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Kinetics of C_xN_y Formation on Electrode Surface Through Electrochemical Method

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Abstract:

Powdered C_xN_y coatings were deposited from acetonitrile on Ni, Si, and C surfaces at a voltage of 500-2000 V by the electrochemical method. Electrolysis products were analyzed by IR spectroscopy, X-ray phase analysis and electron microscopy. According to FTIR data, at frequencies 1370 and 1530 cm^{-1} , absorption bands characteristic for stretching C-N and C=N oscillations are observed. The obtained results indicate that the deposition process occurs in different manner in each specific case, i.e., the kinetics of the electrode depends on the electrode material (Ni, Si, and C).

Keywords: *Electrochemical method, Acetonitrile, Voltage, Electrode, Carbon nitride.*

Introduction

The search of new superhard materials has reached a higher level after publication of [1,2], whose authors theoretically forecast the probability of the existence under normal conditions of crystalline carbon nitride (C_3N_4), which is similar by structure to the known silicon nitride and by hardness to diamond. The calculations performed over further years [3] confirmed the possibility of the existence of crystalline carbon nitride with high mechanical and electrophysical properties.

Most papers report about synthesis of films containing nonstoichiometric nitrogen-carbon compounds using various methods. Generally, film microstructure represents a matrix from amorphous carbon nitride with a low content of crystalline phase grains. In order to synthesize carbon nitride films, many efforts have been devoted to application of physical PVD and chemical CVD methods such as vacuum spraying [4], ion beam deposition [5], ion laser deposition [6], graphite-target spraying in nitrogen plasma [7], et al. All of them are deposition from a gaseous phase. They require complex equipment, high vacuum and high temperature, which adversely affect synthesis of such metastable mixtures as C_3N_4 , alongside with difficult control over experiment conditions.

Over recent years the authors [8] have proposed and used an electrochemical method for deposition of carbon nitride films from a liquid phase. As the latter, organic solvents such as acetonitrile [8], solution of urea in methanol [9], and solution of hexamethyldysalazane in methanol [10] were used.

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This work deals with conditions for production of carbonitride C_xN_y coatings by the electrochemical method on various electrodes in acetonitrile [14].

Experimental

In the investigation, an electrochemical cell was used similar to the one described in [8-10]. The source of direct current made it possible to apply voltage on the electrodes in the range 0-2400 V. The distance between the electrodes was 10 mm. As a working liquid, acetonitrile CH_3-CN of the trade "pure for analysis" was used; it underwent distillation before the experiments. The temperature of electrochemical processes was in the range 18-70 °C. Electrodes were chosen from carbon, silicon, and nickel. The effect of a polar electrode on the kinetics of electrode processes, which was shown up by the change in the current density, I (mA/cm^2), over time, τ (min), was studied in the C-C, Si-Si, Ni-Ni, C-Si, and C-Ni systems. Since the rates of the processes were small and the deposition yields were low, it became necessary to conduct experiments with large electrodes up to 90 cm^2 and a volume of acetonitrile of 600 cm^3 , thanks to which there appeared a possibility to take up powdered products of electrolysis for analyses. The products were analyzed by X-ray diffraction (XRD), IR spectroscopy with the Fourier transformation (FTIR), and X-ray photoelectron spectroscopy (XPS). IR spectroscopic investigations were carried out on a Fourier spectrometer FSM-1201 in the frequency 4000-400 cm^{-1} .

Results and discussion

The molecule of acetonitrile as an organic substance is characterized by the following principal parameters: the bond length between atoms; valence angles, atom charge, dipole moment, polarity, and polarizability, which in strong magnetic fields change. In any electrochemical process, the nature and state of the electrode surfaces play an important part. The properties of electrodes, in their turn, depend on the chemical element, valence, crystalline structure, surface energy as well as on electrical, magnetic, thermalphysic and other properties. This is especially related to processes proceeding in electrochemical systems where as an electrolyte, organic liquid substances (solvents), which have high electrical resistivity, are used. They do not dissociate into anions and cations like aqueous solutions of electrolytes, which operate at low voltage (3-30 V). That is why investigation of the kinetics of electrode processes near the boundary organic solvent/solid electrode is of great interest, firstly, from the scientific viewpoint and, secondly, thanks to the possibility of producing needed substances and materials via electrochemical processes.

