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Запропоновано отримання багатошарових електрохромних плівок на основі $Ni(OH)_2$ і $Co(OH)_2$ катодним темплатним методом. Отримані плівки показали електрохімічну активність і електрохромні властивості. Найкращі електрохромні характеристики показала плівка, яку отримували послідовно в розчинах із додаванням полівінілового спирту, що містять нітрат кобальту і нікелю 2 і 78 хвилин відповідно

Ключові слова: $Ni(OH)_2$, $Co(OH)_2$, електрохромізм, електрохромні матеріали, CoOOH, полівініловый спирт, багатошарові покриття

Предложено получение многослойных электрохромных пленок на основе $Ni(OH)_2$ и $Co(OH)_2$ катодным темплатным методом. Полученные пленки показали электрохимическую активность и электрохромные свойства. Наилучшие электрохромные характеристики показала пленка, которую получали последовательно в растворах сдобавлением поливинилового спирта, содержащих нитрат кобальта и никеля 2 и 78 минут соответственно

Ключевые слова: $Ni(OH)_2$, $Co(OH)_2$, электрохромизм, электрохромные материалы, CoOOH, поливиниловый спирт, многослойные покрытия

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A STUDY OF MULTILAYERED ELECTROCHROMIC PLATINGS BASED ON NICKEL AND COBALT HYDROXIDES

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1. Introduction

Electrochromism is a phenomenon, which is characterized by substance changing its optical properties under applied electrical current. Electrochromic materials can change different optical characteristics: color, transparency, opacity, reflectivity. Electrochemical systems often find application in electrochromic devices. Materials, in which electrochemical processes occur, are characterized by changes of optical properties which occur in parallel to changes in composition and oxidation state of elements that constitute the compound.

Electrochromic devices allow controlling the amount of light and heat that pass through. The properties can be used for various purposes. Creation of temperature regime and suitable lighting, visual separation of rooms, creation of mirrors with adjustable reflectivity, creation of indicators for slow changing values (environment temperature, pressure,

prices, currency exchange rates), etc. [1]. Change of optical properties in electrochromic devices can occur within a wide range. This range is determined by the nature of the electrochromic material and its thickness. For electrochemical electrochromic materials, the flow of electrical current is only necessary for the change of optical properties. And usually, the additional current is not required to maintain the achieved state [2].

The electrochromic device is composed of two transparent conductors that are facing each other, and electrochromic material deposited on each of them. Between electrodes, there is thickened liquid or in some cases polymer electrolyte. The operation of electrochromic devices is based on reversible redox reaction. Two reversible processes occur at the electrodes:

$$\text{Cathode: } A_{ox}[\text{colorless}]+n\bar{e}\leftrightarrow A_{red}[\text{colored}], \quad (1)$$

$$\text{Anode: } B_{red}[\text{colorless}]-n\bar{e}\leftrightarrow B_{ox}[\text{colored}]. \quad (2)$$

Intensity of optical changes in electrochromic devices depends on the amount of charge passed through it and its polarity.

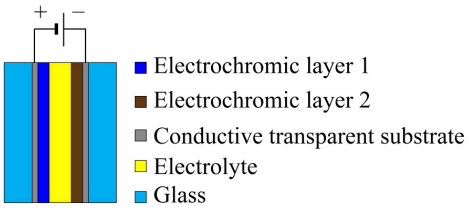

Fig. 1. Schematic of electrochromic device with electrochemical electrochromic films

Thin films of nickel hydroxide and oxide [3, 4], nickel hydroxide doped with other metals [5], are one of the electrochemical materials used as electrochromic materials [6]. Nickel hydroxide is also an active material of hybrid supercapacitors [7] and alkaline accumulators [8], so the study on new synthesis methods [9, 10] and properties of this material [11] is still a relevant scientific problem.

