

Electrochemical synthesis of catalytic active alloys

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The aspects of man-caused gaseous waste purification from hydrocarbons, nitrogen oxides and carbon using supported catalytic neutralizers are analyzed. The replacement of platinum metals in catalysts by alloys and oxide compounds is discussed to be an actual task. The use of hydrogen release reaction is proposed to estimate the catalytic activity of synthesized materials. Electrochemical methods are shown to be of good prospects in catalytic material design. Current exchange dependence on "metal-hydrogen" and "metal-oxygen" bond energy is used for alloy property prediction. The modes for synthesis of nickel-palladium, nickel-copper and nickel-tungsten alloys with maximum catalytic activity are optimized. The synergism of nickel-tungsten and nickel-copper alloys is shown.

Проанализированы особенности очистки техногенных газовых выбросов от углеводородов, оксидов азота и углерода с использованием каталитических нейтрализаторов. Отмечена актуальность замены платиноидов в катализаторах на сплавы и оксидные соединения. Предложено использовать реакцию выделения водорода для оценки каталитической активности синтезируемых материалов. К перспективным способам дизайна каталитических материалов на металлических носителях отнесены электрохимические методы. Для прогнозирования свойств сплавов использована зависимость тока обмена от энергий связи "металл-водород" и "металл-кислород". Оптимизированы режимы синтеза сплавов никель-палладий, никель-медь и никель-вольфрам, состав которых соответствует максимальной каталитической активности. Показано, что сплавы никель-вольфрам и никель-медь обладают синергетическим эффектом.

Neutralization of toxic gaseous emissions from vehicles, mining equipment, domestic waste processing plants, food and other low productivity works is an actual problem in most advanced countries. A strong impulse to the development of catalytic purification methods as well as to creation of variously designed neutralizers was given [1] by implementation of block carrier systems, which are capable to work in wide temperature range, in particular at the "cold" start of engines. The replacement of ceramic block carriers by metallic ones is promoted [2] by: a rather large flow section; high specific surface and heat conductivity, providing the rapid heating; uniform catalytic layer temperature and the lowered risk of local overheats; high mechanical and impact

strength; the production flexibility, allowing to make catalysts of different and sizes.

The traditional catalytic neutralizers based on platinum group metals (Pt, Rh, Pd) provide a considerable reduction of concentration of unburned hydrocarbons and nitrogen oxides (NO_x). Due to the low availability and high price of platinum group metals, a great number of researches has been directed to content of these materials in catalytic systems and even to their complete replacement. An important part in solving this problem belongs to the transition metal oxides (Cu, Cr, Mn, Fe, Co, Ni) as well as mixed and composite oxides, for example spinels and perovskites, and also to various alloys [3]. But problems of providing the durable adhesion and catalytic layer homo-

geneous distribution on the carrier as well as ways to its specific area value and porosity enhancement, i.e. providing the method for manufacturing a stable ignoble catalyst on metallic carrier, remain unsolved to date.

One of the most effective complex solutions for a number of mentioned problems consists in the electrochemical techniques of the carrier pretreatment, surface shaping and the deposition of variable composition and thickness coatings with high adhesion, possessing catalytic properties and corrosive resistance. Preferred should be the pulse electrolysis modes, providing the flexible control of the alloy composition, regulation of the phase composition and the coating purity, and reduction of internal stresses in the materials. This work is devoted to solving the problem of catalytically active system electrodeposition on metallic carriers.

A vital problem in platinum metal replacement is the catalytic activity prediction for ignoble metals and alloys in heterogeneous redox reactions, which depends on their ability to adsorb molecules as well as to influence the electron density redistribution and interatomic bond breaking. The "metal — reagent active center" bond energy can be believed to be a quantitative characteristic of such property. From this point of view, it is possible to use the model reaction of hydrogen reduction to estimate the synthesized material catalytic activity, because this electrochemical process also includes the adsorption stage, and its rate depends on the electrode nature and "metal — hydrogen" (E_{M-H}) bond energy [4]. It is just the hydrogen current exchange density that is considered to be the universal process characteristic, because it is independent of the electrode potential. In our work [5], it has been suggested that *d*-metals located on different sides of the $j_0^H - \Delta E_{H-O}^M$ dependence (Fig. 1), where ΔE_{H-O}^M is the difference between "metal-hydrogen" and "metal-oxygen" bond energy, are able to form catalytic active alloys. This hypothesis was verified taking the electrodeposited nickel-copper, nickel-palladium and nickel-tungsten alloys as examples.

