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ELECTROCHEMICAL ALLOYS BASED ON IRON FAMILY METALS: THE EFFECT OF ELECTROLYSIS CONDITIONS

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Abstract

One of the main tasks of process chemists and material scientists is to create polyfunctional materials with a high level of specified properties. Controlling the structure and composition by varying the electrolysis parameters allows us to produce coatings with unique characteristics. Cobalt coatings have high hardness, corrosion resistance, reflectivity and magnetic properties. The additional inclusion of refractory components in the composition of coatings is one of the most promising ways to control their functional properties, and hence the scope of application, due to the unique physicochemical and physicomechanical properties of such alloys. The process of forming ternary Co-Ni-Zr alloys in the pulse mode from a citrate electrolyte on a copper substrate has been investigated. The effect of stirring, electrolyte pH and current density on the composition, surface morphology and current efficiency of ternary cobalt electrolytic alloys was studied. The resulting coatings are characterised by a uniform surface without cracks. The use of the pulse mode with the ratio of pulse duration $1 \cdot 10^{-3}$–$20 \cdot 10^{-3}$ s and pause duration $2 \cdot 10^{-3}$–$20 \cdot 10^{-3}$ s and the amplitude of cathodic current density 1–10 A/dm^2 makes it possible to obtain cobalt-based alloys with zirconium content up to 2 wt. %. It was found that an increase in the acidity of the electrolyte solution does not favourably affect the current efficiency, and the dependence of the zirconium content is extreme. The modes of electrosynthesis of coatings with cobalt-nickel-zirconium alloys with a given level of surface development are substantiated.

Keywords: alloys; refractory metals; cobalt; pulse mode; current efficiency; electrolyte solution.

ЕЛЕКТРОХІМІЧНІ СПЛАВИ НА ОСНОВІ МЕТАЛІВ РОДИНИ ФЕРУМУ: ВПЛИВ УМОВ ЕЛЕКТРОЛІЗУ

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Анотація

Однією з головних задач хіміків-технологів, а також матеріалознавців є створення поліфункціональних матеріалів з високим рівнем заданих властивостей. Керування структурою та складом за рахунок варіювання параметрами електролізу дозволяє отримати покриття з унікальними ознаками. Кобальтові покриття мають високу твердість, корозійну тривкість, відбивну здатність та магнітні властивості. Додаткове включення до складу покриттів тугоплавких компонентів є одним із найперспективніших способів управління їхніми функціональними властивостями, а отже, і сферою застосування, зумовленими унікальними фізико-хімічними та фізико-механічними властивостями таких сплавів. Досліджено процес формування тернарних сплавів Co-Ni-Zr в імпульсному режимі з цитратного електроліту на мідній підкладці. Вивчено вплив перемішування, pH електроліту та густини струму на склад, морфологію поверхні та вихід за струмом потрійних електролітичних сплавів кобальту. Отримані покриття відрізняються рівномірною поверхнею без тріщин. Використання імпульсного режиму за співвідношення тривалості імпульсу $1 \cdot 10^{-3}$–$20 \cdot 10^{-3}$с і тривалості паузи $2 \cdot 10^{-3}$–$20 \cdot 10^{-3}$с та амплітуді катодної густини струму 1–10 А/дм^2 надає можливість одержати сплави на основі кобальту з вмістом цирконію до 2 мас. %. Виявлено, що підвищення кислотності розчину електроліту не сприятливо впливає на вихід за струмом, а залежність вмісту цирконію носить екстремальних характер. Обґрунтовано режими електросинтезу покриттів сплавами кобальт-нікель-цирконій із заданим рівнем розвитку поверхні.

Ключові слова: сплави; тугоплавкі метали; кобальт; імпульсний режим; вихід за струмом; розчин електроліту.