All of the previous investigations have been carried out using the same electrode pair carbon/silicon, with carbon being as an anode and silicon as a cathode. How this system behaves after changing electrode polarity vice versa was completely unclear. Therefore, the aim of our work was to study the kinetic behavior of electrodes made from systems of carbon, silicon, and nickel elements, different in their chemical nature and properties in acetonitrile. We expected the carbonitride C_xN_y to be the product of the electrolysis. We were interested in the behavior of the systems in the cases of electrodes from the same material as well as from different materials.

Tab. I represents various electrochemical systems of electrodes studied in acetonitrile at chosen electric field intensity, indicates the electrode on which the electrolysis products form, and gives their visual characteristics.

Tab. I. Electrochemical electrode/acetonitrile systems

Symbol of System	System of electrodes	Intensity of electric field, V	Formation of coating on:	Characteristic of coating
a	C ⁺ -C ⁻	500-2000	no coating	
b	C ⁻ -Si ⁺	500-2000	Si ⁺	Powdered coating of gray-yellow color
c	C ⁺ -Si ⁻	500-2000	Si ⁻	Powdered coating of brown-yellow color
d	Si ⁺ -Si ⁻	500-2000	Si ⁺	Powdered coating of gray-yellow color
e	C ⁺ -Ni ⁻	500-2000	no coating	
f	Ni ⁻ -Ni ⁺	300-1500	Ni ⁻	powdered coating of yellow-green color

As follows from these data, in such systems as C⁺ - C⁻ and C⁺-Ni⁻ in the U range 500-2000 V, the formation of coating is not observed. From the other systems, namely C⁻-Si⁺, C⁺-Si⁻, Si⁺-Si⁻, and Ni⁺-Ni⁻, powdered coatings different in color form. It is worth noticing that the polarity of electrodes in the C-Si system determines the electrode (+ or -) on which electrolysis products form. In the C-Si system they can form on both Si⁺ and Si⁻ electrodes (see Tab. I, symbols *b* and *c*). In the case of the Si⁺-Si⁻ system, the electrolysis products form on Si⁺ whereas in the Ni⁺-Ni⁻ system on the negative Ni⁻ electrode.

The data obtained indicate that the nature of electrodes significantly affects the kinetics of interaction in the acetonitrile/electrode system. Fig. 1 (*a-f*) demonstrates the dependences of changes in the current density, *I* (mA/cm²), on the experiment duration, τ (min), for the systems investigated. It should be noticed that for C⁺-C⁻ (*a*) and C⁺-Ni⁻ (*e*) systems, electrolysis products form on the electrode surfaces in the presence of current in the circuit, which is lower than in the other systems by an order of magnitude. This evidences the fact that electric energy is spent on the decomposition of acetonitrile into individual radicals, which form new species of molecules of organic substances (the composition of the liquid phase was not analyzed) and on heating of liquid phase (from 18 to 70 °C).

In the C-C system (Fig. 1*a*) at the initial stage up to 50 min, the current sharply decreases, then after 100 min it increases and practically reaches the initial value within 400 min. In our opinion, this is associated with the change in the chemical composition, physical and physicochemical properties of the liquid phase. The same phenomenon, that is, an increase in the current over time, was observed in other systems such as C⁻-Si⁺ (Fig. 1*b*) and C⁺-Si⁻ (Fig. 1*c*), however, to a much lesser extent. For Si⁺-Si⁻ (Fig. 1*d*), C⁺-Ni⁻ (Fig. 1*e*), and Ni⁺-Ni⁻ (Fig. 1*f*) systems, a decrease in the initial current density by 2-3 times occurs and over time up to 400 min this tendency remains but to a lower extent. The current density in the systems characterized by the formation of electrolysis products is 10-50 fold higher than in the other systems. Such different behaviors of electrode pairs in acetonitrile at high electric field intensities indicate complicated electrode processes and strong influence of the nature and polarity of the electrodes in an electrochemical system.

The XRD spectra demonstrate that the electrolysis products formed on the electrodes are X-ray amorphous; crystalline phases are not observed. The powdered materials forming in the Ni⁺-Ni⁻ systems (deposited on Ni⁻) underwent heat treatment at 300 and 900 °C in air. The X-ray spectra obtained are shown in Fig. 2. With increasing the heat treatment temperature, a crystalline structure corresponding to NiO and Ni appears. We suppose that in this case

metal-organic nickel compounds form, which decompose under treatment in air with the formation of nickel oxides.

