

**ELECTROCHEMICAL SYNTHESIS
OF ULTRAMIKRODISPERSED NICKEL OXIDE
POWDER AS THE WAY TO REDUCE ENVIRONMENTAL
LOAD OF PRODUCTION OF CARBON
NANOMATERIALS**

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Abstract: The possibility of a significant reduction in material costs and the number of pollutants by using an electrochemical method for synthesis of ultramicrodispersed nickel oxide powders on alternating current has been shown. The effect of frequency of alternative sinusoidal current and solution concentration on the rate of synthesis of ultramicrodispersed nickel oxide powder has been revealed. Efficient synthesis modes of ultramicrodispersed nickel oxide powder have been presented. The physico-chemical characteristics of produced ultramicrodispersed nickel oxide powders have been examined. The technological scheme of production of ultramicrodispersed nickel oxide powder with a closed cycle of water and reagents has been described; the possibility of its use in a catalytic synthesis of carbon nanofibers has been verified.

Introduction

The desire to reduce the environmental burden of chemical production has led to a rapid increase in scientific, industrial, and commercial interest in the application of electrochemical technologies for the synthesis of various organic and inorganic compounds. At present, the production of ultramicrodispersed nickel oxide powders, which are used in the catalytic synthesis of carbon nanomaterials as nickel catalyst precursor is of great interest [1–4].

The existing ways to get ultramicrodispersed nickel oxide powder – sol-gel method, the “wet” combustion require various toxic chemicals, as well as a

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large number of emissions of pollutants that create environmental problems for industrial implementation [5, 6]. Thus, during the production of one kilogram of ultramicrodispersed nickel oxide powder by “wet” combustion method about 336 dm³ of nitrogen dioxide is emitted in the atmosphere. The production of one kilogram of nickel oxide by homogeneous sol-gel method outputs 0.64 dm³ nitric acid and 2.8 dm³ of ethanol thermal decomposition which leads to the formation of 360 dm³ of nitrogen dioxide and 1672 dm³ of carbon dioxide. One of the stages of preparing a catalyst for heterogeneous sol-gel method is a synthesis of the precursor by co-precipitation of nickel. The chemical reaction is accompanied by the hydrolysis of ammonia generated by dissolving nickel nitrate in aqueous ammonia. A by-product of the reaction is ammonium nitrate, which is removed by washing with water. The production of one kilogram of catalyst requires 10 dm³ of water to remove 1.714 kg of produced ammonium nitrate. The combustion of 1.07 dm³ of ethanol produces 821.3 dm³ of carbon dioxide. The synthesis of the catalyst with citric acid (citrate method) is accompanied by a significant amount of nitrogen oxides and carbon dioxide: nitrogen oxides 804.545 and 4827.433 dm³ of carbon dioxide per kilogram of catalyst. The method of the explosion of metal wire, as described in [7, 8], is characterized by low productivity, the complexity of the process equipment and high cost of electricity per unit of output.

The disadvantages of the considered methods require the development of methods of synthesis of ultramicrodispersed metal oxide powders to organize the production of carbon nanomaterials by pyrolysis of hydrocarbons with a lower environmental load. These requirements are met by the electrochemical synthesis on a sinusoidal alternating current, which is carried out without the use of expensive equipment and reagents [9, 10].

Experimental

For the electrochemical preparation of the ultramicrodispersed nickel oxide powder a special apparatus is designed that enables to vary the frequency of sinusoidal alternative current (AC) in the range of 10...500 Hz [9–11]. The electrodes for the preparative electrolysis are made of nickel of H-0 grade in the form of rectangular plates with a surface area of 1 cm². The electrolysis is carried out in a glass cell with a jacket of 200 ml. The electrodes and thermometer are mounted in the teflon lid. The constant temperature of the solution in the cell is maintained by a thermostat with an accuracy of 0.5 K. The dissolution rate of nickel is determined by weighing.

