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TECHNOLOGY OF INORGANIC SUBSTANCES AND MATERIALS

Amorphous and Crystalline Nickel Oxide Films Obtained by the Extraction–Pyrolysis Method for Electrochromic Cells

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Abstract—This paper reports studies of thin films of nickel oxide obtained by the extraction–pyrolysis method on glass and quartz substrates at temperatures of 380–600°C. The films have been characterized by atomic force microscopy and X-ray diffraction. It is shown that amorphous and crystalline nickel oxide films are formed on the glass. The grain size depends on the annealing temperature, while increased annealing temperatures lead to recrystallization and a decrease in the grain size in NiO films from 130 to 35 nm.

Keywords: nickel extract, extraction–pyrolysis technology, thin film, annealing, electrochromic cell
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INTRODUCTION

The tremendous interest in thin films of nickel oxide is due to their use in many fields of science and technology. Nickel oxide is a multifunctional material. NiO is a wide-bandgap semiconductor with *Eg* of 3.69 eV at room temperature [1]. Nickel oxide layers are widely used as electrodes in electric energy storage devices, as well as anodes in industrial electrolytic plants for water decomposition [2]. The antiferromagnetic properties of α-NiO cause interest in the use of its layers in magnetic cooling systems, magnetic recording, and data storage [3]. Nickel oxide films are frequently used as electrochromic (EC) layers in various devices because of their electrochromic properties: thin films of NiO and $Ni(OH)_2$ are visually transparent, while superstoichiometric nickel oxides (i.e., NiOOH and Ni_2O_3) are colored. The electrochromic effect in thin films of nickel oxide is reversible. Transparent Ni^{2+} changes its color to brownish Ni^{3+} after oxidation and, therefore, transmittance decreases, while the reduction of Ni^{3+} leads to discoloration of the film during reverse cycling.

NiO films are usually used as a counter electrode (ion-storage material) in cells with EC layers of tungsten oxide.

It is known that the properties of an oxide film depend on the method of its preparation and technological parameters. To obtain oxide films on the surface of large-area glasses, it is advisable to use solution methods that do not use vacuum equipment, since solution methods have several advantages, including the possibility of producing oxide films on a large-area glass. In this work, the extraction–pyrolysis method was used to obtain InSnO and NiO films.

Nickel Oxides and Electrochromism Mechanism

Nickel oxide is a nonstoichiometric crystalline compound NiO_x, where $x \approx 1$. Nonstoichiometry results in a color change from green to black due to vacancies in the NiO crystal lattice resulting in the presence of Ni^{3+}. There are two main phases of nickel(II) hydroxide, namely $Ni(OH)_2$ of α- and β-types (Fig. 1). β-$Ni(OH)_2$ crystallizes in a hexagonal system, described as a hexagonal close-packed (hcp) structure of hydroxyl ions with Ni(II), which occupies half of the octahedral voids. In the layered structure, each layer consists of a hexagonal planar arrangement of Ni(II) ions with coordinated octahedral oxygen. These levels are stacked in layers along the *c* axis with a distance between the layers of 4.5 Å. To explain the electrochemical mechanism of the coloration/discoloration process, it was shown [5] that a chemical reaction occurs during the activation period

$$NiO + H_2O \rightarrow Ni(OH)_2.$$

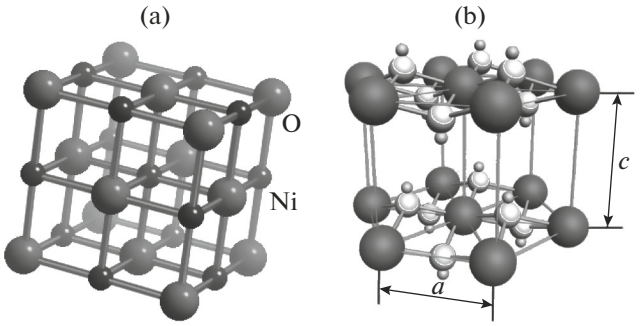

Fig. 1. Crystal lattice of (a) β-NiO and (b) α-NiO, β-Ni $(OH)_2$, β-NiO(OH) [4].

