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ХАБАРШЫСЫ**

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КАРАГАНДИНСКОГО
УНИВЕРСИТЕТА**

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МАЗМУНЫ — СОДЕРЖАНИЕ — CONTENT

ТЕХНИКАЛЫҚ ФИЗИКА

ТЕХНИЧЕСКАЯ ФИЗИКА

TECHNICAL PHYSICS

<i>Yarkimbaev Sh.S., Fedorov E.M., Redko V.V., Galtseva O.V., Jiang X.</i> Study of physical control methods for metric parameters of extended products in cable industry	7
<i>Sagidugumar A.N., Turlybekuly A., Dogadkin D., Pogrebnjak A.D., Kantay N., Sadibekov A.</i> Phase transformations during the doping of zinc chloride and silver nitrate into calcium phosphates	18
<i>Goldshteyn A.E., Abakumov Kh.Kh.</i> The use of a two-frequency eddy current method for measuring the electrically conductive wall thickness under significant variations in the test parameter and the lift-off	24
<i>Sagidugumar A.N., Dogadkin D.S., Azamatov B.N., Turlybekuly A., Rudenko S.O.</i> Calcium phosphate coating formed on titanium scaffold by plasma electrolytic oxidation	32
<i>Altayeva G.S., Razina O.V., Tsyba P.Yu.</i> Cosmography in the multifield cosmological model	37
<i>Kambarova Zh.T., Saulebekov A.O., Kopbalina K.B.</i> Calculation of the electron-optical scheme of a new type mirror energy analyzer of charged particles	49
<i>Bespal'ko A.A., Utsyn G.E., Fedotov P.I.</i> Experimental Studies of Mechanical-Electrical Transformations during the Destructive Processes Developing in Dielectric Materials	58

КОНДЕНСАЦИЯ ЛАНҒАН КҮЙДІҢ ФИЗИКАСЫ

ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ

PHYSICS OF THE CONDENSED MATTER

<i>Kveglis L.I., Noskov F.M., Kalitova A.A., Nasibullin R.T., Nyavro A.V., Cherepanov A.N., Olekhovich A.E., Saprykin D.N.</i> Influence of the size of iron nanoclusters on their magnetization	68
<i>Lyashuk O., Serilko L., Hevko I., Serilko D., Lutsiv I., Vovk Y., Levkovich M., Tson O.</i> The investigation of a physical pendulum motion, which move along a horizontal axis	75
<i>Aimukhanov A.K., Seisembekova T.E., Zeinidenov A.K., Kambar D.S.</i> The impact of SnO ₂ photoelectrode's thickness on photovoltaic properties of the solar cell FTO:SnO ₂ :PTB7-TH:ITIC/Mo/Ag	86
<i>Pavlov A.V., Sagdoldina Zh.B., Kassymov A.B., Magazov N.M., Kengesbekov A.B.</i> Physical and Chemical Processes of Structure Formation of (BeO+TiO ₂)-Ceramics with the Addition of TiO ₂ Nanoparticles	92
<i>Paltusheva Zh.U., Alpysbaiuly N., Kedruk Y.Y., Zhaidary A.D., Aitzhanov M.B., Gritsenko L.V., Abdullin Kh.A.</i> Photocatalytic activity of zinc oxide – graphene oxide composites	102
<i>Bigozha O.D., Seitmuratov A.Zh., Taimuratova L.U., Kazbekova B.K., Aimaganbetova Z.K.</i> Longitudinal magnetoresistance of uniaxially deformed n-type silicon	111
<i>Rozhkova X.S., Aimukhanov A.K., Zeinidenov A.K., Alexeev A.M.</i> Influence of the environment on the morphology, optical and electrical characteristics of the PEDOT:PSS polymer	117
<i>Baitimbetova B.A., Tolubayev K.S., Ryabikin Yu.A., Murzalinov D.O., Zhautikov B.A., Dairbekova G.S.</i> The study of carbon nanomaterials by IR-Fourier spectroscopy, obtained by the action of an ultrasonic field on graphite	127

ЖЫЛУФИЗИКАСЫ ЖӘНЕ ТЕОРИЯЛЫҚ ЖЫЛУТЕХНИКАСЫ
ТЕПЛОФИЗИКА И ТЕОРЕТИЧЕСКАЯ ТЕПЛОТЕХНИКА
THERMOPHYSICS AND THEORETICAL THERMOENGINEERING

Zhussanbayeva A.K., Mukamedenkyzy V., Kossov V.N., Akzholova A.A. Numerical research of characteristic mixing times of isothermal three-component steam-gas systems 133

АВТОРЛАР ТУРАЛЫ МӘЛІМЕТТЕР — СВЕДЕНИЯ ОБ АВТОРАХ — INFORMATION ABOUT AUTHORS 141

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Study of physical control methods for metric parameters of extended products in cable industry

The paper discusses the problems of electrical cables metric (geometric) parameters measurement. The methods of measuring the eccentricity of the electric cables (contact, ultrasonic, X-ray, and inductive-optical) are considered. The advantages and disadvantages of using these methods of technological control of cable products are shown. A study of the inductive-optical conversion method for measuring the eccentricity of a single-core cable, including the circuit for switching on the windings of the inductive converter, is proposed; the design of this converter is presented. The proposed solution makes it possible to achieve good conversion linearity when the conductor is displaced in the control zone. Wherein there is no need to use a system of mechanical drives for centering the magnetic transducer. In addition, the proposed scheme enables to combine the magnetic and optical transducer constructively in the same plane, which ensures to reduce its longitudinal dimensions relative to known analogues. The device prototype for eccentricity control is created based on the proposed transducer; its technical characteristics are confirmed. Direction of further research is determined as part of the development of the industrial design of the device.

Keywords: cable industry, contact methods, contactless methods, geometric characteristics, eccentricity, inductive method, cable core, linearity.

Introduction

Cables and wires are among vital products in modern everyday life. The cable industry is one of the leading and most rapidly developing sectors of the national economy. It has some features, such as a high manufacturability, energy intensity, resource intensity and a high degree of production automation. The maximum indicator of quality is achieved by improving the technology for control of the main product parameters during production and technological-process automation. Therefore, it is necessary to perform the in-process control of both electrical and geometric parameters of cable products [1–2].

The existing control systems (mainly foreign) of the diameter and eccentricity of the electric cable do not meet the requirements of modern Russian consumers in terms of price and number of operational characteristics. It is also unacceptable that there are virtually no instruments by domestic manufacturers of measuring equipment in a strategic area of cable manufacturing.

Controlling the damage of the conductor to the center of the insulating material in the manufacture of products for the cable industry is essential. Eccentricity is the most important parameter for a given type of product and technical and operational characteristics.

Continuous eccentricity control also reduces the consumption of expensive insulation materials (polyvinyl chloride, polyethylene, polyamide, etc.) in the production of signal and power wires and cables. The need

to measure the output of the extrusion die (core insulation temperature of $\sim 130^\circ\text{C}$) and the process continuity does not allow the use of contact and destructive eccentricity control methods. Figure 1 shows the section of the insulated core of the electrical cable, where the distance from the center of the conducting core to the center of the cable sheath (segment e) is its eccentricity, and the segments e_x and e_y are projections of eccentricity along the corresponding axes.

To perform the in-process control of insulation eccentricity, many types of devices are produced based on capacitive, inductive-optical, and X-ray measurement methods. Instruments manufactured by companies that are world leaders in the development and production of control devices for the cable industry, such as Sikora Industrielektronik (Germany), Zumbach Electronic Automatic (Switzerland), ERMIS + (Russia) show the highest characteristics [3].

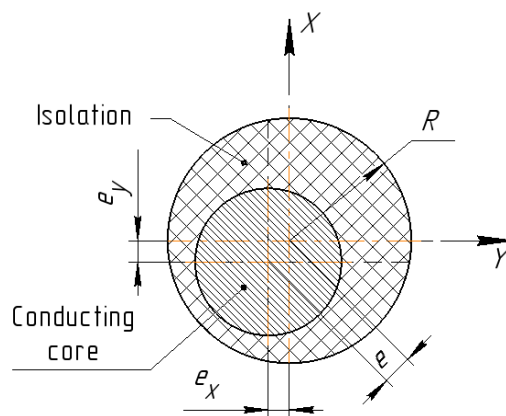


Figure 1. Section of the controlled insulated conductor of the electrical cable

Destructive and contact control methods

The essence of the destructive method of eccentricity control is the selection by the plant quality control service of samples of finished cable products and measurement of eccentricity on their section and, if required, other geometric parameters using measuring microscopes and other available tools that provide the necessary accuracy.

Destructive methods of controlling the eccentricity of cores and cables are not inherent methods of the in-process technological control. This measurement method refers to methods of output and quality control of the finished product or semi-finished product. The method allows rejection of the manufactured products by eccentricity, but it cannot be used to quickly intervene in the production process to eliminate the defect.

The results of these destructive diagnostic methods are distorted or inaccurate for a number of reasons. For example, as a result of deformation, geometric parameters of the structural parts of the product change during control, and control of an individual sample cannot guarantee the quality control of the entire cable coil, which can be several kilometers in length.

The output control of the eccentricity of the finished product alone is not enough to ensure its compliance with the required quality standards. Therefore, the in-process control of eccentricity is required using the developed methods and means of control, both contact and non-contact.

Eddy current methods

The operation principle is based on the use of eddy current resonance sensors that determine the distance to the surface of the conductor located in an insulated core. A pair of sensors is installed on opposite sides of the controlled core. Difference in signals of these sensors is proportional to deviation of the conductor center from the center of the measuring system, which is combined with the insulation center. As a result, the difference in sensor signals depends only on eccentricity along the measurement axis. To control eccentricity simultaneously in two directions perpendicular to each other, two pairs of sensors are installed so that sensitivity axes of each pair are located at an angle of 90° [4].

Alignment of the center of the measuring system with the center of insulation in different devices is implemented in two versions. The simplest version (Figure 2) suggests a mechanical contact method of centering with the help of two pairs of profiled rollers through which the controlled core passes. Sensors with wear-resistant coating that protects them from abrasion are pressed against the insulation surface of the moving core.

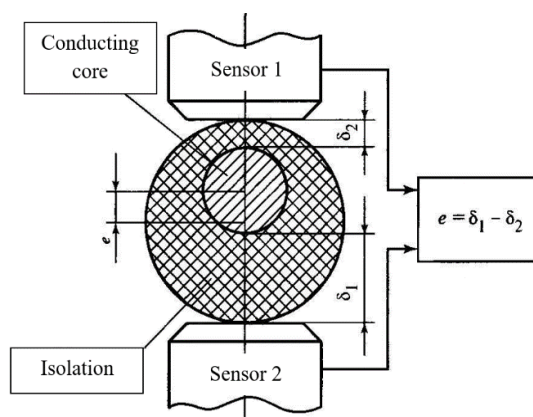


Figure 2. Eccentricity measurement principle with mechanical contact alignment method

This measuring system can be installed on the extrusion line only behind the cooling bath, where the applied insulation acquires the required rigidity. When using such a device, a high-quality drying of the core after cooling must be carried out, since moisture on the insulation surface impairs the accuracy of the device readings.

Non-contact methods

Contact methods used to control eccentricity have serious drawbacks described above. In particular, devices that employ contact methods cannot be installed behind the extruder since the material of the overlay cable sheath at this place is not fully solidified. Therefore, they cannot be used in the automatic extrusion control system. The measurement error of these systems does not meet modern requirements. In addition to contact and destructive methods, methods for non-contact control of cable eccentricity have been developed and implemented in the process.

Ultrasonic methods

Ultrasonic methods are used to control not only the outer diameter of the cable product but also the thickness of its insulation and eccentricity [5].

The method employs the ultrasonic principle (using echo pulse) illustrated in Figure 3. Piezoelectric transducer converts electric energy of short electric pulses into mechanical energy of acoustic waves. When propagating sound waves pass from one medium to another (for example, from water to a polymeric material), part of the energy of these waves is reflected towards the piezoelectric transducer. The waves are reflected from both the outer and inner surfaces of the coating.

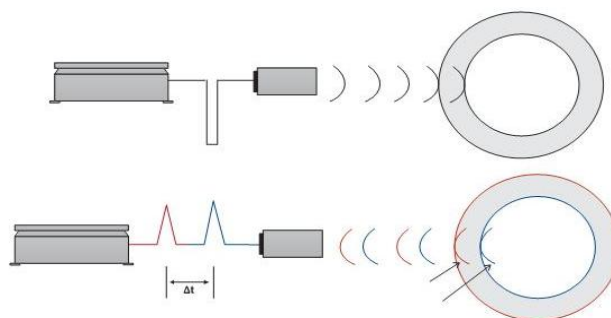


Figure 3. Use of echo pulse in measuring thickness of cable product coating

Thus, it is possible to measure the coating thickness, which will be equal to the production of the velocity of the acoustic wave propagation multiplied by the difference in time of the wave reflection from the outer and inner front surfaces of the coating Δt . The material thickness L can be calculated based on the value of the wave travel time and its velocity using the following ratio:

$$L = v\Delta t / 2, \quad (1)$$

where v is speed of the sound in the material of the measured product sheath, Δt is time of signal passage. The magnitude of the relative change in the signal amplitude can be used to detect defects or measure wave attenuation in the material.

When several pairs of ultrasonic transducers are used, eccentricity, diameter and thickness of the insulation of the product can be measured along two, three or more measuring axes, as shown in Figure 4.

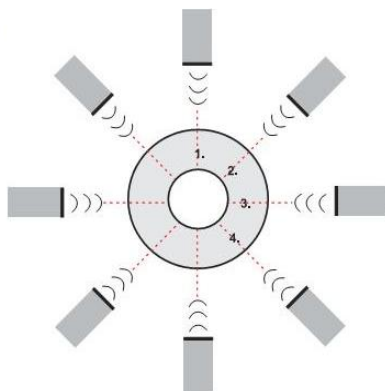


Figure 4. Four-coordinate measurement of cable eccentricity by ultrasonic method

As in the case of diameter measurement, ultrasonic methods of measuring eccentricity have the same disadvantages related to the emission character of primary transducers, which imposes a limitation on the use of such systems in cable enterprises [6–10].

Measurement of eccentricity by ionizing radiation

Due to the development of reliable X-ray sources, the emergence of high-resolution digital X-ray sensors, as well as the gigantic increase in computing power in recent years, new opportunities have opened up for the use of X-ray methods for measuring the internal structure of manufactured cable products, particularly computed tomography.

The main principle of tomography is to provide instrumental imaging of the insides of the object, typically not perceived by the human eye. This involves the use of a ray, which, unlike human vision, has an internal vision of the test object. Such properties are inherent to an X-ray beam, which is physically a high-energy electromagnetic wave formed on the anode of an X-ray source.

The X-ray beam is used to visualize the internal components of the test object. Absorption of some relative amount of X-ray energy is a typical property of a material, which is based on a simple empirical rule: the greater the atomic weight of the element, the higher the ability of the element to absorb beam energy. As a result, materials such as metals or alloys thereof have a high X-ray absorption coefficient, while low atomic weight elements such as polymers have a sufficiently low absorption coefficient depending on the type of polymer and additive material [11].

The X-RAY 2000 is specially made for the measurement of the wall thickness, eccentricity and the inner and outer diameter of single layer hoses and tubes as well as for single layer cables to measure the wall thickness, the concentricity and the outer diameter. Figure 5 shows an example device of this type (Sikora) [10].



Figure 5. X-RAY 2000, Sikora (X-ray meter)

When the beam passes through the test object, the beam energy is partially absorbed, and this depends on the distribution of the material inside the object. The resulting shadow images contain information about the test object. In the past, photographic plates were used to visualize information about an object obtained using a beam. Currently, high-resolution amorphous-silicon digital detectors are used to process digital image information obtained using a beam. The ordered digital data can be rendered by an image recording device or used for further calculations to control the internal geometry of the cable product.

The main advantage of X-ray measuring systems over others is that they can be used to control not only single-core cables and wires but also cable products of a complex multi-layer and multi-core structure.

The high cost of such systems (over 25 million rubles) makes them unprofitable and impractical for control of single-core cables of small cross-section, where cheaper measuring devices that employ other methods of measuring eccentricity can be applied. Another disadvantage is the use of X-rays, which pose a health hazard to the cable plant personnel [12–15].

Inductive-optical method of eccentricity measurement

Inductive transducers are now widely used for non-contact control of many parameters of products made of conductive materials. These transducers have a number of valuable qualities, the main of which are high sensitivity, simplicity of the device, small dimensions and weight, low inertia, etc. Inductive sensors allow appropriate selection of the supply current frequency to increase the sensitivity to a certain controlled value and reduce it in relation to other factors acting on the sensor. For example, by choosing the optimal conversion frequency of the inductive transducer, it is possible to reduce the effect on measurement results of the transverse offsets of the wire, as well as to offset from external electromagnetic interference [16–19].

Eccentricity is measured by using two transducers together on this method. The first is optical. The diameter and position of the cable sheath is measured here. Second, transformer converter is a definition electrically conductive core. Based on the joint data obtained, eccentricity is determined.

Figure 6 shows the design of the converter. The used magnetic converter is essentially a transformer. The functions of the exciting windings are performed directly by the conductor, and the inductive transducer is responsible for the functions of the measuring winding. To let the excitation current flow through the conductor, an inductor is used, which is a ring-shaped core in the form of a transformer. The primary winding is connected to the generator output, and the secondary winding is a conductor through which the core ring is passes.

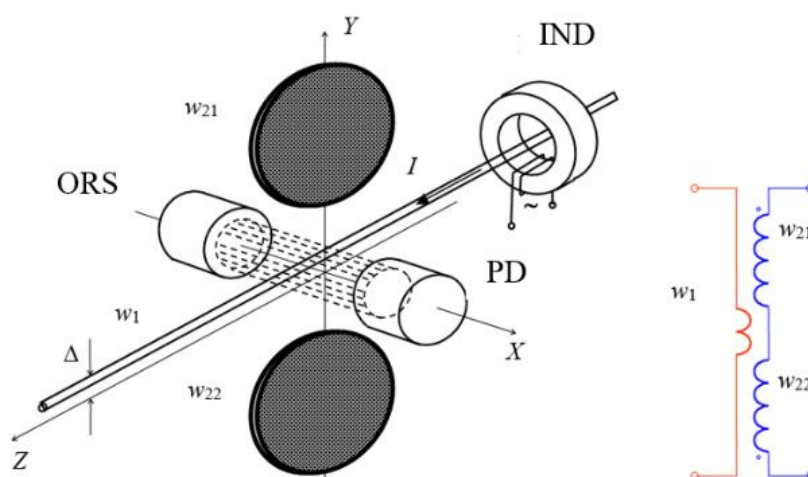


Figure 6. Design of the inductive-optical transducer: ORS — optical radiation source; PD — photodetector; IND — inductor; w_1 — conductor with current (excitation winding); w_{21} , w_{22} — measuring winding sections

The differential induction transducer has two identical sections w_{21} and w_{22} with windings located in the plane ZOY. The geometric axis of the induction transducer symmetry OZ coincides with its electric axis, which is characterized by a zero signal of the transducer, when the axis is aligned with the longitudinal axis of the conductor. When the conductor axis is displaced relative to the OZ axis in the ZOY plane, a signal is generated at the output of the induction transducer, which is functionally associated with the Δ offset value. Figure 6 shows only one induction transducer for measuring OY displacement. In fact, there is another simi-

lar transducer for measuring OX displacement, the windings of which are located in the orthogonal plane ZOX .

Experimental

An inductive-optical method for measuring the eccentricity and diameter of a single-core electric cable has been developed based on the above methods. The method implies a combined use of an optical method for measuring the displacement of the outer cable sheath in a diverging laser beam and an inductive transformer method for measuring the displacement of the cable conductor.

The proposed design includes a mutually inductive transducer with measuring windings that have four rectangular sections connected in series, which are designed to measure the conductor axis coordinates in one of the orthogonal planes. Each of the oppositely connected sections of the transducer described above is replaced by a pair, according to the sections connected (Figure 7). The optimal ratio of the transducer geometric parameters can provide high linearity of the conversion function and the signal independence in the winding designed for measuring the displacement along one axis on the displacement along the orthogonal axis in a wide range of displacements measured.

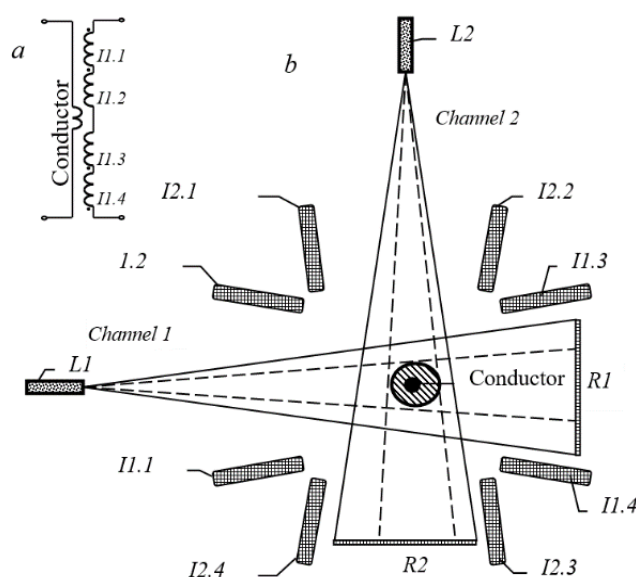


Figure 7. Inductive-optical transducer: *a* — winding connection circuit of the magnetic transducer of one channels; *b* — transducer design

Figure 7 shows a cross-section of the combined inductive-optical transducer with a plane perpendicular to the measured cable, where $I1.1-I1.4$ and $I2.1-I2.4$ are windings of the inductive transducer, which measures the cable core displacement in the first and second channels; $L1$, $P1$ and $L2$, $P2$ are the semiconductor laser module and the multi-element receiver of both measuring channels of the optical measuring system, which controls the position of the outer cable sheath.