The qualitative phase analysis of nickel powder is determined by X-ray diffraction analysis. X-ray analysis of the samples is carried out at ARL X'tra diffractometer using monochromatic X-rays, whose source is X-ray tube with copper anode $\lambda = 1,50452, \text{ \AA}$. The research of thermal stability of nanomaterials is carried out in air atmosphere with derivatograph Q-1500D.

Experimental data and discussion

The passage of symmetrical sinusoidal AC through the nickel electrodes in alkaline solution leads to their intense destruction and to the formation of the ultramicrodispersed nickel oxide powder. The experiments prove that the increase in the concentration and current density increases the rate of nickel

destruction [12, 13]. The maximum rate of a powder formation is observed in 17 M NaOH solution at the current density of 2.5 A/cm^2 and the temperature of 343 K (the increase and decrease in the temperature lead to the decrease in the destruction rate of nickel electrode). There is a gradual clouding of the solution in the electrolysis process. The formed slurry is distributed evenly over the entire volume of the electrolytic cell.

The results of investigation of the effect of frequency of AC sinusoidal current in the range 20...500 Hz, the rate of destruction of the nickel electrodes show that the maximum rate of nickel destruction in all the investigated solutions of sodium hydroxide is observed at the frequency of 20 Hz alternating current, which is almost three times higher than when using the frequency 50 Hz. At frequencies above 100 Hz the rate of destruction of nickel electrodes practically does not depend on the frequency of the AC (Fig. 1).

It must be noted, that the color of the destruction products of nickel depends on the applied AC frequency. So, in 17 M NaOH at the frequencies of the alternating current higher than 50 Hz the color of the product has a greenish color that proves the formation of divalent nickel compounds at these current frequencies. Black powders are developed at lower frequencies and it is a characteristic of trivalent nickel compounds (Ni_2O_3 and NiOOH).

To determine the shape and geometrical dimensions of the particles of ultramicrodispersed nickel oxide powder the studies were carried out using transmission and scanning electron microscopes. The electron microscopic photographs (Fig. 2) show that the precursor of nickel catalyst particles is relatively flat with the formation of agglomerates and the particle size from 10 to 500 nm.

The X-ray analysis of nickel oxide powder dried at 373 K showed that the powder of nickel oxide is X-ray amorphous (Fig. 3). The results of X-ray analysis suggest that the 573 K is observed the beginning of crystallization of X-ray amorphous samples. Radiographs revealed reflexes corresponding interplanar distances 0.242, 0.207, 0.1474, 0.1259 nm, which aggregate hardened samples can be identified as nickel oxide (II). With increasing the treatment temperature to 873 K the particles become more regular form and powder crystallization occurs. Micrographs clearly show the dependence of particle size on the hardening temperature (Fig. 4). The average particle size calculated by Selyakov-Scherrer formula [14, 15] for the particles hardened at 573 and 873 K is respectively 6 and 37 nm.

We carried out the experiments on the synthesis of pyrolytic carbon nanostructures using ultramicrodispersed nickel oxide powder obtained by electrolysis. To prepare the slurry the nickel oxide powder

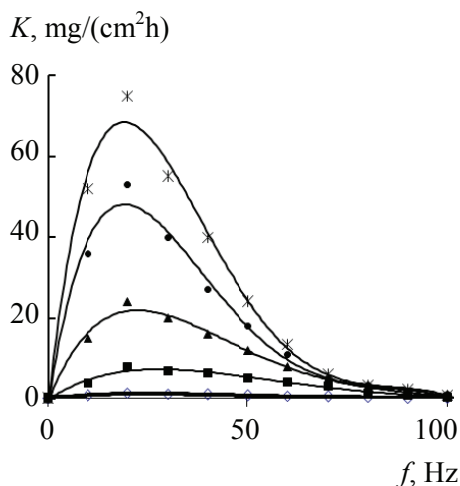
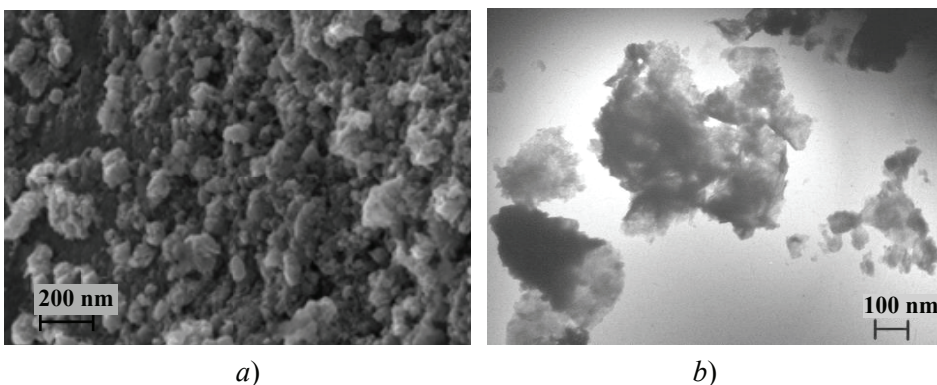


