

## Galvanochemical formation of functional coatings by the cobalt-tungsten-zirconium alloys

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The functional properties of ternary Co–W–Zr(ZrO<sub>2</sub>) alloys obtained in a pulsed mode from pyrophosphate-citrate electrolytes are discussed. The obtained coatings are characterized by a uniformly developed surface without cracks and a sufficiently high and reproducible microhardness. It was determined that the size of the globules on the alloy surface decreases with increasing of the current density to 10 A/dm<sup>2</sup>. It was found that increase of temperature favorably affects the current efficiency of the alloy and the microhardness of the Co–W–Zr(ZrO<sub>2</sub>) coating. The modes of electrosynthesis of the coatings by cobalt-tungsten-zirconium alloys are substantiated, an their influence on the functional properties of the alloy and current efficiency is investigated.

**Keywords:** ternary alloys, microhardness, the current efficiency, electrolysis regimes.

Обсуждаются функциональные свойства тернарных сплавов Co–W–Zr(ZrO<sub>2</sub>), осажденных в импульсном режиме из пирофосфатно-цитратных электролитов. Полученные покрытия отличаются равномерно развитой поверхностью без трещин, что обеспечивает достаточно высокую и воспроизводимую микротвердость. Установлено, что размеры глобул на поверхности сплава уменьшаются с увеличением плотности тока до 10 А/дм<sup>2</sup>. Выявлено, что повышение температуры благоприятно влияет на выход по току сплава и микротвердость покрытия Co–W–Zr(ZrO<sub>2</sub>). Обоснованы режимы электро-синтеза покрытий сплавами кобальт-вольфрам-цирконий, исследовано их влияние на функциональные свойства и выход по току.

**Гальванохімічне формування покриттів сплавами кобальт-вольфрам-цирконій.**  
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Обговорюються функціональні властивості тернарних сплавів Co–W–Zr(ZrO<sub>2</sub>), осаджених в імпульсному режимі з пірофосфатно-цитратних електролітів. Отримані покриття відрізняються рівномірно розвиненою поверхнею без тріщин, що забезпечує досить високу і відтворену микротвердість. Визначено, що розміри глобул на поверхні сплаву зменшуються зі збільшенням густини струму до 10 А/дм<sup>2</sup>. Встановлено, що підвищення температури сприятливо впливає на вихід за струмом сплаву і микротвердість покриття Co–W–Zr(ZrO<sub>2</sub>). Обґрунтовано режими електросинтезу покриттів сплавами кобальт-вольфрам-цирконій і досліджено їх вплив на функціональні властивості і вихід за струмом.

## 1. Introduction

Tungsten and its alloys are widely used in the most important areas of the up-to-date technology due to their unique physical and chemical properties. However, due to the deficit of natural tungsten, the preference is given to the coatings of tungsten alloys whose specific parameters surpass those of the pure metal.

The addition of refractory metals to the ternary iron alloy considerably improves hardness, corrosion resistance and heat resistance of the deposited coatings [1, 2]. A large number of publications are devoted to the electrodeposition of tungsten alloys containing such metals [3–7]. It has been established that the tungsten-containing alloys produced by the galvanic method show a higher corrosion resistance in comparison to that of the pure metals of iron family due to the tungsten inertness and a lower coating porosity. Most scientific papers are devoted to the deposition of binary alloys: nickel-tungsten, iron-tungsten and cobalt-tungsten. To expand the field of application of refractory metal alloys, we switched to ternary alloys, the physical-mechanical and chemical properties of which, as a rule, exceed the properties of binary alloys.

Electrochemical systems that include zirconium are of interest to researchers as promising heterogeneous catalysts used for some processes of organic synthesis [8, 9] and also as heat resistant carriers and composite materials [10]. Though zirconium-containing composite coatings show unique properties [11–13], the research data on the production of zirconium-containing cathode coatings are rather scanty.