Figure 7 shows the design of an inductive measuring transducer, which differs in its windings located in planes intersecting at an angle of 60° and passing through the longitudinal axis of symmetry of the transducer. Similar to the transducer presented in Figure 6, the controlled conductor performs the function of the excitation winding. Each of the pair of measuring windings designed for measuring the conductor axis coordinates along one of the orthogonal axes has two sections connected in series.

Solid lines indicate the dependences of the coordinate factor $K(x,y)$ on the change in the measured y coordinate and on the change in the x coordinate, when the conductor is displaced in the orthogonal direction for the proposed transducer with an optimal ratio of the geometric parameters x_1 and y_1 in Figure 8. The dotted lines indicate similar dependencies for the prototype transducer.

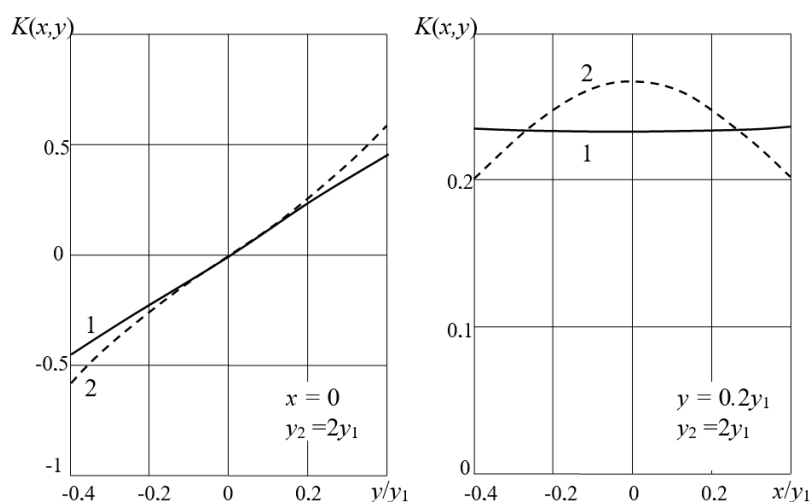


Figure 8. Dependence of the coordinate factor $K(x,y)$ on the change in the measured coordinate of the conductor axis $y(a)$ and on the change in the orthogonal coordinate $x(b)$ for the proposed transducer (1) and the prototype transducer (2)

Figure 9 shows a graph of the coordinate factor dependence, at which the winding section is set at an angle of 60° .

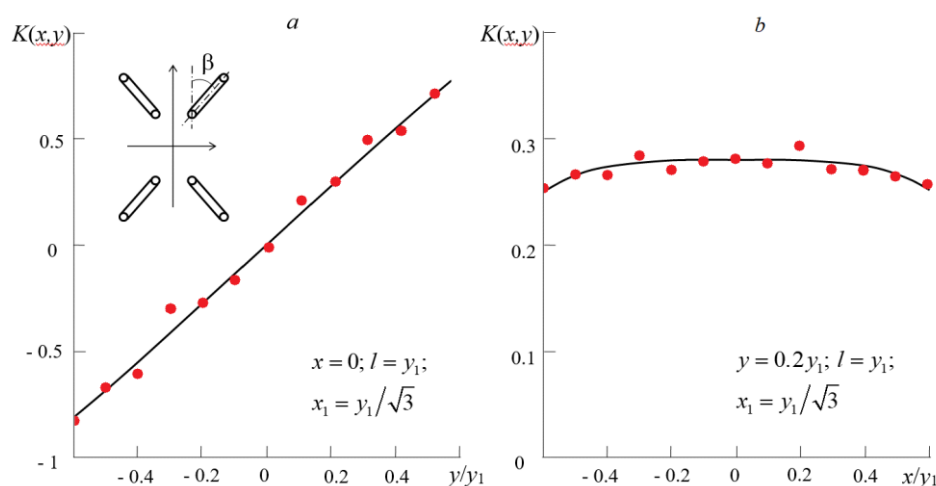


Figure 9. Theoretical and practical dependence of $K(x,y)$ on the measurement of the coordinate of the axis of the conductor y (a) and on the change in the coordinate x (b)

During the experimental part, samples of wire of various diameters were taken. Measurements were carried out by displacing it from the center of the axis of the indicator and optical unit. The results are shown in Table 1.

Table 1

Experimental results

D, [mm]	Cx0, [mm]	Cy0, [mm]	Cx, [mm]	Cy, [mm]	Ux, [mV]	Uy, [mV]
1	2	3	4	5	6	
0.2	0	0	-0.003	0.001	-0.3	0.1
	1	1	0.997	1.006	99.7	100.6
	1	-1	0.999	-1.002	99.9	-100.2
	-1	-1	-0.998	-1.002	-99.8	-100.2
	-1	1	-1.003	1	-100.3	100
0.5	0	0	0	0.002	0.0	0.2
	1	1	0.998	0.999	99.8	99.9
	1	-1	1.001	-1	100.1	-100

1	2	3	4	5	6	
	-1	-1	-0.999	-0.999	-99.9	-99.9
	-1	1	-1.002	0.997	-100.2	99.7
1	0	0	-0.002	-0.004	-0.2	-0.4
	1	1	1.001	0.998	100.1	99.8
	1	-1	0.998	-0.997	99.8	-99.7
	-1	-1	-1	-1.003	-100.0	-100.3
	-1	1	-1.002	0.998	-100.2	99.8
1.2	0	0	0	-0.003	0.0	-0.3
	1	1	0.995	0.997	99.5	99.7
	1	-1	1	-1	100.0	-100
	-1	-1	-0.997	-0.999	-99.7	-99.9
	-1	1	-1	1.002	-100.0	100.2
1.5	0	0	0.002	-0.001	0.2	-0.1
	1	1	0.999	1	99.9	100
	1	-1	1.001	-0.998	100.1	-99.8
	-1	-1	-1.002	-1.002	-100.2	-100.2
	-1	1	-1.001	0.998	-100.1	99.8

An experiment was carried out to compare the conversion function of the proposed converter. As we can see on the graph, the values obtained experimentally characterize good linearity and an order of magnitude less dependence on the conductor displacement in the orthogonal direction.

The discrepancy between the results of mathematical and physical modeling is within the total error of the measuring instruments used in the experiments.

Results and Discussion

Transducer new design with fundamental differences from the existing foreign measuring instruments is proposed (Figure 9). Owing to the magnetic transformer mutually inductive converter, the conversion function has significant linearity, which eliminates the need for electric drives that center the measuring unit in automatic mode relative to the measurement object. Also, it becomes possible to conveniently arrange inductive and optical sensors into a single split system due to the more convenient orthogonal arrangement.

Conclusions

An inductive-optical method for measuring the eccentricity and diameter of a single-core electric cable has been proposed based on the combined use of the optical method for measuring the displacement of the outer cable sheath in a diverging laser beam and the inductive transformer method for measuring the displacement of the conducting core. The proposed inductive method, in contrast to analogs, has a linear transformation function due to the features of the implementation of the measuring transducer. This study is underway. Further, a technical implementation is planned to determine the numerical difference between the used method and the proposed one.

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Ш.С. Яркимбаев, Е.М. Федоров, В.В. Редько, О.В. Гальцева, Цзян Ксю

Кабель өнеркәсібінің ұзартылған бұйымдарының метрикалық параметрлерінің физикалық бақылау әдістерін зерттеу

Мақалада электр кабельдерінің метрикалық (геометриялық) параметрлерін өлшеу мәселелері, сонымен қатар, электр кабельдерінің эксцентриситеттерін өлшеу әдістері (контакттілі, ультрадыбыстық, рентгендік және индуктивті-оптикалық) қарастырылған. Кабельдік бұйымдарды технологиялық бақылаудың осы әдістерін қолданудың артықшылықтары мен кемшіліктері көрсетілген. Индуктивті түрлендіргіштің орамдарын қосу тізбегін қоса алғанда, бір ядролы кабельдің эксцентриситетін өлшеудің индуктивті-оптикалық түрлендіру әдісін зерттеу және осы түрлендіргіштің конструкциясы ұсынылған. Ұсынылған шешім өткізгіштің басқару аймағында орын ауыстырған кезде жақсы конверсиялық сызықтылыққа қол жеткізуге мүмкіндік береді. Бұл жағдайда магниттік түрлендіргішті орталықтандыру үшін механикалық жетектер жүйесін пайдаланудың қажеті жоқ. Сондай-ақ ұсынылған схема магниттік және оптикалық түрлендіргішті бір жазықтықта конструктивті түрде біріктіруге мүмкіндік береді, бұл белгілі аналогтарға қатысты оның бойлық өлшемдерін азайтуға мүмкіндік жасайды. Ұсынылған түрлендіргіш негізінде эксцентристік бақылауға арналған құрылғының түпүлгісі жасалды; оның техникалық сипаттамалары расталды. Әрі қарайғы зерттеулердің бағыты құрылғының өнеркәсіптік үлгісін әзірлеу бөлігі ретінде анықталды.

Кілт сөздер: кабель өнеркәсібі, контакттілі әдістер, контактсыз әдістер, геометриялық сипаттамалар, эксцентристік, индуктивті әдіс, кабель тарамы, сызықтық.

Ш.С. Яркимбаев, Е.М. Федоров, В.В. Редько, О.В. Гальцева, Цзян Ксю

Исследование методов физического контроля метрических параметров протяженных изделий кабельной промышленности

В статье рассмотрены вопросы измерения метрических (геометрических) параметров электрических кабелей, а также методы измерения эксцентриситета электрических кабелей (контактный, ультразвуковой, рентгеновский и индуктивно-оптический). Показаны преимущества и недостатки использования данных методов технологического контроля кабельной продукции. Предложено исследование индуктивно-оптического преобразовательного метода измерения эксцентриситета одножильного кабеля, включающего схему включения обмоток индуктивного преобразователя; представлена конструкция этого преобразователя. Предлагаемое решение позволяет добиться хорошей линейности преобразования при перемещении проводника в зоне контроля. При этом нет необходимости использовать систему механических приводов для центрирования магнитного преобразователя. Кроме того, предложенная схема позволяет конструктивно совместить магнитный и оптический преобразователи в одной плоскости, что позволяет уменьшить его продольные размеры по сравнению с известными аналогами. На основе предложенного преобразователя создан прототип устройства контроля эксцентриситета; его технические характеристики были подтверждены. Направление дальнейших исследований определено в рамках разработки промышленного образца устройства.

Ключевые слова: кабельная промышленность, контактные методы, бесконтактные методы, геометрические характеристики, эксцентриситет, индуктивный метод, жила кабеля, линейность.

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Phase transformations during the doping of zinc chloride and silver nitrate into calcium phosphates

This article shows the results of a study on a biocomposite material based on calcium phosphate doped with ZnCl and AgNO₃. Calcium phosphates are mainly used in dentistry and orthopedics due to their excellent biocompatibility, osteoconductive properties and similarity to the inorganic components of human bone. The main objective of the study is to investigate the morphology, elemental and phase composition, and physico-chemical properties of the obtained material. The test material is obtained in the form of a suspension and subjected to ultrasonic treatment. The microstructure and phase composition of the obtained biocomposites are studied by SEM, XRD, FTIR methods. It is possible to obtain dicalcium phosphate dihydrate (DCPD) by the presented methods, and the results demonstrate a partial replacement of calcium atoms by zinc atoms. X-ray phase analysis shows that Ca(HPO₄)(H₂O)₂ phases as well as CaZn₂(PO₄)₂(H₂O)₂ and AgCl phases were formed during the reaction. Fourier transform infrared spectroscopy revealed that the obtained samples contain the groups HPO₄²⁻ and PO₄³⁻, with the group PO₄³⁻ replacing the group CO₃²⁻. The biocomposite materials could be of great interest in the biomedical field, including the development of coatings that prevent or delay the development of bacterial biofilm.

Keywords: biocomposite material, calcium phosphates, morphology, Ag-doped, hydroxyapatite, bioactivity, biocompatibility, osteoconductive.

Introduction

Currently, biomaterials are an area of great interest in medicine, especially new biomaterials with osteoinductive properties and a bactericidal effect [1]. The fact is that during surgery, there is a risk of bacterial infection. In the event of septic inflammation of the tissues that come into contact with the implant, bacteria can adhere to the surface of the implant and form a biofilm [2]. This leads to the development of "implant-associated infections", which are one of the main complications of orthopedic surgery. Such infections must be treated with systemic antibiotics, which are not always effective because there is another problem - antibiotic resistance of microorganisms [3]. One of the ways to solve these problems is to create materials that have antibacterial properties in addition to biocompatibility.

Silver nanoparticles are effective in treating wounds and ulcers. Currently, antimicrobials containing silver nanoparticles are widely used [4]. It has been shown that AgNO₃ demonstrates significant antibacterial activity against various types of bacteria, both Gram-positive and Gram-negative: *Salmonella*, *Staphylococcus*, and *Pseudomonas*, etc. [5]. In the works of the authors Qiuju Zhou et al. it has been reported that AgNO₃-doped nanocomposite microparticles showed good cytocompatibility and effective antibacterial activity against Gram-negative *E. coli* and Gram-positive *S. aureus* [6]. Zinc ions also show an antibacterial effect. In addition, trace elements of zinc are present in human bone tissue and stimulate the process of osteoinduction and play an important role in the human immune system [7].

The use of biocomposite materials with antimicrobial activity based on calcium phosphates in medicine is promising because human bone tissue is a natural nanocomposite material [8, 9], in which hydroxyapatite nanoparticles (HA) are embedded in collagen fibrils and contain microelements, such as Si, Fe, Zn, Cu, I, Ag, etc., which affect bone tissue, its formation and properties. As an inorganic bone component, HA nanoparticles have excellent biocompatibility, osteoconductivity, and are widely used as a basis for bone tissue engineering, as well as a material for coating implants [10,11].

Calcium phosphates was mainly used in dentistry and orthopedics as dental fillers, coatings for titanium dental implants, as bone substitutes, and for bone reconstruction and regeneration, due to their excellent biocompatibility, osteoconductive properties, and similarity to the inorganic constituents of human bone [12–

16]. This work is devoted to the synthesis and comprehensive study of a biocomposite material based on calcium phosphate doped with ZnCl and AgNO₃.

Experimental

The suspension based on calcium phosphate was obtained by dissolving CaCl₂ · 2H₂O: Na₂HPO₄ · 12H₂O in distilled water in the ratio of 1:2. The solution was mixed in a ball mill for 60 min. ZnCl, AgNO₃ were added to the resulting suspension in different ratios (Table 1). The resulting solution was subjected to ultrasonic treatment for about 40 minutes. The solution was mixed again in a ball mill for 40 minutes. Then the solid fractions were separated by centrifugation and dried at room temperature. The resulting composite material was analyzed using analytical equipment.

XRD analysis. The crystallographic structure investigation was performed by the PANalytical X'PertPro diffractometer. The detector diffraction aperture is 100 μm, anode material - Cu/K-Alpha 1,54060 Å.

FTIR analysis. The functional groups study was carried out by PerkinElmer Spectrum BX Fourier transform infrared spectrometer. Spectra were recorded over the range 4000–400 cm⁻¹ at 1 cm⁻¹ resolution.

SEM analysis. Surface morphology was performed on the JSM-6390LV microscope with the INCA Energy Penta FET X3 energy dispersive microanalysis system at 20 kV acceleration voltage. The chemical elements distribution analysis was performed in the selected area.

Table 1

Concentrations of ZnCl, AgNO₃

Samples	AgNO ₃	ZnCl
1	1,5%	3,5%
2	2,5%	2,5%
3	3,5%	1,5%

Results and Discussion

According to the results of X-ray phase analysis (Fig. 1), all samples were found to contain dicalcium phosphate dihydrate (DCPD) (Brushite) Ca(HPO₄) (H₂O)₂ phases, as well as CaZn₂ (PO₄)₂(H₂O)₂ and AgCl phases. ICSD databases were used in the analysis of the obtained data. The main phase is Ca(HPO₄)(H₂O)₂, which crystallizes in a monoclinic unit cell, and the results show that there is a partial replacement of calcium atoms by zinc atoms, and AgCl synthesis also occurred in the reaction. From a comparison of the diffraction patterns (Fig.1) of the obtained samples, a change in the shape of the diffraction lines with an increase in the zinc concentration is visible. This is probably due to deformation in the crystal lattice and a decrease in the size of nanocrystals of zinc-substituted samples.

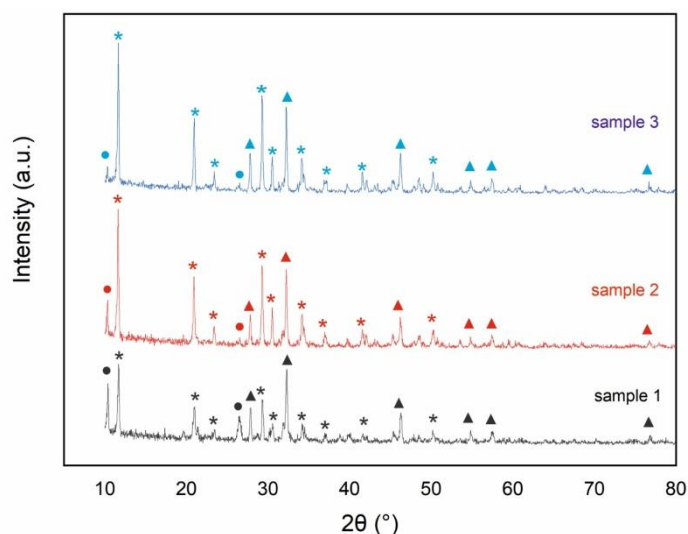


Figure 1. X-ray diffraction patterns of the obtained samples.

* $\text{Ca}(\text{HPO}_4)(\text{H}_2\text{O})_2$ (ICSD code 16738), • $\text{CaZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ (ICSD code 040146), ▲ AgCl (ICSD code 64734).

The surface morphology of the samples was studied (Fig. 2) using a scanning electron microscope (SEM) with INCA analysis. Analysis results illustrate that the samples have similar surface morphology. This indicates that for the samples, the introduction of zinc atoms into the crystal lattice of dicalcium phosphate dihydrate does not change the materials morphology. Images show that these samples have calcium phosphate agglomerates and calcite grains. According to the INCA analysis data (Fig. 2d), we can conclude that white inclusions belong to the AgCl crystals. Our supposition is also proved by XRD analysis data, where the peaks of AgCl (ICSD code 64734) are clearly shown. However, it is difficult to identify certainly because INCA and XRD integrate signals from the material.

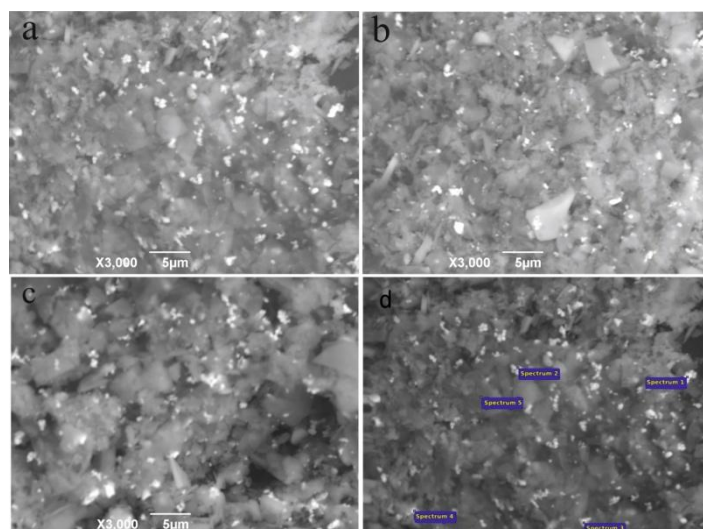


Figure 2. SEM image of samples (a – sample 1; b – sample 2; c – sample 3, d – EDX analysis of the sample 1)

Table 2

Elemental composition of the obtained samples, all results in weight %

Samples	O	Na	Ag	Zn	Cl	Ca	P	Ca/P
Sample 1	58.7±1.38	0	9.3±4.5	8.39±3.4	2.6±0.2	11.18±2.5	9.02±1.6	1.23
Sample 2	55±1.6	1.25	5.58±2.8	5.94±3	2.3±0.13	16±1.07	13.8±0.68	1.16
Sample 3	60±2.1	1.28±0.11	8.44±1.6	1.35±0.22	2.2±0.09	14.076±0.46	11.65±0.46	1.2

From the results of INCA analysis (Table 2), the average Ca/P ratio in Sample 1, Sample 2, and Sample 3 is 1.23, 1.16, and 1.2, respectively. It can be seen that with an increase in Zn concentration, Ca concentration decreases, which could indicate a partial replacement of calcium atoms by zinc atoms, which is confirmed by X-ray diffraction analysis.

