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On the Nature of Decrease in the Particles Size of Nanostructured Nickel Oxide Obtained by the Sol-Gel Method in the Presence of Surfactants

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Abstract—A processes of formation of nanostructured powders of nickel oxide by annealing in the temperature range of 200–700°C of the nickel hydroxide obtained by the sol–gel method at 80°C from solutions of nickel nitrate by precipitation with alkali in the presence of surfactant AF-12 (polyethylene oxide alkylphenyl ether) was investigated. The formation of nanostructured powders of nickel oxide in the presence of a surfactant reduces the size of nanoparticles to 20–25 nm, which is 1.5 times smaller than the particles obtained without a surfactant. The effective influence of surfactant on the particle size begins in the temperature range of its decomposition and evaporation equal 350–400°C.

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Synthesis and study of the properties of metal oxides nanoparticles is at present a promising area of science and industry. The transition metal oxides of nanoscale size can find wide practical application. Among them the nickel oxide should be emphasized, since this compound is interesting due to its physico-chemical properties [1]. The nickel oxide is widely used as catalyst [2]. Among the approaches developed in recent times to obtaining catalysts with high activity there is the use of thin films with particles of a metal or its oxide deposited on them [3].

The particles of nanometer-sized metal oxides, including nickel oxide, may be used as the material for electrodes in lithium power sources, whose electric capacity reaches 700 mA h g^{-1} [4]. Using NiO nano-powder it is possible to reduce the proportion of metal in the cermet anodes of fuel cells to 40–50 wt % with simultaneous reducing the resistivity to $(4–13)\times 10^{-4}$ Ω cm, which is impossible in the case of the nickel–cermet anodes obtained by conventional methods [5]. The nickel oxide is used also as a magnetic material. Therefore the development of simple and effective methods of synthesis of the oxides in nanostructured state is relevant. The most frequently the nanoparticles are synthesized in solution by a sol–gel method that includes exchange and hydrolysis reactions. The ultrafine products obtained in such reactions have a highly developed specific surface and, respectively, their surface energy is high. Therefore the ultrafine systems in most cases are thermodynamically non-equilibrium and the resulting particles tend to aggregate [6, 7]. To prevent the aggregation of fine particles organic surfactants are commonly used (surface active compounds, SAC) [8–10]. In [11] as the surfactants alcohols with various length of hydrocarbon chains are used: ethanol, propanol, and butanol. It is known that the formation of metal oxides by the sol–gel method proceeds consecutively through formation of hydroxide sol, then hydroxide gel, and the subsequent dehydration of the latter followed by high-temperature annealing of the intermediate formed to the metal oxide powder. It was found in [11] that at the temperature of the annealing up to about 400°C the density of cerium oxide powder pre-calcined under a pressure does not depend on the type of alcohol, and only at annealing above this temperature the oxide derived from an alcohol with a long hydrocarbon chain has slightly higher density of the cake. However, to date the nature of the influence of surfactants on the

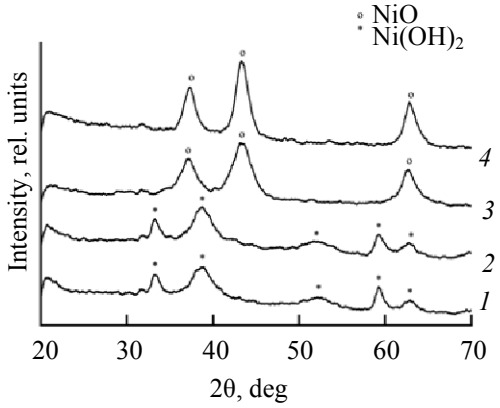

Fig. 1. Diffraction patterns of samples (with AF-12) obtained at different temperatures of dehydration: (*1*) 50°C, (*2*) 200°C, (*3*) 300°C, and (*4*) 400°C.