The alloy coatings were deposited onto steel, nickel, and copper substrates after pretreatment using a standard method [6]. The Ni-Cu alloy were deposited from complex pyrophosphate electrolytes, where the total concentration of copper and nickel salts has not exceed 0.3 mol/dm^3 , that of potassium pyrophosphate 1 mol/dm^3 at $\text{pH} = 8.8-9.0$ and direct current density 50

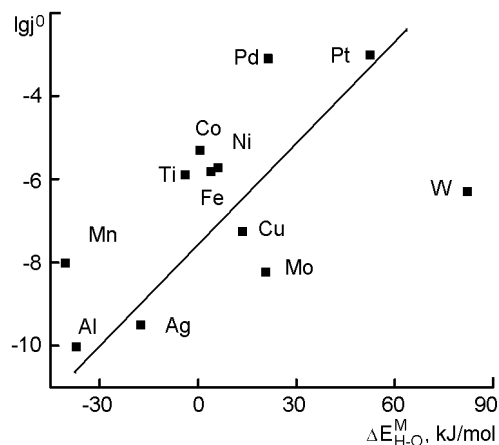


Fig. 1. Hydrogen exchange current density as a function of bond energy difference ΔE_{H-O}^M .

to 100 A/m^2 . Ni-Pd coatings have been obtained from the polyligand ammonium pyrophosphate electrolyte, $\text{pH} = 9.5$ to 10.5 , at 292 K . The cathode current density j_c was varied in the range of 4 to 20 A/m^2 . The Ni-W alloy was deposited from a complex ammonium citrate electrolyte [7] using unipolar pulse current. The tungstate content in the electrolyte was varied in the range of 0.025 to 0.1 mol/dm^3 at the total nickel sulfate and sodium tungstate concentration of 0.2 mol/dm^3 . Citric acid concentration was 0.3 mol/dm^3 , $\text{pH} = 8$. Electrodeposition has been carried out at 343 K and pulse current density amplitude 1000 to 1500 A/m^2 . The Ni content in alloys was determined using photocalorimetry [8], the copper one, by electrolytic deposition on a platinum cathode [9]. The catalytic properties of electrodeposited alloys were estimated basing on the exchange current value in the model reaction of hydrogen reduction from sulfuric acid solution. The cell was de-oxygenated by purging with high purity argon with simultaneous primary cathode work-up of the solution during 30 min . Voltammetric measurements have been carried out under linear step potential polarization mode using a PI-50-1.1 potentiostat and a PR-8 programmer in a standard CSE-2 three-electrode cell.

Electrolysis mode influence on the alloy composition. When Ni-W alloy depositing from a ammonium citrate electrolyte, nickel reduction takes place with depolarization which increases with the cathode current density j_c increase, although we have established that nickel content in the alloy, as well as the current efficiency E_c , are essentially independent of j_c . Ni(II) and W(VI) salt

Table 1. Effect of electrolyte composition on the component content and current efficiency of Ni–W alloy

Ni(II)/W(VI)	1.67	3	3.7	4.7	7
$\omega(\text{Ni})$, %	69.5	76.0	78.1	82.5	84.0
Ce, %	38.5	40	49	50.7	53

concentration ratio in the electrolyte influences the coating composition considerably: as the Ni(II)/W(VI) ratio rises, Ni content in the alloy $\omega(\text{Ni})$ and the alloy current efficiency increase (Table 1).

Consideration of kinetic parameters for partial reactions (d and l) enables to propose the tungsten-nickel (cobalt) alloy deposition mechanism (Fig. 2), where $M \in \{\text{Ni}, \text{Co}\}$; K^z+ , the cation; A^{z-} , the anion; L, the ligand ($L \in \{\text{OH}^-, \text{Cit}^-, \text{NH}_3, \text{H}_m\text{P}_2\text{O}_7^{m-4} \dots\}$); v_d and v_{ds} are bulk and surface diffusion rates of a components from the electrolyte bulk ($x = \infty$) to the electrode ($x = 0$) or the reaction layer ($x = \delta_p$) surface; k_{si} and k_{fi} , rate constants of electrochemical and chemical reactions; K_w , water equilibrium constant; $(X)_{ad}$, ad-atom; $(Y)_{cl}$, crystal lattice atom. This general scheme includes the chemical step corresponding to tungstate ions reduction by hydrogen ad-atoms occurring at high cathode current density realized under pulse electrolysis mode.