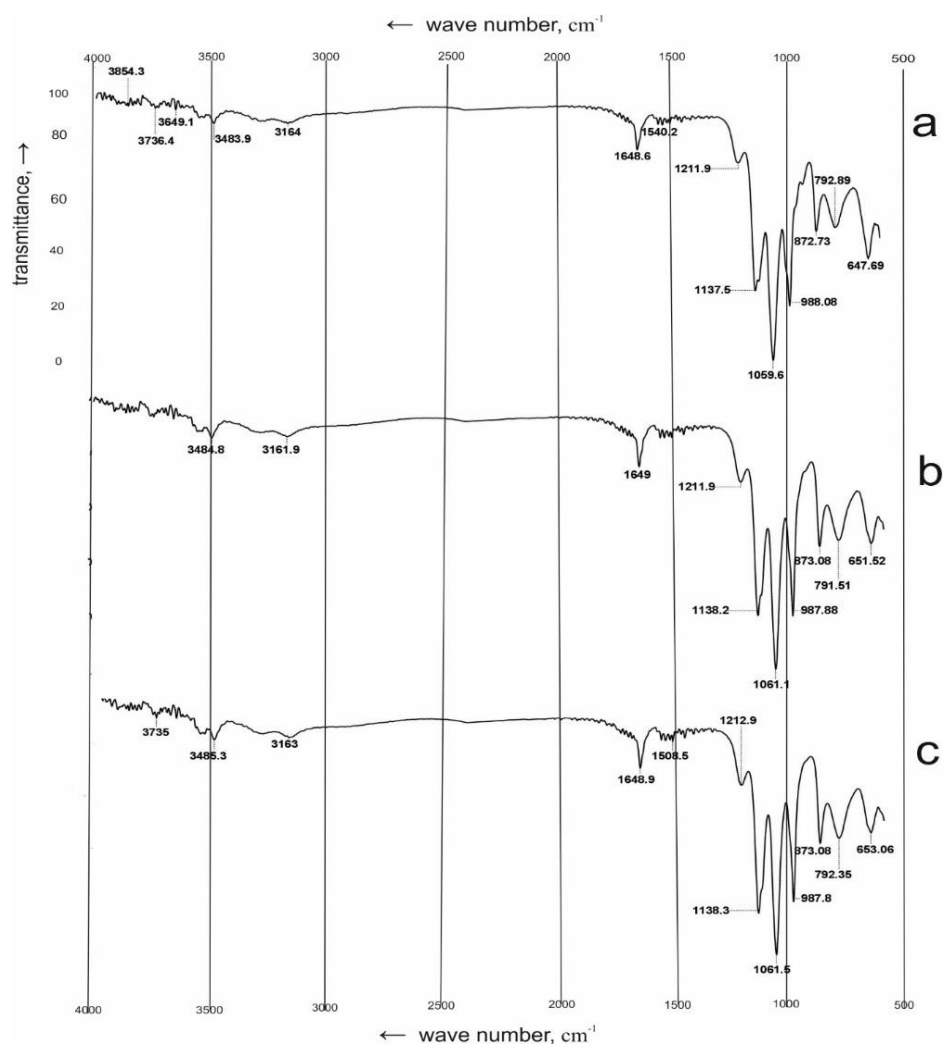


Figure 3. FTIR spectra of the synthesized samples (a – sample 1; b – sample 2; c – sample 3)

In the IR spectra (Fig. 3) of the investigated samples, high-intensity groups of modes in the range of 987.8 and 1061.5 cm^{-1} were observed, which belong to the PO_4^{3-} complex. The vibrational modes at 1038.3 cm^{-1} should be attributed to the asymmetric stretching mode (ν_3) of the P–O bond and bending vibrations of the PO_4^{3-} groups. In addition, vibrational modes in the range of 792 , 873 and 1212 cm^{-1} can be observed in all samples belonging to the HPO_4^{2-} group. The vibrational modes in the range of 653 and 3485 cm^{-1} can be attributed to the group OH. Low-intensity vibrational modes at 1508 and 1648 cm^{-1} show that the PO_4^{2-} group is replaced by the CO_3^{2-} group, which is due to the absorption of CO_2 from the atmosphere during synthesis [17]. In spite of doping with Ag and Zn ions, the relative intensity of CO_2 modes on all samples remained almost constant. When comparing the spectra, the samples doped with Ag and Zn ions show a gradual slight broadening and shift of the absorption bands due to an increase in foreign ions.

Conclusions

The results of X-ray diffraction contributed to the following conclusions: It is possible to obtain dicalcium phosphate dihydrate (DCPD) by the method presented in this work; There is a partial replacement of calcium atoms by zinc atoms; All samples of dicalcium phosphate dihydrate (DCPD) (brushite) contain $\text{Ca}(\text{HPO}_4)(\text{H}_2\text{O})_2$ phases as well as $\text{CaZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ and AgCl phases.

The SEM study outlined that the specimens have similar morphology. Calcium phosphate agglomerates are observed on the surface, as well as crystalline AgCl inclusions $1\text{--}2\text{ }\mu\text{m}$ in size. The INCA analysis demonstrated that with an increase in Zn concentration, Ca concentration decreases, indirectly confirming the partial replacement of calcium atoms by zinc atoms.

According to IR spectroscopy, the obtained samples contain the HPO_4^{2-} and PO_4^{3-} groups, with the PO_4^{3-} group replaced by the CO_3^{2-} group. The results of a comprehensive study provide information for a better understanding of the processes that occur during the synthesis of biocomposite materials.

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Мырыш хлориді мен күміс нитратын кальций фосфаттарына қосу кезіндегі фазалық өзгерістер

Мақалада ZnCl_2 және AgNO_3 қосылған кальций фосфаты негізіндегі биокөмізгіштік материалының зерттеу нәтижелері көрсетілген. Биүйлесімділігі мен остеокондуктивті қасиеттері және адам сүйектерінің бейорганикалық компоненттеріне ұқсастығынан кальций фосфат негізіндегі биокөмізгіштік материалдар, стоматология мен ортопедияда кеңінен қолданылады. Алынған биокөмізгіштің

микроқұрылымы мен фазалық құрамы СЭМ, РФА, ИК-Фурье әдістерімен зерттелді. Дайындалған сынақ материалы суспензия ретінде алынды және ультрадыбыстық өңдеуден өтті. Зерттеудің негізгі мақсаты алынған материалдың морфологиясын, элементтік және фазалық құрамын, сондай-ақ физико-химиялық қасиеттерін зерттеу. Алынған нәтижелерге сәйкес, ұсынылған әдіс бойынша дигидрат дикальцийфосфатын (ДКФД) алуға болатындығы, сонымен қатар нәтижелер кальций атомдарының мырыш атомдарымен ішінара алмастырылатындығы көрсетілген. Рентгенфазалық талдау нәтижелері бойынша реакция барысында $\text{Ca}(\text{HPO}_4)(\text{H}_2\text{O})_2$ фазалары, сондай-ақ $\text{CaZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ және AgCl фазалары пайда болғаны анықталды. ИК спектроскопия әдісімен алынған үлгілерде HPO_4^{2-} және PO_4^{3-} топтары бар екендігі анықталған, сонымен қатар PO_4^{2-} тобымен алмасқанын байқауға болады. Биокөпозиттік материалдар биомедицина саласында үлкен қызығушылық тудыруы мүмкін, соның ішінде бактериялық биопленканың дамуын болдырмайтын немесе баяулататын жабындарды әзірлеу.

Кілт сөздер: биокөпозиттік материал, кальций фосфаты, морфология, гидроксипатит, легирленген Ag, биологиялық белсенділік, биосәйкестік, остеокондуктивтілік.

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Фазовые превращения при допировании хлорида цинка и нитрата серебра в фосфаты кальция

В статье показаны результаты исследования биокөпозитного материала на основе фосфата кальция, допированного ZnCl и AgNO_3 . Фосфаты кальция находят широкое применение, особенно в стоматологии и ортопедии, из-за их превосходной биосовместимости, остеокондуктивных свойств и сходства с неорганическим компонентом костей человека. Микроструктуру и фазовый состав полученных биокөпозитов исследовали методами СЭМ, РФА, ИК-Фурье. Исследуемый материал был получен в виде суспензии и подвергнут ультразвуковой обработке. Основной целью исследования было изучение морфологии, элементного и фазового состава, а также физико-химических свойств полученного материала. Согласно результатам, возможно получение дикальцийфосфата дигидрата (ДКФД) по представленной методике, кроме того, результаты показывают, что происходит частичное замещение атомов кальция атомами цинка. По результатам рентгенофазового анализа было установлено что, в ходе реакции образовались фазы $\text{Ca}(\text{HPO}_4)(\text{H}_2\text{O})_2$, а также $\text{CaZn}_2(\text{PO}_4)_2(\text{H}_2\text{O})_2$ и AgCl . Методом ИК-спектроскопии доказано, что полученные образцы содержат группы HPO_4^{2-} и PO_4^{3-} , кроме того, происходит замещение группы PO_4^{2-} группой CO_3^{2-} . Биокөпозитные материалы могут представлять большой интерес в области биомедицины, включая разработку покрытий, предотвращающих или замедляющих развитие бактериальной биопленки.

Ключевые слова: биокөпозитный материал, фосфат кальция, морфология, гидроксипатит, легированный Ag, биологическая активность, биосовместимость, остеокондуктивность.

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The use of a two-frequency eddy current method for measuring the electrically conductive wall thickness under significant variations in the test parameter and the lift-off

The paper addresses the problem of eddy current testing of the wall thickness of light-alloy drill pipes under significant variations in both the test and the influence parameter of the test object – the lift-off between the eddy current probe and the test object surface. The performance of the two-frequency eddy current method is shown through the use of the signal of the surface eddy current probe of the added high-frequency voltage amplitude as an informative parameter to measure the lift-off and the phase of the added low-frequency voltage. Experimentally obtained dependences of the informative parameters on test and influence parameters are presented. The phase and amplitude-phase multi-parameter methods used to suppress the effect of stray parameters in eddy current testing are analyzed; the effectiveness of their application under significant variations in test and other influence parameters of the test object is shown to be limited. The effectiveness of nonlinear functions for the inverse transformation of the informative parameter into the test parameter to suppress the lift-off effect on test results is estimated. Criteria of choice for informative parameters of the eddy current probe signal are considered. The measurement error caused by the approximation error of the nonlinear functions of the inverse transformation of the informative parameters into the test parameter within the variation ranges of the test and influence parameters is estimated.

Keywords: thickness measurement, surface eddy current probe, signal hodographs, stray parameters, suppression in eddy current testing.

Introduction

One of the important tasks of eddy current testing effectively tackled with surface eddy current probes (ECP) is to measure the wall thickness of pipes made from electrically conductive non-magnetic materials, as well as the thickness of the dielectric coatings of these pipes or the lift-off between the ECP and the pipe surface. A practical example of using the surface ECP is the measurement of the wall thickness of light-alloy drill pipes (LADP) made from D16T duralumin.

Measurement of the wall thickness of electrically conductive pipes using the surface ECP in real inspection is complicated due to possible significant variations in the wall thickness t and the lift-off h between the ECP and the pipe surface, as well as due to the specific electrical conductivity σ of the pipe material and significant impact of these factors on the informative parameters of the ECP signal. These test problems can be solved using well-proven multi-frequency eddy current methods.

The study object is a two-frequency eddy current method used to test the wall thickness of an electrically conductive pipe. The subject of the study is the assessment of its applicability under significant variations in both the test parameter and other influence parameters.

The study aimed to reveal the dependence of the ECT signal on the influence parameters, to choose the informative parameters of the ECP signal, and to choose a method and evaluate its effectiveness for suppression of stray factors, suppression of the lift-off effect in particular. Suppression of the impact of variations in electrical conductivity will be considered in a separate study.

Experimental

Figure 1 schematically shows the design of the surface transformer ECP used in the study, which is supplied with the excitation winding w_1 , measuring winding w_{21} and compensation winding w_{22} . An opposite connection of the measuring and compensating windings in the absence of the test object mutually compensate their initial EMF. An electrically conductive test object located near the ECP causes a signal at the ECP output due to eddy currents generated in the object. In the general case, the amplitude and phase (complex components) of the applied EMF are determined by the amplitude and frequency of the excitation current, ECP design parameters, electromagnetic characteristics of the material and geometric parameters of the test object, and the relative position of the ECP and the test object.

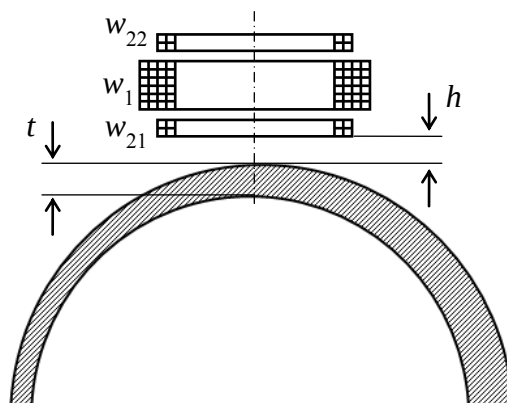


Figure 1. Surface ECP over an electrically conductive pipe

The test object was a pipe made from non-magnetic material with a specific electrical conductivity $\sigma = 16 \text{ MSm/m}$, with a nominal outer diameter $D = 147 \text{ mm}$ and a wall thickness t in the range of (5...12) mm. The distance between the ECP measuring winding and the pipe surface varied in the range of (2...12) mm.

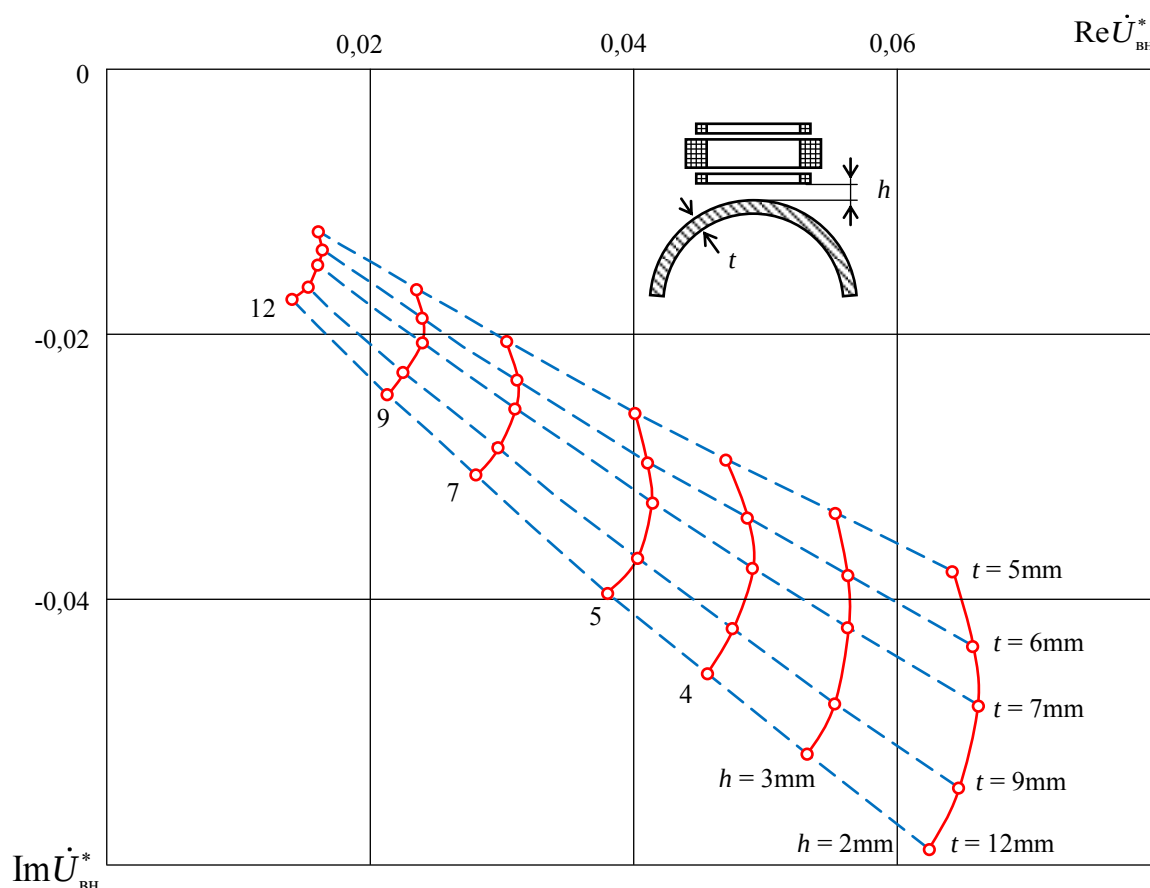


Figure 2. Hodographs of the added relative voltage of the ECP versus variations in the pipe wall thickness and the lift-off

It should be noted that under a wide range of variations in the influence parameters, a higher accuracy of determining the functions of transformation of the influence parameters into the ECP signal informative parameters is required to achieve a high accuracy in the wall thickness measurement with a relative error of less than 3%. The applied mathematical models [1–4] do not provide the required accuracy. Therefore, physical modeling was used to find the transform functions.

During the experiments, a surface ECP with the following structural parameters was used: 40 mm outer diameter of the excitation winding; 32 mm inner diameter of the excitation winding; 10 mm height of the excitation winding; 30 mm diameter of the middle turn of the measuring and compensation windings; 16 mm distance between the planes of the middle turns of the measuring and compensation windings located symmetrically with respect to the excitation winding.

Physical modeling was performed using the SVK-03 eddy current testing system developed at Tomsk Polytechnic University School of Nondestructive Testing to find functional dependencies of the ECP added voltage on the main influence parameters of the electrically conductive test object using different ECPs and excitation current frequencies. The system provides the measurement of the ECP added voltages in the specified ranges of influence parameter variations with a relative error not exceeding 1%.

Figure 2 shows hodographs of the added relative voltage of the ECP versus variations in the pipe wall thickness (solid lines) and the lift-off (dashed lines) for 125 Hz excitation frequency.

At the next stage, informative parameters of the ECP signal were chosen, and the degree of their dependence on the measured and other influence parameters was analyzed. The amplitude of the added voltage [1, 2], the phase of the added voltage [5, 6], both the amplitude and phase of the added voltage [7] and complex components of the added voltage [8, 9] are used as informative parameters to solve various problems of eddy current testing.

When choosing the informative parameter, the main criteria are high sensitivity to the test parameter as compared to the sensitivity to other influence parameters and the monotonicity of the transform function. In most cases of eddy current testing of the electrically conductive wall thickness, the added voltage phase is used as the ECP signal informative parameter [5, 6]. The compliance of this choice with the above criteria can be illustrated based on the analysis of the results presented in Figure 2.

Results and Discussion

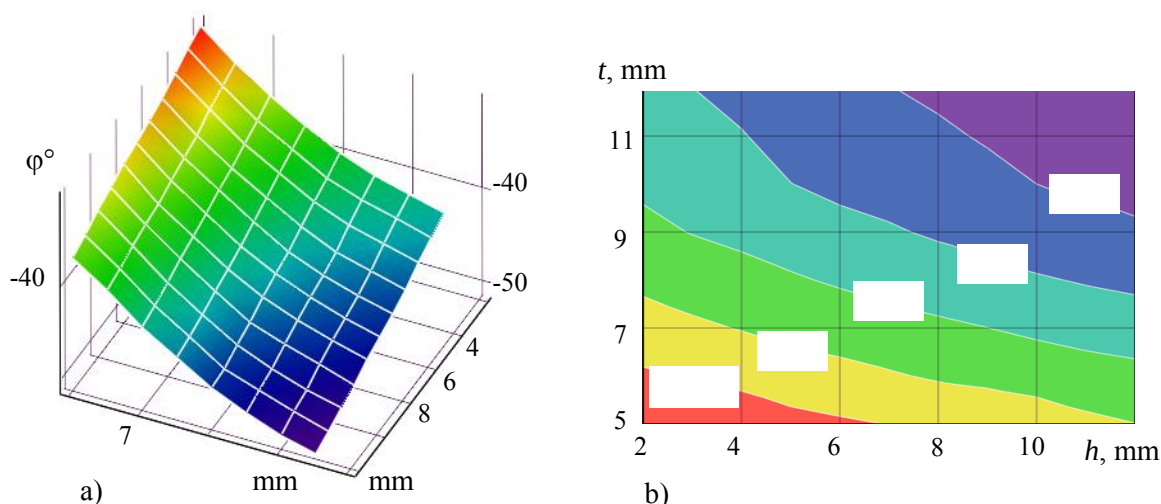


Figure 3. Dependence of the added voltage phase φ on the wall thickness t and the lift-off h : surface plot (a) and level lines of the function $\varphi(t, h)$ (b)

Figure 3 presents the dependence of the added voltage phase on the wall thickness t and the lift-off h , which is a function of two parameters $\varphi(t, h)$. The surface plot (a) illustrates the monotonicity of the dependence $\varphi(t)$, and the level line plot (b) shows a higher sensitivity of the function $\varphi(t, h)$ to the t value variation as compared to its sensitivity to the h value variation. The ratio of the indicated sensitivities corresponds to the tangent of the angle α between the level line (Figure 3b) and the coordinate axis t . If φ does not depend on h , $\alpha \rightarrow \pi/2$ and $\tan \alpha \rightarrow \infty$.

For comparison, Figure 4 shows the dependence of the added relative voltage amplitude on the wall thickness t and the lift-off h . Analysis of the dependence reveals a low sensitivity of the function $A^*(t, h)$ to the t value variation as compared to its high sensitivity to the h value variation and monotonicity of the dependence $A^*(h)$. This indicates that the A^* value is an informative parameter appropriate for measuring the lift-off (thickness of a non-conductive coating) and inappropriate for measuring the thickness of the electrically conductive wall.