β-NiO has a cubic crystal structure of the NaCl-type, *Fm*3*m* space group, and lattice parameter $a = 4.1769$ [4]. Structural changes from NaCl-type NiO (bunsenite) to layered $Ni(OH)_2$ occur due to amorphization of grain boundaries during the contact of the surface of a thin NiO film with liquid KOH electrolyte. NiO grains act as a reservoir of the electrochemically active hydroxide layer. The electrochemical mechanism of the oxidation/reduction process and a reversible color change from transparent to brownish are described by the following reactions:

$$Ni(OH)_2\big|_{colored} \leftrightarrow NiOOH + H^+ + e^-\big|_{discolored},$$

$$Ni(OH)_2 + OH^-\big|_{colored} \leftrightarrow NiOOH + H_2O + e^-\big|_{discolored},$$

$$NiO + Ni(OH)_2\big|_{colored} \leftrightarrow Ni_2O_3 + 2H^+ + 2e^-\big|_{discolored}.$$

Several works reported that the reversible electrochemical oxidation of Ni atoms located in the NiO/electrolyte interface is responsible for the strong EC effect, while the performance of electrochromic nickel oxide depends on the size of nanocrystals [5]. Estrada et al. noted in 1988 that the optical properties of thin films with grains of ca. 7 nm in diameter are stable for at least 5000 cycles, while a significant decrease in stability after 50 cycles was observed in the case of 17-nm grains. The decrease in electrochromic properties after prolonged cycling is associated with the decomposition of the NiOOH phase.

Thin electrochromic films of nickel oxide were prepared by various physical (sputtering, pulsed layer deposition, and electron-beam evaporation) and chemical methods (atomic layer deposition, sol-gel, spray pyrolysis, and anodic deposition) [5–7]. The resulting films differ in stoichiometry, structure, crystallinity degree, grain size, etc. As a result, their electrochromic properties vary significantly.

EXPERIMENTAL

In this work, we used the extraction–pyrolysis method to obtain thin films of nickel oxide on glass and quartz substrates.

To obtain NiO films, an organic extract of nickel ions from a $NiCl_2$ solution was prepared using a mixture of organic acids as an extractant following the equation:

$$NiCl_2 + 2RCOOH + 2NaOH \rightarrow (RCOO)2Ni + 2NaCl + H_2O.$$

Nickel chloride solution (1 M) was mixed with an extractant in a separatory funnel and a 4 M sodium hydroxide solution was added portionwise. First, sodium carboxylate was formed, in which the sodium cation was replaced by a higher valence cation (nickel). As a result, nickel carboxylate was formed in the organic phase. The next two or three washes of the organic phase with the initial nickel chloride solution completely removed sodium from the extract. The concentration of Ni ions in the extract was determined by AAS-1M atomic absorption spectroscopy.

The extracts were dried for DTA study, which was used to determine the temperature of oxide formation.

Thin oxide films were deposited onto precleaned glass and quartz substrates by rolling and are then annealed in an open vertical quartz furnace.

X-ray phase analysis of NiO films on glass and quartz substrates annealed at 300–650°C for 30 min was performed using an X'Pert PRO (PANalytical) diffractometer with CuK_α radiation. Registration was carried out using a PIXcel detector equipped with a graphite monochromator. The survey was carried out at $T = 22$°C in the 2θ range from 3° to 100° with 0.026° step and Δt 50 s.

AFM measurements in the tapping mode were carried out using a Solver P47 multimode scanning probe microscope (NT-MDT) equipped with a 14-μm scanner and an adjustment table (SKM model). The samples were scanned in the air at room temperature. The silicon rectangular NSG30 cantilevers (NT-MDT) had a typical resonant oscillation frequency of about 320 kHz and stiffness constant of ≈40 N/m; the cantilever length was 14–16 μm and the tip radius of curvature was less than 10 nm. Scanning was performed over at least 3–4 sites over the surface. The scanning speed was 40–55 μm/s; the resolution of the resulting image was 256–256 points. As a rule, smoothing or other image processing, except for the deduction of the second-order surface, was not carried out.

The transmission spectra of the obtained cells in the colored and discolored states were measured on a Vertex-80V Fourier spectrometer (Bruker).