Although the equilibrium potentials for copper $E(\text{Cu}^{2+}/\text{Cu})$ and nickel $E(\text{Ni}^{2+}/\text{Ni})$ approach each other due to the complex formation in the pyrophosphate electrolyte, the value $E(\text{Cu}^{2+}/\text{Cu})$ more positive than $E(\text{Ni}^{2+}/\text{Ni})$. However, during codeposition, Ni^{2+} -ion discharge occurs with depolarization while Cu^{2+} , with superpolarization, therefore, both metals co-deposit as an alloy in certain conditions. When current density increases, the nickel content in the alloy drops, but when Ni(II)/Cu(II) salt concentration ratio increases, it grows regularly (Table 2), whereas the temperature rise results in an increasing copper content the alloy. The Ni–Cu alloy current efficiency grows to some extent when Ni(II)/Cu(II) salt concentration ratio and cathode current density increase.

As to nickel-palladium alloy deposition, the variation of the concentration ratio of main components in the electrolyte $\text{Pd}^{2+}/\text{Ni}^{2+}$ from 1:20 to 1:5 results in the decrease of nickel content in the alloy by 15 to 30 % within the current density range of 10 to 15 A/m^2 . So, the maximum nickel

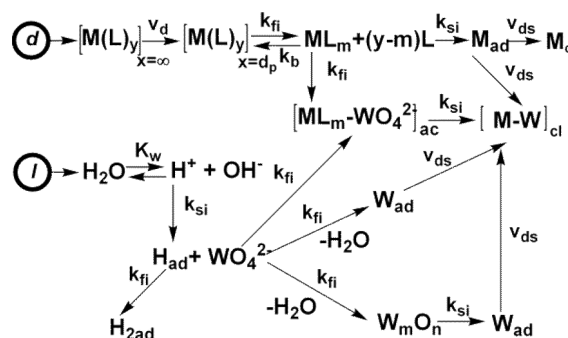


Fig. 2. General scheme of tungsten co-deposition with d-metals.

content in the alloy (42 %) is achieved at the cathode current density 12.5 A/m^2 and the concentration ratio of main components in the electrolyte 1:20. The current efficiency achieves the maximum value 82 % at $j_c = 12.5 \text{ A}/\text{m}^2$ and the alloy-forming component ratio 1:5. Having considered the kinetic criteria, we present the mechanism of Cu(Pd)–Ni alloy deposition (Fig. 3). It includes reactions of polyligand complex dissociation as well as ionic/molecular equilibrium in the electrolyte resulting in formation of various protonated particles. The same reduction mechanism for Cu–Ni and Pd–Ni alloy components can be noted, in contrast to Ni–W alloy ones.

Analysis of the alloy catalytic activity. To prove the correctness of the offered approach to determination of the material properties and adequacy of their quantitative characteristics, catalytic activity of individual metals (platinum, copper, and nickel) has been analyzed by calculating the kinetic parameters of hydrogen reduction process (j_H^0), charge transfer coefficient (α) and the Tafel equation constants **a** and **b**

Table 2. Effect of electrolysis parameters on composition and current efficiency of Ni–Cu alloy

Ni(II)/Cu(II)	T, K	j_c , A/m^2	Ce, %	$\omega(\text{Ni})$, %
1	293	20	98	10.1
		40	93	8.3
	313	20	97	2.4
		40	92	1.3
3	293	20	97	72.1
		40	92	23.8
	313	20	100	58.9
		40	99	19.8

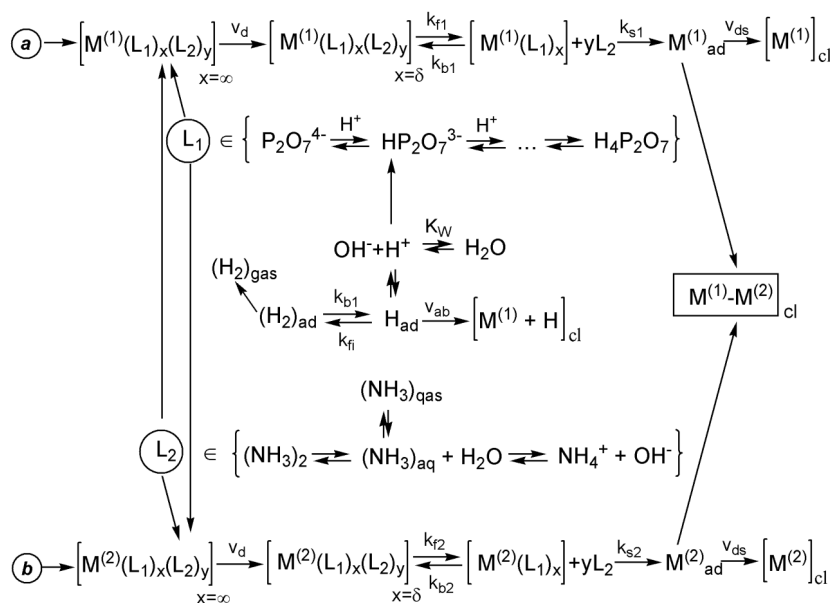


Fig. 3. General scheme of palladium (copper) co-deposition with *d*-metals from polyligand electrolytes.

