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# Photochemical Preparation of Nanometric Nickel Particles. Catalytic Properties

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**Abstract**—Photochemical reduction in the system nickel(II) complex–sodium hypophosphite gave nanometric nickel particles. The size and structure of photostable particles were established. The formation kinetics and catalytic properties of photochemically deposited films in dark chemical deposition reactions were studied.

Over the past years researcher's attention has been attached to development of nanomaterials which have found wide application in science and engineering. One of the possible ways to solving this problem is using nanometric metal particles. Nanometer-scale particles are known to possess unique photoelectric and catalytic properties [1[, which is explained by peculiar features of formation and structuring of small particles. Controlling the size and shape of single particles and their ensembles allows creation of new nanomaterials with preset properties [2].

The aim of the present work was to explore the catalytic properties of the nanosize nickel particles obtained by photochemical reduction in the system nickel(II) complex–sodium hypophosphite.

As the photosensitive system for preparing initial nickel colloids we took a composition used for nickel deposition from aqueous nickeling solutions [3] and comprising the following components (*c*, M): $NiCl_2 \cdot 6H_2O$ (0.1), $NH_4OH$ (0.62), $NH_4Cl$ (0.46), $Na_3C_6H_5O_7$ (0.1), $NaH_2PO_2$ (0.05) (pH 7). The photodeposition of nanometric nickel particles was performed in a quartz cell (optical path 1 mm) by irradiation with a monochromatic light ($\lambda_{exc}$ 365 nm, intensity 1018 quanta $cm^{-2}$ $s^{-1}$). The excitation wavelength was selected with regard for the photosensitivity range of the ammine nickel complex formed in the solution. The catalytic properties of photodeposited nickel films were studied in catalytic reduction of nickel(II) ions from the initial solution. To this end, the nickel film deposited on a quartz surface was placed in a nonirradiated solution of the same composition, and the variation in the optical density (*A*) of the film–solution system was measured in the wavelength range 420–440 nm and time range 0–40 min in the dark and under irradiation. The measurement range was selected on the basis of the absorption spectra of the nickel films. For comparative analysis of the catalytic properties of freshly deposited nickel films of various thickness, the effect of $NH_4BF_4$ additives was studied, taking into account that such compounds enhance surface affinity of nanometric metal particles and thus allow thicker films to be obtained, not tending for peeling. The concentrations of the additives were 0.005–0.01 M. Higher concentrations were found to slow down the photodeposition process. The catalytic properties of nanometric nickel particles were also studied in the photochemical synthesis of Ni–Cu and Ni–Ag bimetallic structures by the successive deposition technique [4].

Film formation and reaction kinetics were studied by spectrophotometry, following the increase in plasmon absorption in the range 350–750 nm. The duration of the induction period was estimated by the absorbance at $\lambda_{max}$ 420 nm. Ultraviolet irradiation ($\lambda_{exc}$ 365 nm) of a thin film (1 mm) of the chemical nickeling solution through a wall of the cell contacting the solution gives rise to photoinduced formation on quartz surface of a thin nickel film. The color of the film varies from dark gray to silver gray, depending on its thickness and photolysis conditions.

The kinetic curve of the photochemical formation of nickel films on quartz (Fig. 1) is S-shaped. The reaction has an induction period whose duration depends on the composition of the photolyte. In our case, it is 60 s. The duration of the induction period is defined by the rate of the photoinduced reduction of the initial $Ni^{2+}$ complex to the intermediate forms $Ni^+$, as well as $Ni^0$ and small metallic nickel clusters. Concurrently, the intermediate forms can be formed and, being strong reducers, reoxidized with oxygen and nickel ions.

$$Ni^{2+} \xrightarrow{h\nu} 2Ni^{+} \xrightarrow{h\nu} Ni^{0},$$

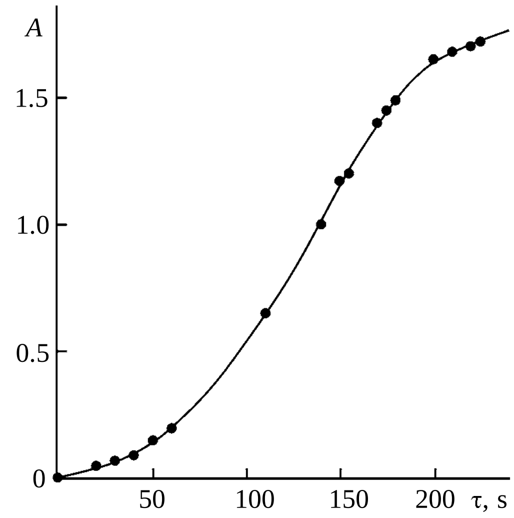

**Fig. 1.** Kinetic curve of photochemical deposition of nickel films from the chemical nickeling solution on quartz surface.