2. Literature review and problem statement

The necessity for improving specific characteristics of electrochromic materials leads to the development of new ways of their synthesis. For instance, one option is the preparation of materials doped with other elements [12–14]. Such approach leads to the preparation of materials with improved activity, which are usually characterized by the presence of a large number of crystal lattice defects or increased interlayer distance within crystals. Such transformations of crystal lattice occur as a result of partial substitution of initial atoms with dopant atoms, inclusion of acid anions and water by crystal lattice. These changes in the material structure can sufficiently ease the occurrence of solid-state reactions.

The other approach for improving specific characteristics of electrochromic materials is the creation of composite materials [15, 16]. Addition of components (usually nanoparticles of metals [17] and non-metals [18]) to electrochromic materials can improve electrical conductivity or transport characteristics of ions within the solid phase. Such approach can improve switching speed of electrochromic material from one state to another, and even increase coloration degree. The downside of such approach is that it can result in materials with worse initial optical properties.

Another approach for creating new electrochromic materials is the search for new methods for the synthesis of nano-ordered structures [19, 20]. The resulting materials have higher activity because of better material utilization, which is explained by high specific surface area. High specific surface area enables faster occurrence of the electrochemical process. The downside of such materials can be meta-stability.

One possible method for altering the properties of electrochromic elements is the modification of the substrate surface, onto which the electrochromic material is to be deposited. For instance, the paper [21] shows that weak etching of the electrode substrate using electrochemical method can significantly affect the properties of the resulting electrochromic element – coloration degree, film uniformity, etc.

Multilayered electrochromic films can be one of the options for improving specific characteristics of these materials. Multilayered films are a variant of previously reviewed composite materials. For instance, the authors of the paper [22] have demonstrated that the multilayered electrochromic film based on WO_3 with layers of $K_6P_2W_{18}O_{62}$ and polyethyleneimine shows better characteristics in comparison to pure WO_3. Due to the fact that the number of papers dedicated to the preparation of multilayered electrochromic materials is rather small, such synthesis method can be promising.

It is known that cobalt compounds have a positive effect on the properties of nickel hydroxide in accumulators [23], supercapacitors [24] and nickel-based electrochromic devices [14, 25]. Activation of nickel oxide electrode with cobalt additive improves the utilization coefficient of active material in alkaline accumulators by 10–15 %. Cobalt is added to the positive electrode in the form of hydroxide [26]. It is stated in the literature that hydroxide is a surface activator, i. e., a significant increase of capacity occurs if cobalt compounds are on the surface of nickel hydroxide [27]. In this regard, it was decided to deposit an electrochromic film based on nickel and cobalt hydroxides, followed by a study of structural, electrochromic and electrochemical characteristics of the prepared films.

3. The aim and objective of the study

The aim of the work was to verify the possibility of preparing multilayered electrochromic films by sequential deposition using cathodic template deposition and study the influence of such deposition on the resulting characteristics of electrochromic films.

In order to achieve the aim, the following objectives were set:

– to deposit multilayered films using cathodic template deposition from solutions containing nickel and cobalt ions, and also polyvinyl alcohol;

– to determine structural, electrochemical and electrochromic properties of multilayered films.

4. Materials and methods used in research

Materials and method for deposition of multilayered electrochromic films. The films were formed by sequen-

tial deposition from different solutions. Cathodic template deposition was used for depositing films [4, 14, 16]. For the deposition of $Ni(OH)_2$ layer, the cathodic chamber of the electrolyzer was loaded with 1M $Ni(NO_3)_2$ solution with the addition of 5 % wt. polyvinyl alcohol (PVA). For deposition of $Co(OH)_2$, the other solution was loaded into the electrolyzer's cathodic chamber – 1M $Co(NO_3)_2$ solution with the addition of 5 % wt. PVA. In both cases, 1M KNO_3 was used in the anodic chamber.

The electrolyzer's frame is made out of Plexiglas and its schematic is shown in Fig. 2.

