

Co-Mo-W Galvanochemical Alloy Application as Cathode Material in the Industrial Wastewater Treatment Processes

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Abstract. The article deals with the role of electrodes materials in improving the industrial wastewater treatment from pollutants by electrochemical action. The instability constants of the complexes and coordinated ligand molecules were calculated. Based on the research conducted regarding the rationalisation of the poly-ligand electrolytes and electrolysis modes, a variative flow scheme of the coatings deposition by triple alloy has been developed. The corrosion resistance characteristics of the coatings obtained in the form of alloy, that were obtained from complex electrolyte that satisfy the necessary coatings requirements for effective treatment of wastewater have been researched. The obtained coatings have better corrosion resistance than in special steels of electrochemical purpose.

Introduction

In Ukraine, according to the State Water Resources Agency [1], over 48.5 thous. tons of harmful pollutants of the second and third hazard classes have been discharged to the surface water in recent years. Over 18% of the total wastewater discharge is contaminated water, non-purified or insufficiently purified at purification works. Water resources are used by sectors of the economy without sufficient measures to prevent their pollution [2]. Most of the contaminator enterprises belong to the utilities sector – 74, to the industry – 18 (the largest ones of them – ironworks – 6). The total number of enterprises discharging the wastewater to the natural water bodies is 539, the total amount of contaminated return water or wastewater discharge – 952 mln m³ per year. Out of this volume more than 95 %, 918,6 mln m³ are discharged by the 100 major contaminators. It happens due to the fact that of taking place the return- or wastewater discharging without a sufficient degree of decontamination for compliance with the established maximum allowable norms in permits for special water use. Almost two-thirds of enterprises from this anti-rating are located in the territory of 5 regions: Dnipropetrovsk – 24; Donetsk – 19; Lviv – 7, Kharkiv – 7, Luhansk – 6. The specified situation needs an increase in wastewater treatment efficiency and deepness. Biochemical technologies allow achieving a deep purification of these effluents [3], but they are characterized by the effects selectivity, need for narrow process modes maintaining, pretreatment technologies application and need for significant areas to arrange basins and reservoirs.

Main Part

The most effective, compact, with a high nomenclature of effects are electrochemical technologies of wastewater treatment. These methods allow extracting valuable products from wastewater for further use at a relatively simple flow scheme without using chemical reagents and with insignificant energy input. When wastewater passing through the electrolyzer inter-electrode space of electrolysis of water and particles polarization occurs, electrophoresis, oxidation-reduction processes, electrolysis products interaction with each other, flotation and coagulation processes

initiation are observed. Localization of the primary electrolysis processes on the electrodes surface determines the electrolyzers design features. One can get rid of these limitations in a distributed electrode system, where bulk electrode particles are located between ordinary plane electrodes. Depending on the electrolyzer voltage and geometrical characteristics, either volume-distributed electrochemical process or multiple microarc discharge occurs in this system [4]. In the latter case, a plasma-chemical technology with reactively active compounds penetration the treated solution is implemented. Electrodes are usually protected by coatings and modified to improve their electrical and technological characteristics [5].

In a standard electrolyzer (Fig.1) on the positive electrode, anode ions yield electrons, i.e., the electrochemical oxidation reaction occurs, on the negative electrode, cathode, electrons attachment occurs, i.e., the reaction of reduction.

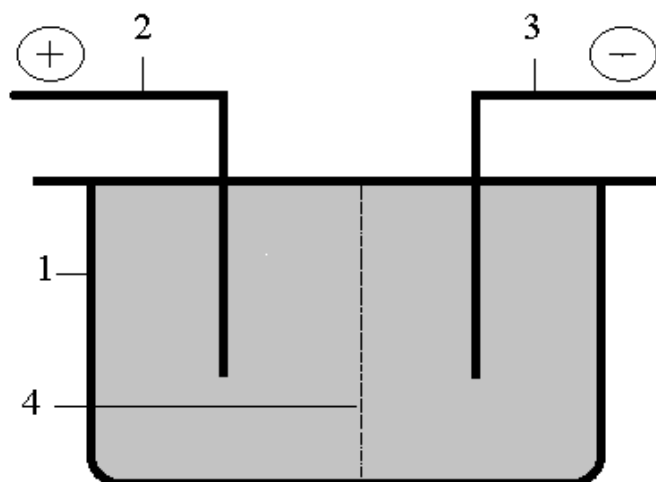


Fig. 1. Electrolyzer diagram: 1 - housing; 2 - anode; 3 - cathode 4 – diaphragm

These processes are actively implemented in the technologies of wastewater purification from dissolved impurities (cyanides, amines, alcohols, aldehydes, nitro compounds, sulphides, mercaptans). In the electrochemical oxidation processes, impurities contained in wastewater fully decompose with the formation of CO_2 , NH_3 and water, or they convert into simpler and non-toxic substances available for removing by other methods.