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Introduction

The formation of multifunctional materials with the highest possible level of specified properties still remains to be a priority task for technologists and materials scientists [1–4]. In this regard, the technologies used for electrochemical synthesis gain more importance due to a number of significant advantages in comparison to the metallurgical method of obtaining materials with their physical application [5–7].

Electrolytic coatings having high hardness act as hard lubricants during metal-to-metal friction, and due to high corrosion resistance [8; 9], the cobalt-coated items can be used in a sulfur-containing gas environment. The diverse magnetic properties of cobalt coatings [9] allow them to be used for space and computer technologies, and high reflectivity enables the manufacture of reflectors and mirrors. Along with the positive properties [10–12] of electrolytic cobalt coatings, disadvantages should also be noted, in particular the high cost of this metal and its salts. Therefore, to reduce the consumption of expensive metal, it is often suggested to partially replace it with other, cheaper metals. To reduce the use of pure cobalt coatings, we have suggested to partially replace cobalt with nickel [13], which is significantly cheaper than cobalt and, like cobalt, it belongs to the iron family.

On the one hand, the addition of refractory components to the coating composition is one of the most promising ways to control their functional properties, and as a matter of fact, the field of their application, due to the unique physical, chemical and physical and mechanical properties of such alloys, and on the other hand, it significantly complicates the technology of their production [14].

Some coatings, including alloy and composite coatings, can only be applied using electrochemical method, because other methods of their application are less economically advantageous or less effective, or cannot be implemented. This is especially topical for alloy coatings that contain such refractory elements as tungsten, zirconium or others [15].

Electrochemical co-deposition of cobalt and nickel with such refractory metals as tungsten, molybdenum, vanadium, zirconium and/or their compounds into composite coatings is complicated by a significant difference in the standard electrode potentials of the alloy-forming components. The use of composite, in particular, the most effective polyligand electrolytes allows us to bring the electrode potentials closer together and, accordingly, to obtain a high-quality coating. The main difficulty relating to this method of implementing the electrochemical technology of alloy application consists in the justified choice of a ligand for the aforementioned complexing elements, and it is a fairly urgent task. In recent years, significant factual material has been collected covering the results of studying the conditions of electrodeposition of alloys based on iron family metals [16–18], but only a few of them have practical application so far. One of the reasons for the limited use of the electrolytic method of coating application with such alloys is the complicated process control.

The aim of this research is to control the composition and structure of the galvanic Co-Ni-Zr alloy by varying the electrolysis parameters.

Experimental

Cobalt-nickel-zirconium alloy coatings were applied onto a copper substrate M0. Preparatory operations for surface treatment of specimens were carried out in accordance with the nature of the studied material [19]. To prepare the citrate electrolyte for deposition of Co-Ni-Zr coatings (Table 1), reagents of “chemically pure” and “analytical grade” were used. To establish ionic equilibrium and stabilize the formed compounds, the electrolyte was held for 8–12 hours.

Table 1

Composition of electrolytes for deposition of coatings with cobalt alloys

Electrolyte composition, mole/dm^3	Coating Co-Ni-Zr
$CoSO_4 \cdot 7H_2O$	0.2
$NiSO_4 \cdot 6H_2O$	0.2
$Zr(SO_4)_2 \cdot 4H_2O$	0.05
$Na_3C_6H_5O_7 \cdot 2H_2O$	0.5

The ligand in this electrolyte has one alcohol group and three carboxyl groups capable of forming coordination compounds with divalent metals, including nickel and cobalt. Stainless steel plates 12X18N10T were used as the anode material during alloy deposition. The coatings were deposited in a pulsed mode in a sealed three-electrode cell using a PI-50-1.1 potentiostat and a PR-8 programmer. During the coating deposition the current amplitude was varied in the range of i = 1–10 A/dm^2, frequency f = 10–250 Hz and the pulse duty cycle was $Q = 2–10$ at a temperature of 20 °C.