NiO films obtained on glass and quartz substrates with a predeposited ITO transparent conductive film as an electrode were used to assemble an electrochromic cell. In this work, electrochromic cells with NiO

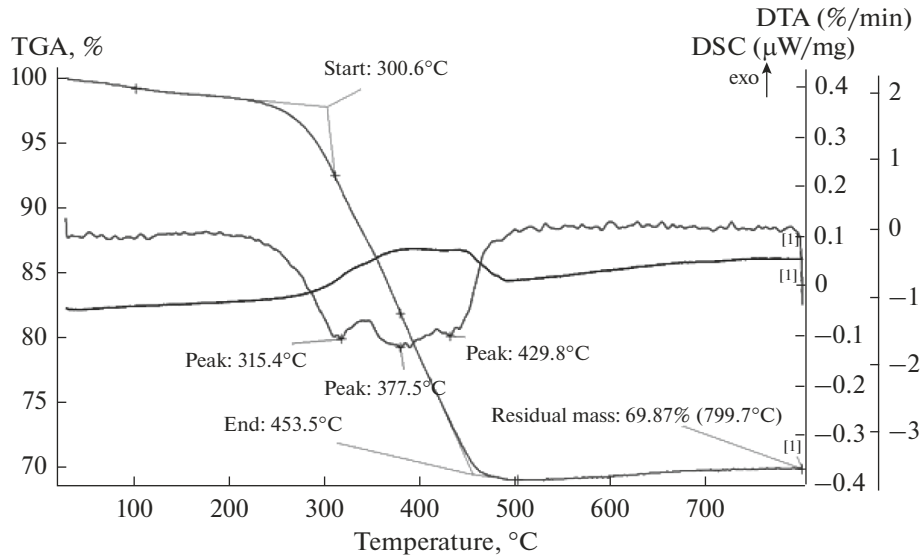

Fig. 2. Thermogram of nickel extract.

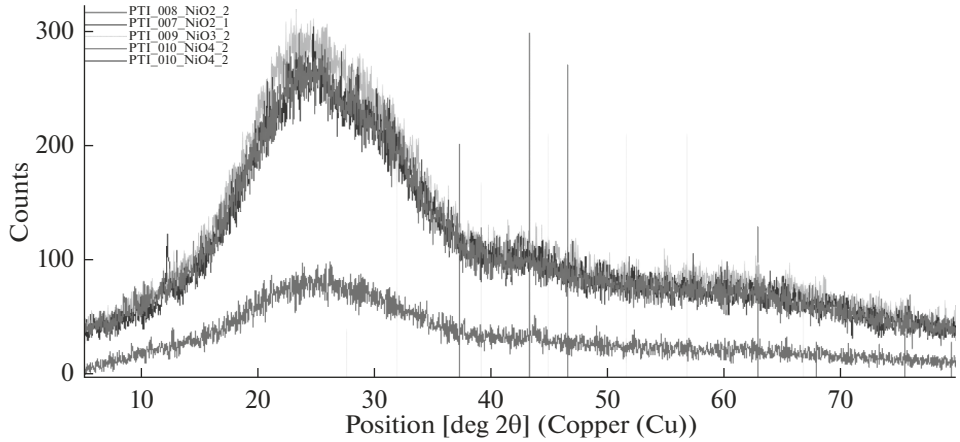

Fig. 3. XRD patterns of films deposited on glass substrates at 500, 600, and 650°C.

films of the amorphous and crystalline structure obtained by the extraction-pyrolysis method were examined

RESULTS AND DISCUSSION

Figure 2 presents a thermogravimetric analysis of nickel extract, which shows the temperature range of the main mass loss, ranging from 300 to 450°C. Mass loss corresponds to the complete removal of the organic part and the formation of nickel oxide. A slight rise in the TG curve with an increase in temperature from 500°C corresponds to the oxidation of nonstoichiometric nickel oxide.

Nickel oxide films were deposited from nickel extract on substrates with an optimal concentration of 2%, as was earlier found in [8]. The thickness of the films was controlled by the number of layers applied.

Studies on the film structure with a thickness of about 300 nm deposited on glass substrates and annealed at various temperatures from 350 to 650°C showed that the films are X-ray amorphous (Fig. 3).

The X-ray diffraction analysis of NiO films deposited on quartz substrates showed that they have a crystalline structure after high-temperature pyrolysis (Fig. 4). Wide peaks at 43.2°, 37.3°, and 62.8° corresponding to cubic nickel oxide were observed in an XRD pattern after annealing the film at 380°C. An increase in the annealing temperature increases the peak intensity due to larger crystallite size (a decrease in the half-width of the peaks), i.e., an increase the crystallinity of the material.