The main issue in the targeted electrodes creation is the balance between their effective period since they are worn due to corrosion and other processes, and cost efficiency and safety of their manufacturing process as well as protective coatings application. Insoluble materials are used as anodes: graphite, magnetite, oxides of lead, manganese, ruthenium, iridium that are applied on titanium base (ORTA etc.) individually or mixed with titanium dioxide. Quite rarely, regarding the cost of material, platinum or platinized titanium (PTA) is used. Cathodes are made of materials that provide for a long service life: molybdenum, graphite, stainless steel as well as other steels plated with molybdenum, tungsten or their alloys. Accordingly, a bulk electrode shall be made of materials capable to function as both anodes and cathodes.

Thus, the electrodes material properties are decisive for the efficiency of both the electrochemical treatment in general and the wastewater electrochemical treatment processes. Requirements for the cost-effectiveness of manufacture, the need for ensuring the necessary electrochemical mode and stability under the conditions of wastewater aggressive environment can be applied to the electrode material. Usually, in practice, coatings with target properties are used for electrodes. On the one hand, these coatings shall be strong, solid and well tenacious to the base, on the other hand, their forming process shall be cost-effective and safer from the point of view of the electrodes used as well as reduce in the side formation of hydrogen [6].

Regarding the coating properties forming, it should be noted that metals are prone to clusters formation. Therefore, issues on forming the alloy properties is an issue on the optimal cluster structure forming to form the target properties. Electrochemical deposition is a convenient way for the targeted formation of structure and cluster composition.

Materials and Research Methods

Individual tungsten and molybdenum coatings cannot be obtained from aqueous solutions, but with the Ferrum family metals (Fe, Co, Ni), they can co-deposit into an alloy of complex electrolytes due to complex formation [7]. A significant complication of the complex formation process in the studied system is the fact that tungstate- and molybdate-ions can act not only as complexing substances but also as ligands, which contributes to the heteronuclear complexes arising.

The complexes instability constants values K_{in} were determined by potentiometry of solutions were alloying components concentration was created, mol/dm³: CoSO₄·7 H₂O – 1·10⁻³... 5·10⁻³, Na₂WO₄·2 H₂O i Na₂MoO₄·2 H₂O – 5·10⁻³...1·10⁻¹; whilst the ligands (Na₃C₆H₅O₇·5.5 H₂O, K₄P₂O₇, C₁₀H₁₄O₈N₂Na₂·2 H₂O) concentration (Na₃C₆H₅O₇·5,5 H₂O, K₄P₂O₇, C₁₀H₁₄O₈N₂Na₂·2 H₂O) was varied in the range of 5·10⁻³...1·10⁻¹. The constant ionic strength ($I_c = 1$) of the solution was maintained through sodium sulphate introduction.

The instability constant on the example of mononuclear cobalt complexes was calculated as:

$$K_{in} = \frac{[Co^{2+}] \cdot [L]^n}{[CoL_n]} \quad (1)$$

where $[Co^{2+}]$, $[L]^n$, $[CoL_n]$ – equilibrium concentrations of free ions of cobalt (II), ligand particles and complex respectively, mol/dm³; n – number of coordinated ligands.

In case of the ligand excess in solution, the unknown values for K_{in} calculation are n and $[Co^{2+}]$. The equilibrium concentrations of free ions of cobalt can be calculated via Nernst equation based on the equilibrium potential values of cobalt in solution:

$$E = E^0 + \frac{R \cdot T}{z \cdot F} \ln c_{M^{z+}} \quad (2)$$

The following ratio was used to calculate the ligand n coordinated molecules:

$$\frac{\Delta E}{\Delta \lg c_L} = -n \left(\frac{R \cdot T}{z \cdot F} \right) \quad (3)$$

where ΔE – change of the electrode potential when the ligand concentration varying; R – universal gas constant; T – temperature; z – the complexing substance ions charge; F – Faraday constant.