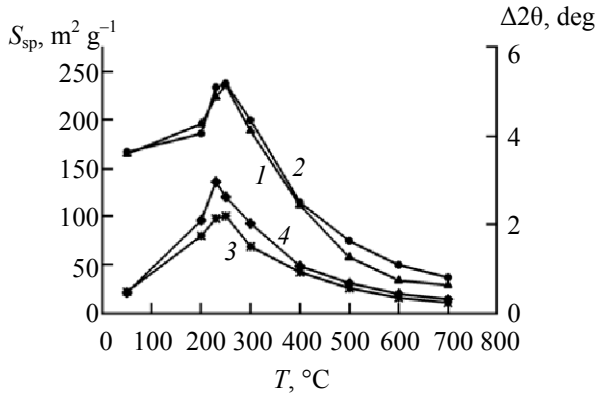

Fig. 2. Dependence of specific surface on temperature of the samples (*1*) obtained without surfactant AF-12 and (*2*) with surfactant AF-12; (*3*) broadening of the reflex (111) on half-height 2θ degrees for the samples without surfactant AF-12; and (*4*) the same in the presence of surfactant AF-12.

gelation and the formation of nanostructured metal oxide powders at annealing in air at elevated temperatures remains unexplored. Yet more natural is an assumption that low molecular weight alcohols evaporate even at low annealing temperatures due to the high pressure of their vapors; this also concerns possible products of decomposition of metal alcoxides [12].

The research performed earlier [13] consisted in the study of the formation mechanism of nanodispersed nickel oxide at the dehydration of nickel hydroxide obtained by the precipitation with alkali from aqueous solutions of nickel nitrate, with iso-propanol as a surfactant, and by subsequent annealing of washed and dried precipitate. Obviously, in the initial stages of formation of sol and gel alcohol is evaporated from the system, therefore to investigate the effect of surfactant on the processes and on the subsequent formation of nanostructured nickel oxide it is necessary to use additionally a surfactant with a much lower vapor pressure. Such requirements are consistent with surfactants with longer hydrocarbon chains.

The aim of this work was to study the effect of long-chain nonionic surfactant AF-12, alkylphenyl ether of polyethylene oxide, $C_9H_{19}(C_6H_4)(CH_2OCH_2)_{12}OH$, introduced into the reaction zone, on the dispersion of nano-structured products formed sequentially in the specified stages of the dehydration of nickel hydroxide and nickel oxide formation process.

The nanostructured nickel oxide powders obtained were studied by various methods described in the experimental section. Fig. 1 shows the results of X-ray phase analysis of the samples synthesized using AF-12. Diffraction patterns of the samples obtained with surfactant AF-12 and without it are identical, as can be seen by comparing the diffraction patterns we registered with those published in [13] for the process without surfactant AF-12. The results indicate that the products of the synthesis dried at 50°C are mixtures of an amorphous phase with a polycrystalline nickel hydroxide. However, annealing even at the temperature 200°C affords a phase of nickel oxide. The large reflection width points to nanocrystallite state of the product. Increase in the annealing temperature leads to the increase in crystallinity and in the nickel oxide fraction. Finally, in the temperature range 300–400°C the phase of nanocrystalline hydroxide disappears and remains only a phase of nickel oxide, whose crystallinity increases with further increase in temperature.

Analysis of the data of measuring the specific surface area of these samples shows that the chosen method of synthesis allows to obtain nanoporous hydrolysis products, which upon subsequent annealing are transformed into nanostructured powders. Figure 2 shows the dependence of specific surface of the samples obtained in the presence of AF-12 and without (curves *1* and *2*) on the annealing temperature, and the broadening of the reflections (111) of Δ2θ diffraction patterns at their half-heights (curves *3* and *4*) characterizing the change in size of pores (for gels), and particles (for powders) of crystallites, respectively. The specific surface area of dispersed samples increases in the temperature range 50–230°C. This

stage is characterized by the formation of xerogels [13], with an increase in porosity associated with the destruction of the hydrogel. The presence of surfactant AF-12 additives shows no effect at this stage. Further increase in annealing temperature leads to a sharp decrease in specific surface area of samples associated with the processes of coalescence of the particles of nickel oxide. In the region of medium temperatures of annealing, the values of specific surface area of powders obtained with surfactant AF-12 and without it remain similar, and only at temperatures above 400°C the value of specific surface area of samples prepared with surfactant AF-12 becomes larger. This suggests that in systems with AF-12 the coalescence of particles at temperatures above 400°C is slightly lower than in the samples without surfactant. The characteristic feature of the process is the weak influence of surfactant AF-12 on the size of crystallites in the whole temperature region of annealing, which follows from the proximity of the values of X-ray coherent scattering in the two processes (Fig. 2, curves *3*, *4*). However, a monotonic decrease in X-ray coherent scattering at increase in temperature above 230°C indicates agglomeration of crystallites. It is worth noting that crystallite size determined from the data of X-ray diffraction method (the broadening of reflexes, Scherrer method), does not necessarily coincide with the size of ultrafine particles, defined from the data on the specific area of the sample surface measured by the method of inert gas adsorption. The particles may contain several crystallites, which have boundaries between themselves and partly with the gas phase. What hinders coalescence of particles of the products of xerogel dehydration at temperatures above 400°C in a system with AF-12?