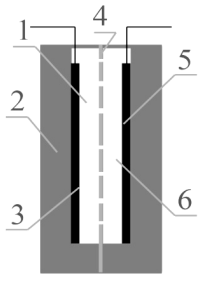

Fig. 2. Schematic of electrolyzer for deposition of films: 1 – cathodic chamber with solution of $Ni(NO_3)_2$ and 5 % PVA; 2 – frame; 3 – cathode; 4 – diaphragm with low permeability coefficient and rubber gasket; 5 – anode; 6 – anodic chamber with KNO_3 solution

Thick nickel foil was used as the anode. The films were deposited onto polished nickel electrode with a working area of S=4 cm^2. The cathodic current density of deposition was 0.625 mA/cm^2. In order to remove the electrolyte residue from the deposited film, after each deposition, the film was placed into distilled water at room temperature for 10 minutes. After the deposition procedure, the prepared electrodes were dried for 1 day at room temperature.

Nickel substrate was chosen for deposition of multilayered films because of the following reasons:

– greater electrical conductivity of nickel in comparison to indium-tin oxide coated glass; results in better distribution of current density across the electrode's height;

– better sensitivity during recording the electrochromic response because of light passing through $Ni(OH)_2$ film two times: light source → $Ni(OH)_2$ film → mirror-like nickel substrate → $Ni(OH)_2$ film → photoresistor.

In order to be able to compare the prepared films by all of their characteristics – optical, electrochemical and structural, it is necessary that the amount of deposited material was equal. However, it is difficult to achieve an absolute match between the thickness of the films. Nevertheless, in order to achieve the maximum possible match, it was decided to set the same deposition time for all the films. Details regarding deposition time for each film are presented in Table 1.

Structure of multilayered electrochromic films. In order to determine the structure of prepared electrochromic films, the XRD analysis for prepared electrodes was conducted using the X-Ray diffractometer DRON-3 (Cu-Kα) (Russia).

Electrochemical and optical characteristics of multilayered electrochromic films. Optical and electrochemical properties of the films were studied by means of cyclic voltamperometry (CVA) with simultaneous recording of the coloration-bleaching process. The cell shown in Fig. 3 was used for these experiments. Polished nickel electrodes with films deposited according to Table 1 were used as a working electrode. Ag/AgCl (KCl sat.) was used as a reference electrode. Nickel foil was used as a counter-electrode. For all the measurements, 0.1 M KOH solution was used as an electrolyte. Optical characteristics were recorded using the ADC E-154 (Russia), the electrochemical measurements were recorded using the potentiostat-galvanostat Ellins p-8 (Russia). Parameters for electrochemical and optical measurements: potential window from +200 to +750 mV, scan rate 1mV/s, number of cycles – 5.

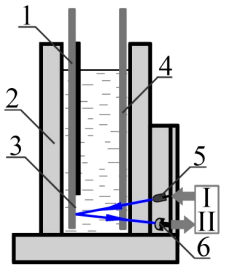

Fig. 3. Cell for recording cyclic voltamperograms: 1 – working electrode; 2 – frame; 3 – electrode's working area; 4 – U-shaped counter-electrode; 5 – LED; 6 – photoresistor; I – stabilized voltage source; II – analog-to-digital converter

One of the properties that characterizes electrochromic parameters was coloration dgree, which was calculated as the difference between the film's light transmittance in the colored and bleached state, which was averaged from 5 cycles.

5. Structural analysis of prepared multilayered electrochromic films

A separate batch of films was prepared according to Table 1 and sent for XRD analysis, without separating films from the substrate (because of high adhesion to the substrate, which was demonstrated in the previously published paper). The recorded XRD patterns for prepared samples are presented in Fig. 4.