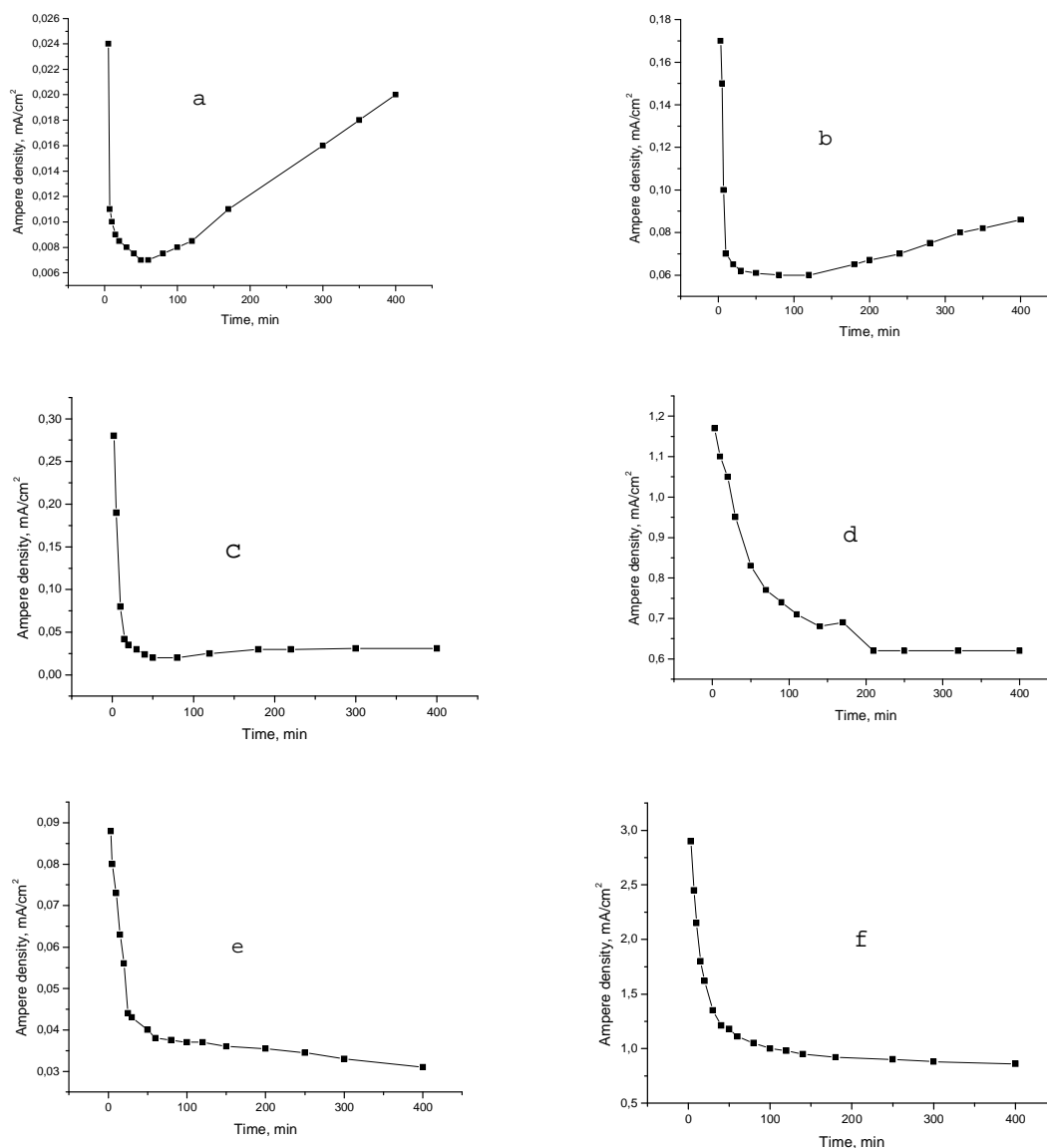
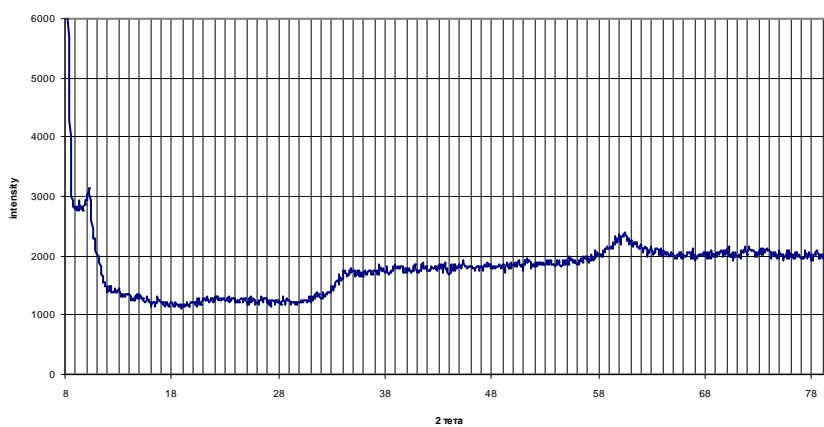