The chemical composition of the obtained cobalt-nickel-zirconium coatings was determined by the X-ray fluorescence method using a portable spectrometer "SPRUT" that has a relative standard deviation of $10^{-3}–10^{-2}$. The analysis was carried out at least at 3 points with subsequent averaging of the obtained values. The error in determining the content of components was ±0.1 wt. %.

The electrolyte acidity was adjusted by adding sodium hydroxide or sulfate acid. The values of the hydrogen index were monitored using a pH-150 M device with an ESL-6307 glass electrode.

The alloy current efficiency was determined gravimetrically based on the assumption that the metals that are part of the coatings are in a completely reduced state. The initial number of reagent and the mass of specimens before and after the deposition of coatings was weighed using an AXIS AD100 electronic scale in accordance with DSTU 7270:2012.

Visual analysis of the surface of electrodeposited coatings in laboratory conditions was carried out using an XSG-109L optical microscope at 200-fold magnification.

Results and discussion

During deposition of the Co-Ni-Zr alloy from a citrate electrolyte, the more electronegative metal, cobalt, is predominantly released. The priority release of cobalt is due to the fact that in the presence of its ions, the electroreduction of nickel ions is inhibited. For the citrate electrolyte developed for deposition of the Co-Ni-Zr alloy, with an increase in pH, the degree of protonation of the ligands is decreased, and accordingly, the strength of the corresponding cobalt and nickel compounds is increased. Their reduction potentials will shift to the negative side approaching the reduction potentials of zirconium [20]. It leads to an increase in the Zr content in the Co-Ni-Zr alloy deposited from the studied electrolyte at pH < 8.5 (Fig. 1). It should also be noted that with the transition to the alkaline region, the risk of formation of the metal hydroxides of the iron subgroup in the electrolyte is increased and it results in their undesirable inclusion in the coating composition. A further increase in pH results in a decrease in the zirconium content in the alloy, and it can be explained by the reduction of zirconium (IV) that exists in an alkaline medium mainly in the form of the oxocompound $HZrO_3$. It was found that an increase in pH values in the range of 6 to 9 results in an increase in the cobalt content in the deposits in the range of 61.7 wt.% to 84.0 wt.%. It is due to an increase in the concentration of hydroxocomposites of the deposited metals and more intensive adsorption of $CoOH^+$ compared to $NiOH^+$ [21; 22].

In the pH range of 6 to 7.5, the coatings with a high level of adhesion to the substrate and a current efficiency of 55 to 60% are formed, a further increase in the electrolyte pH to 9.5 results in a sharp decrease in the current efficiency. This can be explained by the fact that denser compounds are discharged with a higher overvoltage, and, accordingly, the telic process of coating formation is inhibited in favor of the partial reaction of hydrogen emission resulting in a decreased current efficiency.