Table 1

Legend and duration of deposition of layers for different electrochromic films used in the experiment

Film/label	Deposition time of the 1st layer, min	Deposition time of the 2nd layer, min	Deposition time of the 3rd layer, min	Total deposition time, min
$Ni(OH)_2$/Ni80	80	------	------	80
$Ni(OH)_2$–$Co(OH)_2$/Ni78Co2	78	2	------	80
$Co(OH)_2$–$Ni(OH)_2$/Co2Ni78	12	78	------	80
$Ni(OH)_2$–$Co(OH)_2$–$Ni(OH)_2$/Ni39Co2Ni39	39	2	39	80

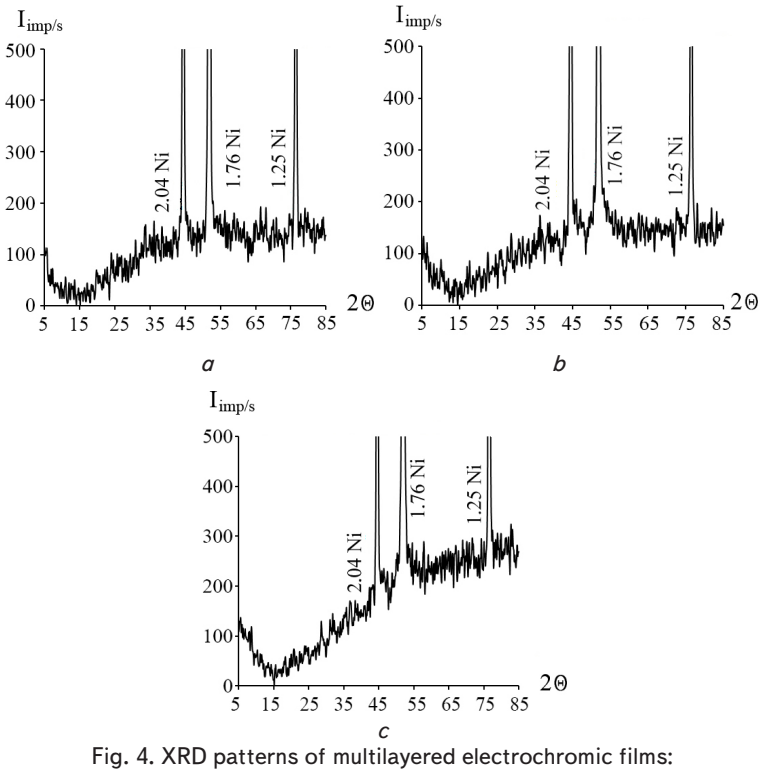

Fig. 4. XRD patterns of multilayered electrochromic films: *a* – Ni78Co2, *b* – Co2Ni78, *c* – Ni39Co2Ni39

All XRD patterns show high and distinguishable peaks that correspond to the metallic nickel substrate. There are no visible peaks that correspond to nickel or cobalt hydroxide, however, an elevation at 2θ=5° is observed.

5. 2. Experimental results of determining optical and electrochromic characteristic of prepared films

All prepared films were studied by means of cyclic voltamperometry (CVA) with simultaneous recording of optical characteristics – Fig. 5. A film deposited from 1 M nickel nitrate with the addition of 5 % PVA (sample Ni80) at 0.625 mA/cm^2 – Table 1 served as a reference sample.

For comparison of CVA graphs, the graphs were determined and compiled in Table 2.

Table 2 also shows current densities for established oxidation and reduction peaks (5th cycle). Because the shape of the peaks is almost the same, it was assumed that the peak current density can characterize the process rate.

When comparing the cyclic voltamperometry curves, a few facts can be stated for all the samples. Anodic and cathodic peak potentials of Ni39Co2Ni39 films differ the most from the reference sample, and this sample also shows the lowest reversibility. The reversibility was evaluated as the value of E_a–E_c. On the other hand, based on the shape of the curves and peak current density values of subsequent cycles, Ni39Co2Ni39 shows the best results when it comes to the stationary regime.

Table 2

Electrochemical parameters calculated from CVA

Sample	Ni80	Ni78Co2	Co2Ni78	Ni39Co2Ni39
E_a, mV	661	675	670	690
E_c, mV	510	526	521	531
E_a–E_c, mV	151	149	149	159
E_p^*	585.5	600.5	595.5	610.5
i_a, mA/dm^2	121	97	112	184
I_c, mA/dm^2	–111	–87	–91	–142

Note: Formal equilibrium potential – E_p^* was calculated as a mean value between established values of anodic and cathodic potential E_a and E_c.