Research Results

Insubstantial complex compounds are formed in the systems Co–WO₄²⁻ and Co–MoO₄²⁻, as evidenced by the instability constants calculated values of compounds 5.7·10⁻⁴ and 8·10⁻⁴ respectively. The inflexion on the dependencies evidences the formation possibility of various composition complexes (Fig.2): thus, at the $c(WO_4^{2-}(MoO_4^{2-}))/c(Co^{2+}) \geq 6:1$ concentration ratio, the $[Co(WO_4)_2]^{2-}$ and $[Co(MoO_4)_2]^{2-}$ composition complexes are formed.

Stability of the monoligand complexes of cobalt with tungsten and molybdenum can be increased by additional ligands introduction – citrate and diphosphate. Based on the dependencies shown in Fig.3, to study the complex formation in the Co–MO₄²⁻–P₂O₇⁴⁻ and Co–MO₄²⁻–Cit³⁻ systems, the constant ratio $Co^{2+}/MO_4^{2-}=1:12$ (where M = W and Mo) was adopted, since the inflexion on the E–lgc_L dependencies are only observed after $\lg c_L \geq -1.4$, which indicates the complex compound formation, and the ligands concentration were varied in the range $c(P_2O_7^{4-}$ and $Cit^{3-})$ of 1:1 to 1:100.

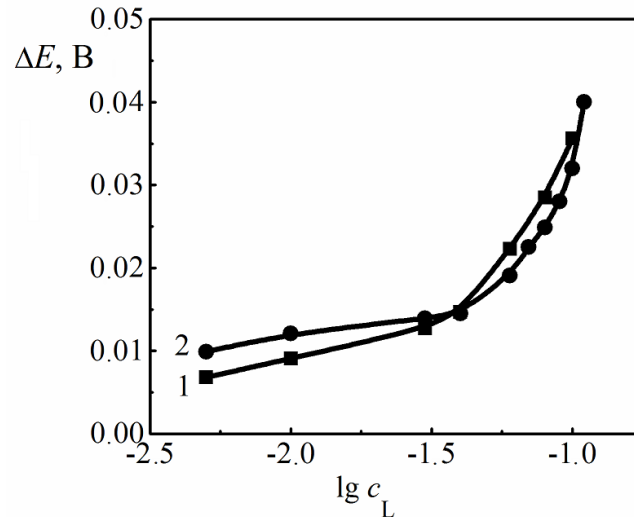


Fig. 2. Operating electrode potential dependence on the tungstate and molybdate concentration at $c(\text{Co}^{2+})=5 \cdot 10^{-3}$, $\text{pH} = 6.3 \dots 7.2$

The linear course of a cobalt electrode potential dependence on the ligands concentration indicates that at all ratios of complexing substance and ligands concentrations, complex compounds of the same composition are formed (Table 1.). Tungsten and molybdenum, in terms of their chemical properties, are very similar to each other, so in the same solutions and their concentrations, the course of 1-2 and 3-4 dependencies in Fig. 3 has a similar trajectory.

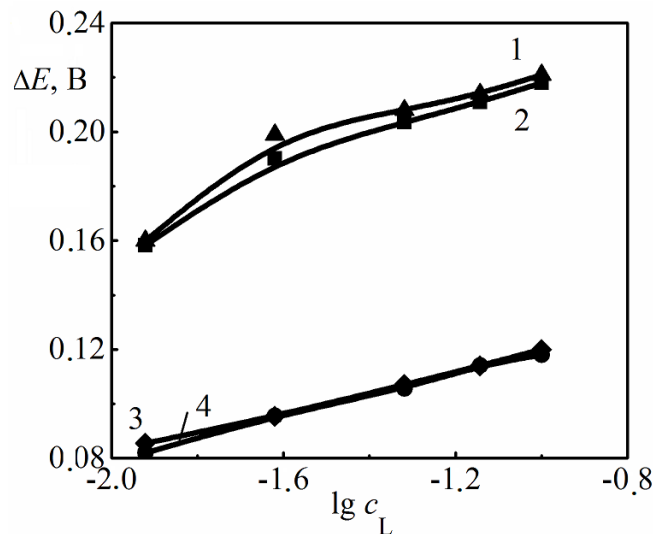


Fig. 3. Electrode potential dependence at the concentration constant of $C(\text{Co}^{2+})=10^{-3} \text{ mol/dm}^3$ on the electrolyte components concentration, mol/dm^3 :