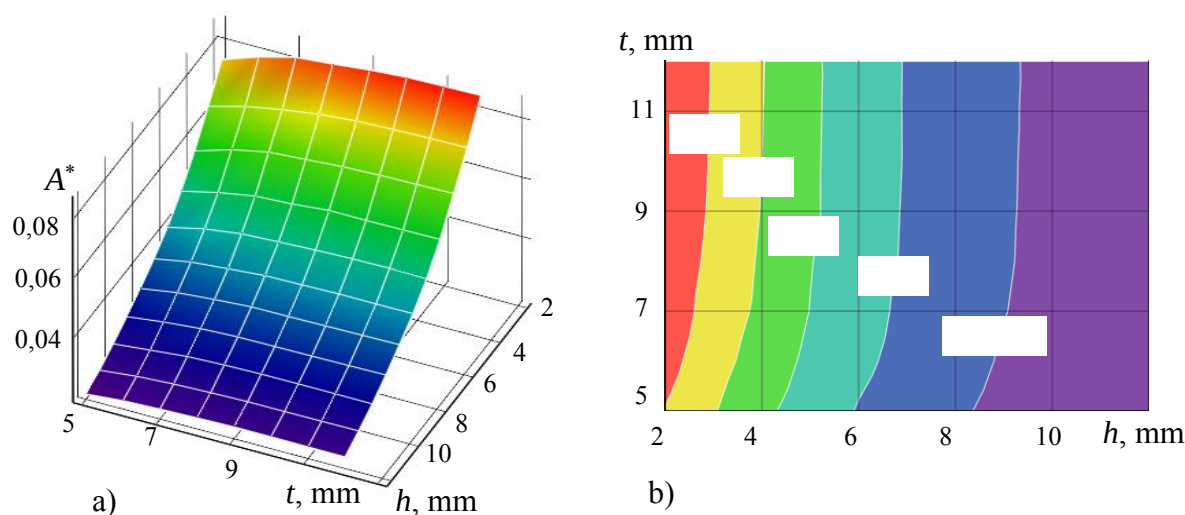


Figure 4. Dependence of the added relative voltage amplitude A^* on the wall thickness t and the lift-off h : surface plot (a) and level lines of the function $A^*(t, h)$ (b)

It should be noted that the dependence of the phase on the lift-off $\varphi(h)$ is relevant for high measurement accuracy when using the added voltage phase $\varphi(t)$ to measure the thickness t of the electrically conductive wall as an informative parameter of the ECP signal. Therefore, the impact of the lift-off h variations on the testing results should be suppressed to effectively measure the thickness t .

The main suppression methods for solving the considered problem are phase [4, 5] and amplitude-phase [1, 2, 9] methods. However, as shown in [7, 8, 10], conventional methods used to suppress the impact of stray parameters do not always provide the desired results. This is because the effective suppression of the influence parameter when using the above suppression methods is possible only if the hodograph of the added voltage versus the parameter variation is a straight line [2, 8]. This can be achieved only in small variation ranges of both measured and influence parameters [9].

The specified limitation can be reduced by nonlinear methods for processing the ECP signal, along with multifrequency excitation of eddy currents [8, 11]. Let us consider a two-frequency eddy current thickness gauge for the wall of light-alloy drill pipes as an example of practical implementation of this method for suppressing influence parameters [12].

To effectively perform testing, the excitation current frequency of the ECP of the eddy current thickness gauge was chosen so that at a high frequency f_1 the penetration depth of the magnetic field was approximately equal to half the wall thickness, and at a low frequency f_2 it exceeded the wall thickness. In this case, the added voltage of the ECP at the first frequency depends on the lift-off h and the specific electrical conductivity of the material σ , and the added voltage at the second frequency depends on the lift-off h , the specific electrical conductivity of the material σ and the wall thickness t .

Data on the wall thickness can be obtained by measuring the added low-frequency voltage phase. In this case, the influence parameters are the lift-off variation and the material-specific electrical conductivity variation, which to a lesser extent affect the value of the added voltage phase. As already indicated, this study considers suppression of the lift-off effect only.

The indicated suppression can be performed using the function of inverse transformation of the relative value of the added high-frequency voltage amplitude A_1 into the value of the lift-off h , which is determined by the numerical analysis of the experimental dependence of the amplitude A_1 on the lift-off h . This dependence with an accuracy sufficient for efficient testing is approximated by the function

$$h = b \ln \left(\frac{A_1}{A_{10}} \right),$$

where b is a coefficient that depends on the outer diameter of the pipe, design parameters of the ECP and the lift-off h variation range; A_{10} is the amplitude value at the minimum h value (determined during setting of the thickness gauge before measurements).

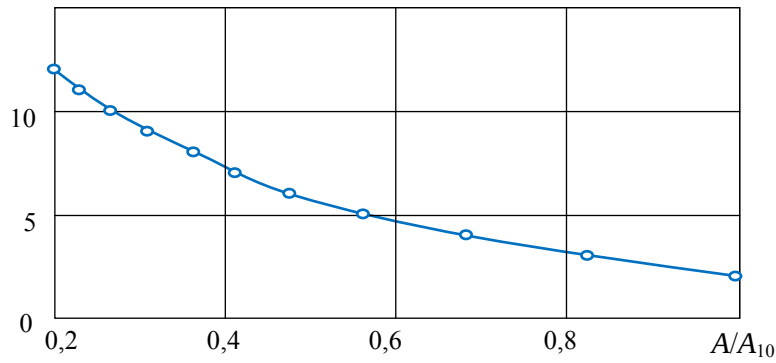


Figure 5. Function of transformation of the relative value of the added high-frequency voltage amplitude A_1 into the lift-off h

Figure 5 presents the plot of the function $h(A_1)$ for the excitation current frequency of 2500 Hz and previously indicated parameter values of the ECP and the test object.

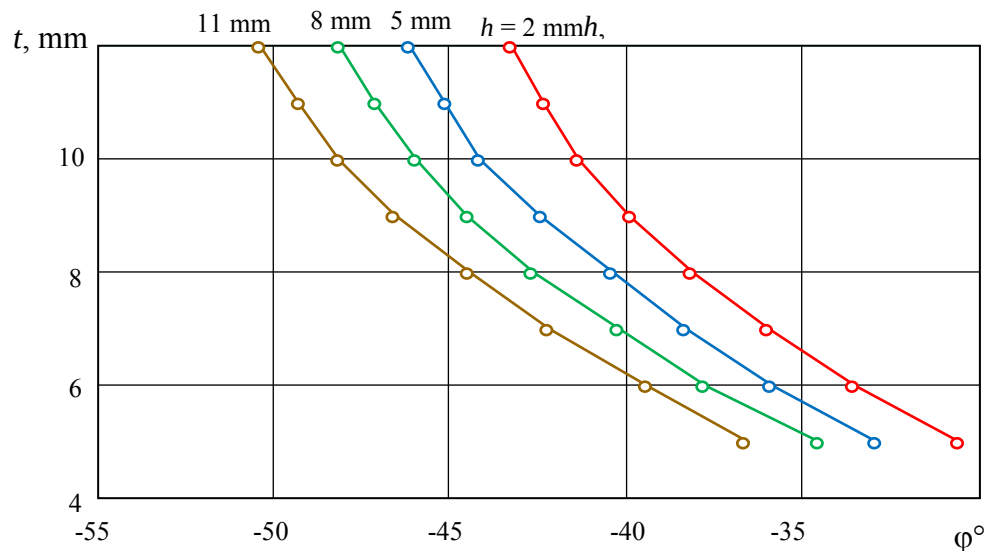


Figure 6. Function of inverse transformation of the added low-frequency voltage phase φ_2 into the pipe wall thickness t for different values of the lift-off h

To determine the desired value of the test parameter, the functional dependence of the pipe wall thickness $t(h, \varphi_2)$ on the lift-off h and low frequency phase φ_2 is used (Figure 6). These functions are approximated by the third-degree polynomials with a sufficient degree of accuracy.

To determine the t value, the discrete values h_i and h_{i+1} corresponding to the thicknesses of the test objects used to determine the dependence presented in Figure 6, which are closest to the measured h value, are first determined. Next, the corresponding values $t_i(h_i, \varphi_2)$ and $t_{i+1}(h_{i+1}, \varphi_2)$ are calculated.

The t value is calculated under the assumption of linearity in a small range of the lift-off h variation in the dependence $t(h)$:

$$t = t_i(h_i, \varphi_2) + \frac{t_{i+1}(h_{i+1}, \varphi_2) - t_i(h_i, \varphi_2)}{h_{i+1} - h_i} (h - h_i).$$

To assess both the quality of suppression of the lift-off variation effect for the measurement result of the pipe wall thickness and the component of the measurement error caused by the approximation error of non-linear functions of the inverse transformation of the informative parameter into the test parameter, the thickness was measured in the indicated variation ranges of the pipe wall thickness and the lift-off.

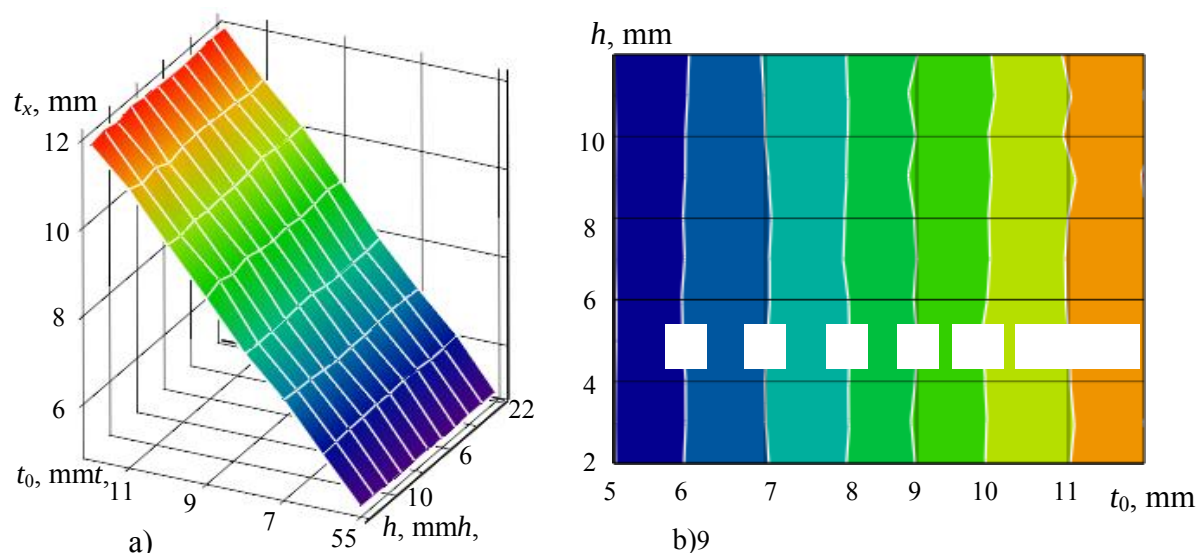


Figure 7. Dependence of the measured wall thickness t_x on the actual value of the wall thickness t_0 and the lift-off h : surface plot (a) and level lines of the function $t_x(t_0, h)$ (b)

Figure 7 presents the measurement results as the dependences of the measured wall thickness t_x on the actual value of the wall thickness t_0 and the lift-off h in the variants of the surface plot (a) and level lines of the function $t_x(t_0, h)$ (b). The plot of the level lines most apparently represents the measurement error. It is evidenced by the mismatch of the level lines (lines of a similar wall thickness) with vertical grid lines.

Figure 8 presents the obtained dependence of the measurement error on the wall thickness t and the lift-off h . The analysis of the dependence shows that this component of the absolute error in the main ranges of the test and influence parameter variations does not exceed ± 0.1 mm.

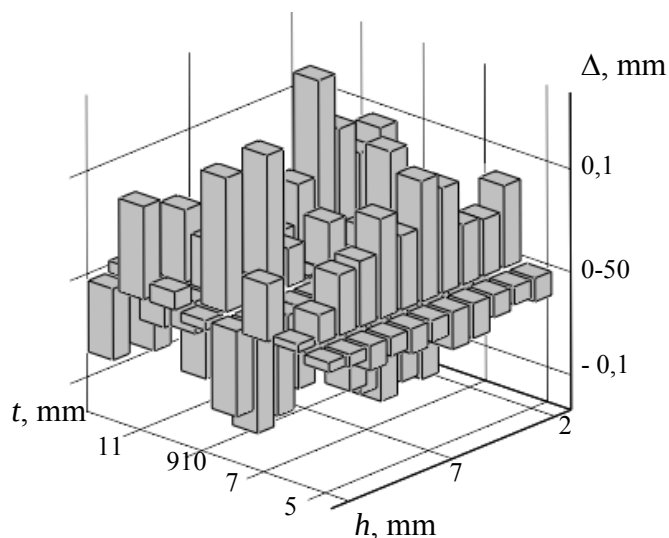


Figure 8. Dependence of the measurement error on the wall thickness t and the lift-off h

Conclusions

Analysis of the results obtained in the study of the two-frequency method for testing the wall thickness of light-alloy drill pipes proved its feasibility under significant variations in both the test parameters and other influence parameters. The requirements for choosing the informative parameters of the ECT signal are presented. The effectiveness of non-linear functions for the inverse transformation of the informative parameter into the test parameter was estimated to suppress the impact of the lift-off variations on the wall thickness measurement results. Due to the error in the approximation of the inverse transformation functions in

the established ranges of variations in the test and influence parameters, the measurement error does not exceed tenths of a millimeter, which is acceptable for solving a wide range of practical tasks.

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А.Е. Гольдштейн, Х.Х. Абакумов

Бақыланатын параметр мен саңылау мәндерінің елеулі өзгерістерімен электр өткізгіш қабырғаның қалыңдығын бақылау үшін екіжілікті құйындыток әдісін қолдану

Бақылау объектісінің бақыланатын және әсер ететін параметрі — құйындыток түрлендіргіші мен бақылау объектісінің беті арасындағы саңылау айтарлықтай өзгерген жағдайда жеңілбалқитын бұрғылау құбырлары қабырғасының қалыңдығын құйындытокпен бақылау есебі қарастырылған. Бұл есепті шешуде қабырға қалыңдығын өлшеу үшін төмен жиілікті кернеудің фазасына енгізілген және саңылауды өлшеуде жоғары жиілікті кернеуге енгізілген амплитудада қолданбалы құйындыток түрлендіргішін ақпараттық сигнал параметрі ретінде қолдана отырып, екіжілікті құйындыток әдісін қолдану тиімділігі көрсетілген. Ақпараттық параметрлер мәндерінің бақыланатыны және әсер ететін параметрлерге эксперименттік түрде тәуелділігі келтірілген. Құйындытоктың бақылау тәжірибесінде қолданылатын фазалық және амплитудалық-фазалық көппараметрлерді кедергі факторларының әсерінен ажырату әдістері талданған; бақылау объектісінің бақыланатын және басқа да әсер ететін параметрлерінің елеулі өзгерістер диапазоны жағдайында оларды реттеу тиімділігінің шектеулілігі көрсетілген. Ақпараттық параметрлер мәндерінің бақыланатын параметр мәніне кері түрлендірудің сызықтық емес функцияларындағы саңылаудың өзгеруін бақылау нәтижесіне алшақтық әсерін пайдаланудың тиімділігі бағаланды. Құйындыток түрлендіргіші сигналының ақпараттық параметрлерін таңдау критерийлері қарастырылған. Бақыланатын және әсер етуші параметрлер өзгерістерінің белгіленген диапазонында ақпараттық параметрлер мәндерін бақыланатын параметр мәніне кері түрлендірудің сызықтық емес функцияларының жуықтау қателігінен туындаған өлшеу қателігінің құрамдас бөлігін бағалау жүргізілді.

Кілт сөздер: қалыңдығын өлшеу, қолданбалы құйынды ток түрлендіргіші, сигнал годографтары, кедергі параметрлері, құйындытокты бақылау кезінде реттеу.

А.Е. Гольдштейн, Х.Х. Абакумов

Использование двухчастотного вихретокового метода контроля толщины электропроводящей стенки при значительных изменениях значений контролируемого параметра и зазора

Рассмотрена задача вихретокового контроля толщины стенки легкосплавных бурильных труб в условиях значительных изменений как контролируемого, так и влияющего параметра объекта контроля — зазора между вихретоковым преобразователем и поверхностью объекта контроля. Показана эффективность применения для решения данной задачи двухчастотного вихретокового метода с использованием в качестве информативных параметров сигнала накладного вихретокового преобразователя амплитуды вносимого напряжения высокой частоты для измерения зазора и фазы вносимого напряжения низкой частоты для измерения толщины стенки. Приведены полученные экспериментально зависимости значений информативных параметров от контролируемого и влияющего параметров. Проанализированы применяемые в практике вихретокового контроля фазовый и амплитудно-фазовый многопараметровые способы отстройки от влияния мешающих факторов; показана ограниченность эффективности их применения в случае значительных диапазонов изменений контролируемого и других влияющих параметров объекта контроля. Оценена эффективность использования для отстройки от влияния на результаты контроля изменений зазора нелинейных функций обратного преобразования значений информативных параметров в значение контролируемого параметра. Рассмотрены критерии выбора информативных параметров сигнала вихретокового преобразователя. Осуществлена оценка составляющей погрешности измерения, обусловленной погрешностью аппроксимации нелинейных функций обратного преобразования значений информативных параметров в значение контролируемого параметра в установленных диапазонах изменений контролируемого и влияющего параметров.

Ключевые слова: измерение толщины, накладной вихретоковый преобразователь, годографы сигнала, мешающие параметры, отстройка при вихретоковом контроле.

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Calcium phosphate coating formed on titanium scaffold by plasma electrolytic oxidation

The article provides the results of the preparation of calcium phosphate coatings by plasma electrolytic oxidation. Calcium phosphate coatings are formed on titanium scaffolds with a porous structure. Titanium scaffolds are products of additive manufacturing equipment by selective laser melting. The morphology of the obtained coating, phase and elemental composition are described, the Ca/P ratio of the coating is determined. The surface of the scaffold is porous due to the baking of powder particles during production. XRD analysis shows the presence of calcium phosphate and oxide compounds. The resulting oxide coating is evenly distributed over the porous surface of the scaffold. Titanium, aluminum and vanadium are located in the areas of the coating free of calcium phosphate particles. The average Ca/P ratio for the resulting coating was 2.48. This value is close to the Ca/P ratio in human bone. It is concluded that the use of the PEO method is promising for the manufacture of scaffolds with a porous structure with calcium phosphate coatings for use in traumatology and orthopedics. The use of titanium scaffolds with a porous structure with calcium phosphate coatings will improve the osseointegration of implants and exclude the possibility of implant failure.

Keywords: titanium, calcium phosphate, plasma electrolytic oxidation, protective coatings, bioactivity, hydroxyapatite, implant, osteogenesis.

Introduction

Currently, artificial materials are widely used in medicine to replace joints and restore bone tissue. Titanium and titanium alloys are used for medical implants since they meet the requirements of modern medicine the most and have high biocompatibility and high corrosion resistance [1], as well as a good strength-to-density ratio. However, due to their limited biological activity, titanium-based materials cannot effectively interact with bone tissue in the early stages of implantation, which can lead to implant failure [2, 3].

To improve biological activity, one of the most effective methods is the deposition of calcium phosphate (CP) coatings on the implant surface by plasma electrolytic oxidation (PEO) [3]. The preparation of such compounds as hydroxyapatite, tricalcium phosphate, octacalcium phosphate, and calcium acid phosphates (brushite, monetite) as part of the coating is preferable because they are similar in composition and properties to the components of natural human bone tissue [4, 5].

Titanium alloys used in medicine are acceptable, but have a significant drawback — this is a discrepancy between the rigidity of the implant and bone tissue, which can lead to a shielding effect, osteoporosis and further loss of the implant [6]. One of the important parameters of bone tissue is porosity, since the porous material provides the necessary conditions for cell growth and division, and can also help to reduce the rigidity of the implant [7], which avoids the shielding effect, which leads to the destruction of bone tissue.

The advantage of the PEO method is the possibility of depositing calcium phosphate coatings on implants of various shapes, including porous ones; this method also makes it possible to obtain coatings with a given phase and elemental composition [7, 8]. In addition, Ag, Zn, and other elements can be used to form a coating with antibacterial properties. ZnO also has luminescent and photoelectric properties and can be used in other directions [9, 10]. Therefore, the optimization of coating parameters and electrolytes for the formation of calcium-phosphate coatings of materials for the replacement and restoration of bone tissue is an urgent problem.

Experimental

Titanium scaffolds with a porous structure were fabricated from titanium alloy powder (Ti-6Al-4V) DIN EN ISO 22674 Rematitan® by selective laser melting (SLM) on an MLab Cusing R (Concept Laser, Germany) additive manufacturing facility.

For coating by the PEO method, a switching power supply “PV-500V/20kW” was used. The surface layer was formed on the surface of scaffolds with a porous structure during PEO processing in an aqueous electrolyte solution using a bipolar mode. A titanium alloy bath (Ti-6Al-4V) was used as a cathode. Electrolyte composition: $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (30-40 g/l), $\text{Ca}_3(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (40-50 g/l). The following parameters were used for coating: pulse frequency – 50 Hz; pulse voltage – 200 V; processing time – 5 min.

The surface morphology and elemental analysis were studied using a JSM-6390LV scanning electron microscope (SEM) equipped with an INCA Energy Penta FET X3 energy dispersive microanalysis system.

X-ray diffraction analysis of the obtained coatings was performed on a PANalytical X'Pert PRO Cu K α diffractometer with a wavelength of 1.54056 Å.

Results and Discussion

The SEM image (Figure 1) shows the surface morphology of the coating obtained by the PEO method. The sample surface has a porous structure and contains titanium particles melted during the additive manufacturing of scaffolds. It can be seen that the resulting oxide coating is evenly distributed over the surface of the sample. Due to the porous surface of the scaffold, additional porosity of the coating surface was formed. The observed coating is the result of CaP transfer from the electrolyte during PEO [11].