In addition, Ni39Co2Ni39 sample demonstrates the highest peak current densities for anodic and cathodic processes. On average, the peak values exceed those of other samples by 57 %.

In turn, the Ni78Co2 and Co2Ni78 samples demonstrated average results by all parameters presented in Table 2.

During the recording of cyclic voltamperograms, the optical changes of the films were also recorded. The coloration-bleaching curves are presented in Fig. 5.

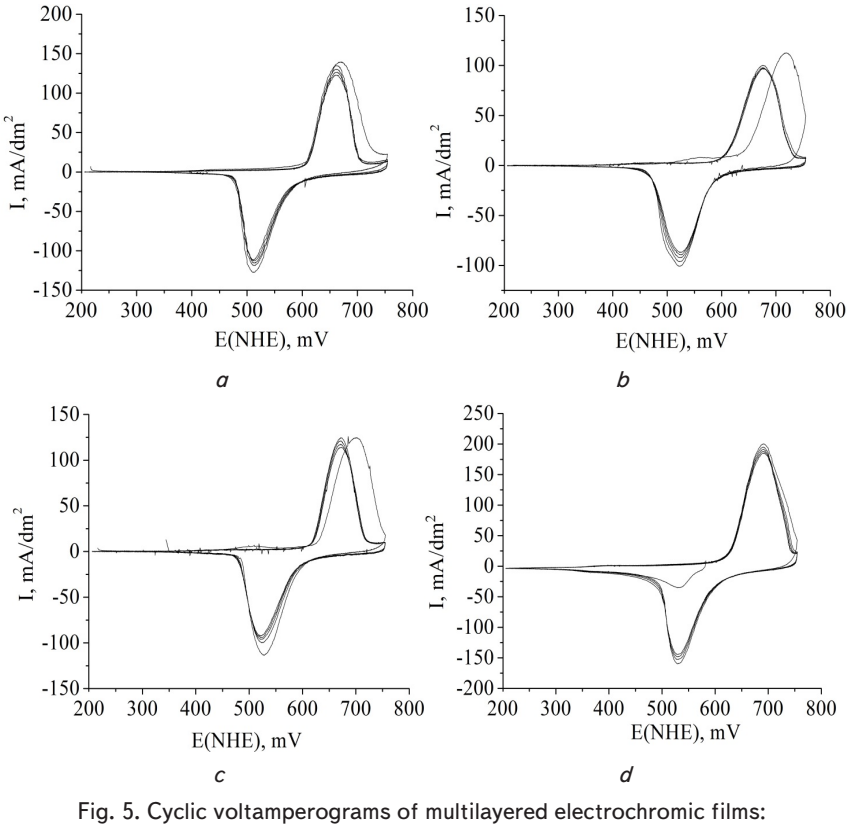

Fig. 5. Cyclic voltamperograms of multilayered electrochromic films: *a* – Ni80, *b* – Ni78Co2, *c* – Co2Ni78, *d* – Ni39Co2Ni39

Analysis of the curves presented in Fig 5 reveals that coloration degree (averaged difference between colored and bleached states) increases in the series – Ni39Co2Ni39, Ni80, Ni78Co2, Co2Ni78. Moreover, the maximum coloration degree was demonstrated by the Co2Ni78 sample. It should also be noted that the shapes of the curves do

not differ significantly from each other. Additionally, the Ni39Co2Ni39 samples did not return to its initial state with each subsequent cycle Fig. 6, *d*.