- 1 – $(\text{WO}_4^{2-}) = 1.2 \cdot 10^{-2}$, $(\text{P}_2\text{O}_7^{4-}) = 1.2 \cdot 10^{-2} \dots 10^{-1}$;
- 2 – $(\text{MoO}_4^{2-}) = 1.2 \cdot 10^{-2}$, $(\text{P}_2\text{O}_7^{4-}) = 1.2 \cdot 10^{-2} \dots 10^{-1}$;
- 3 – $(\text{WO}_4^{2-}) = 1.2 \cdot 10^{-2}$, $(\text{Cit}^{3-}) = 1.2 \cdot 10^{-2} \dots 10^{-1}$;
- 4 – $(\text{MoO}_4^{2-}) = 1.2 \cdot 10^{-2}$, $(\text{Cit}^{3-}) = 1.2 \cdot 10^{-2} \dots 10^{-1}$, $\text{pH} = 8.2 \dots 9.9$

The instability constants values obtained for molybdates and tungstates are almost the same and barely depend on the nature of the second ligand (Table 1).

The research conducted on rationalization of the poly-ligand electrolytes composition and electrolysis modes has formed a background for a variable flow scheme of the triple alloy Co-Mo-W coating deposition development.

The alloys electrochemical synthesis flow process includes preparatory stages (mechanical preparation of the base, chemical degreasing and etching), alloy plating stage, final processes (rinsing, drying) [8].

Table 1. Instability constants of the complex compounds of cobalt

Complexing substance	Ligand	Composition of complex	pH	K_{H}
Co^{2+}	WO_4^{2-}	$[\text{Co}(\text{WO}_4)_2]^{2-}$	6.3÷7.2	$5.7 \cdot 10^{-4}$
	MoO_4^{2-}	$[\text{Co}(\text{MoO}_4)_2]^{2-}$	6.3÷7.2	$8 \cdot 10^{-4}$
	$\text{WO}_4^{2-}, \text{P}_2\text{O}_7^{4-}$	$[\text{WO}_4\text{Co}(\text{P}_2\text{O}_7)]^{4-}$	9.14÷9.9	$1.8 \cdot 10^{-10}$
	$\text{WO}_4^{2-}, \text{Cit}^{3-}$	$[\text{WO}_4\text{Co}(\text{Cit})]^{3-}$	8.9÷9.7	$5.67 \cdot 10^{-7}$
	$\text{MoO}_4^{2-}, \text{P}_2\text{O}_7^{4-}$	$[\text{MoO}_4\text{Co}(\text{P}_2\text{O}_7)]^{4-}$	8.8÷9.7	$2.82 \cdot 10^{-10}$
	$\text{MoO}_4^{2-}, \text{Cit}^{3-}$	$[\text{MoO}_4\text{Co}(\text{Cit})]^{3-}$	8.2÷8.7	$5.87 \cdot 10^{-7}$

Co–Mo–W alloy electrodeposited coatings, refractory components content, surface structure and morphology as well as physical and mechanical properties of which are dependent on the electrolyte composition and electrolysis conditions are formed from the citrate-diphosphate electrolyte. To obtain high-quality coatings by Co–Mo–W alloy deposition, it is recommended to provide for the alloying elements concentrations ratio of $C(\text{Co}^{2+})/C(\text{WO}_4^{2-} + \text{MoO}_4^{2-}) = 1:1$ as well as citrates ligands: diphosphate as 1:2; in the current density range of 2-6 A/dm² at the temperature variation within the interval of 293-333 K. A low content of tungsten (Fig.4.) in alloy provides coatings with fine-crystalline structure and reduces the internal stresses level [9].