Fig. 1. Dependence of the destruction rate of nickel electrodes on the AC frequency at different concentrations of sodium hydroxide, M:
 \diamond – 1; \blacksquare – 5; \blacktriangle – 10; \bullet – 13; \ast – 17



a) *b)*
Fig. 2. Electron microscopic images of nickel powder:
a – transmission EM image; *b* – scanning EM image

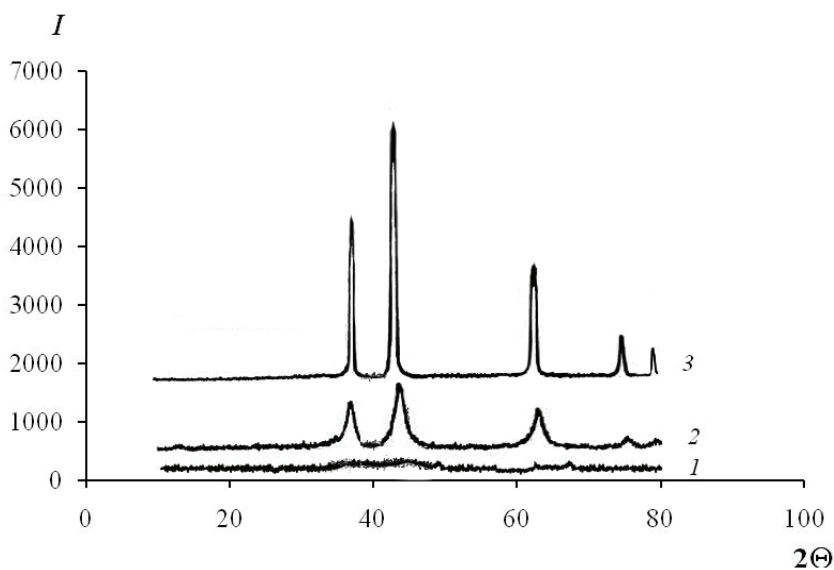
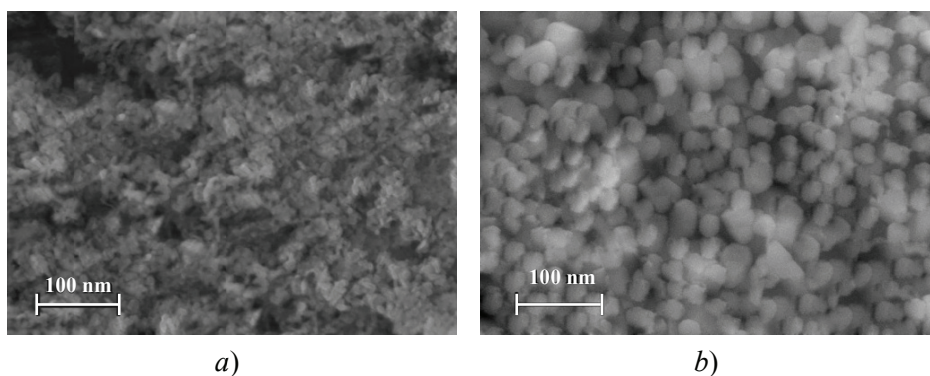