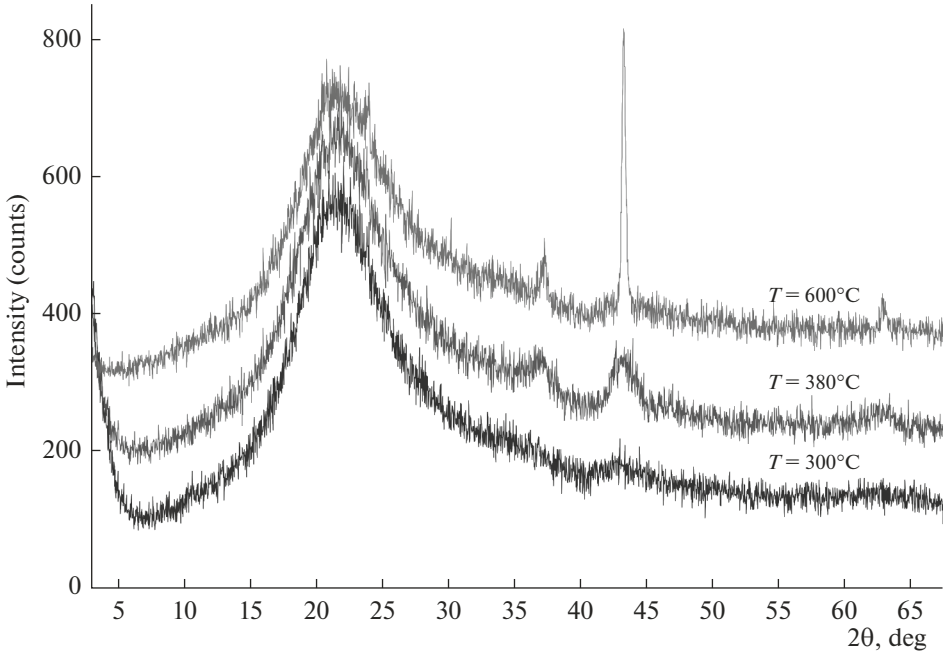

Fig. 4. XRD patterns of films deposited on quartz substrates at 300, 380, and 600°C.

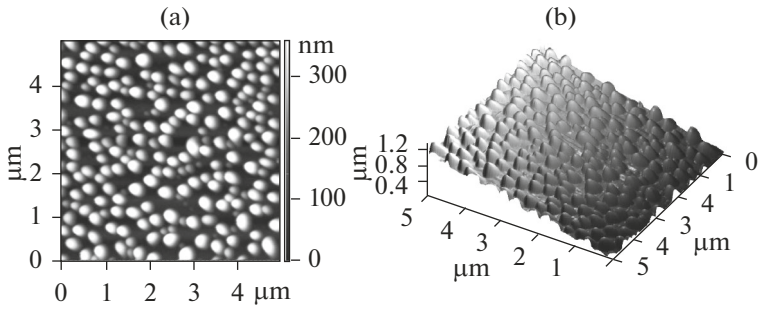

Fig. 5. Surface morphology of NiO film deposited on the glass substrate and annealed at 380°C.

It is known that the structure of the substrate affects the structure of the grown film. The atomic structure of glass, in which atoms are covalently bonded, does not contribute to the crystallization of the nickel oxide film. Quartz crystallizes as trigonal trapezohedron of trigonal syngony. The crystal structure of the quartz substrate promotes the crystallization of the nickel oxide film.

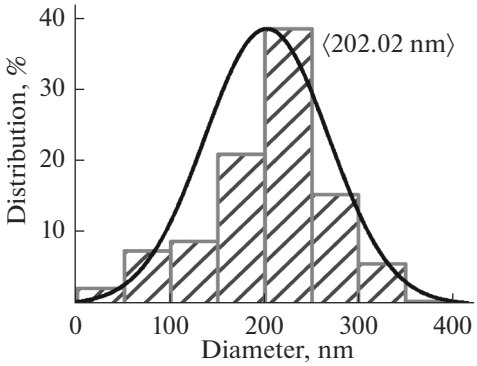

Fig. 6. Particle-size distribution histogram of NiO film deposited on the glass substrate and annealed at 380°C.

The AFM results showed that the films obtained on glass at 380°C had a relief surface with aggregates distributed over the entire surface, the average size of which was 200 nm (Fig. 5). A histogram of the particle-size distribution in the NiO film on glass annealed at 380°C is shown in Fig. 6.

Nickel oxide films on the quartz substrate, deposited at the same temperature of 380°C, had a crystalline structure according to the XRD (Fig. 7). The grain size ranged from 50 to 250 nm. The largest volume fraction of grain sizes was 130 nm.