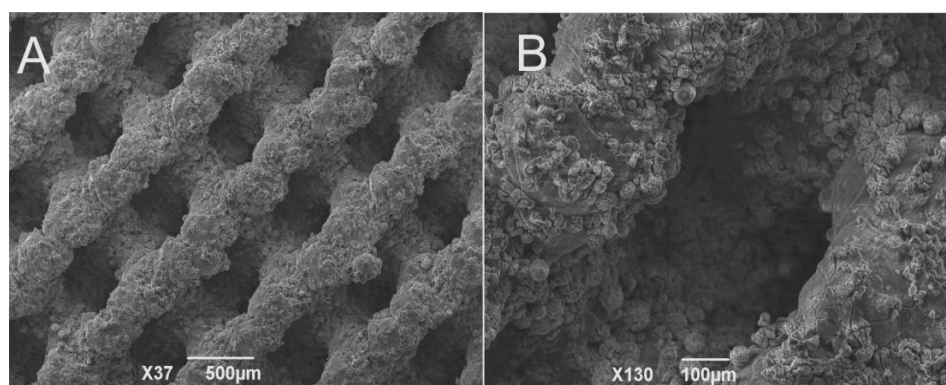


Figure 1. SEM images of the scaffolds surface after PEO

Table 1 and Figure 2 illustrate the results of the energy dispersive X-ray (EDX) analysis. Spectral lines are distinguishable. The elemental composition indicates the presence of an oxide layer, which is the main coating in PEO. According to the presented elemental analysis, it is possible to observe the content of the main elements in the coatings, such as phosphorus, calcium, oxygen, titanium. The average ratio of calcium to phosphorus is 2.48. The Ca/P ratio of the resulting coating is close to the Ca/P ratio in human bone tissue [12].

Table 1

Elemental composition of the obtained CP coatings (wt.%)

Spectrum	O	Na	Al	P	Ca	Ti	V	Total	Ca/P
Spectrum 1	61.27	0.84	2.68	0.94	1.61	31.35	1.30	100	1.7
Spectrum 2	33.37	0.39	1.16	2.24	6.27	53.56	3.01	100	2.7
Spectrum 3	55.18	0.56	2.91	1.30	1.75	36.38	1.92	100	1.3
Spectrum 4	41.38	0.48	1.42	1.95	6.37	46.06	2.35	100	3.2
Average	47.80	0.57	2.04	1.61	4.00	41.84	2.14	100	2.48

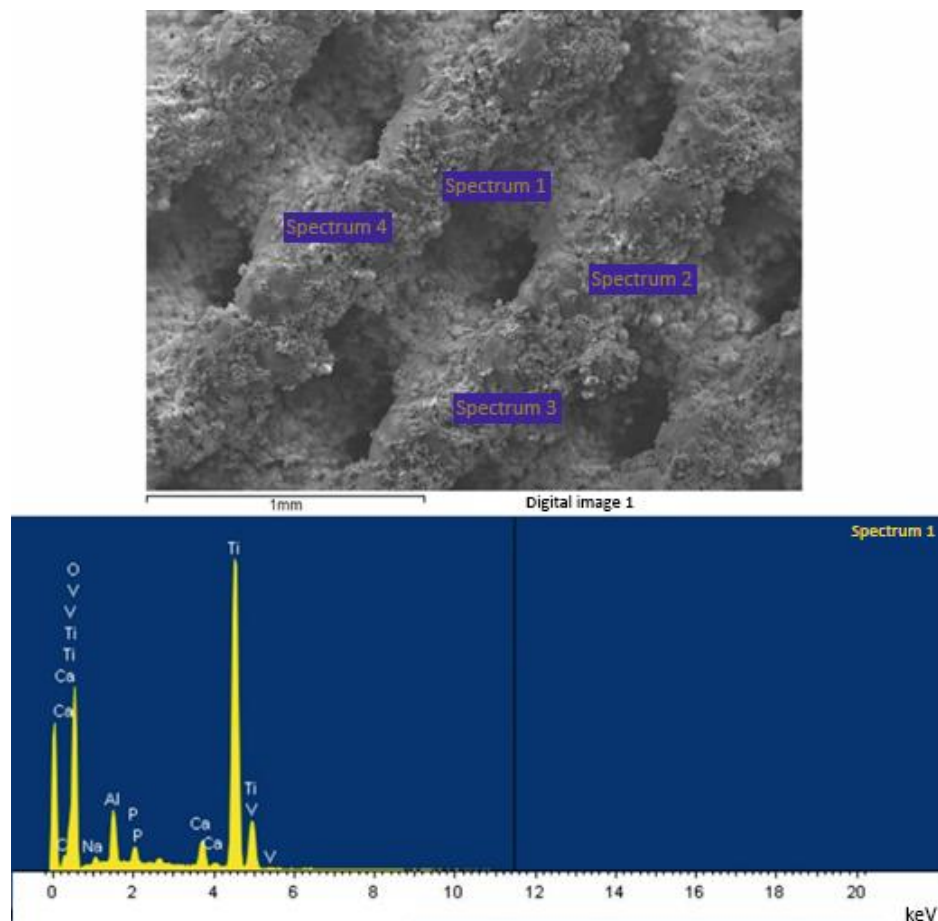


Figure 2. EDX analysis of the obtained CP-coating

On the maps of the distribution of elements, one can observe that phosphorus and calcium are concentrated mainly in the particles that form the surface relief. Titanium, aluminum, and vanadium are located in the areas of the coating free of calcium phosphate particles (Figure 3).

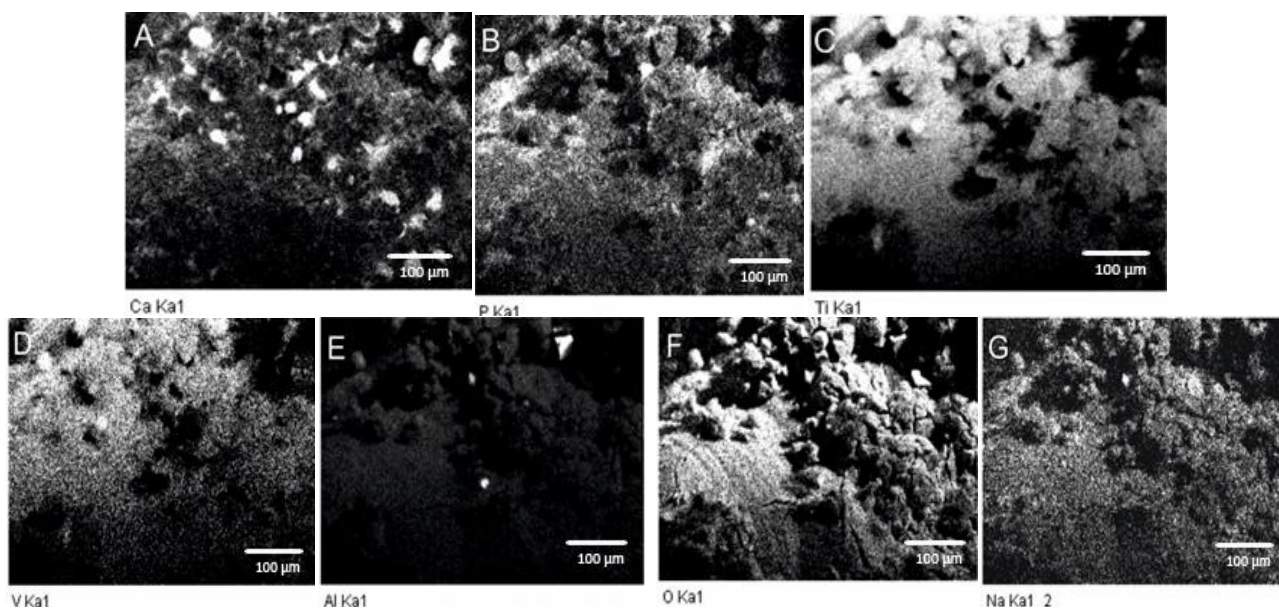


Figure 3. Elements distribution SEM images: (A) - Cl, (B) - P, (C)-Ti, (D)-V, (E)-Al, (F)-O, (G)-Na

Analysis of the XRD pattern (Figure 4) of the resulting coating shows the presence of calcium phosphate and oxide compounds. When analyzing the obtained data, the ICSD databases were used. The presence of a calcium cyclotetraphosphate phase and a titanium oxide coating is confirmed.

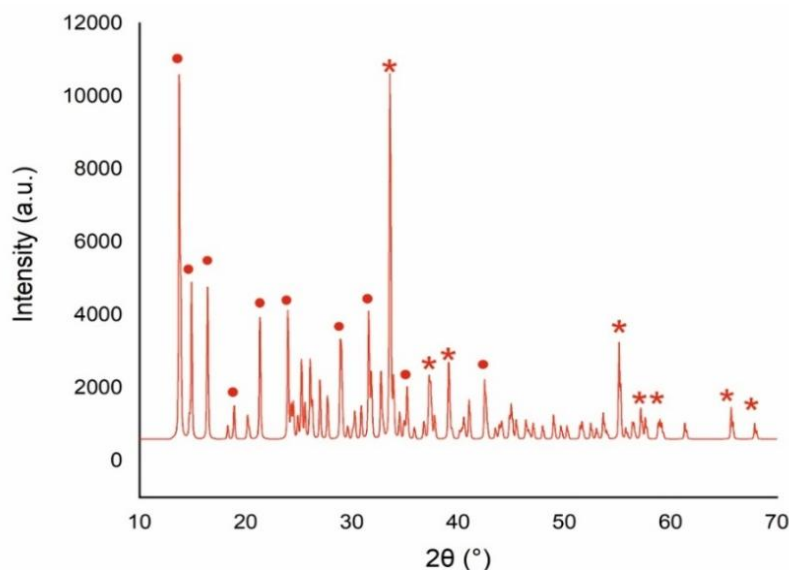


Figure 4 XRD pattern of the resulting coatings
* $\text{Ca}_2[\text{P}_4\text{O}_{12}] \cdot 4\text{H}_2\text{O}$; ● TiO_2

Conclusions

Using the PEO method, calcium-phosphate and oxide coatings were formed on titanium scaffolds with a porous structure obtained by selective laser melting equipment. The phase and elemental compositions, surface morphology were studied, and the Ca/P ratio was determined. It is confirmed that the parameters used for the formation of the coating and the composition of the electrolyte make it possible to obtain an oxide coating with the inclusion of particles of calcium cyclotetraphosphate. The results show the possibility of using the PEO method for modifying titanium scaffolds for subsequent use in medicine, and in particular in traumatology and orthopedics. Modification of the surface of titanium scaffolds will ensure to create bioactive implants, which will positively affect their osseointegration and lead to a decrease in failure rates in the early postoperative periods.

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Плазмалық-электролиттік тотығуы әдісімен қалыптасқан титан скаффолдындағы кальций фосфатты жабын

Мақалада плазма-электролиттік тотығу (ПЭТ) әдісімен кальций-фосфатты жабындарды алу нәтижелері берілген. Кальций фосфатының жабындары кеуекті құрылымы бар титан скаффолдтарында қалыптасты. Титан скаффолдтары селективті лазерлік балқыту әдісімен аддитивті өндіріске арналған жабдықта жасалды. Алынған жабынның морфологиясы, фазалық және элементтік құрамы сипатталған, жабынның Са/Р қатынасы анықталған. Өндіріс процесінде ұнтақ бөлшектерінің қақталуынан скаффолдың беті кеуекті болады. Рентгендік фазалық талдау кальций фосфаты қосылыстары мен оксидті жабынның болуын көрсетеді. Алынған оксид жабыны скаффолдтың кеуекті бетіне біркелкі үлестірілді. Титан, алюминий және ванадий жабынның кальций фосфаты бөлшектері жоқ аймақтарында орналасқан. Алынған жабын үшін орташа Са/Р қатынасы 2,48 болды. Бұл көрсеткіш адам сүйегіндегі Са/Р қатынасына жақын. Травматология және ортопедияда қолдану үшін кальций фосфатты жабындары бар кеуекті құрылымы бар матрицаларды өндіру үшін ПЭТ әдісін қолданудың болашағы туралы қорытынды жасалды. Кальций-фосфат жабыны бар кеуекті құрылымның титан қаңқаларын пайдалану имплантаттардың остеоинтеграциясын жақсартады және олардың қабылданбау мүмкіндігін болдырмайды.

Кілт сөздер: титан, кальций фосфаты, плазманың электролиттік тотығуы, қорғаныш жабындары, биоактивтілігі, гидроксипатит, имплант, остеогенез.

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Кальций-фосфатное покрытие, сформированное на титановом скаффолде методом плазменно-электролитического оксидирования

В статье приведены результаты по получению кальций-фосфатных покрытий методом плазменно-электролитного оксидирования (ПЭО). Покрытия из фосфата кальция формировались на титановых скаффолдах с пористой структурой. Титановые скаффолды были изготовлены на оборудовании для аддитивного производства методом селективного лазерного плавления. Описаны морфология полученного покрытия, фазовый и элементный состав, определено соотношение Са/Р покрытия. Поверхность скаффолда пористая из-за спекания частиц порошка в процессе производства. Рентгенофазовый анализ показывает наличие соединений фосфата кальция и оксидного покрытия. Полученное оксидное покрытие равномерно распределяется по пористой поверхности скаффолда. Титан, алюминий и ванадий располагаются на участках покрытия, свободных от частиц фосфата кальция. Среднее отношение Са/Р для полученного покрытия составляло 2,48. Это значение близко к соотношению Са/Р в кости человека. Сделан вывод о перспективности использования метода ПЭО для изготовления матриц с пористой структурой с кальций-фосфатными покрытиями для применения в травматологии и ортопедии. Использование титановых каркасов пористой структуры с кальций-фосфатными покрытиями улучшит остеоинтеграцию имплантатов и исключит возможность их отторжения.

Ключевые слова: титан, фосфат кальция, плазменно-электролитическое оксидирование, защитные покрытия, биоактивность, гидроксипатит, имплантат, остеогенез.

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Cosmography in the multifield cosmological model

This paper analyzes a cosmological model containing the fermion field, scalar field and vector field with Yukawa interaction. Such a model allows one to research the contribution of various types of matter to the dynamics of the universe. In flat, homogeneous, and isotropic space-time, this coupling can provide the acceleration expansion of the universe. Cosmological reconstruction of dynamical equations is obtained using hybrid solution. This solution is researched by cosmography and energy condition. In the model under study, a zero energy condition, a strong energy condition, and a dominant energy condition are satisfied, and a weak energy condition, which is not mandatory, is not satisfied. It is shown how the cosmographic parameters – the parameters of deceleration q , jerk j , and snap s – can be related to the hybrid value of the scale factor. The resulting analysis makes it possible to relate the model-independent results obtained from cosmography to theoretically substantiated assumptions of gravity. The total density and pressure of the energy of the gravitational field are found in the form of the sum of contributions, which are associated with the bosonic, fermionic, vector fields, as well as the Yukawa type potential. In the model under study, in the early epoch, the bosonic field is responsible for the accelerated regime. Fermionic and vector fields have a positive pressure value, and therefore slow down the accelerated expansion of the universe. At a later time, a transition to a slow mode occurs, as the total pressure tends to zero.

Keywords: scalar field, fermionic field, Yukawa-type interaction, vector field, cosmography, deceleration parameter.

Introduction

The accelerated expansion of the universe was discovered in 1998 based on an SN Ia type brightness curve and its luminosity at maximum. This phenomenon is supported by data of other cosmological observations, such as measurements of the temperature anisotropy of the CMB and the polarization of the cosmic microwave background and large-scale structure in the [1–4]. There are a large of number theoretical models capable of explaining the acceleration expansion and the most popular model assumes that a considerable part of the universe is in the form of dark energy or dark matter [5–17]. An unusual property of dark energy is that it exerts negative pressure on space. Understanding the nature and origin of dark energy is an important question and still an unsolved problem of modern cosmology.

The Standard Model is a successful model of the Big Bang theory. His predictions were confirmed by observations of [18–23], in particular by the expansion of the universe and the existence of relic radiation. Its success is associated with the explanation of the synthesis of light elements and the model of the early universe. The standard model is homogeneous and isotropic at large scales, as evidenced by observations.

The search for the responsible elements for accelerated periods in the evolution of the universe is fundamental in cosmology. Several candidates have been proposed describing both the inflationary period and the modern accelerated epoch: scalar fields, exotic equations of state, and the cosmological constant.

Another way is to consider the fermion field as a gravity source in expansion of the universe [24–26]. In [27–33], gravitation models were researched using multiple sources. The result includes exact solutions, anisotropy to isotropy transition scenarios, and cyclic cosmology.

At considering the fermion field as responsible for acceleration expansion of the universe then different regimes arise. The fermion field rapidly increases and matter is created until it begins to dominate, and as a result, the initial accelerated expansion slows down. When the universe enters the area of dominance of matter, then the fermion field again prevails, which leads to an era of accelerated growth rates of the scale factor. In this case, the fermion field is responsible for inflation in the early Universe and dark energy for the late Universe, without the need for a cosmological study of the constant terms or the scalar field. In the late Universe, energy begins to dominate again and a gradual transition to dark energy occurs, the so-called fermionic energy period, in which the accelerated regime begins and continues in the modern era.

Thus, the purpose of our work is to study the influence of scalar, fermion and massive vector fields and their interaction on the dynamics and evolution of cosmological regimes in a homogeneous and isotropic

spatially flat universe. To achieve the goal and for the selected action, we will perform the following tasks we will find the equations of motion and then construct a solution to these equations using a hybrid scaling factor.

Experimental

Let us consider the general action in the form of

$$S = \int \sqrt{-g} d^4x \left\{ \frac{R}{2} + \frac{1}{2} \partial^\mu \phi \partial_\mu \phi - \frac{1}{2} m_b^2 \phi^2 + \frac{i}{2} [\bar{\psi} \Gamma^\mu D_\mu \psi - (D_\mu \bar{\psi}) \Gamma^\mu \psi] - \right. \\ \left. - V(\bar{\psi} \psi) - \lambda \bar{\psi} \phi \psi + \frac{1}{2} m_v^2 A_\mu A^\mu - \frac{1}{4} F_{\mu\nu} F^{\mu\nu} \right\}.$$

Here sources of gravity are the fermion field and its potential $V(\bar{\psi} \psi)$

$$L_f = \frac{i}{2} [\bar{\psi} \Gamma^\mu D_\mu \psi - (D_\mu \bar{\psi}) \Gamma^\mu \psi] - V(\bar{\psi} \psi), \quad (1)$$

where ψ and $\bar{\psi} = \psi^\dagger \gamma^0$ represent the spinor field and its adjoint, respectively. The covariant derivatives in (1)

$$D_\mu \psi = \partial_\mu \psi - \Omega_\mu \psi + iq A_\mu \psi,$$

$$D_\mu \bar{\psi} = \partial_\mu \bar{\psi} + \bar{\psi} \Omega_\mu - iq \bar{\psi} A_\mu.$$

Here q is a constant which couples the fermion field with the vector field A_μ . Moreover, Ω_μ is the spin connection

$$\Omega_\mu = -\frac{1}{4} g_\rho \sigma [\Gamma_{\mu\delta}^\rho - e^b (\partial_\mu e_\delta^b)] \Gamma^\delta \Gamma^\sigma,$$

where $\Gamma_{\sigma\lambda}^\nu$ is the Christoffel symbols.

The Lagrangian density of a massive scalar field ϕ without self-interaction potential

$$L_b = \frac{1}{2} \partial^\mu \phi \partial_\mu \phi - \frac{1}{2} m_b^2 \phi^2,$$

where m_b is mass of the scalar field.

The Lagrangian density of the massive vector field A_μ

$$L_v = \frac{1}{2} m_v^2 A_\mu A^\mu - \frac{1}{4} F_{\mu\nu} F^{\mu\nu},$$

where m_v is mass of the vector field and $F_{\mu\nu} = \partial_\mu A_\nu - \partial_\nu A_\mu$.

The Lagrangian density corresponds to the Yukawa interaction between the fermionic and the scalar fields

$$L_Y = -\lambda \bar{\psi} \phi \psi,$$

where λ is the coupling constant of the Yukawa potential.