It should be noted that the data presented here indicate that the surfactant AF-12 is not washed out completely at the stage of purification of precipitate. The results of thermal analysis of the process of annealing the samples with surfactant AF-12 and without it in an atmosphere of He and Ar/O_2 mixture (ratio 4:1) are shown in Fig. 3. The mass loss up to temperature 250°C is connected with the loss of free water and adsorbed isopropanol. At this temperature the product composition corresponds to the formula $Ni(OH)_2$ [13], although the phase analysis gives a mixture of hydroxide and nickel oxide. The remaining amount of OH groups corresponds to the formation of the xerogel. Above this temperature begins the xerogel dehydration [13].

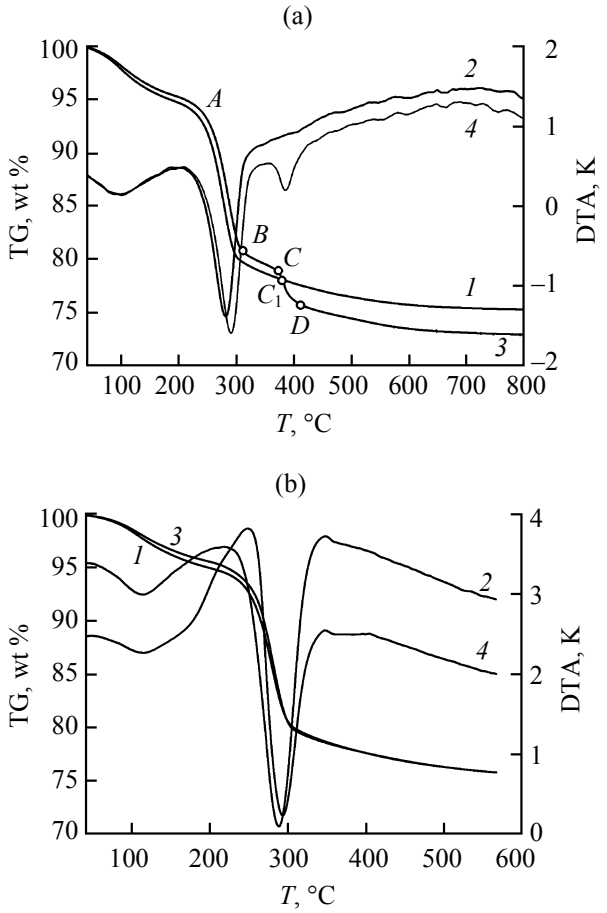

Fig. 3. (a) The curves of thermal analysis of samples in helium: (*1*) TG without surfactant AF-12, (*2*) DTA without surfactant AF-12, (*3*) TG with AF-12, (*4*) DTA with AF-12; (b) The curves of thermal analysis of samples in an argon–oxygen mixture: (*1*) TG without surfactant AF-12, (*2*) DTA without surfactant AF-12, (*3*) TG with AF-12, (*4*) DTA with AF-12.

The mass loss curves of the samples without AF-12 in He and Ar/O_2 are identical, while the DTA curves are identical only qualitatively (Fig. 3b) and indicate the *endo*-effects associated with the samples dehydration and evaporation of adsorbed isopropanol. The curve of mass loss of the sample with surfactant AF-12 (Fig. 3b) in the presence of oxygen is identical to the curve for the sample without surfactant, but is characterized by a lesser rate of mass loss. For the sample with an AF-12 the *endo*-effect appears after a significant *exo*-effect that can be associated only with thermal transformation of the surfactant AF-12, and threrafter the rate of dehydration of the sample with decomposed AF-12 increases, and at 290°C the mass loss of samples with AF-12 and without become comparable.