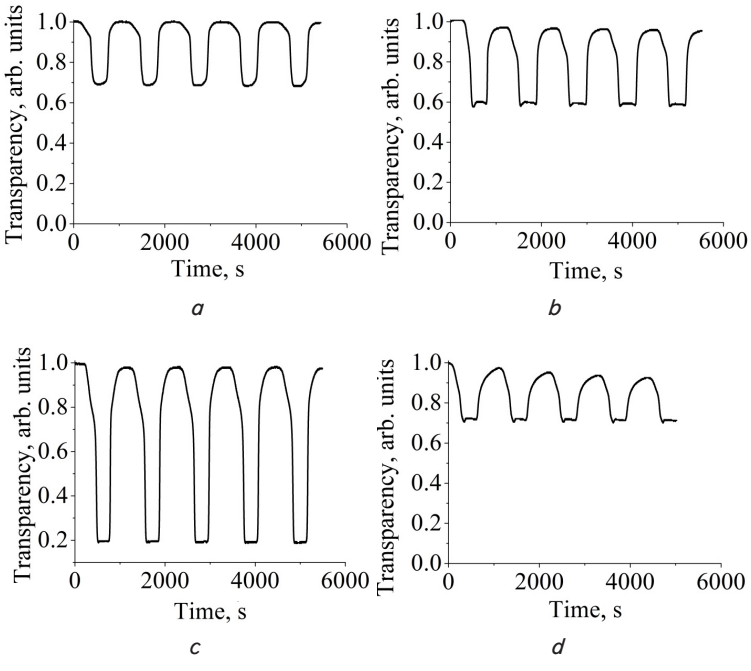

Fig. 6. Coloration-bleaching curves for multilayered electrochromic films: *a* – Ni80, *b* – Ni78Co2, *c* – Co2Ni78, *d* – Ni39Co2Ni39

6. Discussion of results the study on the structure, electrochemical and optical characteristics of multilayered electrochromic films

Based on the results of XRD analysis, it can be said that all the films are X-ray amorphous, i. e., the crystals in the crystal lattice are very small and comparable to the wavelength, which is 1.54 Å for Cu-Kα radiation. Thus, it can be said that all the films have a large number of defects and likely contain large amounts of structural water. The latter is related to the fact that defected crystals tend to incorporate foreign substance, which in case of hydroxide prepared from aqueous solution is water. It can also be added that the prepared multilayered films are similar to α-$Ni(OH)_2$, because there is a series of peaks in the region of small angles at 2θ equal to 5–10°. The absence of peaks corresponding to cobalt hydroxide is likely related to its low content.

Upon analysis of CVA curves for deposited films, the following can be said. First, all the films have fast activation rate, because the peak currents of the second cycle don't differ much from those of the first cycle. Second, the potential values of reduction peaks are similar for all the films, unlike the potential values for oxidation peaks, which do differ. Upon comparing the oxidation and reduction currents, the samples can be arranged in the order of increasing peak values: Ni78Co2, Co2Ni78, Ni80 and Ni39Co2Ni39. By dividing the absolute current value of the cathodic peak by the absolute current value of the anodic peak, we get a value that approximately characterizes reversibility of the electrode. Based on this value, the films can be arranged in the following order, from lowest to highest: Ni39Co2Ni39 (0.77), Co2Ni78 (0.81), Ni78Co2 (0.90) and Ni80 (0.92). To sum up the comparison results, it can be concluded that electrochemical characteristics of all the films are similar and differences are within a small margin. Only the Ni39Co2Ni39 sample notably differs from other films.

The coloration degree and cycle stability are the main qualitative characteristics of such materials. Based on that, when comparing coloration-bleaching curves (Fig. 6), it can be said that Co2Ni78 demonstrates the best characteristics – coloration degree of about 80 %, unlike other films, which on average show 25–40 %. It is also thought that the shape of the coloration-bleaching curves should ideally be rectangular. It should be pointed out that the most stable curve shape and optical values in the colored and bleached state are demonstrated by the Ni80 and Co2Ni78 samples, and the least stable are Ni39Co2Ni39 and Ni78Co2.