Fig. 1 Change in the current density, I (mA/cm²), over time, τ (min), under electrochemical interaction of acetonitrile in the systems:

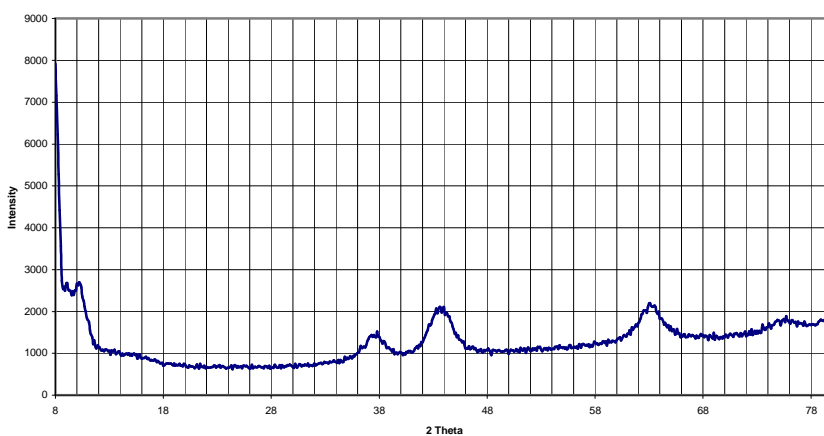
- C^+-C^- , $U=1900$ V, no deposit ;
- C^-Si^+ , $U=1200$ V, deposit on Si^+ ;
- C^+Si^- , $U=2300$ V, deposit on Si^- ;
- Si^+Si^- , $U=1000$ V, deposit on Si^+ ;
- C^+Ni^- , $U=2300$ V, no deposit ;
- Ni^-Ni^+ , $U=300$ V, deposit on Ni^- ;

The IR spectrum from the electrolysis product of the $C^- - Si^+$ -acetonitrile system is presented in Fig. 3. The formation of powdered deposit of gray - yellow color on Si^+ is

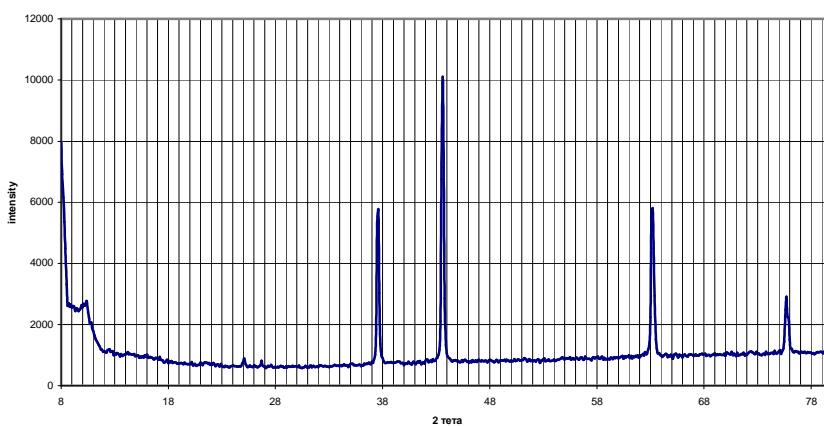
evident (symbol *b*, Table) (electric field intensity 1370 V, temperature 20-72 °C, process duration 18 h).



a)



b)



c)

Fig. 2. XRD spectrum from the coating obtained in the Ni-Ni-acetonitrile system on the negative Ni- electrode: (a) deposit without heat treatment; (b) heat treatment at 300 °C; (c) heat treatment at 900 °C.