basing on polarization dependences (Table 3). The comparison of kinetic parameters (see Table 3), calculated from experiment results and known from literature sources (theor.) [10], evidences their good agreement, and thus confirms the reasonability of proposed procedure application when determining the optimum catalytic alloy composition. The polarization measurements testify that among studied materials Ni–W alloys that possess the highest catalytic activity when $\omega(W)$ being within limits of 15 to 35 %. This $\omega(W)$ range corresponds completely to theoretical calculation data (Fig. 4b), thus reflecting the correctness of approaches developed in [5]. Moreover, the maximum activity of coatings, deposited on nickel substrate, is to be noted. This is probably due to the lowered internal stress level and the more perfect coating structure formation on substrates of similar nature. The $\lg j_H^0$ value differences observed for Ni–W alloy obtained on other

substrates might be explained by different coating porosity (and thus true surface area) which is diminished at rising overpotential of hydrogen evolution and its absorption during the alloy deposition in the Ni > Fe > Cu sequence. Thus, the hydrogen current exchange values on nickel, which is catalytically more active and similar to the coating in nature, are somewhat higher than on other substrates.

The Ni–Cu alloys have lower catalytic activity in comparison with Ni–W alloys, independent of the composition and substrate material. At the same time, the catalytic activity of both alloys exceeds the activities of alloy-forming components (Fig. 5), since Ni and Cu as well as Ni and W are located on different sides of the dependence (see Fig. 1). This fact completely corresponds to theoretical ideas concerning the synergic effect probability. The j_H^0 value for Ni–Cu alloy is close to that of nickel, so the interval of maximum $\lg j_H^0$ values obtained for

Table 3. Kinetic parameters of hydrogen evolution process on metals

Electrode material	-a		-b		α		$-\lg j_H^0$	
	exp.	theor.	exp.	theor.	exp.	theor.	exp.	theor.
Pt	0.11	0.10	0.022	0.030	–	–	3.65	3.33
Ni	0.68	0.63	0.120	0.110	0.49	0.54	5.67	5.72
Cu	0.96	0.87	0.124	0.120	0.48	0.50	7.74	7.25
W	–	–	–	–	–	–	–	6.4

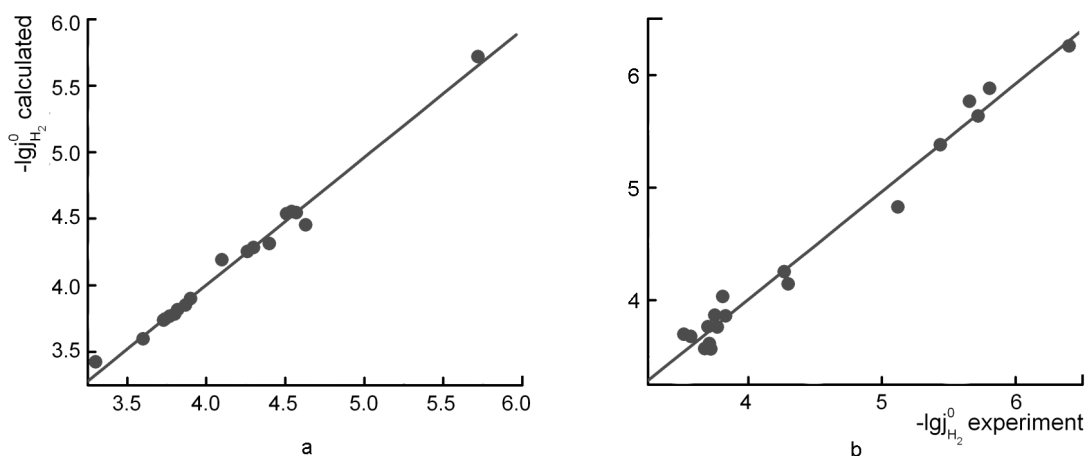


Fig. 4. Correlation between experimental and calculated values of hydrogen exchange current density for Ni-Pd (a) and Ni-W (b) alloys.

alloys with nickel content 85 to 95 %, permits to consider the contribution from this metal to the alloy properties to be dominant. The $\lg j_H^0$ values for the Ni-Cu alloys also depend on the substrate material, but the difference between them is insignificant, so the results obtained on the steel substrate that is widely used in practice, are illustrated. The maximum exchange current is attained for the alloy of 85 % nickel and 15 % copper. Hydrogen evolution overvoltage values on Ni-Cu alloys are considerably lower as compared to η_H on copper and, as well as exchange currents, are practically independent of the substrate material, although exceed Ni-W alloy overvoltage almost at 0.15 V. The catalytic activity of Ni-Pd alloy directly changes from the properties of the first metal to those of the second one (Fig. 5, curve 1) without any synergic effect because Ni and Pd are located on the same side of the dependence (see Fig. 1). Such behavior is in a complete agreement with calculated j_H^0 values (see Fig. 4a).

