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**PLASMOCHEMICAL PREPARATION OF SILVER NANOPARTICLES: THERMODYNAMICS AND KINETICS ANALYSIS OF THE PROCESS (p. 4–9)****Margarita Skiba**Ukrainian State University  
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The thermodynamics and kinetics analysis of the plasmochemical formation of silver nanoparticles is performed. The thermodynamics analysis is made on the basis of calculation of the Gibbs free energy of formation of silver nanoparticles in an aqueous medium by various methods. It was found that the Gibbs free energy in aqueous solutions increases with decreasing size of silver particles. Based on experimental data, it was determined that the average size of plasmochemically prepared particles depends on the initial concentration of silver ions in the solution and equals 36.5–60.1 nm for 0.25–3.0 mmol/l.

The kinetics of chemical conversion in aqueous solutions of silver nitrate under plasma treatment conditions in a gas-liquid plasmochemical batch reactor is investigated. The curves of  $\text{Ag}^+$  dependence on duration of plasmochemical treatment of solutions and initial concentration of silver ions are given. It is found that the process of plasmochemical formation of silver nanoparticles is the second-order reaction. The rate constant of formation of silver nanoparticles is  $k=0.07\text{--}1.53\text{ mol}^{-1}\cdot\text{dm}^3\cdot\text{min}^{-1}$  depending on the initial concentration of silver ions. It is shown that the formation of silver nanodispersions under plasma discharge impact is characterized by the presence of the peak  $\lambda_{\text{max}}=400\text{--}440\text{ nm}$ .

**Keywords:** low-temperature plasma, discharge, formation, process, Gibbs free energy, thermodynamic potential, Nernst equation, rate constant.

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**DETERMINING THE PHYSICAL-CHEMICAL CHARACTERISTICS OF THE CARBON-THERMAL REDUCTION OF SCALE OF TUNGSTEN HIGH-SPEED STEELS (p. 10–15)**

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We determined that scale of the high-speed steel R18 is composed of the phases of  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ , with the presence of alloying elements as the replacement atoms. The microstructure is disordered and non-uniform. In the examined area, in addition to Fe, we revealed the presence of, % by weight: W – 16.34, Cr – 2.68, V – 1.82, and others. The content of O was 15.32 %. It was established that the reduction of scale at 1,523 K proceeds with the formation of  $\alpha$ -Fe and carbides  $\text{Fe}_3\text{W}_3\text{C}$ ,  $(\text{Fe}, \text{Cr})_7\text{C}_3$ ,  $\text{W}_2\text{C}$ ,  $\text{V}_2\text{C}$ ,  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_2\text{C}$ . Manifestation of carbides of alloying elements decreased with an increase in the degree of reduction. The microstructure of reduction products is heterogeneous, containing particles with a different content of alloying elements and has a spongy structure. The conditions are provided for the absence of phases subject to sublimation. We conducted experimental-industrial tests of using the metallized scale while smelting high-speed steel with a degree of disposal of alloying elements at the level of 92–94 %. Improvement of environmental safety was implemented by the replacement of reduction melting with the newest methods of powder metallurgy employing the solid-phase reduction.

**Keywords:** alloyed technogenic wastes, high speed steel, carbon-thermal reduction, microscopic analysis, carbide formation.

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**COMPARATIVE INVESTIGATION OF ELECTROCHEMICALLY SYNTHESIZED ( $\alpha+\beta$ ) LAYERED NICKEL HYDROXIDE WITH MIXTURE OF  $\alpha$ -Ni(OH)<sub>2</sub> AND  $\beta$ -Ni(OH)<sub>2</sub> (p. 16–22)**

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Nickel hydroxides, owing to their high electrochemical activity are promising materials for chemical power sources (alkaline accumulators, lithium accumulators and hybrid supercapacitors), electrochromic devices, electrochemical oxidation of organic compounds. The most promising is nickel hydroxide that contains both  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>. The aim of the research was to determine the properties of model mechanical mixtures with different ratios between  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> and to prove the hypothesis about the layered structure of nickel hydroxide samples synthesized in the slit diaphragm electrolyzer by means of comparative study.