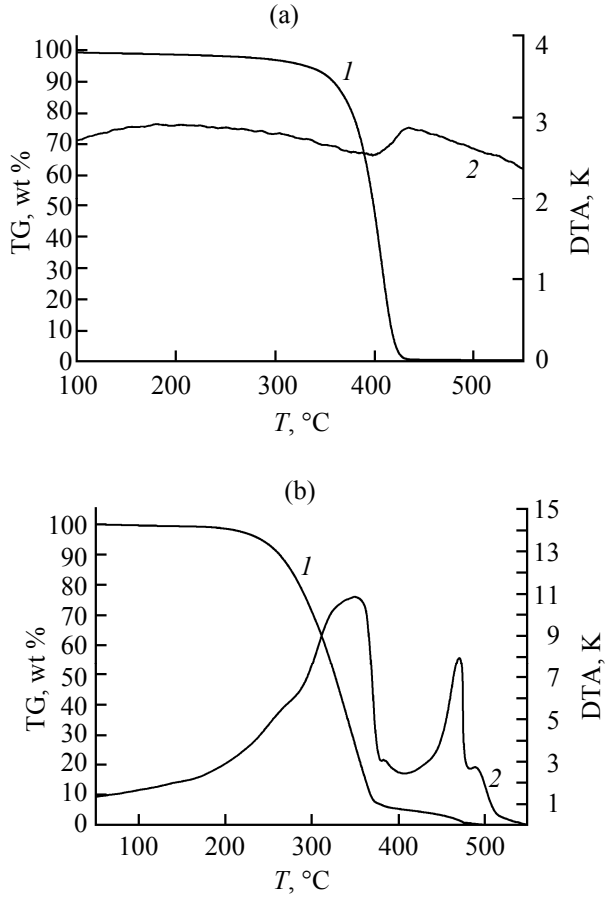

Fig. 4. (a) The curves of thermal analysis of AF-12 in helium. (*1*) TG and (*2*) DTA. (b) The curves of thermal analysis of AF-12 in the presence of oxygen: (*1*) TG and (*2*) DTA.

In contrast to these transformations, the curve of mass loss of the sample with surfactant AF-12 in an inert atmosphere is characterized by two steps (Fig. 3a). To the point *C* the mass loss curves are almost identical. There is only a slight slowdown in the relative loss of mass. After this point, there is an additional rather sharp mass loss which may be associated with the transformation of the surfactant AF-12, as evidenced by the second *endo*-effect.

Figure 4 demonstrates the results of thermal analysis of AF-12 in the atmosphere of He and Ar/O_2, which implies that in an inert atmosphere (Fig. 4a) there is only a process of evaporation increasing sharply at about 350°C. This indicates a low vapor pressure of the AF-12 at the temperature of formation and dehydration of hydrogel and xerogels below 300°C. Thus, the deceleration in the mass loss before point *C* can be explained only by blocking the surface of the particle with the effective surfactant. It should be noted that the concentration AF-12 in the initial solution 5.5×10^{-4} mol l^{-1} was chosen not to exceed the limit of the critical concentration of the micelle formation. Washing the product of the synthesis with water reduces the content of AF-12 in the system considerably. The found mass loss between points *C* and *D* equals to 2.8 mg, and taking the initial sample mass 56.7 mg as 100%, this corresponds to the amount of water loss due to dehydration of the xerogel ~0.6 mg (C–C_1) and to removal of ~2.2 mg of AF-12 from the system due to evaporation and decomposition (C_1–D). From these data and taking into account the specific surface area of the product at 375°C according to Fig. 2, we obtain the amount of adsorbed surfactant AF-12 equal to 3×10^{-6} M. The obtained amount of adsorbed surfactant corresponds to the degree of the surface coverage of the dehydration products at the point *C* equal to 10%. However, it should be taken into account that the molecule of AF-12 contains 12 adsorption-active CH_2OCH_2 groups that on adsorbtion on the surface increase the degree of its coverage with the surfactant. Thus, it is the presence of adsorbed surfactant AF-12 that leads to a marked inhibition of the dehydration of the products at the temperature below 400°C. After evaporation of AF-12 at ~375°C the process of dehydration of the xerogel is continued.

At the thermal transformation of AF-12 surfactant in the presence of oxygen (Fig. 4b) the mass loss of AF-12 in the region of 250–375°C is accompanied by a strong *exo*-effect. In the temperature range 370–430°C the mass loss is slowing and is characterized by a decrease in the *exo*-effect. But at the end of this stage there is a strong two-step *exo*-effect. Such a transformation of AF-12 in the presence of oxygen can be attributed to its thermal decomposition in the first stage and the formation of solid products of decomposition, presumably resin or even graphite. In the second stage, apparently, there is a burn-out of these products. Similar effects are observed on the derivatograms of dehydration of hydrogels in an atmosphere of Ar/O_2 (Fig. 3b). The set of described transformations of surfactant AF-12 results in the partial suppression of coalescence of particles at the temperatures above 400°C, which follows from Fig. 2 (curves *1* and *2*).