Existing ideas on the mechanism of co-deposition of tungsten and iron family metals are diverse and contradictory and a general vision or the theory that would explain a mechanism of this process is not yet available. Many authors believe that an essential specific feature of the formation of this alloy is an induced co-deposition [14–16] and it is understood as conjugated and not as combined reduction of the components of the alloy. Moreover, clear ideas on the mechanism of the incorporation of zirconium into the composition of cathode deposits are also absent, because it is known that zirconium is not reduced at a cathode from water solutions. Unfortunately, none of the theories available today allow us to predict the composition and, as a consequence, the properties of the resulting coatings. The generally used methods to control the pa-

rameters of electrochemical deposition, in particular, the electrolyte composition and electrolysis modes, in order to obtain the coatings of a specified composition with required properties have not been clearly accentuated. All the above reasons require an experimental study of the electro-deposition of Co–W–Zr(ZrO<sub>2</sub>) alloys.

The purpose of this research was to study the effect of the electrolyte acidity and the electrolysis parameters on the chemical composition of the surface coating, its surface morphology and structure as well as on the physical and mechanical properties of the coatings of a ternary Co–W–Zr(ZrO<sub>2</sub>) alloy.

## 2. Experimental

The coatings were obtained from complex pyrophosphate-citrate electrolytes [17] of the following composition, mol/dm<sup>3</sup>: cobalt (II) sulfate 0.1–0.3; sodium tungstate 0.05–0.1; zirconium (IV) sulfate 0.01–0.05; potassium pyrophosphate 0.1–0.5; sodium citrate 0.1–0.5. To improve the electrical conductivity, sodium sulfate was added to the electrolyte in an amount of 0.5 mol/dm<sup>3</sup>. The electrolyte for the deposition of the Co–W–Zr(ZrO<sub>2</sub>) alloy was prepared from analytically pure reagents which were dissolved in a small amount of distilled water; after that the solution was mixed in a certain sequence based on the results of the ionic equilibria study.

The copper substrate (M0) was pretreated according to the procedure described in [18]. Electrodeposition was carried out by a pulsed current with varying temperature from 15 to 60°C, pH, and current density  $j = 2\text{--}12 \text{ A/dm}^2$  [19]. The following time parameters of the deposition were maintained: pulse duration ( $t_{on}$ ) of  $5 \cdot 10^{-3}$  s, and current interruption time (pause duration  $t_{off}$ ) of  $1 \cdot 10^{-2}$  s. In this paper, we do not consider the influence of the frequency and duty cycle of pulses on functional properties. Pulse electrodeposition modes were set using a PI-50-1.1 potentiostat and a PR-8 programmer. Stainless steel plates were used as insoluble anodes. The pH values of the electrolytes were measured by a pH-150M instrument using an ESL-6307 glass electrode. The current efficiency (CE) of the alloy was calculated by the gravimetric method, based on the deposition duration and considering the electrochemical equivalent of the alloy.

The chemical composition of the obtained coatings was determined by a SPRUT spec-

trometer. The analysis was carried out at least at 3 points, followed by averaging of the obtained values. The elemental composition and surface morphology of the coatings were analyzed on a ZEISS EVO 40XVP scanning electron microscope (SEM). Images were obtained by recording secondary electrons by scanning with an electron beam, which made it possible to study topography with high resolution and contrast [20, 21]. The error in measuring the content of the components was  $\pm 1$  wt. %

The microhardness of the substrate material (copper), as well as the coatings of cobalt-tungsten-zirconium alloys was determined by indentation of a diamond pyramid using a PMT-3 hardness tester; the load of  $P = 0.1$  kg and a holding time of 10 s. The experiment was carried out after aging the coatings for 24 h at room temperature.  $H_v$  values were calculated by the formula:

$$H_v = 1854P/d^2,$$

where  $d$  is the diagonal of the indentation spot of the pyramid, in microns. The measurements were carried out at least at 3 points with subsequent averaging of the data. The confidence interval was  $\pm 10$  %.