The XRD patterns of samples composed of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> mixture show peaks corresponding to separate phases. By means of cyclic voltamperometry, it was discovered; that mixture samples do not show an oxidation peak during the first cycle, while two reduction peaks that correspond to reduction of  $\alpha$  and  $\beta$  components are observed on the cathodic curve. A synergetic effect, which results in significant improvement in electrochemical activity of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> mixture was discovered – specific reduction peak current values are 2.3 A/g (20 %  $\alpha$ -phase), 3.5 A/g (30 %  $\alpha$ -phase), 6.9 A/g (50 %  $\alpha$ -phase), which exceed those of initial  $\beta$ -Ni(OH)<sub>2</sub> (1.5 A/g) and  $\alpha$ -Ni(OH)<sub>2</sub> (2.0 A/g). By means of XRD analysis, it was discovered; that Ni(OH)<sub>2</sub> samples synthesized in the SDE are composed of  $\alpha$  and  $\beta$  and a series of intermediate structures. These samples demonstrate high electrochemical activity: presence of a defined oxidation peak during the first cycle, single reduction peaks with high specific currents of 6.5–11.7 A/g. The comparative analysis has revealed that electrochemically synthesized samples are composed of  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub>, but are not a mixture of these phases, owing to significantly different electrochemical behavior from mixture samples. Using mechanical modeling, the layered ( $\alpha+\beta$ ) structure of samples electrochemically synthesized in the slit diaphragm electrolyzer has been proved by contradiction.

**Keywords:** ( $\alpha+\beta$ ) layered structure, nickel hydroxide, slit diaphragm electrolyzer, mixture of  $\alpha$  and  $\beta$  nickel hydroxides.

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**ASPECTS OF MAKING OF A COMPOSITE MATERIAL WHEN USING RED MUD (p. 23–28)**

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A composite material was developed with the polymeric binder at the elevated concentration of a technogenic raw material, 75 % by weight of red mud, as the filler. Dependence of indicators of composite properties on the content of the filler at the differentiation of varieties of polymer binders was established. When applying the binder Acronal 290 D, the water absorption minimum is 3.2–3.5 % by weight, the maximum is 5.0–5.3 % by weight. When applying Pliolite AC-4, the water absorption minimum is 0.83–0.96 % by weight, the maximum is 3.0–3.2 % by weight. When replacing the binder from the aqueous dispersion with the varnish dispersion, it is observed that water absorption level decreases by two times, but the character of dependence of this indicator on concentration of the filler remains unchanged. Analysis of hydrophobicity as a factor of improvement of operational properties of the composite showed that

the maximum values of wetting angle of 130–136 degrees are registered at the concentration of the filler of 75 % by weight.

We established features of the porous structure of the composite as a factor of influence on its properties. Total porosity and development of its varieties depend on the type of the polymeric binder. Indicators of total porosity are at the level of 9.3–11.8 % against 8.6–23.9 %, and the indicators of open porosity are at a significantly lower level of 0.96–3.15 versus 3.49–5.32 over the same range of changes in the concentrations of the filler when using Pliolite AC-4 compared to Acronal 290 D.

It was shown that the developed material is distinguished by decorative (red color) and physical-technical characteristics that are important for modern architecture, which contributes to solving comprehensively the tasks on extending the range of composites and on the industrial waste disposal.

**Keywords:** polymeric composite, filler, red mud, porous structure, styrene-acrylate, cellulose thickener.

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### RESEARCH INTO EFFECT OF COMPLEX NANOMODIFIERS ON THE STRENGTH OF FINE-GRAINED CONCRETE (p. 29–33)

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We studied the effect of nanomodifiers, which consist of a mixture of a surface-active substance that creates micelles, and mineral modifying admixtures. A special feature of present research is studying a simultaneous effect of surface-active substances that create micelles, and mineral modifying admixtures, on a change in the strength of fine-grained concretes.

The modifying admixtures that are most widely used at present are microsilica and metakaolin. They have, however, certain disadvantages. The shortcomings of microsilica include a lack of stability in its properties as it represents the industrial waste. Metakaolin is rather costly because of high energy costs for its production. That is why we employed microsilica, lime, gypsum, and natural kaolin as the modifying admixtures in this research.

It was established in the course of our study it that the use of nanomodifiers, which consist of micelles solutions and mineral modifying admixtures, strengthens the rate of formation and the magnitude of strength of fine-grained concretes. The results of research showed that the processes of strength formation of concrete, when using gypsum or lime as a modifying admixture, speed up by 1.5–2 times at the initial period of its hardening (3 days). Subsequently, the rate of concrete strength formation, when it has a nanomodifier based on lime or gypsum, continues to exceed the rate of formation of strength of the concrete, which contains only MSAS,

and concrete without additives. At the age of 28 days the nanomodified concrete demonstrates strength that is 70–110 % larger than the strength of concrete without additives.