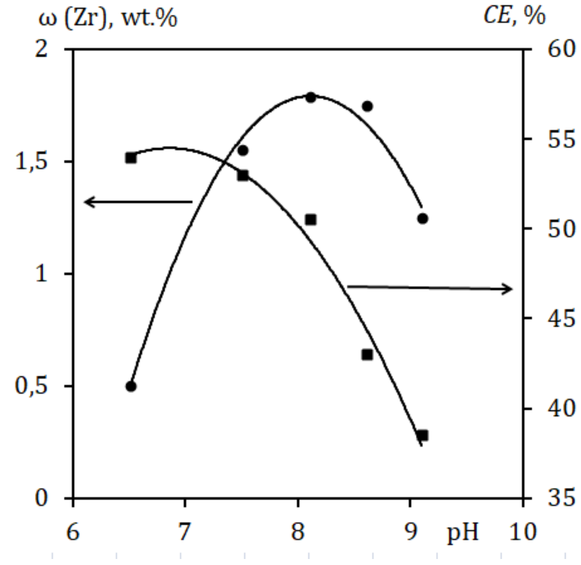
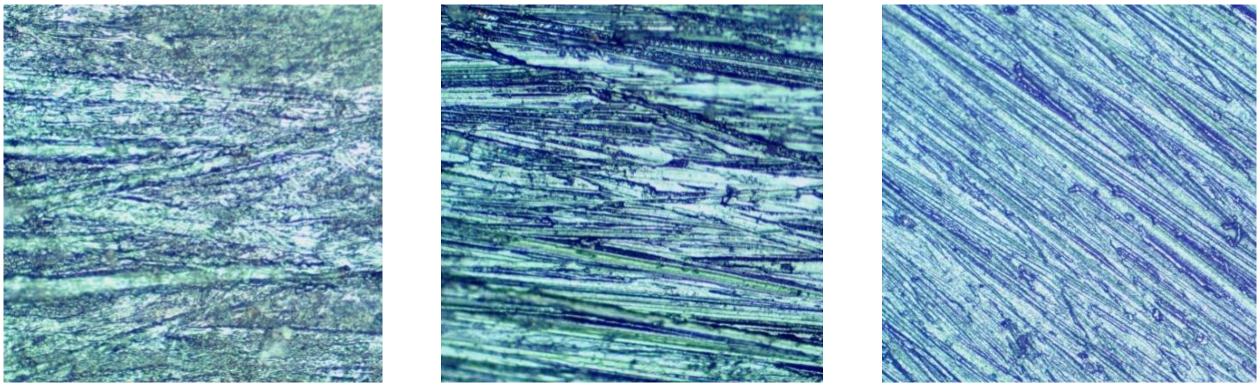


Fig.1. The influence of the acidity of the electrolyte of the deposition of the Co-Ni-Zr electrolytic alloy on the zirconium content and the current efficiency

It has been experimentally established that zirconium is not deposited together with cobalt and nickel in the galvanostatic mode at room temperature, whereas uniform fine-crystalline coatings of Co-Ni-Zr alloys are formed from the multiplex citrate electrolyte in the pulsed mode in the current density range of *i* = 2 - 10 A/ dm^2 (Fig. 2).

The reason for such behavior can be explained from the standpoint of the effect of the combined partial reaction of hydrogen emission on the mechanism of the alloy formation reaction. We believe that the reactive hydrogen ad-atoms formed in the cathode pulse chemically reduce zirconium compounds during the pause period, similar to the formation of ternary alloys/composites with the participation of tungsten and molybdenum oxoanions [23 - 25]. The dependence of the zirconium content on the pulse/pause period duration ratio speaks in favor of this opinion.



Co – 58.8
Ni – 41.1
Zr – 0.1
***i* = 1 A/dm^2**

Co – 60.9
Ni – 38.3
Zr – 0.8
***i* = 6 A/dm^2**

Co – 77.8
Ni – 20.2
Zr – 1.8
***i* = 10 A/dm^2**

Fig. 2. Morphology (x200) and composition ω (wt. %) of Co-Ni-Zr coatings, precipitated by a unipolar pulsed current

In the range of pulse current amplitude of 2 to 10 A/dm^2 and constant pulse/pause duration ratio of t_i / t_p = 2 ms / 2 ms, the zirconium content in the Co-Ni-Zr alloy is increased linearly (Fig. 3) and it reaches a maximum of ~1.8 wt.%, a further increase in the current density results in a decreased content of the transition metal in the alloy.