In order to study the evolution of a homogeneous and isotropic spatially flat universe, we use the Friedmann-Robertson-Walker metric

$$ds^2 = -dt^2 + a(t)^2 (dx^2 + dy^2 + dz^2), \quad (2)$$

where $a(t)$ is scale factor of the universe, and the Ricci scalar is expressed as

$$R = 6 \left(\frac{\ddot{a}}{a} + \frac{\dot{a}^2}{a^2} \right),$$

Here we consider the case of time-like vector field, namely

$$A_\mu = (A_0(t), 0, 0, 0).$$

This case is the only possible ansatz compatible with a homogeneous and isotropic space-time. We assume that the self-interaction potential of the fermion field is $V(u) = \xi u^n$, where ξ and n are constants and $u = \bar{\psi} \psi$ is biliner function. Then the corresponding point-like Lagrangian has the form of

$$L = 3a\dot{a}^2 - a^3 \frac{i}{2} (\bar{\psi}\gamma^0\dot{\psi} - \dot{\bar{\psi}}\gamma^0\psi + 2iqA_0\bar{\psi}\gamma^0\psi) +$$

$$+ a^3 \left\{ \xi u^n - \frac{1}{2} \dot{\phi}^2 + \frac{1}{2} m_b^2 \phi^2 + \lambda \bar{\psi}\phi\psi - \frac{1}{2} m_v^2 A_0^2 \right\}. \quad (3)$$

From the Euler-Lagrange equations and energy-momentum tensor, the complete system of equations of motion corresponding to the Lagrangian (3) take the form

$$3H^2 = \rho, \quad (4)$$

$$2\dot{H} + 3H^2 = -p, \quad (5)$$

$$\ddot{\phi} + 3H\dot{\phi} + \lambda u + m_b^2 \phi = 0, \quad (6)$$

$$A_0 = q \frac{\bar{\psi}\gamma^0\psi}{m_v^2}, \quad (7)$$

$$\dot{\bar{\psi}} + \frac{3}{2} H \bar{\psi} - i \bar{\psi} [qA_0 + n\xi u^{n-1} \gamma^0 + \lambda \phi \gamma^0] = 0, \quad (8)$$

$$\dot{\psi} + \frac{3}{2} H \psi + i [n\xi u^{n-1} \gamma^0 + qA_0 + \lambda \phi \gamma^0] \psi = 0, \quad (9)$$

$$\dot{\rho} + 3H(\rho + p) = 0, \quad (10)$$

where

$$\rho = \frac{1}{2} \dot{\phi}^2 + \frac{1}{2} m_b^2 \phi^2 + \xi u^n + \lambda \bar{\psi}\phi\psi + \frac{1}{2} q^2 \frac{(\bar{\psi}\gamma^0\psi)^2}{m_v^2}. \quad (11)$$

$$p = \frac{1}{2} \dot{\phi}^2 - \frac{1}{2} m_b^2 \phi^2 + \xi(n-1)u^n + \frac{1}{2} q^2 \frac{(\bar{\psi}\gamma^0\psi)^2}{m_v^2}. \quad (12)$$

The equations (4), (5) are the Friedmann equations; the equation (6) is the Klein-Gordon equation; the equation (7) is the vector field equation; (8) and (9) are Dirac equations; the equation (10) is the conservation law; (11), (12) are the energy density and pressure, respectively.

We can assume that the total energy density of the gravitational field as the sum $\rho = \rho_b + \rho_f + \rho_Y + \rho_A$ is associated with the bosonic, fermionic fields, as well as the Yukawa potential and the vector field, respectively. Their expressions are of the form

$$\rho_b = \frac{1}{2} \dot{\phi}^2 + \frac{1}{2} m_b^2 \phi^2, \quad (13)$$

$$\rho_f = \xi u^n, \quad (14)$$

$$\rho_A = \frac{1}{2} q^2 \frac{(\bar{\psi}\gamma^0\psi)^2}{m_v^2}. \quad (15)$$

$$\rho_Y = \lambda \bar{\psi}\phi\psi. \quad (16)$$

Total pressure of the gravitational field in the form as $p = p_b + p_f + p_A$ is associated with bosonic, fermionic and vector fields, respectively. The pressure of a Yukawa type potential is zero. Their expressions are of the form

$$p_b = \frac{1}{2} \dot{\phi}^2 - \frac{1}{2} m_b^2 \phi^2, \quad (17)$$

$$p_f = \xi(n-1)u^n, \quad (18)$$

$$p_A = \frac{1}{2} q^2 \frac{(\bar{\psi}\gamma^0\psi)^2}{m_v^2}, \quad (19)$$

$$p_Y = 0. \quad (20)$$

Results

The system of equations (4)–(12) has the following solution in the form of a hybrid function

$$a = a_0 e^{\alpha t} t^\beta, \quad (21)$$

where a_0 , α and β are constants and $\alpha > 0$. By solving equations (11) and (12) together and taking into account the hybrid dependence on the scale factor, we can find the form of the scalar field function

$$\phi = \frac{-\frac{\lambda c}{a_0^3 e^{3\alpha t} t^{3\beta}} + \sqrt{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\beta} - 4m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha\beta}{t} - \frac{2\beta(3\beta-1)}{t^2})}}{2m_b^2}.$$

From equation (7), we obtain a solution for the vector field

$$A_0 = \frac{\dot{c}}{m_b^2 a_0^3 e^{3\alpha t} t^{3\beta}},$$

where we have previously derived the relation simplifying further calculations from the Dirac equations (8),

$$(9) \bar{\psi} \gamma^0 \psi = \frac{\dot{c}}{a^3}, \quad \dot{c} \text{ is constant.}$$

For the fermionic field, we will search for a solution in the form

$$\psi_k = E_k(t) e^{iF_k(t)}, \quad k = 0, 1, 2, 3. \quad (22)$$

Expanding the Dirac equations (8), (9) in component terms and substituting in them the general form of the fermion field (22), we find the exact value of the coefficients

$$\begin{aligned} E_k &= E_{k0} a^{-\frac{3}{2}}, \\ F_k &= -\frac{q^2 \dot{c} 3^{\frac{3}{2}\beta-1} e^{-\frac{3}{2}\alpha t} t^{-3\beta} (\alpha t)^{\frac{3}{2}\beta} - \text{WhittakerM}(-\frac{3}{2}\beta, -\frac{3}{2}\beta + \frac{1}{2}, 3\alpha t)}{m_b^2 a_0^3 \alpha (-1+3\beta)} - \\ &- n \xi \left(\frac{c^{n-1} (n-1)^{3\beta(n-1)} \alpha^{3\beta(n-1)-1} 3^{3\beta(n-1)-1} (\text{WhittakerM}(1-3\beta(n-1), 3\alpha(n-1)t))}{a_0^{3(n-1)}} \right) - \\ &- \frac{\lambda c (1-3\beta) 3^{3\beta-1} \alpha^{3\beta-1}}{2a_0^3 m_b^2 (3\beta-1)} + F_{k0} + \int N dt, \end{aligned}$$

where E_{k0} and F_{k0} are integration constants, $F_k = -F_m$, ($k=0,1$; $m=2,3$) and we introduced the notation

$$N = \frac{\sqrt{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\beta} - 4m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha\beta}{t} - \frac{2\beta(3\beta-1)}{t^2})}}{2m_b^2}.$$

From the form of the self-interaction potential of the fermion field chosen above, taking into account the form of the scale factor, we find its dependence on time t

$$V = \xi \left(\frac{c}{a_0^3 e^{3\alpha t} t^{3\beta}} \right)^n.$$

The total energy density and pressure of the model under study from the Friedman equations (4) and (5) are equal to

$$\begin{aligned} p &= -3\left(\alpha + \frac{\beta}{t}\right)^2 + \frac{2\beta}{t^2}, \\ \rho &= 3\left(\alpha + \frac{\beta}{t}\right)^2. \end{aligned}$$

The component-wise contributions of each of the fields to the total density (13)–(16), respectively, are

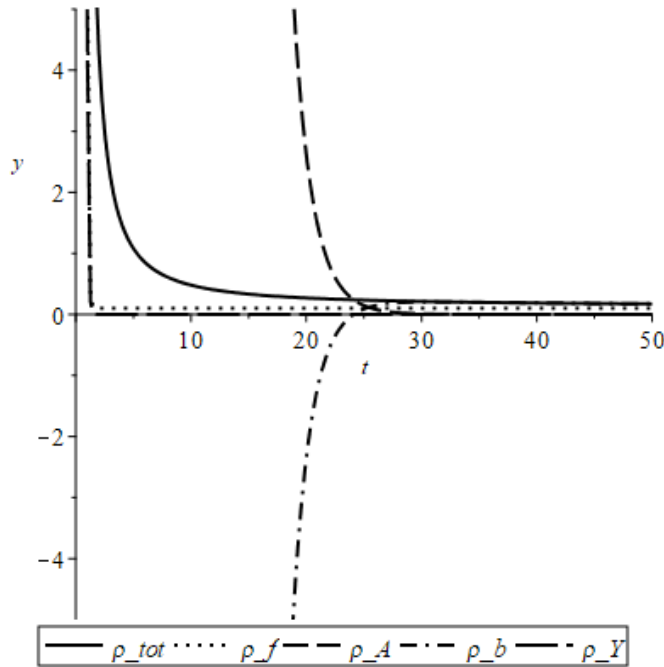
$$\rho_b = -\frac{\frac{\lambda c}{a_0^3 e^{3\alpha t} t^{3\beta}} \sqrt{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\alpha} - 4m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha t}{t} - \frac{2\beta(3\beta-1)}{t^2})}}{4m_v^2} +$$

$$+ \frac{1}{2} \dot{\phi}^2 - \frac{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\alpha} - 2m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha\beta}{t} - \frac{2\beta(3\beta-1)}{t^2})}{4m_v^2},$$

$$\rho_f = \xi \left(\frac{c}{a_0^3 e^{3\alpha t} t^{3\beta}} \right)^n,$$

$$\rho_Y = -\frac{-\frac{\lambda^2 c^2}{a_0^6 e^{6\alpha t} t^{6\beta}} + \frac{\lambda c}{a_0^3 e^{3\alpha t} t^{3\beta}} \sqrt{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\alpha} - 4m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha t}{t} - \frac{2\beta(3\beta-1)}{t^2})}}{2m_b^2},$$

$$\rho_A = \frac{1}{2} q^2 \frac{\dot{c}^2}{a_0^3 e^{3\alpha t} t^{3\beta} m_v^2},$$

Figure 1. Energy density ρ depends on time t , at

$$m = 10^{-6}, \xi = 5, c = 1, n = 2, a_0 = 1, \alpha = 0.2, q = 2, \dot{c} = 10, \phi = 2, \lambda = 2$$

Figure 1 shows the total energy density ρ (solid line), fermionic field density ρ_f (dotted line), vector field density ρ_A (dash line), scalar field density ρ_b (dash-dotted line), potential density Yukawa type ρ_Y (open line). The component-wise contributions of each of the fields to the total pressure (17)–(20), respectively, are

$$p_b = -\frac{\frac{\lambda c}{a_0^3 e^{3\alpha t} t^{3\beta}} \sqrt{\lambda^2 c^2 a_0^{-6} e^{-6\alpha t} t^{-6\alpha} - 4m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha t}{t} - \frac{2\beta(3\beta-1)}{t^2})}}{4m_v^2} +$$

$$\begin{aligned}
& + \frac{1}{2} \dot{\phi}^2 + \frac{\lambda^2 c^2 a_0^{-6} e^{6\alpha t} t^{-6\alpha} - 2m_b^2 (\xi(2-n)c^n (a_0 e^{\alpha t} t^\beta)^{-3n} - 6\alpha^2 - \frac{12\alpha\beta}{t} - \frac{2\beta(3\beta-1)}{t^2})}{4m_v^2}, \\
& p_f = \xi(n-1) \left(\frac{c}{a_0^3 e^{3\alpha t} t^{3\beta}} \right)^n, \\
& p_A = \frac{1}{2} q^2 \frac{c^2}{a_0^6 e^{6\alpha t} t^{6\beta} m_v^2}, \\
& p_Y = 0.
\end{aligned}$$

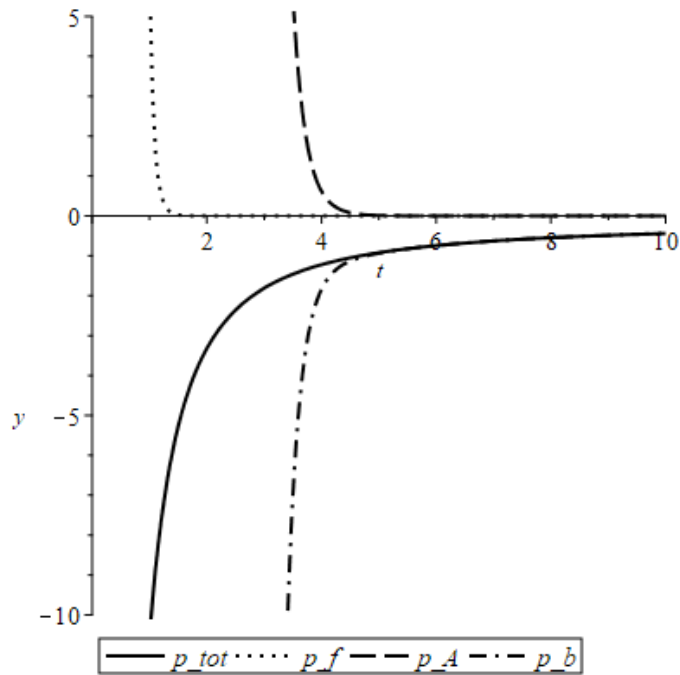


Figure 2. Pressure p and energy density ρ component contributions versus time t , at $m = 10^{-6}$, $\xi = 5$, $c = 1$, $n = 2$, $a_0 = 1$, $\alpha = 0.2$, $q = 2$, $c = 10$, $\phi = 2$, $\lambda = 2$

Figure 2 shows the total pressure of the model p (solid line), pressure of the fermionic field p_f (dotted line), pressure of the vector field p_A (dash line) pressure of the scalar field p_b (dash-dotted line).

In the model under consideration, the scalar and fermion fields have negative pressure, while the massive vector field has a slight positive pressure. The Yukawa field does not contribute. In the early epoch, the bosonic field is responsible for the accelerated regime, but in later time, a transition to the slow regime occurs since the total pressure tends to zero.

Cosmography

Cosmography ensures to test cosmological models that do not contradict the cosmological principle [34]. The components of the dark energy introduced by us into the model change the equations of motion, but do not affect the relationship between the kinematic characteristics. The expansion of the scale factor in a Taylor series in the vicinity of the current time instant t_0 leads to an expression that depends only on the metric (2) and is completely independent of the model [35, 36].

$$a(t) = a_0 + \dot{a}(t_0)(t-t_0) + \frac{1}{2!} \ddot{a}(t_0)(t-t_0)^2 + \frac{1}{3!} \dddot{a}(t_0)(t-t_0)^3 + \frac{1}{4!} \dots a^{(4)}(t_0)(t-t_0)^4, \quad (23)$$

where 0 means the current value of the quantity and terms above the fifth order have been omitted. Functions in terms of derivatives of the scale factor and their values at the hybrid law scale factor (21) are Hubble parameter

$$H(t) = \frac{1}{a} \frac{da}{dt} = \alpha + \frac{\beta}{t}.$$

Deceleration parameter

$$q(t) = -\frac{1}{a} \frac{d^2 a}{dt^2} \left(\frac{1}{a} \frac{da}{dt} \right)^{-2} = -1 + \frac{2\alpha\beta t}{\alpha^2 t^2 + \beta^2}.$$

Jerk parameter

$$j(t) = \frac{1}{a} \frac{d^3 a}{dt^3} \left(\frac{1}{a} \frac{da}{dt} \right)^{-3} = 1 + \frac{3\alpha\beta t(\alpha t + \beta)}{\alpha^3 t^3 + \beta^3}.$$

Snap parameter

$$s(t) = \frac{1}{a} \frac{d^4 a}{dt^4} \left(\frac{1}{a} \frac{da}{dt} \right)^{-4} = 1 + \frac{\alpha\beta t(4\alpha^2 t^2 + 6\alpha\beta t + 3\alpha\beta t + 4\beta^2)}{\alpha^4 t^4 + \beta^4}.$$

The parameters of deceleration, jerk, and snap are dimensionless. Using them, one can rewrite the equation (23) as

$$a(t) = a_0 \left[1 + H_0(t-t_0) - \frac{1}{2!} q_0 H_0^2(t-t_0)^2 + \frac{1}{3!} j_0 H_0^3(t-t_0)^3 + \frac{1}{4!} s_0 H_0^4(t-t_0)^4 \right].$$

An accelerated increase in the scale factor occurs at $q < 0$. An accelerated increase in the expansion rate, $H > 0$, corresponds to $q < -1$.

Energy conditions

In general, relativity and modified theories of gravity, the distribution of mass, momentum and angular momentum must have values for any field and are described by the energy momentum tensor or matter tensor. However, Einstein's field equation does not impose restrictions on the types of state of matter or non-gravitational regions admissible in the space-time model. This is a strong point, since general relativity should be as independent as possible from any assumptions of non-gravitational physics. The weak point is that the Einstein equation admits solutions by properties that most cosmologists regard as non-physical, i.e., too unusual to fit in the real [34] universe.

The energy conditions are such criteria. They describe the properties characteristic of all states of matter and all non-gravitational areas that are studied in physics. Energy conditions can eliminate many non-physical solutions of the Einstein equations. In cosmology, these four energy conditions are of great importance.

Null Energy Condition (NEC)

$$\rho + p \geq 0.$$

Weak Energy Condition (WEC)

$$\rho \geq 0, \quad \rho + p \geq 0.$$

Strong Energy Condition (SEC)

$$\rho + 3p \geq 0, \quad \rho + p \geq 0.$$

Dominant Energy Condition (DEC)

$$\rho \geq 0, \quad -\rho \leq p \leq \rho.$$

For hybrid solution (21), the energy-momentum components are read as follows

NEC

$$2\beta t^{-2} \geq 0 \tag{24}$$

WEC

$$3\left(\alpha + \frac{\beta}{t}\right)^2 \geq 0, \quad 2\beta t^{-2} \geq 0. \tag{25}$$

SEC

$$-6\left(\alpha + \frac{\beta}{t}\right)^2 + \frac{6\beta}{t^2} \geq 0, \quad 2\beta t^{-2} \geq 0. \quad (26)$$

DEC

$$3\left(\alpha + \frac{\beta}{t}\right)^2 \geq 0, \quad -3\left(\alpha + \frac{\beta}{t}\right)^2 \leq -3\left(\alpha + \frac{\beta}{t}\right)^2 + \frac{2\beta}{t^2} \leq 3\left(\alpha + \frac{\beta}{t}\right)^2. \quad (27)$$

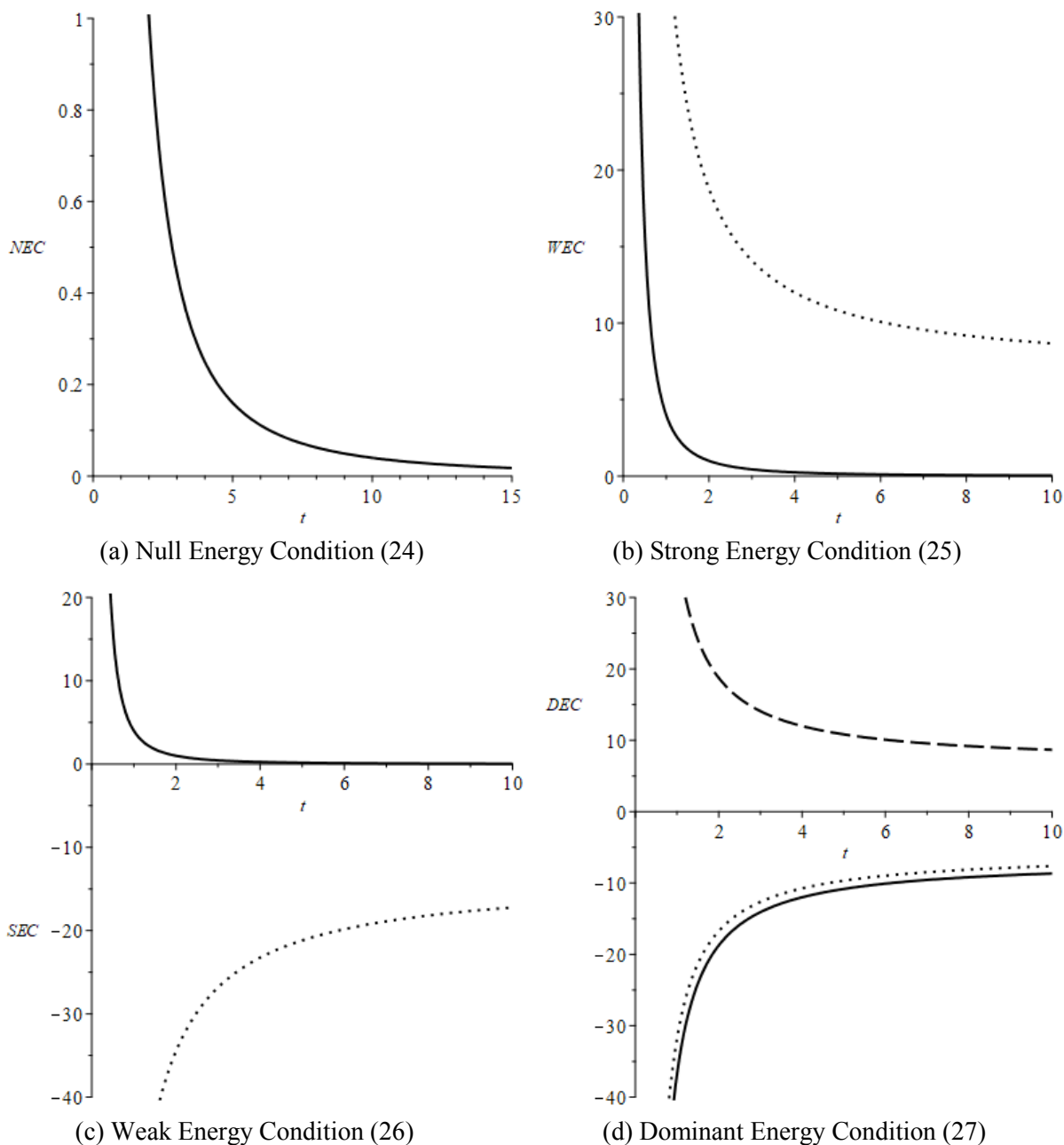


Figure 3. Energy Condition

Figure 3a shows NEC ($\rho + p$ is a solid line); the curve $\rho + p$ does not cross the abscissa axis, that is, over the entire time interval $\rho + p \geq 0$. Figure 3b shows WEC (ρ is a solid line, $\rho + p$ is a dotted line); curves $\rho + p$ and ρ are above the abscissa axis throughout the entire time interval, that is, conditions $\rho \geq 0$ and $\rho + p \geq 0$ are satisfied throughout the entire time interval. Figure 3c shows the SEC ($\rho + 3p$ is a dotted line, $\rho + p$ is a solid line); the $\rho + 3p$ curve is located below the abscissa axis, that is, the $\rho + 3p \geq 0$ condition is violated and the SEC is not fulfilled. Figure 3d shows DEC (ρ is a dash line, $-\rho$

is a solid line, p is a dotted line); the curve ρ is located above the abscissa axis and curve p lies between curves $-\rho$ and ρ , that is, the condition $\rho \geq 0$ and $-\rho \leq p \leq \rho$ is satisfied throughout the entire time interval. These conditions impose simple and model-independent constraints on behavior of the energy density and pressure. For our model, the zero energy condition, the strong energy condition, the dominant energy condition are satisfied, and the weak energy condition, which is not mandatory, is not satisfied.