### 3. Results and discussion

#### 3.1. The effect of the electrolyte pH

The practice shows that the electrolyte acidity significantly affects the efficiency of the process, in particular, the current efficiency (CE) and the quality of coatings, hence, their physical and mechanical properties. Even a slight change in the acidity of the electrolyte can lead to disruption of the electrolysis process and poor quality of the deposited coatings. A specific feature of pyrophosphate-&-citrate electrolytes used for the deposition of the alloy is that the strength of appropriate cobalt clusters increases with a decrease in the protonation degree of the ligands (citrate and pyrophosphate); as a consequence, the reduction potential will shift to the negative range and approach the tungstate reduction potentials [22]. However, it is worth to note that the threat of the formation of cobalt hydroxides in the electrolyte increases with the transition to the alkaline domain; this leads to their undesirable inclusion in the coating composition. In addition, the solution acidity has an essential effect on the ionic equilibrium in tungstate solutions; in addition, as the pH factor increases, the polyforms dissociate into the mono-tungstates, the size

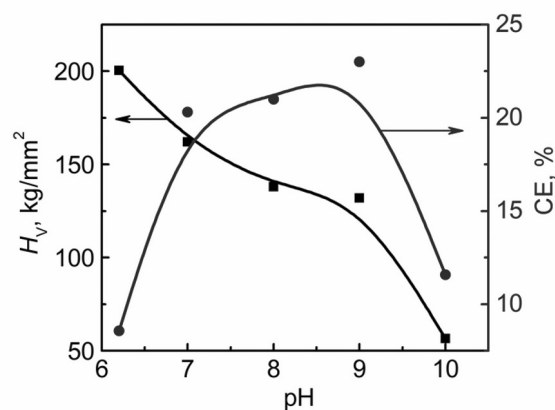


Fig. 1. The effect of the solution acidity on the microhardness and CE of the deposit Co-W-Zr(ZrO<sub>2</sub>). The pulse electrolysis mode:  $j = 8$  A/dm<sup>2</sup>,  $t_{on} = 5 \cdot 10^{-3}$  s,  $t_{off} = 1 \cdot 10^{-2}$  s. Temperature  $T = 25^\circ\text{C}$ .

and ability of which to formation of heteronuclear clusters and their reduction significantly increase [23].

The reaction of metal reduction proceeds simultaneously with the reaction of hydrogen evolution and the latter strongly affects the formation of a pure alloy. One of the main reasons for deterioration of the electrolyte stability is the alkalization of a near-electrode layer due to the side reaction of hydrogen evolution [24] that consumes up to 80 % of the current, as regards the processes under consideration (Fig. 1). In addition, when the electrolyte pH exceeds 8, the current efficiency of the Co-W-Zr(ZrO<sub>2</sub>) alloy sharply decreases and at  $\text{pH} \geq 10$  the insoluble deposit forms. This process lead to the formation of hydroxides and basic cobalt salts and as a result, the coating quality deteriorates along with their microhardness (Fig. 1).

#### 3.2. The effect of the electrolyte temperature

The temperature can have a double effect on the formation of galvanic coatings. On the one hand, the ion diffusion rate increases with temperature thus providing an opportunity for an increase in the current density which is still low for the formation of dendrites and spongy precipitates. On the other hand, an increase in the electrolyte temperature results in an increased rate of the crystal growth that contributes to the formation of a coarse-grained structure. When the temperatures are not too high ( $T \leq 50^\circ\text{C}$ ), the effect of the first factor is stronger and results in an improved quality of coatings and, as a consequence, the microhardness of the deposit increases (Fig. 2).

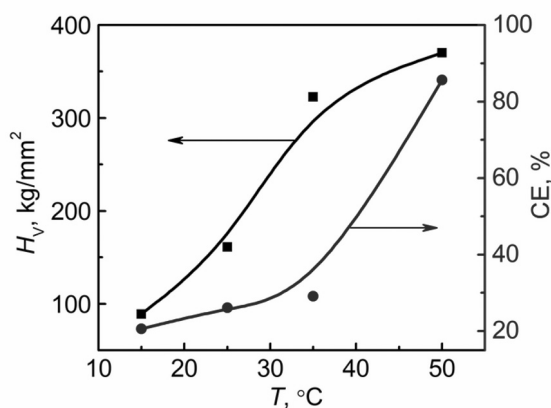


Fig. 2. The effect of temperature on the microhardness and CE of the deposit Co–W–Zr(ZrO<sub>2</sub>). The pulse electrolysis mode:  $j = 8 \text{ A/dm}^2$ ,  $t_{on} = 5 \cdot 10^{-3} \text{ s}$ ,  $t_{off} = 1 \cdot 10^{-2} \text{ s}$ . Temperature  $T = 25^\circ\text{C}$ ; pH = 8.