Fig. 3. Radiographs of nickel oxide powder obtained at a frequency of AC sinusoidal 20 Hz, $T = 343\text{ K}$, $i = 2,5\text{ A/cm}^2$ and calcined at temperature, K:
1 – 373; *2* – 573; *3* – 873



a) *b)*
Fig. 4. Micrographs of nickel oxide powder obtained at a frequency of AC sinusoidal 20 Hz, $f = 35\text{ kHz}$ ultrasonic $T = 343\text{ K}$, $i = 2,5\text{ A/cm}^2$ and calcined at temperature, K:
a – 573; *b* – 873

weighing 100 mg was diluted in 10 ml of B-70 gasoline. 10×50 mm glass-ceramic plate coated with slurry of nickel powder was placed in a Petri dish. The Petri dish was fixed on an electric heater with the heating temperature of 363 K; after the evaporation of gasoline we monitored the distribution of sedimentated powder by means of an optical microscope. Glass-ceramic plates prepared in this way were placed into a pyrolytic reactor. A set of experiments was carried out at three temperature values – 873, 923 and 973 K respectively, the rest of the technological parameters such as the consumption of hydrogen and propane, and the duration of the synthesis process remained unchanged. The reactor was purged with hydrogen at the flow rate of 2 cm³/s to achieve the predetermined temperature at the range of 873...973 K. When the predetermined temperature was achieved, propane with the flow rate of 1 cm³/s was supplied to the reaction zone during 15 min, at the same time the hydrogen flow rate was reduced to 0.1 cm³/s. After 15 minutes, the supply of propane was interrupted, heating was cut off and the flow of hydrogen was increased to 1 cm³/s. When the glass ceramic plate was cooled to 313...333 K, the reactor was opened and the glass ceramic plate was removed from it. The derived carbon nanomaterial was mechanically removed from the surface of the glass ceramic plate, and was placed on the polymer film which was 20...25 nm thick, fixed on 3 mm copper grid. The derived object (a copper grid with the film) was put under the electron microscope, and the synthesized carbon nanostructures were examined. The obtained carbon nanomaterial was a conglomerate of nanotubes with a diameter of 10 to 80 nm.

Figure 5 shows photographs of nanomaterial samples (*a*) – without pretreatment (with visible particles of the catalyst) and (*b*) – with the cleaning of the catalyst. To clean the nanomaterial of catalyst particles we used concentrated hydrochloric and nitric acid at 363 K for 15 minutes.

To evaluate the thermal stability of the synthesized carbon nanomaterial derivatograph was obtained (Fig. 6).

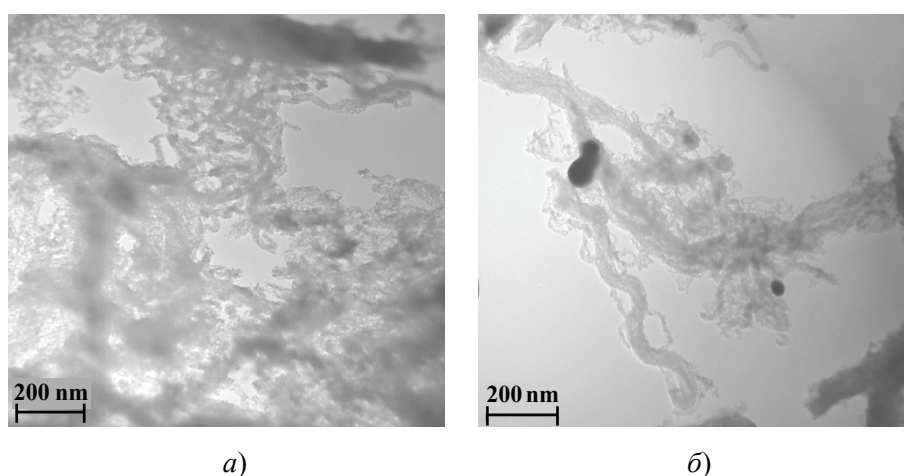


Fig. 5. Electron microscopic images of carbon nanostructures synthesized by ultramicrodispersed nickel oxide powder