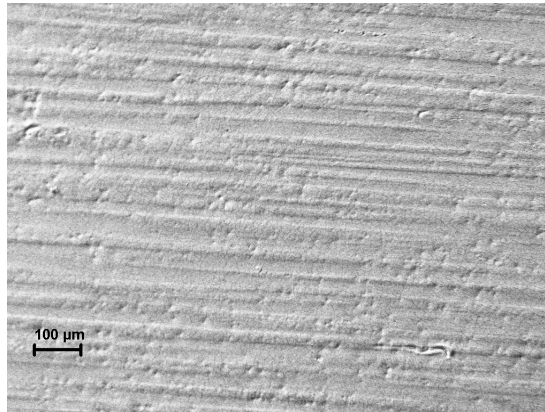


Fig. 4. Alloy photomicrograph and chemical composition (wt %): Co-53.93, Mo-24.94, W-3.96, O-7.59, C-9.58, Na-0.5

It is known that to intensify the cyanides oxidation process, sodium chloride is preliminarily added to wastewater, therefore, one has to analyze the corrosion behaviour of the synthesized alloy in a neutral medium with addition of ions chloride [10]. It has been established that for synthesized coatings the corrosion behaviour depends on the acidity of medium, composition and morphology.

The synthesized materials corrosion resistance determining was carried out by the polarization resistance method through anode and cathode voltamperograms recording (Fig.5). The corrosion current density j_{cor} was determined through extrapolation in the intersection point of the partial anode and cathode polarization dependencies linear sections near the corrosion potential E_{cor} (sections up to 50 mV) in Tafel coordinates $\lg j - \Delta E$ [11].

According to the known value of corrosion current, the corrosion rate depth indicator k_h was calculated using the equation as well as the resistance index was determined (Table 2.):

$$K_h = \frac{8.76 \cdot k_{\text{all}} \cdot j_{\text{kor}}}{\rho_{\text{all}}} \quad (4)$$

where k_{all} – electrochemical equivalent of metal or alloy, C/kg; j_{cor} – corrosion current density, A/m²; ρ_{all} – alloy density, kg/m³.

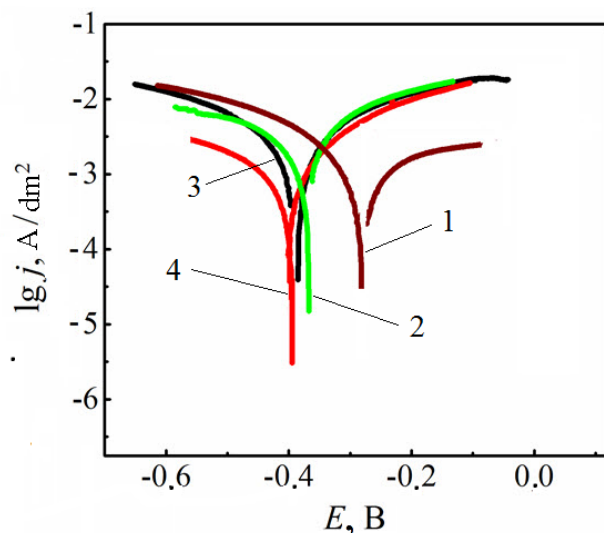


Fig. 5. Alloy Co-Mo-W polarization dependencies in a neutral medium (pH=7, 3 % NaCl) at the total content of refractory components, wt %: 1– 20,2 – 33 ,3 – 38,4 – 45

Table 2. Alloy coatings corrosion resistance characteristics obtained from a complex electrolyte

Alloy composition, [wt %]			pH=7		
Co	Mo	W	E_{cor} , [B]	k_h , [mm/year]	Resistance rating
74.3	10.6	15.1	-0.29	0.001	1-2
70.1	16.1	13.8	-0.31	0.0017	2
68.3	18.8	12.9	-0.35	0.004	2
Comparison constants [12]					
09G2S			-	2.0961	8
St3PS			-	0.5935	7
VT20			-	0.1324	5
12H17			-	0.0788	5

Conclusion

Thus, based on the experimentally established non-stability constants, the complex electrolyte composition for triple alloy deposition was justified. Analysis of the corrosion studies has shown that application even of a thin layer of deposited alloy does not reduce its productivity and operational efficiency and, at the same time, is more economically and resource-efficient compared, for example, with a casting alloy. Therefore, the properties of the developed alloy coating are correspondent and meet the requirements specified to the cathodes material properties for wastewater electrochemical treatment. The obtained coatings have better corrosion resistance than in special steels of electrochemical purpose.

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