An increase in the current efficiency with the temperature can also be explained not only by the accelerated diffusion of electrode-active particles to the cathode surface and an increased limiting current density but also by the acceleration of the conjugate metal reduction reactions that occur with the formation of an alloy. As the temperature rises, the rates of chemical stages accompanying the electrodeposition of tungsten-containing alloys from complex electrolytes also increase [17]. A preceding stage of the release of the ligands from complex ions is attributed to such reactions; this contributes to the acceleration of the metal discharge. The next stage of the chemical reduction of intermediate tungsten oxides by hydrogen ad-atoms, which occurs during a pause, also refers to such reactions. In this regard, the fraction of current required for the evolution of gaseous hydrogen decreases and the efficiency of the alloy current increases.

### 3.3. The effect of the current density

Mechanical properties and internal stresses in the coatings are defined by the microstructure. By varying electrolysis conditions, we can form the coatings with a different degree of the structure dispersion and, therefore, with different properties. The crystalline structure of deposited alloys depends on the two processes, namely, the formation of crystal nuclei on the cathode and the growth of crystals from the crystalline nuclei. The specific features of the coating structure directly affect the morphology of the surface formed during deposition; the current density at the cathode

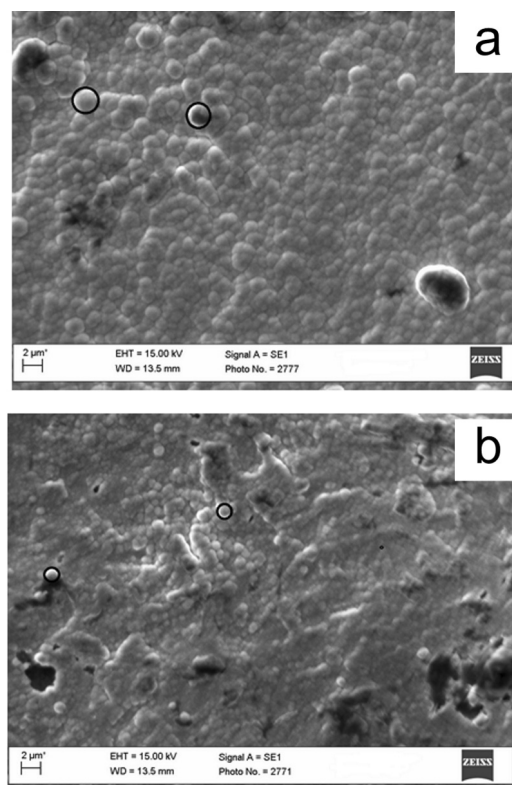


Fig. 3. The morphology of the coatings Co–W–Zr(ZrO<sub>2</sub>) deposited by  $j = 4 \text{ A/dm}^2$  (a) and  $j = 6 \text{ A/dm}^2$  (b). The pulse electrolysis mode:  $j = 6 \text{ A/dm}^2$ ,  $t_{on} = 5 \cdot 10^{-3} \text{ s}$ ,  $t_{off} = 1 \cdot 10^{-2} \text{ s}$ . Temperature  $T = 25^\circ\text{C}$ ; pH = 8.

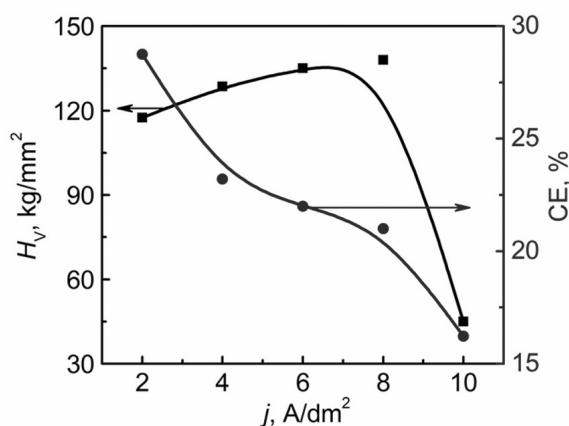


Fig. 4. The effect of current density on the microhardness and CE of the deposit Co–W–Zr(ZrO<sub>2</sub>). The pulse electrolysis mode:  $j = 8 \text{ A/dm}^2$ ,  $t_{on} = 5 \cdot 10^{-3} \text{ s}$ ,  $t_{off} = 1 \cdot 10^{-2} \text{ s}$ . Temperature  $T = 25^\circ\text{C}$ .