$$2Ni^0(2Ni^+) \xrightarrow{O_2} Ni^{2+} + NiO,$$
$$Ni^0 + Ni^{2+} \longrightarrow 2Ni^+.$$

Such a short induction period can be associated with the low redox potential of the $Ni^{2+}/Ni^0$ pair, as a result of which film formation begins if a $Ni^{2+}$ complex is present in the solution. Once the induction period has been complete, fast autocatalytic precipitation of metallic nickel and film stabilization occur. The observation of a plateau on the curve suggests complete reduction of nickel from the solution. According to electron microscopy data, film formation begins with the formation of isolated particles on separate surface regions. The mean particle size is 30–40 nm. On further irradiation the particles grow to 50 nm and group into torus ring structures. On microphotographs we can see hexagonal ring growth steps around holes. Therewith, the torus ring size is 110–160 nm, and the hole is 20–40 nm. Such structure is probably formed because of strong gas evolution attendant on nickel reduction [5].

$$Ni^{2+} + 2H_2PO_2^- + 2H_2O \longrightarrow Ni + 2H_2PO_3 + H_2 + 2H^+.$$

The particle size distribution is shown in Fig. 2. Further photolysis no longer increases particle size, and 50 nm can be considered a photostable size of nickel particles under the conditions used. It is important to note that the film structure is invariable throughout the whole photolysis time. Torus ring holes are even observed in microphotographs of an almost completely filled surface.

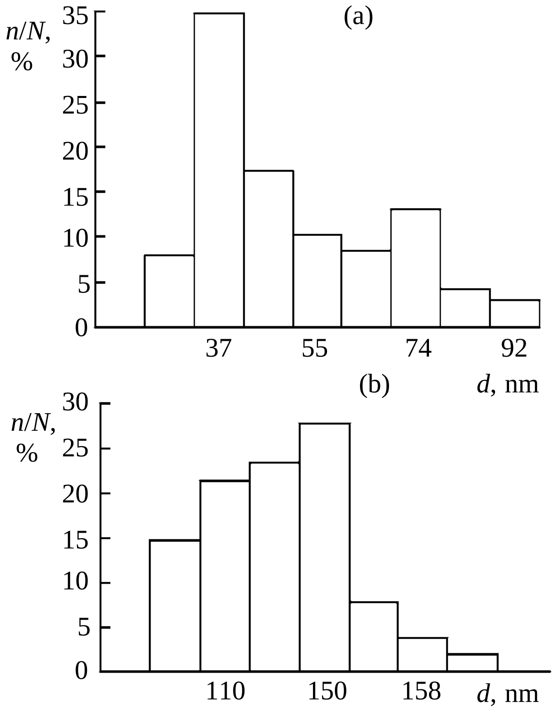

**Fig. 2.** Particle size distributions after (a) 80-s and (b) 150-s irradiation. (*n*) Number of particles of diameter *d* and (*N*) total number of particles in the film.

Furthermore, upon prolonged irradiation large crystalline particles formed in the film (150–200 nm). Diffraction studies revealed intrinsic structural differences between particles forming torus rings and large crystals. The diffraction patterns of the latter show sharply defined rings, whereas torus rings are rather blurred. Photodeposited films are characteristically strongly bound to quartz surface. The strong adhesion of nanometric nickel particles is probably explained [6, 7] by the initial formation of $Si–O–Ni^{\delta+}$ inclusions play the role of nucleation centers for the subsequent formation of colloid particles. Such bonds can form when there are $\equiv Si–O–H$ groups or siloxane bridging oxygen atoms on the surface.

By electron microscopy and spectroscopy we found that the mechanism of nickel photodeposition is similar to those established earlier [5] for nanometric silver and gold particles and involves formation of particle intermediates in the near-surface layer of the photolyte, followed by their diffusion to quartz surface and chemisorption.

The nickel films formed by photolysis act as catalysts of chemical deposition [2], ensuring complete growing from nonirradiated solutions (Fig. 3). Thus, we observed increase in the optical density of a film (*A* 0.28) contacting the irradiated solution in the dark.

Therewith, the duration of the induction period was dependent on the thickness of the initial metallic film. As seen from Fig. 3, the induction period decreases about 5 times when the film thickness increases from 0.2 to 1.2 *A* units. It was found that the films preserve their catalytic activity within 5–7 min after irradiation. Thereafter chemical deposition no longer occurs. This fact can be explained by oxidation of nickel particles and formation on their surface of oxide and hydroxide forms, as evidenced by the observation of characteristic bands in the XPE spectra at 853.4 and 855.5 eV, respectively.

The nickel films obtained by photochemical deposition proved to be stable and preserved their optical properties within 2 years.