Conclusions

We have investigated the scalar, fermion, and massive vector fields' influence and their interactions on the dynamics and evolution of cosmological regimes under conditions of a homogeneous and isotropic spatially flat universe. Observing the behavior of pressure of the scalar field with respect to the fermion and vector fields, we can infer that it is this field, to a greater extent, that is responsible for the accelerated regime in the early universe. An extended set of parameters was found to describe the kinematics of cosmological expansion: the deceleration parameter q , the jerk parameter j , and the snap parameter s . All the resulting parameters satisfy the latest observational data for $\alpha > 1$. Pressure in the model under consideration is negative and tends to zero at a later time. Therefore, at a later time, there is a transition to a slow mode.

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Мультиөрісті космологиялық модельдегі космография

Авторлар фермиондық өрісті, скалярлық өрісті және Юкава әсерлесуі бар векторлық өрісті қамтитын космологиялық модельді талдаған. Бұл модель материяның әртүрлі типті түрлері Әлемнің динамикасына қосқан үлесін зерттеуге мүмкіндік береді. Жазықтықта, біртекті және изотропты кеңістік-уақытта бұл байланыс Әлемнің үдемелі ұлғаюын қамтамасыз ете алады. Динамикалық теңдеулерді космологиялық реконструкциялауда гибриді теңдеулер шешімнің көмегімен жорамалдап алынады. Бұл шешім космография және энергетикалық күй арқылы зерттеліп қарастырылды. Зерттелетін бұл модельде нөлдік энергия шарты, күшті энергия шарты, басым энергетикалық шарты қанағаттандырылады, ал міндетті емес әлсіз энергия шарты қанағаттандырылмайды. Космографиялық параметрлердің – q баяулату параметрі, j серпілу параметрі және s басу параметрлерінің масштаб коэффициентінің гибриді мәніне қалай байланысты болуы анықталып көрсетілген. Алынған талдауда космографиядан және алынған модельден тәуелсіз нәтижелерді гравитацияның теориялық негізделген болжамдарымен байланыстыруға мүмкіндік береді. Гравитациялық өріс энергиясының жалпы тығыздығы мен жалпы қысымы бозондық өріс, фермиондық өріс, векторлық өрістермен, сондай-ақ Юкава типінің потенциалымен байланысты үлестер қосындысы түрінде болып табылады. Зерттелетін модельде ерте дәуірде бозондық өріс жеделдетілген режимге жауапты болып табылады. Фермиондық өріс және векторлық өрістер оң қысым мәніне ие, сондықтан Әлемнің үдемелі ұлғаюын баяулатады. Кейінірек баяу режимге көшу жүреді, өйткені жалпы қысым нөлге ұмтылады.

Кілт сөздер: скалярлы өріс, фермиондық өріс, Юкава типті әсерлесу, векторлық өріс, космография, тежеу параметрі.

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Космография в мультиполевой космологической модели

Авторами проанализирована космологическая модель, содержащая фермионное поле, скалярное поле и векторное поле с взаимодействием Юкавы. Такая модель позволяет исследовать вклад различных типов материи в динамику Вселенной. В плоском, однородном и изотропном пространстве времени эта связь может обеспечивать ускоренное расширение Вселенной. Космологическая реконструкция динамических уравнений получена с помощью гибридного решения. Это решение исследуется космографией и энергетическим состоянием. В исследуемой модели выполняется нулевое энергетическое условие, сильное энергетическое условие, доминирующее энергетическое условие и не выполняется слабое энергетическое условие, которое не является обязательным. Показано, как можно связать космографические параметры — параметры замедления q , рывка j и щелчка s с гибридным значением масштабного фактора. Полученный анализ дает возможность связать независимые от модели результаты, полученные из космографии, с теоретически обоснованными предположениями гравитации. Найдены полная плотность и давление энергии гравитационного поля в виде суммы вкладов, которые связаны с бозонным, фермионным, векторным полями, а также потенциалом типа Юкавы. В исследуемой модели в раннюю эпоху бозонное поле является ответственным за ускоренный режим. Фермионное и векторное поля имеют положительное значение давления и, следовательно, замедляют ускоренное расширение Вселенной. В позднее время происходит переход в замедленный режим, так как общее давление стремится к нулю.

Ключевые слова: скалярное поле, фермионное поле, взаимодействие типа Юкавы, векторное поле, космография, параметр замедления.

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Calculation of the electron-optical scheme of a new type mirror energy analyzer of charged particles

Further studies of the electron-optical properties of electrostatic multipole-cylindrical fields, synthesized from the fields of a cylindrical mirror and circular multipoles, are continued in the work. The implementation of electron spectroscopy methods is based on the use of complex equipment, one of the main elements of which is an electron energy analyzer of low and medium energies. Application of the multipole approach to the synthesis of deflecting fields makes it possible to develop effective methods for energy analysis of charged particle beams. The electron-optical scheme of new type mirror energy analyzer of charged particle beams based on an electrostatic axially symmetric octupole-cylindrical field is proposed in the work. An axially symmetric octupole-cylindrical field is constructed as a superposition of a basic cylindrical field and a circular octupole. When the fields were added, the central circle of the octupole was combined with the zero equipotential of the logarithmic field. The motion of charged particles in the electrostatic octupole-cylindrical field. An integrodifferential equation for the motion of charged particles in an electrostatic octupole-cylindrical field is derived. Calculation of trajectories in an energy analyzer with an octupole-cylindrical field was performed on the basis of the method of expansion into a fractional-power series of the particle motion equation presented in the integrodifferential form. Coefficients of the series, representing the trajectory of motion in an analytical form, accessible for further studies of the electron-optical characteristics of the octupole-cylindrical field, are obtained. Based on an octupole-cylindrical field, high luminosity energy analyzers can be built to determine the composition of charged particle beams with energies from units of eV to tens of keV in space plasma.

Keywords: energy analyzer of charged particles, electron mirrors, electrostatic axially symmetric octupole-cylindrical field, approximate-analytical calculation, motion of charged particles.

Introduction

The operation of all analyzing devices is based on the use of the features of the movement of charged particles in the fields created by the corresponding electrode systems. The suitability of a particular field for the purposes of energy analysis is characterized by the dispersion of the field in terms of energies.

In reflector-type analyzers, charged particles enter between the electrode plates and, if their energy matches the tuning energy, move in the region of the equipotential surface, then fall on the detector. The advantage of these analyzers is the ability to analyze high-energy charged particles beams with a relatively small potential difference between the electrodes. The disadvantage is a small specific dispersion and a strong influence of edge fields. Deflectors, in addition to surface analysis, have found wide application in mass spectrometry, as well as in the analysis of high-energy particles. This has found application in space plasma research. For these purposes, an electrostatic hemispherical analyzer with a circular field of view, called “top-hat” was widely used [1]. This analyzer was designed in the laboratory of the University of Texas (USA). Then it was successfully used in various projects in the USA and Europe.

Until now, top-hat energy analyzers have been successfully used in experimental space plasma physics [2–5].

The measurement of charged particles with energies from a few eV to tens of keV is a significant part of space experiments. A plasma of such energy inhabits the solar wind, planetary ionospheres, interplanetary space, the earth's ionosphere, and the magnetosphere. Near the earth, the study of the boundaries of particle precipitation is necessary for fundamental studies of the magnetosphere.

The cylindrical mirror type energy analyzers have found wide application in the study of resonant phenomena in gases, in spectroscopy for chemical analysis, to obtain spectra of secondary electrons, photoelectrons, auto-electrons, Auger electrons, as well as in space research, in the study of the interaction of atomic particles with the solid body surface and plasma diagnostics. The cylindrical mirror analyzer has become the

basic element of electron spectrometers for various purposes, produced in the countries near and far abroad by leading instrument-making companies [6, 7].

The class of potential fields, called multipole-cylindrical, was first substantiated and classified by Zashkvara V.V. and Tyndyk N.N. in [8, 9]. Application of the multipole approach to the synthesis of deflecting fields makes it possible to develop effective methods for energy analysis of charged particle flows. This method is based on the principle of superposition of the simplest fields of cylindrical type and various order circular multipoles.

The electron-optical schemes of mirror energy analyzers based on electrostatic quadrupole-cylindrical [10], hexapole-cylindrical [11], and decapole-cylindrical fields [12] were previously studied in sufficient detail. In particular, the monograph [13] is devoted to the study of their electron-optical characteristics and potential capabilities, to the search for optimal electron-optical schemes with high focusing properties and energy resolution.

In previous studies, a family of equipotentials of cylindrical octupoles with a plane of symmetry and antisymmetry was calculated [14]. Calculation and analysis of equipotential portraits of electrostatic axially symmetric octupole-cylindrical fields for different weight contributions of the cylindrical field and the circular octupole were carried out.

In the present work, the electron-optical scheme of a new type of energy analyzer based on an electrostatic octupole-cylindrical field is investigated, and a trajectory calculation in an electrostatic octupole-cylindrical field is carried out.

1. Focusing field of the energy analyzer

The field is built based on the superposition of the fields of a cylindrical mirror and a circular octupole. The potential distribution for the proposed electrostatic system can be expressed as follows:

$$U(r, z) = \mu \ln r + \omega U_{oct}(r, z) \quad (1)$$

here

$$U_{\text{oct}}(r, z) = \frac{1}{4!} z^4 + \frac{1}{2} z^2 \left\{ \frac{1}{4} (1 - r^2) + \frac{1}{2} \ln r \right\} + \frac{1}{64} r^4 + \frac{1}{16} r^2 - \frac{1}{8} \ln r \left[\frac{1}{2} + r^2 \right] - \frac{5}{64} \quad (2)$$

is circular octupole, μ is coefficient specifying the weight contribution of the cylindrical field $\ln r$, ω is weight component of the circular octupole.

The octupole-cylindrical field was chosen as the object of research, in which the component of the cylindrical field is equal to the multipole part.

Figure 1 shows a schematic view in the longitudinal section (upper part) of the electron-optical scheme of an energy analyzer based on an octupole-cylindrical field, where the value of the weight contributions of the cylindrical field $\mu = 1$ and octupole $\omega = 1$. Potential distribution Eq. (1) differs significantly from the classical field cylindrical mirror.

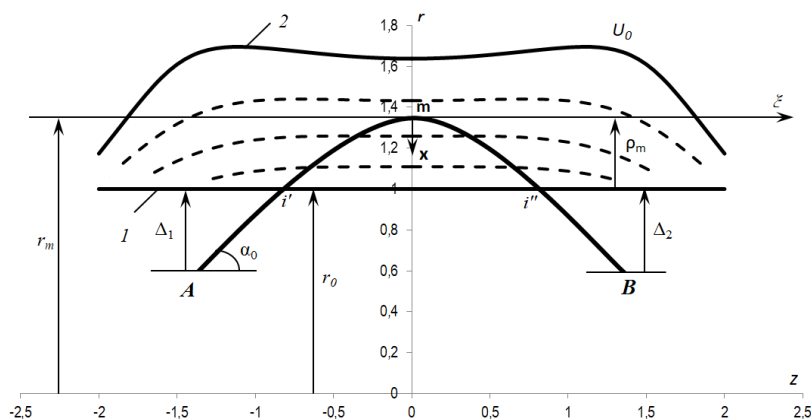


Figure 1. Schematic view in longitudinal section (upper part) of the electron-optical scheme of the energy analyzer based on an octupole-cylindrical field: 1 – inner cylindrical electrode, 2 – outer deflecting electrode, A – ring source of charged particles, i' – entrance ring window, i'' – exit ring window, B – ring image

The analyzer contains two coaxial electrodes, the inner electrode 1 has a cylindrical shape of radius r_0 and is under zero potential the outer electrode 2 has a curvilinear profile and is under the deflecting potential U_0 . The field is created between the electrodes that decelerate and deflect charged particles and has the properties of an electrostatic mirror. The profile of the outer deflecting electrode 2 repeats the equipotential surface of the electrostatic octupole-cylindrical field. The cylindrical electrode 1 cuts through the entrance i' and exits i'' windows for the movement of the charged particles beam.

According to the scheme, the charged particles beam from the ring source A through the entrance window i' in the inner cylinder 1 enters the energy analyzer field, further reflected by the field, then through the exit window i'' on the inner cylinder 1 returns to the zero potential region and focused into the ring image B.

2. Calculations

Consider the motion of a charged particle in the octupole-cylindrical field. To calculate the trajectories of charged particles motion in the octupole-cylindrical field, let us move the reference point of the trajectory to its vertex $\mathbf{m}$ and place the origin x, ξ at the same point (see Fig. 1). All linear dimensions are calculated in the radii of the inner cylindrical electrode r_0 to maintain the following dimensionless parameters:

$$\frac{r}{r_0} = \frac{r_0 + r_0 \rho}{r_0} = 1 + \rho, \quad x = \frac{r_m - r}{r_0} = \rho_m - \rho, \quad \xi = \frac{z}{r_0}. \quad (3)$$

The distribution of the octupole-cylindrical field Eq. (1) in the new coordinates x, ξ ((for any μ and ω) has the following form:

$$U(x, \xi) = U_0 g(x, \xi) = U_0 g_x, \quad (4)$$

where

$$g(x, \xi) = g_x = \mu \ln(R - x) + \omega \left[\frac{1}{4!} \xi^4 + \frac{1}{2} \xi^2 \left\{ \frac{1}{4} [1 - (R - x)^2] + \frac{1}{2} \ln(R - x) \right\} + \right. \\ \left. + \frac{1}{64} (R - x)^4 + \frac{1}{16} (R - x)^2 - \frac{1}{8} \ln(R - x) \left[\frac{1}{2} + (R - x)^2 \right] - \frac{5}{64} \right], \quad R = 1 + \rho_m. \quad (5)$$

The motion of a charged particle in the octupole-cylindrical field for the case under study: the contributions of the cylindrical field and the circular octupole, respectively, $\mu = 1$, $\omega = 1$, in this case, the potential distribution in this system is described in the x, ξ coordinate system as follows:

$$U(x, \xi) = U_0 g(x, \xi) = U_0 g_x, \quad (6)$$

where

$$g(x, \xi) = g_x = \ln(R - x) - \frac{1}{4!} \xi^4 - \frac{1}{2} \xi^2 \left\{ \frac{1}{4} [1 - (R - x)^2] + \frac{1}{2} \ln(R - x) \right\} + \\ - \frac{1}{64} (R - x)^4 - \frac{1}{16} (R - x)^2 + \frac{1}{8} \ln(R - x) \left[\frac{1}{2} + (R - x)^2 \right] + \frac{5}{64}. \quad (7)$$

The motion of a charged particle in the axially symmetric octupole-cylindrical field (6) has the following form:

$$m\ddot{x} = qU_0 \varepsilon_1, \quad \varepsilon_1 = -\frac{\partial g(x, \xi)}{\partial x}, \quad (8a)$$

$$m\ddot{\xi} = qU_0 \varepsilon_2, \quad \varepsilon_2 = -\frac{\partial g(x, \xi)}{\partial \xi}. \quad (8b)$$

According to the law of conservation of energy when moving in a static potential field, the change in the kinetic energy of a charged particle is determined by the passed potential difference. Further, integrating the sum of Eqs. (8a) and (8b) along the particle trajectory from the vertex $\mathbf{m}$ to an arbitrary point, we obtain the law of conservation of energy for a particle moving in the electrostatic octupole-cylindrical field, which relates the change in the kinetic energy of the particle to the potential difference:

$$\frac{mv_m^2}{2} - \frac{m}{2} (\dot{x}^2 + \dot{\xi}^2) = -q(U_m - U(x, \xi)) = -qU_0(g_0 - g_x), \quad (9)$$

here $U_m = U_0 g(x_m, \xi_m) = U_0 g_0$ is field potential at point m, while $x_m = \xi_m = 0$, $g_x = g(x, \xi(x))$; $g_0 = g(x, \xi)|_{x=0, \xi=0}$.

By integrating Eq. (8 b) within the range from point m to an arbitrary point of the trajectory, we can determine the value of $\frac{m\dot{\xi}^2}{2}$. At the same time, we take into account that $v_m^2 = \dot{\xi}_m^2 + \dot{x}_m^2 = \dot{\xi}_m^2$, since at the vertex of the trajectory $\dot{x}_m = 0$. Further, using the relation $\dot{\xi} = \frac{d\xi}{dt} = \frac{d\xi}{dx} \frac{dx}{dt} = \xi' \dot{x}$, we obtain

$$\frac{mv_m^2}{2} - \frac{m\dot{\xi}^2}{2} = qU_0 \int_x^{x_m} \frac{\partial g(x, \xi)}{\partial \xi} \frac{d\xi}{dx} dx = qU_0 \int_0^x \frac{\partial g(x, \xi)}{\partial \xi} \xi' dx. \quad (10)$$

According to the scheme (Fig. 1), $\frac{m\dot{\xi}^2}{2} = \frac{mv_0^2}{2} = W \cos^2 \alpha_0$ at $x = \rho_m$, therefore, Eq. (10) can be rewritten relatively $\frac{mv_m^2}{2}$ as follows:

$$\frac{mv_m^2}{2} = W \cos^2 \alpha_0 + qU_0 f_m, \quad (11)$$

where

$$f_m = \int_0^{\rho_m} \frac{\partial g(x, \xi)}{\partial \xi} \xi' d\xi. \quad (12)$$

Substituting Eqs. (11) and (12) into Eq. (10), we obtain the integro-differential equation of motion of a charged particle in the octupole-cylindrical field (6):

$$(\xi')^2 [g_0 - g_x + f_x] = P^2 \operatorname{ctg}^2 \alpha_0 + f_m - f_x, \quad (13)$$

or

$$(\xi')^2 = \frac{P^2 \operatorname{ctg}^2 \alpha_0 + f_m - f_x}{g_0 - g_x + f_x}, \quad (14)$$

where

$$f_x = \int_0^x \frac{\partial g(x, \xi)}{\partial \xi} \xi' dx, \quad (15)$$

and $P_0^2 = \frac{W}{qU_0} \sin^2 \alpha_0$ is the reflection parameter relating the geometric and energy parameters of the octupole-cylindrical field.

The solution of the integro-differential equation (13) can be found as an expansion in a power series with indeterminate coefficients. These coefficients can be calculated from Eq. (13) by substituting a power series into it.

The integro-differential equation (13) has a singular point at the point $x=0$, since the factor $(\xi')^2$, in this case, vanishes, therefore, to integrate the equation, the method of expanding the solution of the equation ξ into a fractional power series is used [15]:

$$\xi = \sqrt{x} \sum_{n=0}^{\infty} C_n x^n, \quad (16)$$

or

$$\xi = \sqrt{x} (C_0 + C_1 x + C_2 x^2 + C_3 x^3 + C_4 x^4 + C_5 x^5 + C_6 x^6 + \dots). \quad (17)$$

The radial component $R = 1 + \rho_m$ of the turning point of the trajectory, necessary for calculating the value of ξ , can be determined by using the integro-differential equation of the trajectory (13) for the point $x = \rho_m$. In this case:

$$(\xi')^2 = \operatorname{ctg}^2 \alpha_0, \quad g_{x=\rho_m} = 0,$$

and

$$g_0 + f_m = P^2.$$

Substituting g_0 from Eq. (3) into Eq.(16) we arrive at the expression:

$$\ln R = \frac{8(P^2 - f_m) + \frac{1}{8}R^4 + \frac{1}{2}R^2 - \frac{5}{8}}{\left(\frac{17}{2} + R^2\right)}.$$

The value R can be determined by the method of successive approximations. As a zero approximation, the parameters of a cylindrical mirror analyzer are used: $R_0 = \exp(P^2) = 1 + P^2 + \frac{1}{2}P^4 + \frac{1}{6}P^6 + \frac{1}{24}P^8 + \dots$ and $f_{m_0} = 0$.