Thus, it was proved that in order to control processes of cement setting and strength formation of an artificial stone, which is obtained in the process of cement hydration, it is possible to use the micellar catalysis. Applying the micelles filled with modifying admixtures increases the absolute magnitude of compressive strength of fine-grained concretes.

The results obtained make it possible to reduce consumption of Portland cement when manufacturing fine-grained concretes, or to significantly reduce the time needed to fabricate monolithic structures from the specified concretes.

**Keywords:** fine-grained concrete, micelles, surface-active substances, nanofiller, nanomodifier, strength.

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## DEVELOPMENT OF NANOMODIFIED RAPID HARDENING FIBER-REINFORCED CONCRETES FOR SPECIAL-PURPOSE FACILITIES (p. 34–41)

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Experimental studies confirmed that the development of rapid-hardening concretes with high resistance to a high-velocity impact for special-purpose facilities is achieved through the multilevel modification of the structure. The introduction of dispersed fibers ensures optimization of a structure at the macro- and mesolevel. At the micro- and nano-levels – by energetically active ultra- and nanofine mineral additives and a high-reducing polycarboxylate superplasticizer. We established high efficiency of the influence of an organo-mineral nanomodifier containing polycarboxylate superplasticizer, micro- and nano-silica on the workability of the concrete mixture and the kinetics of concrete hardening based on it. We detected a directional formation of the structure and the preset properties of concretes of highly flowing mixtures at both early and late stages of hardening. We established that the early strength of nanomodified concretes increases by 4.8–5.1 times, and strength after 28 days – by 2.0–2.3 times. The study showed that an increase in the number of contacts, reduction in size and the number of initial defects and increasing the homogeneity of nanomodified concrete leads to the creation of a dense, fine-porous, less defective structure. Ensuring such a structure of nanomodified fiber-reinforced concretes leads to an increase in deformation characteristics, specifically stiffness and elasticity, which make it possible to withstand greater stresses at a constant value of relative deformations. We carried out

tests on resistance of nanomodified fiber-reinforced concretes under conditions of action of a high-velocity impact that indicate their increased impact viscosity. Thus, we can argue about the relevance of a mechanism for the formation of regulated properties of nanomodified fiber-reinforced concretes and about practical attractiveness of the proposed technological solutions.

**Keywords:** nanomodification, dispersed reinforcement, organo-mineral additive, rapid-hardening concrete, deformation properties, high-velocity impact.

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## DEVELOPMENT OF THE ELECTROCHEMICAL SYNTHESIS METHOD OF ULTRAFINE COBALT POWDER FOR A SUPERALLOY PRODUCTION (p. 41–47)

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The electrochemical synthesis method for the preparation of ultrafine cobalt powder from the sulfate-ammonium electrolyte for the preparation of superalloys; has been developed. It was proposed to introduce ammonia to the electrolyte until pH=11. The electrolyte composition and the mechanism behind electrochemical processes during cobalt powder synthesis have been studied. The formation of the Co<sup>2+</sup>ammine complex has been observed. The precipitate dissolved in the mother liquor during a week, with the formation of a purple-red solution. By recording cathodic and cyclic cathodic-anodic curves, it was discovered that the solution with dissolved precipitate contained Co<sup>3+</sup>. It was revealed that the synthesis process occurs in two stages «Co<sup>3+</sup>-Co<sup>2+</sup>-Co<sup>0</sup>», which results in the increased polarization and formation of ultrafine cobalt powder. The influence of electrolyte temperature on electrolysis and powder characteristics has been studied. It was revealed that higher temperatures lead to larger particle size and formation of compact metal particles. It has been determined that the maximum electrolyte temperature should not exceed 30 °C. It is shown that under these conditions, the Co powder is composed of spherical particles that form coral-like aggregates with the size of 35–150 μm, which can be easily ground. The cobalt powder forms with the cathodic current yield of 39 % and specific power consumption of 48 kW·h/kg, which indicates a high effectiveness of the developed method.