In the IR spectra from the powder formed on the silicon electrode, in addition to the characteristic C-N and C=N bands in the frequency range 1370 and 1530 cm^{-1} , absorption bands appear, which can be related to Si-N oscillations in the frequency range 450-1150 cm^{-1} . The presence of the absorption frequencies 2170-2200 cm^{-1} can be prescribed to the valence oscillations of the end C \equiv N bonds. The absorption bands in the ranges 2800-3000 and 1210 cm^{-1} are connected with the valence and deformation CH oscillations, respectively. The IR spectra from powders have absorption bands in the frequency range 3100-3600 and 1640 cm^{-1} , which can be related to the valence and deformation NH oscillations, respectively. From the IR spectra obtained, a conclusion can be drawn that under interaction of acetonitrile with a silicon electrode, composite $\text{C}_x\text{N}_y\text{-Si}_3\text{N}_4$ coatings form.

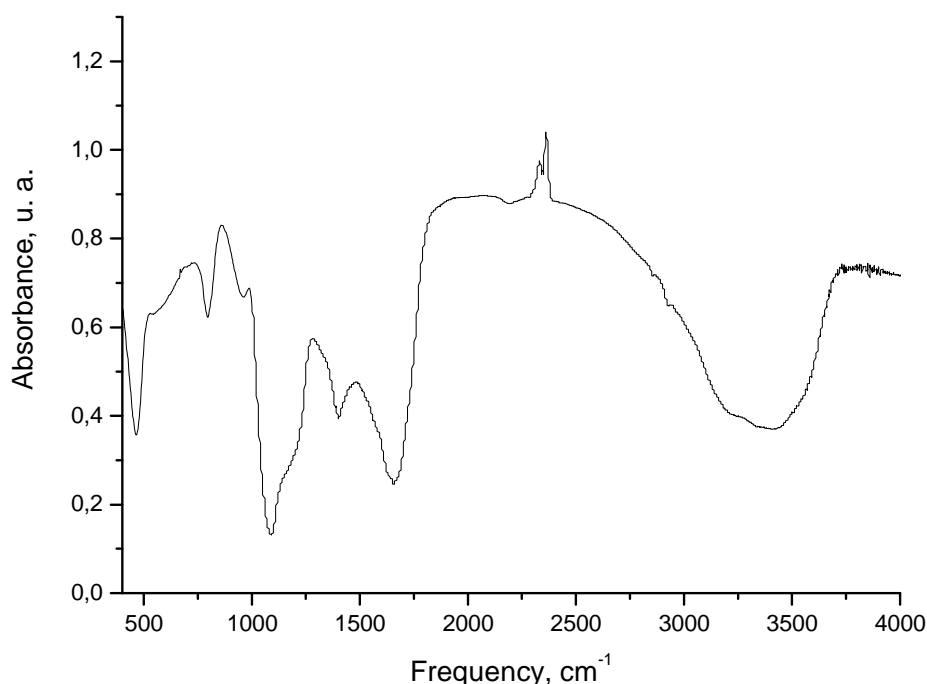


Fig. 3 FTIR spectrum from the C-Si⁺-acetonitrile system; coating on Si⁺ at U= 1370 V, T= 20-72 °C, τ = 18 h.

For the Ni-Ni (*f*) system, in addition to the abovementioned bonds, the presence of the Me-C and Me-O bonds is characteristic, which manifest themselves in the bands within the frequency range 400-800 cm^{-1} .

The powdered products of the electrochemical synthesis deposited on the Si⁺ electrode of the Si-Si-acetonitrile system were analyzed using x-ray photoelectron spectroscopy. Fig. 4 shows XPS spectra, which indicate the presence of nitrogen and oxygen in the electrolysis products. The C1s spectrum decomposes into two components with bound energies of 284.6 and 287.8 eV, which are related to the C-C and C-N bonds, respectively. The N1s spectrum also decomposes into two peaks, 399.3 and 405.1 eV. The N1s peak located at 399.3 eV corresponds to the nitrogen bound with sp^2 C. The origin of the N1s peak at 405.1 eV is not clear yet. The oxygen O1s spectrum has one peak with an energy of 532 eV. The presence of oxygen in the coating obtained is caused by its adsorption on the surface of material.