Using the found values of pycnometric density ρ (Fig. 5) and the specific surface area S_{sp} (Fig. 2) of the samples, we found the average diameters of particles in the ash, hydrogel, xerogel, and nanostructured nickel oxide in a spherical approximation, from the

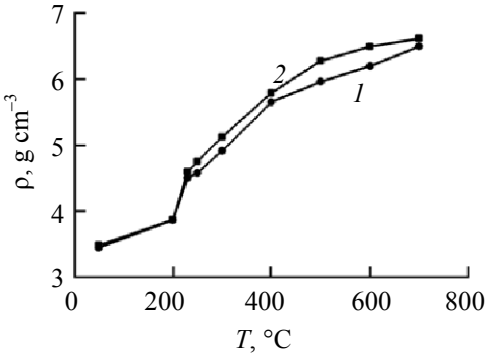

Fig. 5. Density vs. change in temperature of dehydration of samples obtained: (*1*) with surfactant AF-12 and (*2*) without surfactant AF-12.

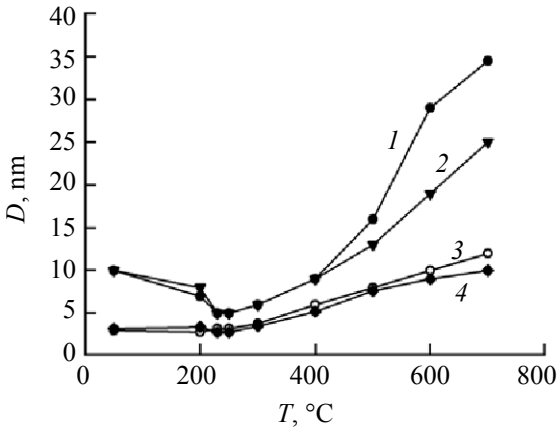

Fig. 6. Dependence on the temperature of dehydration of particle sizes of samples synthesized at 80°C: (*1*, *3*) without surfactant AF-12, (*2*, *4*) with surfactant AF-12; the values are found by equations from [14] and [15], respectively.

known equation connecting these values [14]. The calculation results for the samples obtained with surfactant AF-12 and without it, at different annealing temperatures, are shown in Fig. 6, curves *1* and *2*. As can be seen, in both cases after the synthesis of nickel hydroxide the particles with a diameter of about 10 nm are formed. Analysis of changes in particle size during annealing shows that at 230°C their smallest size is reached, equal 4–5 nm, and at further increase in temperature the enlargement of their size is observed. No significant difference occurs between the sizes of particles obtained with and without the addition of surfactant AF-12 at annealing to ~400°C. Figure 6 demonstrates the changes in the crystallite size obtained with the Scherrer equation [15]. As follows from the results obtained, the particle sizes exeed 2–3 times the size of the crystallites. This means that each particle contains on the average 10 to 20 crystallites. The established facts indicate that the coalescence of the crystallites occurs at their interface, where the presence of the AF-12 surfactant is practically excluded.

From the figure it also follows that above 400°C the NiO particle size in a system with AF-12 is less than in the system without it, and in the final product annealed in the 600–700°C the particle size is by 30–50% smaller. Figure 7 shows photographs of nickel oxide after annealing at 700°C confirming the accuracy of the values of particle sizes found above by indirect methods.

Thus, it is found that the formation of nanostructured powders of nickel oxide by sol–gel method from nitrate solutions by precipitation of nickel

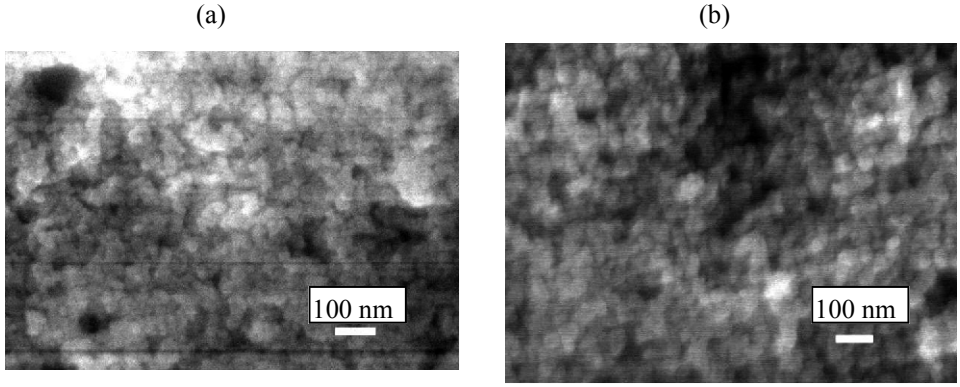

Fig. 7. Photomicrographs of the particles of nickel oxide dehydrated at 700°C obtained using scanning electron microscopy: (a) synthesized with surfactant AF-12 and (b) synthesized without surfactant.