**Keywords:** cobalt (+3) ammine complex, cobalt powder, superalloys, dendrite.

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## CHEMICAL DEPOSITION OF CDS FILMS FROM AMMONIAC-THIOUREA SOLUTIONS (p. 48–52)

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This paper investigates the process of chemical deposition of CdS films from ammonia-thiourea solutions. It was established that a change in the turbidity of solution occurs in the process of chemical deposition. The results of visual observations and measurement of turbidity of solution allowed us to establish that these dependences could be used to monitor the status of the process. Visual observations correlate with the obtained dependences for turbidity and suggest that the chemical deposition of CdS includes the accumulation of colloidal-dispersed precipitate in the volume of solution, agglomeration of CdS particles, and a stationary mode of the CdS film growth at the surface of a sample. The first stage of the process

is matched by a sharp increase in the turbidity of solution; the second stage is accompanied by the emergence of a maximum in the dependence. No significant change in turbidity occurs at the third stage. The observation of morphology of the resulting precipitate allowed us to establish working concentrations of reagents in solution, which ensure obtaining a high-quality CdS film with a thickness not less than 100  $\mu\text{m}$ . The working concentrations of cadmium chloride, ammonia, and thiourea are, respectively, 1.8, 0.6, and 8.4  $\text{g}\cdot\text{l}^{-1}$ .

It was assumed that the CdS formation is accompanied by the formation of thiourea. This is confirmed by data on the analysis of a working solution. An analysis of the solution revealed high concentrations of the  $\text{CO}_3^{2-}$  ions, which are a product of the thiourea decomposition. The data obtained are a preliminary stage in the development of a technology of chemical deposition of CdS films from ammonia-thiourea solutions.

**Keywords:** photoelectric converters, cadmium sulfide, chemical deposition, turbidity, ammoniac-thiourea solutions.

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**RESEARCH INTO EPOXIDATION PROCESS OF THE C<sub>9</sub> FRACTION HYDROCARBONS AND UNSATURATED CO-OLIGOMERS BY PEROXYETHANOIC ACID (p. 53–60)**

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We have studied regularities of the epoxidation process of the C<sub>9</sub> fraction of liquid by-products of the pyrolysis of hydrocarbons and co-oligomers based on the C<sub>9</sub> fraction with peracetic acid. It is established that the use of the specified system makes it possible to achieve high values of conversion for double bonds and the selectivity of epoxidation process, sufficiently high yield of epoxy-containing co-oligomers. We established the possibility to use the C<sub>9</sub> fraction of liquid by-products of hydrocarbon pyrolysis (the accompanying product of ethylene production) as a raw material for obtaining epoxides, which is a rational method in order to dispose of the fraction. We analyzed experimental dependences of reagents consumption and the formation of epoxide in the reaction of the C<sub>9</sub> fraction epoxidation. It was established that the resulting values for selectivities of the epoxidation process by double bonds when obtaining epoxy-containing co-oligomers are the highest in the case of epoxidation of co-oligomers, synthesized by the heterogeneous catalytic co-oligomerization of the C<sub>9</sub> fraction S9 hydrocarbons using, as a catalyst, activated bentonite clay. The synthesized epoxy-containing co-oligomers retain residual unsaturation. It is obvious that the unsaturated bonds of styrene, vinyl toluene,  $\alpha$ -methyl styrene, allylbenzene links at the ends of a co-oligomer macromolecules are easily epoxidized. The selectivity of epoxidation of co-oligomers, obtained by different methods of co-oligomerization of the C<sub>9</sub> fraction hydrocarbons (homogeneous catalytic, heterogeneous catalytic, initiated, and thermal) is different (60.2–96.1 %) and depends on the nature of the starting co-oligomer. Using the methods of <sup>1</sup>H NMR-, Raman-, and infrared spectroscopy, we confirmed the high content of epoxy groups in the composition of epoxy-containing co-oligomers and the progress of the epoxidation reaction.

Applying the method of <sup>1</sup>H NMR spectroscopy, we established the presence of epoxy groups formed based on the resulting vinyl double bonds of co-oligomers. Due to the content of oxirane oxygen and a high reaction ability of the oxirane ring, epoxy-containing co-oligomers can act as the raw material for subsequent obtaining of various chemical substances: glycols, carbonyl compounds, plasticizers, polymers.

**Keywords:** C<sub>9</sub> fraction, epoxy-containing co-oligomers, epoxidation selectivity, epoxy number, IR spectroscopy, Raman spectroscopy, <sup>1</sup>H NMR spectroscopy.

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