It was found that at the given energy and intensity of luminous flux the minimal irradiation time of the photolyte, required for the subsequent autocatalytic nickel deposition to occur is 40 s. This time is needed to create in the system a minimal concentration of catalytically active nickel particles. It can be considerably shorter (less than 25 s), if the solution contains no citrate ions which stabilize nanometric particles and adversely affect their catalytic activity.

To find out what is the optimal composition of the solution for effective photochemical synthesis of thick nickel films with a good adhesion, we studied the effect of the concentration of sodium hypophosphite of the rate of dark deposition. It was established that the increase of the concentration of sodium hypophosphite from 0.01 to 0.2 M shortens the induction perion 2–6 times, depending on the thickness of the initial film. This is explained by a regular increase of the number of catalytically active nickel particles on the surface. Therewith, however, loose films are formed, tending for peeling. For enhanced adhesion we made use of fluorinaning additives, such as $NH_4BF_4$ which effects etching of quartz surface and forms microscopic defects, thus favoring chemisorption of metal particles. This additive stabilizes the photosensitive system, as evidenced by a longer inductive period. Optimal $NaH_2PO_2:NH_4BF_4$ ratios were determined (see table), which allow preparation of electroconducting films of nanometric nickel particles with a good adhesion. The optimal concentration of $NH_4BF_4$ in the chemical nickeling solution was found to be 0.005 M.

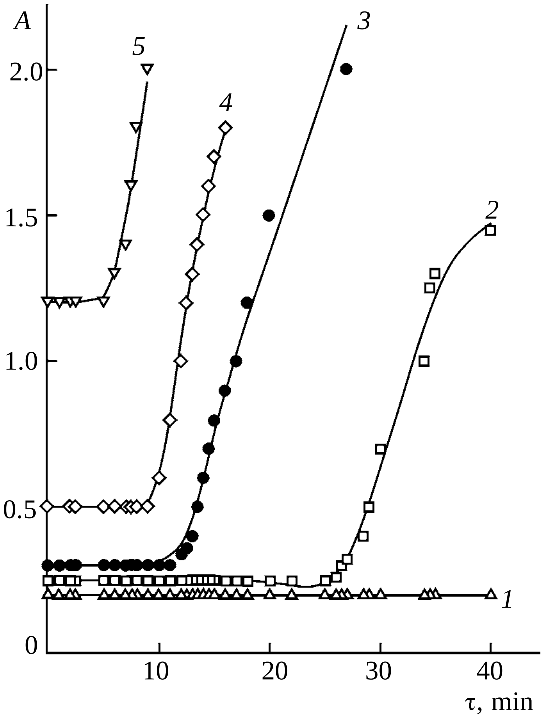

**Fig. 3.** Kinetic curves of dark growth of nickel films of various length from nonirradiated chemical nickeling solutions. $A_0$: (*1*) 0.2, (*2*) 0.25, (*3*) 0.3, (*4*) 0.5, and (*5*) 1.2.

It is known [8] that bimetallic nanometer-scale particles provide a high selectivity, owing to the possibility of varying their donor-acceptor properties determined by the nature of the metal and the structure of the bimetallic particle. In the present work we could prepare bimetallic nanometric particles on the basis of nickel, silver, and copper. The variation of the absorption spectra in the course of photocatalytic deposition of Ni–Cu and Ni–Ag bimetallic structures points to fast precipitation on the nickel film of copper and silver particles, as evidenced by the appearance and growth of characteristic copper and silver plasmon absorption bands at $\lambda_{max}$ 630 and 420 nm, respectively. Prolonged irradiation does not affect the positions of the plasmon absorption maxima.

Duration of the induction period ($\tau_{ind}$) in the dark growing of nickel films as a function of the initial film thickness (*A*) and photolyte composition [$c(Ni^{2+})$]

| *c*, M | | $\tau_{ind}$, min | | |
|---|---|---|---|---|
| $NaH_2PO_2$ | $NH_4BF_4$ | *A* 0.25 | *A* 0.5 | *A* 0.8 |
| 0.01 | – | 25 | 13 | 6 |
| 0.05 | – | 25 | 13 | 5 |
| 0.1 | – | 18 | 6 | 3 |
| 0.2 | – | 13 | 2 | 1 |
| 0.1 | 0.005 | 50 | 27 | 15 |
| 0.1 | 0.01 | 90 | 33 | 23 |
| 0.1 | 0.02 | 100 | 35 | 27 |

This fact suggests formation of “nucleus–shell” structures in both cases, which involves complete “screening” of nickel nuclei with copper and silver shells.

## EXPERIMENTAL

Film formation was followed and kinetic measurements were performed on an SF-121 spectrophotometer. The particle size was determined using a Hitachi HU-11 electron microscope. The XPE spectra were obtained on a Perkin–Elmer PHI-400 spectrometer, Mg$K_\alpha$ excitation ($h\nu$ 1253.6 eV).

## ACKNOWLEDGMENTS

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