has the strongest effect. Therefore, the crystal nucleation rate increases faster with increasing current density compared to crystal growth; as a result, the grain size

Table. The effect of the current density on the elemental composition of the deposits Co–W–Zr(ZrO<sub>2</sub>). The pulsed mode of electrolysis:  $t_{on} = 5 \cdot 10^{-3}$  s,  $t_{off} = 1 \cdot 10^{-2}$  s. Temperature  $T = 25^\circ\text{C}$ ; pH = 8.

$j$ , A/dm <sup>2</sup>	Composition of the coating, wt.%				
	Co	W	Zr	C	O
4	69.8	20.6	0.7	3.4	5.5
6	78.1	8.2	1.9	3.8	8.0
10	79.1	4.2	2.4	3.8	10.5

decreases and the coatings become fine-grained (Fig. 3). When the cathode current density  $j$  exceeds 10 A/dm<sup>2</sup>, loose Co–W–Zr(ZrO<sub>2</sub>) deposits are formed due to difficult diffusion in comparison to the diffusion at the charge transfer stage. In addition, the alkalization of the near-cathode layer increases, thus, the probability of the formation of cobalt hydroxides increases too; these inclusions into the coating can degrade their properties.

An increase in the current density amplitude results in a decrease in the current efficiency of the alloy (Fig. 4); this might be due to considerable vibrations of the cathode potential, which facilitate the removal of hydrogen bubbles from the electrode surface and the  $H_{ad} \leftrightarrow H_2$  reaction equilibrium shifts towards the formation of molecular hydrogen.

The dependence of microhardness  $H_v$  of the coating on the cathode current density has an extreme behavior. The value of  $H_v$  increases with increasing current density  $j$  in the range of 2 to 8 A/dm<sup>2</sup> (Fig. 4). It is explained by a decrease in the size of conglomerate grains and globules on the coating surface. In addition, low current densities contribute to a more homogeneous distribution of the coating over the substrate surface due to a low crystallization rate. At current density  $j = 10$  A/dm<sup>2</sup>, the microhardness of the Co–W–Zr(ZrO<sub>2</sub>) coating decreases abruptly due to the formation of loose cracking layers on the surface, which, apparently, contain hydroxides.

This assumption is confirmed by the analysis of the experimental data. It has been established that the Co–W–Zr(ZrO<sub>2</sub>) coatings contain nonmetal admixtures, in particular oxygen and carbon (Table 1). This allows us to consider such coatings as a nanocomposite which includes incompletely reduced zirconium oxides and, possibly, tungsten oxides. With an increase in the current density, the content of oxygen in

the alloy increases from 5.5 to 10.5 wt.%, while the content of carbon in the coating composition remains actually unchanged. An increase in the concentration of oxygen in the alloy leads to a decrease in the content of the crystalline phase in the form of solid solutions and an increase in the proportion of amorphous deposits.

#### 4. Conclusions

The ternary Co–W–Zr(ZrO<sub>2</sub>) alloys deposited in a pulsed mode from a pyrophosphate-&-citrate electrolyte have a uniformly developed surface without cracks, which ensures a sufficiently high microhardness of the coatings. The studies of the influence of electrolysis parameters on the microhardness of galvanic coatings have shown that the properties of the ternary Co–W–Zr(ZrO<sub>2</sub>) coatings depend on the pH of the electrolyte, its temperature and the pulse current density.

It was determined that the size of globules on the alloy surface decreases with increasing current density up to 10 A/dm<sup>2</sup>. It was found that an increase in temperature favorably affects the efficiency of the alloy current and the microhardness of the Co–W–Zr(ZrO<sub>2</sub>) coatings. The modes of electro-synthesis of cobalt-tungsten-zirconium nanocomposite coatings are substantiated, and their influence on the functional properties and current efficiency of the alloy is investigated.

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