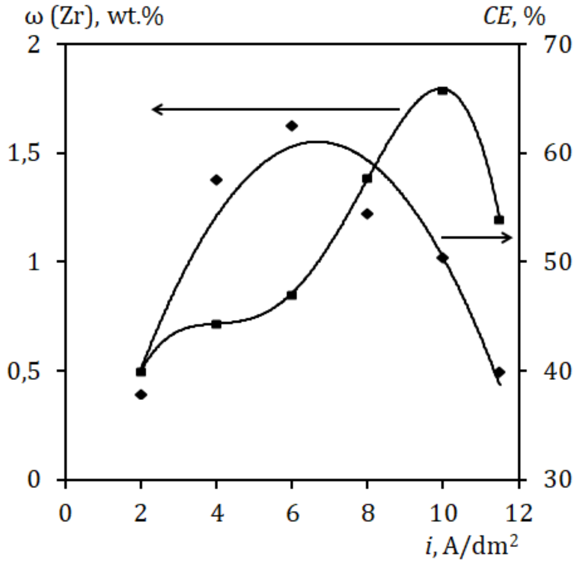


Fig. 3. The effect of current density on the zirconium content and current efficiency of the Co-Ni-Zr electrolytic coating

The dependence of the current efficiency of the electrolytic Co-Ni-Zr alloy on the current density has also an extreme pattern (Fig. 3), in particular the current efficiency is increased from 20 % to 63 % with an increase in current density in the range of 5 to 7 A/dm^2, while a further increase in *i* reduces the process efficiency to 40 %. Such behavior may be associated with the intensification of the side reaction of hydrogen release with significant fluctuations in the cathode potential. Electrolyte stirring also has a significant effect on the surface morphology and chemical composition of the alloys. Thus, at room temperature, microcracked coatings of the Co-Ni-Zr alloy are formed, in which the mass fraction of zirconium during precipitation under stirring conditions is no more than 0.4 mass % and it is decreased with an increase in the number of revolutions of the magnetic stirrer (rpm) according to Fig. 4.

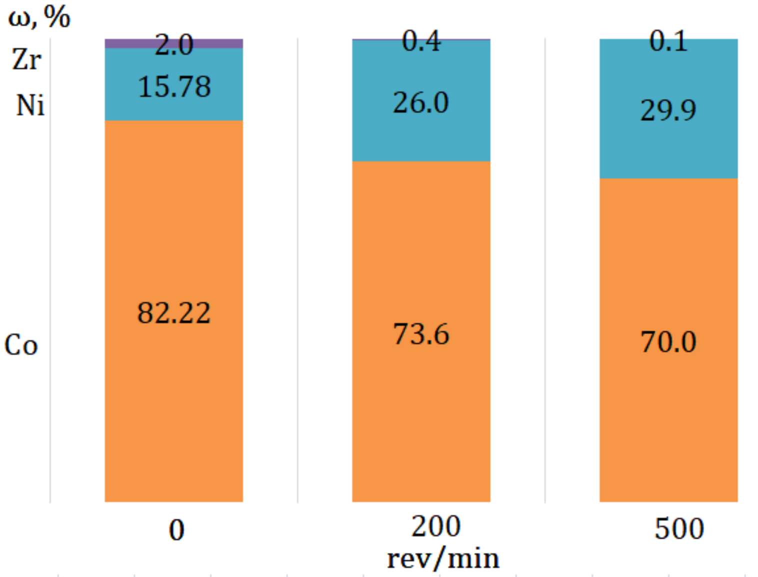


Fig. 4. The influence of stirring on the composition of the Co-Ni-Zr electrolytic coating

The reason for this phenomenon may lie in the direct effect of stirring on the formation of adhesive equilibrium in the near-electrode layer, which, on the other hand, can serve as a tool for controlling the coating composition.

Conclusion

Thus, on the basis of the conducted studies, it was found that electrolytic coatings Ternary Co-Ni-Zr with a zirconium content of up to 2.0 wt. %. Ternary Co-Ni-Zr alloys deposited in a pulsed mode from citrate electrolytes are characterized by a uniformly developed surface and the absence of a crack network on the surface.

Based on the studies carried out to determine the effect of electrolysis parameters on the composition of galvanic coatings, the modes of electrosynthesis of coatings with cobalt-nickel-zirconium alloys have been substantiated. The control of the composition of galvanic alloys in a quite wide range of alloying components concentrations is being achieved by varying the parameters of the pulse electrolysis, which allows adapting of the deposition technology to the needs of the modern market.

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