hydroxide with a solution of alkali in the presence of AF-12 can reduce the size of particles 1.5-fold compared with the particles obtained without it. Effect of low molecular weight alcohols, for example, isopropanol, on the particle size stops at the stage of gelation due to the high vapor pressure of these substances and, consequently, due to their evaporation from the system. To reduce the rate of accretion of the nickel oxide nanosize particles at temperatures above 400°C, it is useful to add into the system a high-molecular surfactant of AF-12 type, which has low vapor pressure and high temperature of decomposition into volatile products. Reducing the rate of accretion of particles in these systems is probably the result of the blocking the surface with organic tar or graphite, which eventually burn out.

EXPERIMENTAL

We used Ni $(NO_3)_2 \cdot 6H_2O$ of analytical grade, NaOH of analytical grade, isopropyl alcohol of qualification OP-1 high purity. Solutions of nickel nitrate of concentration ~0.25 M and sodium hydroxide of 1.0 M, 350 ml each (to a solution of nickel nitrate was added 50 ml of isopropanol) were placed in different vessels and introduced into the reactor containing 10 ml of hot solution of NaOH at a rate of about 100 drops per minute at continuous stirring with a mechanical stirrer within 1.5–2.0 h. Amount of the added isopropanol was 0.06 g per one cm^3 of solution, which corresponded to the number of the alcohol molecules 10^{17} per 1 cm^2 of the surface of formed nanostructured nickel hydroxide, as determined by the results of the synthesis. It is known that for the formation of an adsorbed monolayer it is enough to have ~10^{14} molecules. After deposition of the precipitate, the stirring was continued for 30 min. The temperature of deposition of nickel hydroxide was 80°C, which was maintained during the experiment using a water bath. The precipitated hydroxide was washed on a Büchner funnel with a large amounts of water (~ 2 l) to a neutral medium and dried at 50°C to a constant weight, then it was ground in an agate mortar. The achievement of permanent weight indicated that free water and not chemisorbed isopropyl alcohol were evaporated from the system. By analogy with the known facts of the stability of chemisorbed monolayer of alcohol on the surface of some transition metal oxides (Cr, Fe, Mo) [16], in this case the existence of an adsorbed monolayer of alcohol on the surface of nickel hydroxide was accepted after washing with water at room temperature and drying at 50°C.

A similar procedure of investigation was used at the introduction to the system of a surfactant with a long hydrocarbon chain. We used alkylphenyl ether of polyethylene oxide with the number of ethoxy groups 12 (AF-12), which is chemically stable in alkaline and acidic media [17]. The surfactant was added dropwise in equal amounts in the initial nitrate and precipitant solutions. The concentration of AF-12 in the reaction medium was about 5.5×10^{-4} mol l^{-1}, which corresponded to the critical concentration of micelle formation. However, at subsequent washing of the precipitated product an abundant water foaming was observed and washing out of AF-12 till the final stage of purification.

Yield of the final product with respect to nickel was 100% for both processes. Samples of nickel hydroxide obtained after drying at 50°C were subjected to gravimetric analysis with thermal treatment in air at 200, 230, 250, 300, 400, 500, 600, and 700°C, for 2 h at each temperature. The phase composition of samples (X-ray phase analysis) was studied on a DRON-3M instrument, radiation CuK_α, λ = 1.54178 Å. Thermal analysis of the processes of dehydration of products and transformation of AF-12 was performed using a NETZSCH micro thermal balance TG 209 F1 (heating rate 10 deg min^{-1}, flow of inert gas 70 ml min^{-1} (He or a mixture of Ar/O_2 = 4/1). The specific surface of samples S_{sp} was determined on an adsorption analyzer Sorbtometr-M with a relative standard deviation of ±5%. The density of samples was determined by pycnometric method with an uncertainty of ±(0.2–0.5%), as a working fluid was used bidistilled water. The morphology of nickel oxide particles was studied with a scanning electron microscope EX-23000 BU.

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