The Co2Ni78 sample has demonstrated the best optical characteristics. This fact can be explained by the following assumed mechanism. Cobalt hydroxide is oxidized in the first cycle to CoOOH, which is a semiconductor. On the backwards scan, it is not reduced to the initial hydroxide, which is a known behavior for this material when working in the nickel oxide electrode of alkaline accumulators [28]. Thus, this layer plays the role of electrically conductive "bridge" that connects the substrate and the electrochromic layer of nickel hydroxide (II).

In conclusion, it can be said that the conducted research revealed the possibility of preparing multilayered electrochromic films by subsequent deposition of layers using the cathodic template deposition technique. Such approach can give rise to a relatively simple deposition of multilayered films of hydroxides and oxides of nickel, cobalt and other metals. The developed deposition method is also convenient for the preparation of new catalysts, magnetic compounds, sensors, etc. Additionally, deposition time and current density are process parameters that enable control over film thickness in a wider range. On the other hand, it is still necessary to carry out additional studies in order to determine the morphology of prepared films, deposition rate, and distribution of layers in the films, which will be conducted later.

7. Conclusions

1. The electrochromic films based on $Ni(OH)_2$ with $Co(OH)_2$ have been prepared using sequential deposition using cathodic template deposition and their properties have been studied. All prepared films are similar in structure and consist of alpha-like hydroxide.

2. The film prepared by depositing a layer of cobalt hydroxide from cobalt nitrate solution with 5 % polyvinyl alcohol for 2 minutes and a layer of nickel hydroxide from nickel nitrate solution with 5 % PVA, for 78 minutes, demonstrated a high coloration degree (80 %) with the shape of the coloration-bleaching curve close to rectangular. The latter is likely related to cobalt hydroxide being oxidized to CoOOH, which can serve as a conductor between the electrochromic layer and the substrate, improving the distribution of current along the surface.

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Проведено теоретичні та експериментальні дослідження можливостей використання гібридного лазерно-ультразвукового зміцнення та оздоблювання металевих виробів. Запропоновано методику для оцінки градієнту температур при використанні сканувального лазерного променя та ультразвукового інструменту. Визначено температуру початку деформаційної дії ультразвуковим інструментом в процесі термодеформаційного зміцнення та оздоблювання великогабаритних сталевих поверхонь

Ключові слова: лазерно-ультразвукове зміцнення, сталь 45, термокінетична модель, термофізична модель, твердість, шорсткість

Проведены теоретические и экспериментальные исследования возможностей использования гибридного лазерно-ультразвукового упрочнения и отделки металлических изделий. Предложена методика для оценки градиента температур при использовании сканирующего лазерного луча и ультразвукового инструмента. Определена температура начала деформационного действия ультразвуковым инструментом в процессе термодеформационного упрочнения и отделки крупногабаритных стальных поверхностей

Ключевые слова: лазерно-ультразвуковое упрочнение, сталь 45, термокинетическая модель, термофизическая модель, твердость, шероховатость

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SURFACE HARDENING AND FINISHING OF METALLIC PRODUCTS BY HYBRID LASER-ULTRASONIC TREATMENT

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1. Introduction

The surface hardening is one of the effective ways to increase the wear resistance of parts in modern production due to changes in the chemical composition, modification, as well as changes in the surface microrelief and the structure of the surface layer. Given that a large number of machine parts work in extreme conditions, traditional surface hardening methods often do not allow getting the required qualitative indicators that fully meet the operation conditions. Moreover, the use of high-strength materials is often economically unprofitable.

Laser or plasma surface treatment is used to solve these problems in production processes. It should be noted that the laser surface hardening technology allows treating complex shaped parts with minimal zones of thermal influence in comparison with traditional processes (induction, flame and bulk hardening) [1–3]. Currently, laser surface hardening is successfully used to improve the wear resistance of responsible parts [4]. It is known that the combined method of surface-plastic deformation (SPD) is carried out after laser heat treatment (LHT) under a separate scheme at ambient temperature. In contrast to the combined method, the