NiO films obtained on quartz at a pyrolysis temperature of 600°C have an even denser granular structure (Fig. 8), with grain sizes from 25 to 50 nm and the

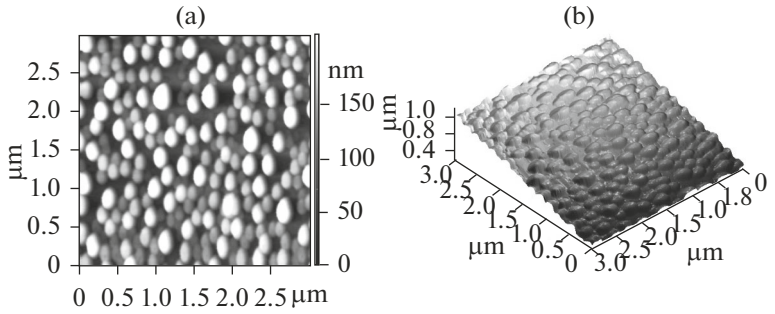

Fig. 7. Surface morphology of NiO film deposited on the quartz substrate and annealed at 380°C.

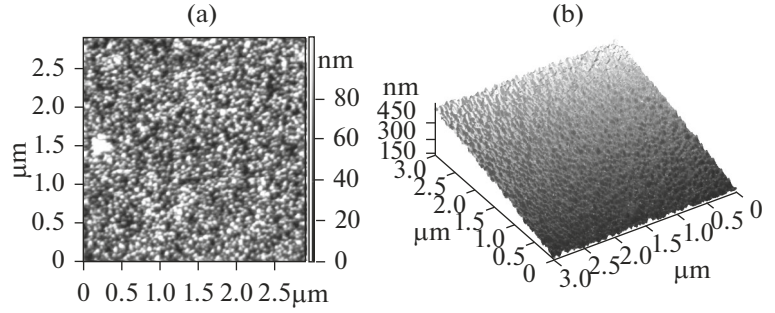

Fig. 8. Surface morphology of NiO film deposited on the quartz substrate and annealed at 600°C.

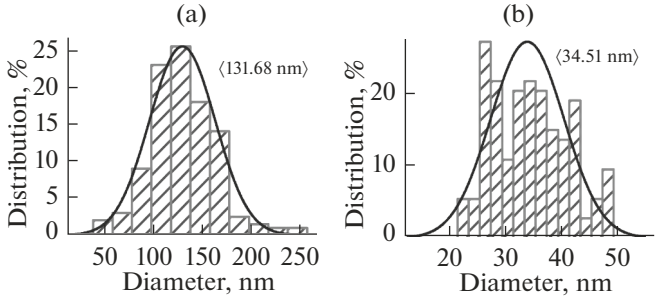

Fig. 9. Particle-size distribution histogram of NiO films deposited on the glass substrate and annealed at (a) 380 and (b) 600°C.

largest fraction of 32–36 nm, as well as a film roughness of about 15 nm. Figure 9 shows grain-size diagrams of NiO films obtained on quartz at (a) 380 and at (b) 600°C.

From the data that were obtained, it follows that films of nickel oxide on the glass are formed as amorphous aggregates of medium size 200 nm.

Nanocrystalline NiO films were obtained on the quartz substrate. Moreover, at an annealing temperature of 380–450°C, the particle size is 130 nm on average. With increasing annealing temperature, recrystallization occurs due to internal stresses in the film, and the average particle size decreases to 35 nm.

A change in the histogram of the particle-size distribution after annealing could occur as a result of crystallites cracking due to the exit of hydroxyl groups (OH) from the lattice and compaction of the structure.

The studied films were used as electrodes in EC cells. A ten-layer film is optimal for providing the EC effect. The cell also included a counter electrode with a ZrO/TiO_2 as the ion-storage film. This material has a slight EC effect [6]. The cell was filled with $LiClO_4$ + PC + DME electrolyte.

Optical studies of EC cells containing nickel oxide films annealed at different temperatures showed that, for a cell with NiO_{380} (Fig. 10) in the discolored state,