Consideration of the study results allows to conclude that nickel-tungsten alloys with tungsten content of 15 to 35 % deposited on nickel or its alloys are the most perspective catalytic materials of non-platinum group for the gas waste purification. The tungsten content increase in the specified range favors the coating amorphization [6], resulting in the stress relaxation and increased corrosion resistance, a sufficiently high catalytic activity being retained at the same time.

Ni-W alloy with an optimum $\omega(\text{Ni})$ content interval has been deposited from an

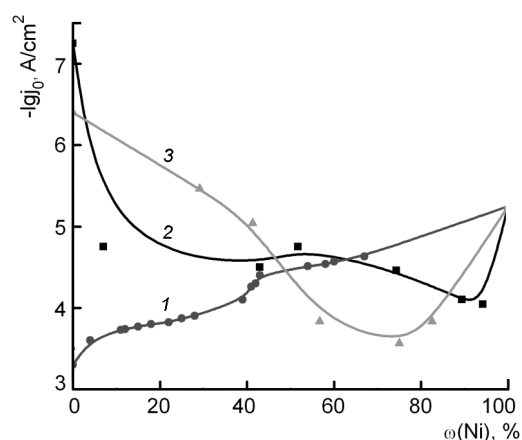


Fig. 5. Ni content influence on catalytic activity of Ni-Pd (1), Ni-Cu (2), Ni-W (3) alloys.

electrolyte with Ni(II)/W(VI) salt concentration ratio of 4 to 7 at the pulse current density 1200 A/m^2 , current pulses having been interchanged with pauses for the internal stress relaxation in the coatings. For Ni-Cu alloy, the optimum nickel content is provided at $j_c = 20 \text{ A/m}^2$, temperature 293 K and maximum Ni(II)/Cu(II) salt concentration ratio in the electrolyte.

The synthesized optimum composition Ni-W and Ni-Pd alloys were tested at stands simulating the diesel engine work [11]. The hydrocarbon and CO reduction in the emissions purification by 92–95 %, nitrogen oxide (NO_x) by 20–25 % was attained, the reaction ignition temperature being lowered. The optimistic work results concerning the noble metal replacement in neutralizers confirm the possibility of the hydrogen reduction model reaction use to

estimate the material catalytic activity in gaseous reactions.

To conclude, the influence of electrolysis parameters on the composition of nickel-copper, nickel-palladium and nickel-tungsten alloys established in experiments has provided preconditions for obtaining the materials with different component contents. The analysis of hydrogen exchange currents on individual metals in comparison with the catalytic activity in gaseous reactions has confirmed the reasonability of hydrogen reduction model reaction use for the estimation of the catalytic nickel-based alloys. The experimental kinetic parameters of hydrogen reduction reaction obtained for different nickel alloys agree well with predictions of the material catalytic activity based on chemical, physical and other characteristics of alloy-forming components. This opens new approach to replace noble metals in different catalytic systems. The catalytic synergism effect for nickel-copper and nickel-tungsten alloys has been established, optimum nickel alloy compositions have been defined and technological regimes of their deposition have been developed.

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Електрохімічний синтез каталітично активних сплавів

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Проаналізовано особливості очищення техногенних газоподібних викидів від вуглеводнів, оксидів нітрогену та вуглецю із застосуванням каталітичних нейтралізаторів. Відзначено актуальність заміни платиноїдів у каталізаторах на сплави і оксидні сполуки. Запропоновано використовувати реакцію виділення водню для оцінки каталітичної активності матеріалів, що синтезують. До перспективних засобів дизайну каталізаторів на металевих носіях віднесено електрохімічні методи. Для прогнозування властивостей сплавів використано залежність струму обміну від енергій зв'язку "метал-водень" і "метал-кисень". Оптимізовано режими синтезу сплавів нікель-паладій, нікель-мідь і нікель-вольфрам, склад яких відповідає максимальній каталітичній активності. Показано, що сплавам нікель-вольфрам та нікель-мідь притаманний синергетичний ефект.