrodes, and at –1.1 V on the Co coated electrode (Fig. 2, a curves 1, 2, 3 and 4). The HER polarization on Co-V coated electrodes is 0.15–0.2 V lower compared to Co coated electrode.

Analysis of the polarization dependences, rebuilt in the Tafel coordinates, (Fig. 3) made it possible to determine the kinetic parameters of the HER for electrodes studied (Table 1).

The decrease in overvoltage of HER on Co-V alloy coating is explained by the presence of vanadium, which has electrocatalytic properties. As the vanadium content in the alloy increases, the value of the hydrogen evolution overvoltage decreases.

The universal kinetic characteristic of the process is the exchange current density (j_0) of the HER, reflecting the influence of the electrode nature on the kinetics of direct and reverse reactions. Unlike the overvoltage of HER, the value of j_0 does not depend on the current density. Therefore, it is this value that makes it possible to compare the catalytic properties of materials in electrode reactions and evaluate them. For Co-V coated steel 20 electrodes, the j_0 value indicates a higher activity of these materials in comparison with the cobalt coated electrode.

The obtained values of overvoltage and current exchange for a cobalt-vanadium coating with vanadium contents in the range of 0.8-1 mass % are close to the values of the corresponding parameters for a platinum electrode in alkaline solutions (Table 1).

The microhardness of the obtained coating is 150 – 200 kg·mm^{-2} higher, than that of cobalt electroplated from a sulphate solution (Fig 4).

With increasing vanadium content in the alloy, the microhardness of the Co-V coating also increases; this improves the performance characteristics of electrodes that can be used in concentrated solutions and aggressive environments.

4. Conclusions

(i) Cobalt-vanadium alloy coatings were electrodeposited from a citrate electrolyte via pulsed modes. According to the results of X-ray

dispersive analysis, the resulting cobalt-vanadium alloy coatings contain 0.2-1.0 mass % vanadium.

(ii) The microhardness of the obtained Co-V coating is 150 – 200 kg·mm^{-2} higher, than that for a cobalt coated electrode.

(iii) Electrodes with the Co-V coating have the electrocatalytic activity of hydrogen evolution reaction and can be recommended as cathodes for the electrochemical hydrogen production, which will reduce the energy consumption of this process by 10-15 %.

References

1. Ved M. V. Sakhnenko M.D. Catalytic and protective coatings with alloys and complex oxides: electrochemical synthesis, prediction of properties. Kharkiv: NTU «KhPI», 2010; 272p. [In Ukraine]
2. Kozin L.H., Volkov S.V., Skryptun I.N. Modern Hydrogen Energetics and Ecology. Kyiv: PH "Akademperiodyka", 2019; 364 p.
3. Gamburg Yu. D, Zangari G. Theory and practice of metal electrodeposition. New York: Springer, 2011; 378 p.
4. Popov K. I., Djokic S. S, Nikolic N. D., Jovic V. D. Morphology of electrochemically and chemically deposited metals. New York: Springer, 2016; 368 p.
5. B. Bairachniy, Yu. Zhelavska, O.Smirnova, A.Pilipenko, O.Finohenov. *Materials Today: Proseedings*. **50**(4), 448 (2022).
6. UA Patent № 123411 (2021)
7. M.D.Sakhnenko, Yu. A Zhelavska, S.I. Ziubanova, V.O. Proskurina. *Bulletin of the National Technical University "KhPI"*. **49** (1270), 5 (2021)
8. M.D. Sakhnenko, Yu. A. Zhelavska, S.I. Zyubanova, N.V. Horokhivska, S.I. Rudneva. *Voprosy khimii i khimicheskoi tekhnologii*. **3**, 165 (2024)
9. UA Patent № 155542 (2024)
10. V.B. Bairachnyi, N. Rudenko, Yu. Zhelavska, A. Pilipenko. *Materials Today: Proseedings*. **6**, 299 (2019).