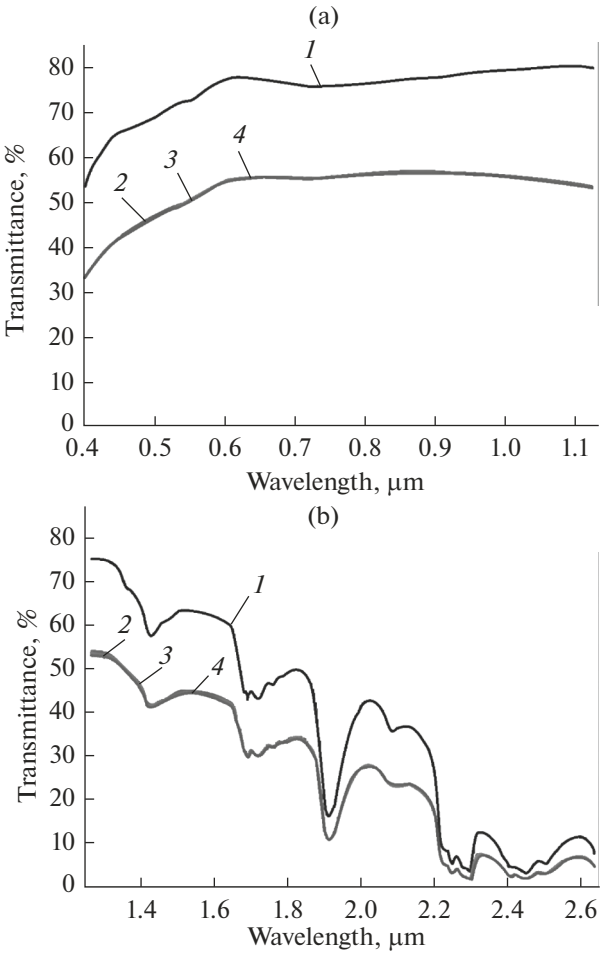

Fig. 10. Transmittance in the (a) visible and (b) infrared range of NiO 380°C on quartz.

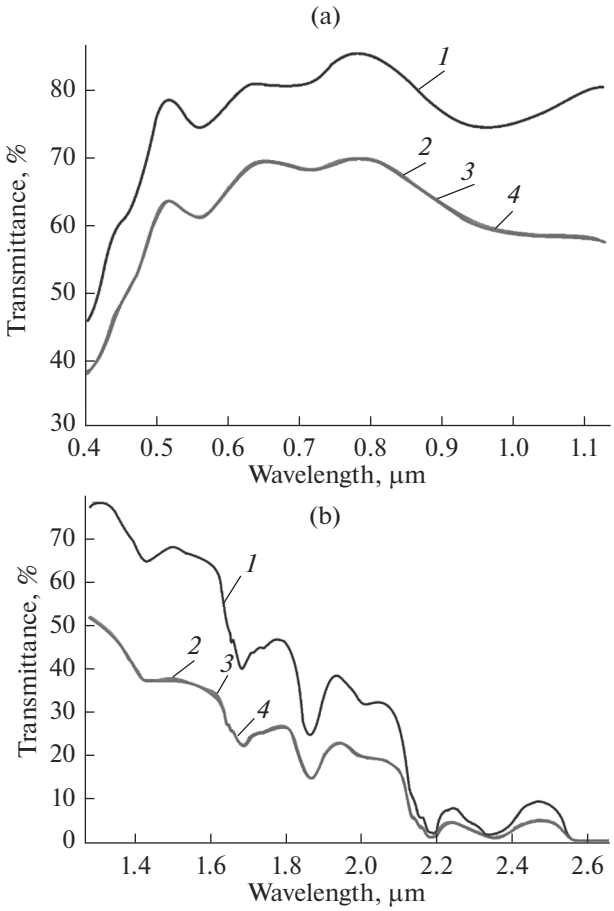

Fig. 11. Transmittance in the (a) visible and (b) infrared range of NiO 600°C on quartz.

the transmission is 60–80% in the visible spectrum and 10–75% in the mid-IR range, while in the colored state it is 40–55% in the visible and 10–55% in the mid-IR range. For a cell with NiO_{600} (Fig. 11) in the discolored state, the transmittance was 50–85% in the visible region of the spectrum and 10–80% in the mid-IR range, while it is 40–68% in the visible and 10–52% in the mid-IR range in the colored state.

The decomposition of the organic component during pyrolysis is accompanied by the release of gaseous products, mainly carbon dioxide. We are developing a method for utilizing pyrolysis gases.

CONCLUSIONS

Based on the data that were obtained, it can be concluded that, in the discolored state, the cell containing NiO_{600} is more transparent than the cell containing NiO_{380}, but, at the same time, the staining efficiency of this cell is lower than that of the cell with the amorphous film.

When using these films in windows of buildings or vehicles, they can provide the necessary level of natural illumination of the premises in the discolored or intermediate/darkened state while maintaining the optical visibility of the surrounding outside areas.

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