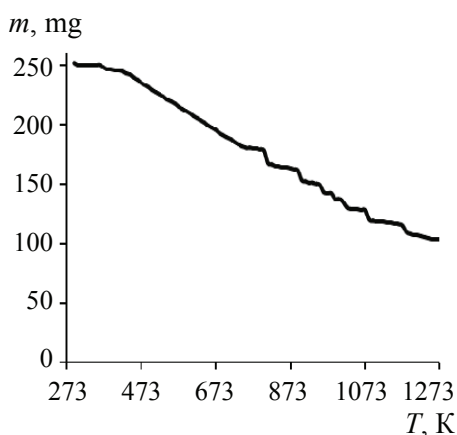


Fig. 6. Derivatograph of carbon nanomaterial heating

The study of the derivatograph established the temperatures (803, 893, 963, 1023, 1083 and 1178 K) at which an abrupt change of the mass of heated nanomaterial occurs, apparently, due to the removal of nanocarbon structural formations (soot and multi-walled nanotubes). After heating the sample of carbon nanomaterial up to 1273 K the powder mixture is ultramicrodispersed carbide and nickel oxide is produced.

We established conditions for efficient preparative electrochemical synthesis [16–19] taking into account the data of electron microscopy, X-ray

diffraction and derivatographic studies that formed the basis of the technological scheme of production of ultramicrodispersed nickel oxide powder (Fig. 7). The stage of washing of the target product is the most time-consuming operation in the scheme of nickel oxide powder. The traditional method of washing of the electrolyte requires 1 dm³ of gel per 100 dm³ of water. To reduce this figure studies were carried out, as a result of which it was established that the neutralization of alkali in the first stage of the washing solution of acetic acid leads to the formation of large flakes of sodium acetate and a decrease in the amount of water to clean nickel oxide from the electrolyte solution. First, the resulting suspension settles for days, and then it is separated by decantation. Alkali, after monitoring its concentration in the recycle was used as the electrolyte.

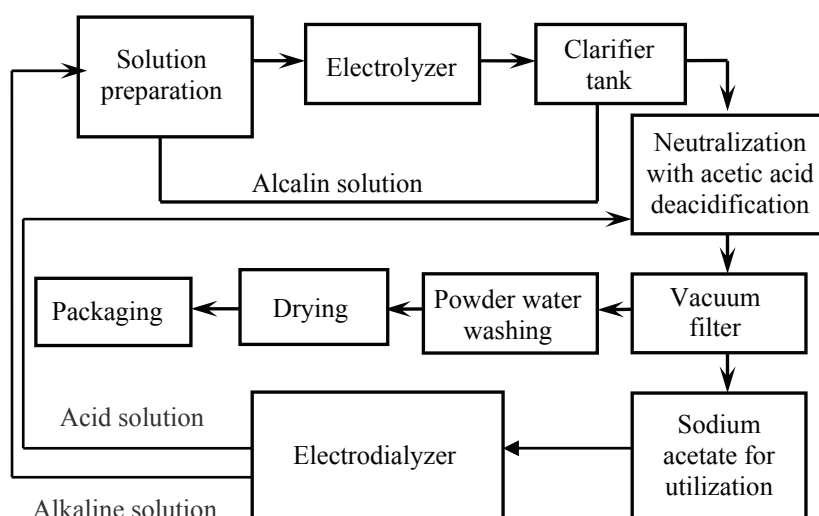


Fig. 7. Technological scheme of the nickel oxide powder synthesis by electrolysis by means of sinusoidal AC

The trapped sediment nickel oxide alkaline solution is neutralized with 80 % acetic acid. The resulting reaction solution of sodium acetate is filtered more easily than a concentrated solution of alkali and washing time is reduced by 50 % compared with currently used technology. At the same time the washing of gel requires 1 to 50 dm³ of water, which in general reduces the amount of wash water to 50 %. This method of separation of nickel oxide powder from the reaction solution does not change the physical-chemical characteristics of the target product. The resulting neutralization of sodium acetate solution is directed to electro dialysis.