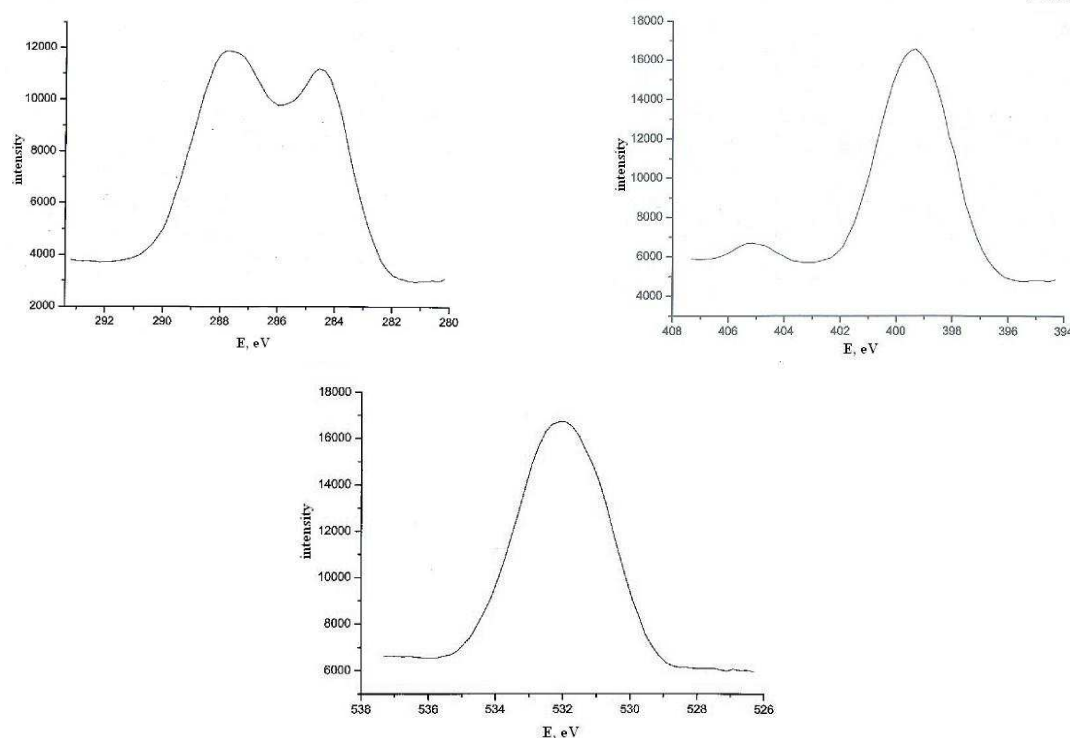


Fig. 4 XPS spectrum from the C_xN_y coating obtained in the Si-Si-acetonitrile system on Si^+ electrode: (a) C1s, (b) N1s, (c) O1s.

The atomic composition of the electrolysis product is: C = 44.9 %, N=24.6%, O=24.4%, and Si=6.1%. The N/C ratio in the coating is equal to 0.54, which is high enough in comparison with the C-Si-acetonitrile system [8, 10].

Conclusions

For the first time, the kinetics of electrode processes proceeding at the boundary organic solvent (acetonitrile)/solid electrode has been studied at temperature 18-70 °C and direct electric field intensity of 400-2000 V. As electrodes, C, Si, and Ni were used. The cases when in the electrochemical cell electrodes were made from the same material or from combination of different materials have been considered. In the case of different materials, the electrochemical kinetics is markedly affected by the polarity of electrodes, which determines the character of forming electrolysis products. In the case of the C^+-C^- and C^+-Ni^- electrode systems, the formation of electrolysis products is not observed. In the studied systems of elements C, Si, and Ni under electrolysis in acetonitrile, oxides, carbonitrides, and composite powdered $C_xN_y-Si_3N_4$ materials form depending on the electric field intensity and electrode polarity. By using X-ray phase analysis, IR spectroscopy, and X-ray photoelectron analysis, it has been established that in the coatings obtained there are single and double carbon-nitrogen bonds and the N/C ratio is equal to 0.54.

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Садржај: Превлаке од праха C_xN_y су нанете електрохемијском методом из ацетонитрила на површине Ni, Si, и C под напоном од 500-2000 V. Производи електролизе су анализирани IR спектроскопијом, рентгенском анализом и електронском микроскопијом. У складу са FTIR подацима на фреквенцијама од 1370 и 1530 cm^{-1} примећени су апсорпциони опсежи који су карактеристични за истегање C-N и C=N осцилатора. Добијени резултати су указали да се процес наношења одвија на различите начине за сваки специфичан случај. Кинетика електрода зависи од материјала од кога је електрода (Ni, Si, и C).

Кључне речи: Електрохемијска метода, ацетонитрил, напон, електрода, карбонитрид.