The developed process consists of the following stages: 1) preparing a solution of sodium hydroxide; 2) the electrolysis of nickel on an alternating current (frequency 20 Hz) in sodium hydroxide solution; 3) upholding of the gel nickel oxide from alkaline solution; 4) separation of the precipitate by decantation nickel oxide (filtrate-containing alkali is sent for re-use); 5) neutralization with acetic acid of alkali seized by sediment nickel oxide; 6) separation of the precipitate nickel oxides from sodium acetate on the filter (sodium acetate is directed to electro dialysis, electro dialysis products are used in recycle); 7) washing of nickel oxide powder with distilled water; 8) drying the resulting product; 9) packaging of the desired product.

Cost calculation of production of 1 kg of ultramicrodispersed nickel oxide powder by electrolysis on alternating current for 2010 prices (unit capacity of 200 kg/year) was performed by the standard technique.

The following table shows comparative data on the consumption of reagents and waste in the methods of synthesis and electrochemical wet combustion.

Consumption of reagents and the amount of waste to obtain 1 kg of nickel catalyst precursor

Name raw materials (electrochemical synthesis)	The consumption rate, kg	Name raw materials (the method of "wet combustion")	The consumption rate, kg	Waste	
				Electrochemical synthesis	The method of "wet combustion"
Sodium hydroxide. NaOH*	2	Glycine NH ₂ CH ₂ COOH	2,40	-	360 dm ³ NO ₂ ; 1672 dm ³ CO ₂
Nickel. Ni	0,59	Magnesium nitrate Mg(NO ₃) ₂ ·6H ₂ O	0,48		
Acetic acid. CH ₃ COOH*	0,1	Nickel nitrate Ni(NO ₃) ₂ ·6H ₂ O	3,60		

*Sodium hydroxide and acetic acid used in the recycle.

The economic efficiency of the developed process is ensured by the reduction in production costs by 30 %, which is 195.2 thousand rubbles per year (in 2010 prices), compared to the existing conventional method of preparing the catalyst by the “wet” combustion and a significant reduction in the cost of waste disposal.

Conclusion

Thus, we have developed the method and technological scheme of synthesis of ultramicrodispersed nickel oxide powder on the sinusoidal alternating current with frequency of 20 Hz, current density of 2.5 A/cm² (asymmetry current 2.5:1) and ultrasound exposure of 17 M NaOH at 343 K, that reduces the environmental burden of production of carbon nanomaterials by catalytic pyrolysis of hydrocarbons, eliminates the emission of pollutants, and reduces the cost of the desired product by 30 %, compared with the existing conventional method for preparing a catalyst by “wet” combustion, and significantly decreases the cost of waste disposal.

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Электрохимический синтез ультрамикродисперсного порошка оксида никеля – путь снижения экологической нагрузки производства углеродных наноматериалов

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Ключевые слова и фразы: гидроксид натрия; оксид никеля; переменный синусоидальный ток; углеродное нановолокно.

Аннотация: Показана возможность значительного снижения материальных затрат и количества поллютантов за счет применения электрохимического метода синтеза ультрамикродисперсных порошков оксида никеля на переменном токе. Установлено влияние частоты переменного синусоидального тока и концентрации раствора на скорость синтеза ультрамикродисперсного порошка оксида никеля. Приведены эффективные режимы синтеза ультрамикродисперсного порошка оксида никеля. Исследованы физико-химические характеристики полученных ультрамикродисперсных порошков оксида никеля. Описана технологическая схема производства ультрамикродисперсного порошка оксида никеля с замкнутым циклом использования воды и реагентов, и подтверждена возможность его использования в каталитическом синтезе углеродных нановолокон.

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