So the equation for determining ρ_m :

$$\rho_m = \exp \left[\frac{8(P^2 - f_m) + \frac{1}{8}R^4 + \frac{1}{2}R^2 - \frac{5}{8}}{\left(\frac{17}{2} + R^2\right)} - 1 \right].$$

The left side of Eq.(13) was found from the calculations:

$$\begin{aligned} & \left(\frac{d\xi}{dx} \right)^2 \left[g_0 - g_x + \int_0^x \frac{\partial g(x, \xi)}{\partial \xi} \xi' dx \right] = \\ & = h_0 [b_1 - e_1] x + \left[h_0 \left(\frac{b_2}{2} - e_2 \right) + h_1 (b_1 - e_1) \right] x^2 + \\ & + \left[h_0 \left(\frac{b_3}{3} - e_3 \right) + h_1 \left(\frac{b_2}{2} - e_2 \right) + h_2 (b_1 - e_1) \right] x^3 \\ & + \left[h_0 \left(\frac{b_4}{4} - e_4 \right) + h_1 \left(\frac{b_3}{3} - e_3 \right) + h_2 \left(\frac{b_2}{2} - e_2 \right) + h_3 (b_1 - e_1) \right] x^4 + \\ & + \left[h_0 \left(\frac{b_5}{5} - e_5 \right) + h_1 \left(\frac{b_4}{4} - e_4 \right) + h_2 \left(\frac{b_3}{3} - e_3 \right) + h_3 \left(\frac{b_2}{2} - e_2 \right) + h_4 (b_1 - e_1) \right] x^5 + \\ & + \left[h_0 \left(\frac{b_6}{6} - e_6 \right) + h_1 \left(\frac{b_5}{5} - e_5 \right) + h_2 \left(\frac{b_4}{4} - e_4 \right) + h_3 \left(\frac{b_3}{3} - e_3 \right) + h_4 \left(\frac{b_2}{2} - e_2 \right) + h_5 (b_1 - e_1) \right] x^6. \end{aligned} \quad (18)$$

Further, the integral on the right side of Eq.(13) is found:

$$\begin{aligned} & P^2 \operatorname{ctg}^2 \alpha_0 + f_m - f_x = P^2 \operatorname{ctg}^2 \alpha_0 + F(\rho_m) - \\ & - \left\{ b_1 x + \frac{b_2 x^2}{2} + \frac{b_3 x^3}{3} + \frac{b_4 x^4}{4} + \frac{b_5 x^5}{5} + \frac{b_6 x^6}{6} + \dots \right\} - \phi(x). \end{aligned} \quad (19)$$

Thus, both parts of the equation of motion of a charged particle in the octupole-cylindrical field (13) are presented in the form of power series. Further, by equating the terms at the same powers of x in expressions (18) and (19), the coefficients of series Eq. (16) are determined. The coefficients of series allow for further analyzing the corpuscular-optical parameters of the considered system.

The results of calculating the coefficients of the C_n series (16), which determine the trajectories of motion of charged particles in the investigated octupole-cylindrical field, are given below. We equate the terms at the same powers in Eqs. (18) and (19), and the following system of equations is obtained:

$$h_0 (b_1 - e_1) = -b_1, \quad (20a)$$

$$h_0\left(\frac{b_2}{2}-e_2\right)+h_1(b_1-e_1)=-\frac{b_2}{2}, \quad (20b)$$

$$h_0\left(\frac{b_3}{3}-e_3\right)+h_1\left(\frac{b_2}{2}-e_2\right)+h_2(b_1-e_1)=\frac{b_3}{3}, \quad (20c)$$

$$h_0\left(\frac{b_4}{4}-e_4\right)+h_1\left(\frac{b_3}{3}-e_3\right)+h_2\left(\frac{b_2}{2}-e_2\right)+h_3(b_1-e_1)=\frac{b_4}{4}, \quad (20d)$$

$$h_0\left(\frac{b_5}{5}-e_5\right)+h_1\left(\frac{b_4}{4}-e_4\right)+h_2\left(\frac{b_3}{3}-e_3\right)+h_3\left(\frac{b_2}{2}-e_2\right)+h_4(b_1-e_1)=\frac{b_5}{5}, \quad (20e)$$

$$h_0\left(\frac{b_6}{6}-e_6\right)+h_1\left(\frac{b_5}{5}-e_5\right)+h_2\left(\frac{b_4}{4}-e_4\right)+h_3\left(\frac{b_3}{3}-e_3\right)+h_4\left(\frac{b_2}{2}-e_2\right)+h_5(b_1-e_1)=\frac{b_6}{6}. \quad (20f)$$

The problem of determining the trajectories of charged particles in the field under study is reduced to calculating the coefficients in expression (16). Expressions for the coefficients h_i , e_i and b_i are obtained:

$$h_0 = \frac{C_0^2}{4}, \quad (21a)$$

$$h_1 = \frac{3C_0C_1}{2}, \quad (21b)$$

$$h_2 = \frac{9C_1^2}{4} + \frac{5C_0C_2}{2}, \quad (21c)$$

$$h_3 = \frac{7C_0C_3}{2} + \frac{15C_1C_2}{2}, \quad (21d)$$

$$h_4 = \frac{25C_2^2}{4} + \frac{9C_0C_4}{2} + \frac{21C_1C_3}{2}, \quad (21e)$$

$$h_5 = \frac{11C_0C_5}{2} + \frac{27C_1C_4}{2} + \frac{35C_2C_3}{2}, \quad (21f)$$

$$h_6 = \frac{49C_3^2}{4} + \frac{13C_0C_6}{2} + \frac{33C_1C_5}{2} + \frac{45C_2C_4}{2}. \quad (21g)$$

$$e_0 = -\frac{3}{16}\rho_m - \frac{5}{32}\rho_m^2 - \frac{1}{16}\rho_m^3 - \frac{1}{64}\rho_m^4 + \ln(1+\rho_m)\left(\frac{19}{16} + \frac{1}{4}\rho_m + \frac{1}{8}\rho_m^2\right), \quad (22a)$$

$$e_1 = \frac{3}{16} + \frac{5}{16}\rho_m + \frac{3}{16}\rho_m^2 + \frac{1}{16}\rho_m^3 + \frac{C_0^2}{2}\rho_m(1+\rho_m) - \dots, \quad (22b)$$

$$e_2 = \frac{3}{32} - \frac{C_0^2}{2} - \frac{\rho_m C_0^2}{2} - \frac{C_0^4}{24} - \frac{1}{8}\rho_m - \frac{19}{16(1+\rho_m)^2} - \frac{1}{8}\ln(1+\rho_m) - \dots, \quad (22c)$$

$$e_3 = \frac{1}{16} + \frac{C_0^2}{4} + \frac{1}{4(1+\rho_m)}\left(1 + \frac{1}{2}\right) - \frac{19}{16(1+\rho_m)^3} + \frac{\rho_m C_1^2}{2} + \frac{\rho_m^2 C_1^2}{4} - \dots, \quad (22d)$$

$$e_4 = -\frac{1}{64} - \frac{C_1^2}{2} - \rho_m C_0 C_2 + \rho_m C_0 C_3 + \rho_m C_1 C_2 + \frac{1}{2(1+\rho_m)^2} - \frac{3\rho_m}{8(1+\rho_m)^4} + \dots, \quad (22d)$$

$$e_5 = \frac{C_1^2}{4} + \frac{1}{8(1+\rho_m)^3} - \frac{19}{16(1+\rho_m)^5} - \frac{\rho_m}{4(1+\rho_m)^5} - \frac{\rho_m^2}{8(1+\rho_m)^5} + \frac{\rho_m C_2^2}{2} - \dots, \quad (22e)$$

$$e_6 = -\frac{1}{8(1+\rho_m)^4} + \frac{1}{4(1+\rho_m)^5} - \frac{C_2^2}{2} - \frac{C_1^4}{24} - \frac{19}{16(1+\rho_m)^6} + \frac{\rho_m}{4(1+\rho_m)^5} - \dots. \quad (22f)$$

$$b_1 = \frac{\rho_m C_0^2}{4} \left(1 + \frac{\rho_m}{2} \right) - \frac{C_0^2}{16} \ln(1 + \rho_m), \quad (23a)$$

$$b_2 = -\frac{C_0^2}{4} - \frac{C_0^4}{12} + \rho_m C_0 \left(C_1 - \frac{C_0}{4} \right) + \frac{C_0^2}{16(1 + \rho_m)} + \dots, \quad (23b)$$

$$b_3 = \frac{C_0^2}{8} - \frac{C_0^3 C_1}{2} - C_0 C_1 (1 + \rho_m) + \frac{3\rho_m}{2} \left(\frac{C_1^2}{2} + C_0 C_2 \right) \left(1 + \frac{\rho_m}{2} \right) + \dots, \quad (23c)$$

$$b_4 = \frac{C_0 C_1}{2} - \frac{3C_0 C_2}{2} - \frac{3C_1^2}{4} - C_0^2 C_1^2 - \frac{2C_0^3 C_2}{3} + 3 \left(\frac{C_1^2}{2} + C_0 C_2 \right) \left(\frac{1}{8(1 + \rho_m)} - \frac{\rho_m}{2} \right) + \dots, \quad (23d)$$

$$b_5 = -2C_1 C_2 - 2C_0 C_3 - C_0^3 C_4 - \frac{3C_0 C_2}{4} - \frac{5C_0^2 C_1 C_2}{2} + \frac{3C_1^2}{8} - \dots, \quad (23e)$$

$$b_6 = C_0 C_3 + C_1 C_2 - 3 \left(C_0 C_1^2 C_2 + C_0^2 C_1 C_3 \right) - \frac{1}{2} \left(5C_1 C_3 + 5C_0 C_4 - 3C_0^2 C_2^2 \right) - \dots, \quad (23f)$$

$$b_7 = -3 \left(C_2 C_3 + C_1 C_4 + C_0 C_5 \right) + \frac{5}{4} \left(\frac{C_2^2}{2} - C_0 C_4 + C_1 C_3 \right) - \frac{7}{6} \left(C_1^3 C_2 + C_0^3 C_5 \right) - \dots \quad (23g)$$

Considering the system of Eqs. (21)–(23), the coefficients C_i are found. The approximate-analytical method makes it possible to describe with high accuracy the trajectories of motion of charged particles in the field under consideration.

Conclusions

The electron-optical scheme of a new type of mirror energy analyzer based on an electrostatic octupole-cylindrical field has been studied. The calculation of particle trajectories in an electrostatic octupole-cylindrical field is performed. The problem of integrating the differential equations of motion of charged particles and the analytical description of the trajectory equation in the electrostatic octupole-cylindrical mirror is solved. The coefficients of the fractional-power series are obtained, which are necessary for describing the trajectories of motion in an analytical form, accessible for further studies of the electron-optical characteristics of the octupole-cylindrical field.

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Жаңа типті зарядталған бөлшектердің айналы энергия талдағыштың электронды-оптикалық сұлбасын есептеу

Мақалада цилиндрлік айна мен дөңгелектік мультипольдер өрістерінен синтезделген электрстатикалық мультипольді-цилиндрлік өрістердің электронды-оптикалық қасиеттеріне одан арғы зерттеулер жүргізілген. Электрондық спектроскопия әдістерін іске асырудың негізгі элементтерінің бірі төмен және орта энергиялы электрондарының энергия талдағышы болып табылатын күрделі құрал-жабдықты қолдануға негізделген. Ауытқушы өрістерді синтездеуге мультипольдік әдіс-тәсілді қолдану зарядталған бөлшектер ағындарын энергия талдауының тиімді әдістерін дамытуға мүмкіндік береді. Бұл жұмыста электрстатикалық осьтік симметриялық октупольді – цилиндрлік өріс негізінде зарядталған бөлшектер ағындарының жаңа типті айналы энергия талдағышының электронды-оптикалық сұлбасы ұсынылған. Аксиалды-симметриялық октупольді-цилиндрлік өріс базалық цилиндрлік өріс және дөңгелектік октупольдің суперпозициясы түрінде құрастырылған. Берілген өрістерді қосу кезінде дөңгелектік октупольдің орталық шеңбері логарифмдік өрістің нөлдік эквипотенциясымен біріктіріледі. Электрстатикалық аксиалды-симметриялық октупольді-цилиндрлік өрісте зарядталған бөлшектердің қозғалысы зерттелген. Электрстатикалық октупольді-цилиндрлік өрістегі зарядталған бөлшектердің қозғалысының интегралды-дифференциалдық теңдеуі алынған. Энергия талдағыштың октупольді-цилиндрлік өрісінде бөлшектердің траекториялық есептеуі интегралды-дифференциалдық түрде берілген зарядталған бөлшектердің қозғалыс теңдеуінің бөлшекті-дәрежелі қатарға жіктеу әдісі негізінде жүргізілген. Октупольді-цилиндрлік өрістің электронды-оптикалық сипаттамаларын одан әрі зерттеуге мүмкіндік беретін аналитикалық түрдегі қозғалыс траекториясын беретін қатар коэффициенттері есептелінген. Октупольді-цилиндрлік өріс негізінде ғарыштық плазмадағы ЭВ біріктерінен оңдаған кэВ дейінгі энергияға ие зарядталған бөлшектер ағындарының құрамын анықтауға арналған жарық күшті электрстатикалық энергия талдағыштарын құрастыруға болады.

Кілт сөздер: зарядталған бөлшектердің энергия талдағышы, электронды айналар, электрстатикалық осьтік симметриялық октупольді-цилиндрлік өріс, жуық-аналитикалық есептеу, зарядталған бөлшектердің қозғалысы.

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Расчет электронно-оптической схемы зеркального энергоанализатора заряженных частиц нового типа

В статье продолжены дальнейшие исследования электронно-оптических свойств электростатических мультипольно-цилиндрических полей, синтезированных из полей цилиндрического зеркала и круговых мультиполей. Реализация методов электронной спектроскопии основана на использовании сложного оборудования, одним из главных элементов которого является энергоанализатор электронов низких и средних энергий. Применение мультипольного подхода к синтезу отклоняющих полей дает возможность для развития эффективных методов энергоанализа потоков заряженных частиц. Авторами предложена электронно-оптическая схема зеркального энергоанализатора потоков заряженных

частиц нового типа на основе электростатического осесимметричного октупольно-цилиндрического поля. Осесимметричное октупольно-цилиндрическое поле сконструировано в виде суперпозиции базового цилиндрического поля и кругового октуполя. При сложении полей центральная окружность октуполя совмещалась с нулевой эквипотенциалью логарифмического поля. Исследовано движение заряженных частиц в электростатическом октупольно-цилиндрическом поле. Выведено интегро-дифференциальное уравнение движения заряженных частиц в электростатическом октупольно-цилиндрическом поле. Расчет траекторий частиц в зеркальном энергоанализаторе с октупольно-цилиндрическим полем выполнен на основе метода разложения в дробно-степенной ряд уравнения движения заряженных частиц, представленного в интегро-дифференциальной форме. Получены коэффициенты ряда, представляющие траекторию движения в аналитическом виде, доступном для дальнейших исследований электронно-оптических характеристик октупольно-цилиндрического поля. На основе октупольно-цилиндрического поля могут быть построены светосильные энергоанализаторы, предназначенные для определения состава потоков заряженных частиц с энергиями от единиц эВ до десятков кэВ в космической плазме.

Ключевые слова: энергоанализатор заряженных частиц, электронные зеркала, электростатическое осесимметричное октупольно-цилиндрическое поле, приближенно-аналитический расчет, движение заряженных частиц.

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Experimental Studies of Mechanical-Electrical Transformations during the Destructive Processes Developing in Dielectric Materials

A mechanical-electrical method for testing fractures developing within the stress-strain state changes of dielectric rock samples, as an example, is discussed here. The paper discusses the results of numerical and experimental studies of changes in the electromagnetic responses parameters under the pulse deterministic acoustic excitation of rock samples with different composition and texture. The paper presents the results of mathematical calculations of the stress concentration on cracks located along and across the sample axis, perpendicular to which deterministic acoustic pulses were introduced. The cracks presented in the sample volume are stress concentrators. With a different number and sizes of cracks perpendicular to the propagation of an acoustic pulse, the intensity of stresses and their type differ significantly. This circumstance indicates the influence of the structure of the samples and their dielectric properties on the parameters of electromagnetic signals when recording the results of mechanical and electrical transformations. Thus, the use of the method of mechanical-electrical transformations under compression can be used in testing the processes of the onset of crack formation and the development of fracture in solid-state dielectric materials and products.

Keywords: dielectrics, rocks, numerical modeling, acoustic impact, uniaxial compression, electromagnetic emission, mechanoelectric transformations, electromagnetic signal.

Introduction

The development of destruction of solid dielectric structures is accompanied by occurrence of alternating electromagnetic fields. This phenomenon is being addressed to employ the parameters and characteristics of electromagnetic emission for testing imperfection and to study development of destruction of solid dielectric materials. Alternating electromagnetic fields arise from mechanical-electrical transformations (MET) in solid-state structures when their stress-strain state changes under mechanical load with subsequent acoustic emission inside the test material. Electromagnetic radiation due to various types of destruction mechanisms has been proven to emerge in all-dielectric materials [1–12]. During MET processes, electromagnetic signals (EMS) are generated due to the changed charge state of materials or their interfaces. The presence, occurrence, and quantitative or qualitative change of electric charges and their vibrations under acoustic excitation are a prerequisite for EMS generation.

In [13], the issues of charging layers of rocks of different textures and compositions are considered in detail. In [3], Khatiashvili and Perelman experimentally and theoretically proved that acoustic wave-induced generation of EMS, which is a consequence of the oscillatory movements of double electric layers and fluctuation-charged edges of microcracks, and release and vibration of charged dislocations. EMS parameters depend on the amplitude-frequency spectrum of the acoustic field excited by linear deformations of the sources.

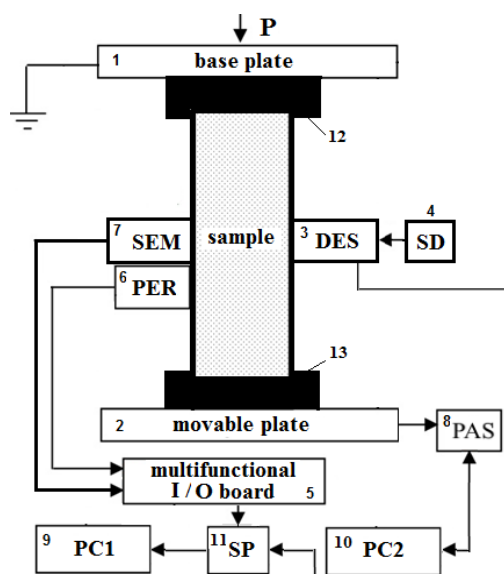
Mechanisms of EMS generation and source types were summarized to distinguish processes that induce separation of electric charges and form electric dipoles. These processes include: uneven distribution of electric charges on crack edges when ionic or other types of bonds are broken; in inhomogeneous field of mechanical stresses, charged defects start to migrate in the area of crack formation; at the interface of mineralized water released during heating with the rock; friction-induced electrification during movement of structural elements. On the other hand, the change in the dipole moment is determined by the breakdown between the charged sides of the crack, charge relaxation if the current flows through the dielectric body outside the crack; electron emission; vibrations of charged surfaces.

Thus, EMS generation is due to the change in the charge state of the test material during development of cracks of various scales or double electric layers at the interface of media, minerals, and aqueous solutions. During crack development, acoustic emission methods can be employed, which use acoustic pulses emitted by growing cracks of different lengths and record electromagnetic signals when the charged edges of these cracks vibrate. These are mechanical-electrical methods.

Experimental

Experimental studies of mechanical and electrical transformations were carried out on samples of rocks from the Tashtagol iron ore deposit, which have different ratios of magnetite and calcite. These minerals are distinguished by their ultimate strength: $(12-50) \times 10^6$ Pa - for calcite [14]; $(14-21.5) \times 10^7$ Pa - for magnetite ore and skarns of the Tashtagol deposit, calculated from the date of destruction of samples in experiments. In addition, calcite and magnetite differ significantly in their electrical characteristics. So the specific electrical resistance (ρ) of calcite is $(10^7 - 10^{12})$ Ohm $\cdot$ m, and magnetite is $(10^{-5} - 10^4)$ Ohm $\cdot$ m [14, 15]. The magnetite content in the ore samples used ranged from 60 to 77 percent. In addition, skarn samples containing magnetite were used. Samples for experiments were made from cores with a diameter of $(42 \pm 1) \times 10^{-3}$ m and a length of $(80 \pm 5) \times 10^{-3}$ m.

Investigations of the electromagnetic emission (EME) characteristics under uniaxial compression loads were carried out on the stand, the block diagram of which is shown in Figure 1. In the course of the experiment, the sample was placed between the support (1) and the movable plate (2) of the IP500.1 automated press, which developed the force P on the sample up to 500 kN.



1 — base plate of the IP500.1 press; 2 — movable press plate IP500.1; 3 — dynamic excitation system to control the energy of the impact of the ball; 4 — spring device PU for accelerating the ball for introducing a deterministic acoustic pulse into the sample; 5 — multifunctional input-output board NI BNC 2120; 6 — PER piezoelectric receiver; 7 — electromagnetic differential capacitive sensor; 8 — press automatic system; 9 — personal computer PC1 for visualization and amplitude-frequency analysis of acoustic and electromagnetic signals; 10 — personal computer PC2 for operating with the press; 11 — software block; 12, 13 — holders for centering the sample.

Figure 1. Block diagram of the stand for uniaxial compression of the test samples.

The load and loading rate of the sample was set using a specialized program from a PC2 computer (10) through the press automatic system (8) to the actuator of the servo valve. Moreover, changes in the load could be set linear, stepwise, or cyclical. For centering the samples, special holders 12 and 13 were used. Recording of information on changes in the sample deformation due to applied forces and their type was recorded and displayed on the PC2 computer monitor. Uniaxial compression was carried out at a constant rate of 0.3 Pa/s. Acoustic impulse excitation of the samples by the impact of the ball was carried out using a spring device for accelerating the impacting ball SD (4) through the impact energy control system DES (3) [12, 23]. The shape of the acoustic pulse was close to the bell-shaped Gaussian distribution, and its duration at the 0.1 of maximum amplitude was 50×10^{-6} seconds. A point impact with a ball weighing 8.6×10^{-4} kg was applied in the middle of the free cylindrical part of the sample. After flying through 3, the ball hit a hardened steel plate 2×10^{-3} meters thick, excited a deterministic acoustic pulse, which passed through a layer of mineral oil between the plate and the sample into the sample. The hardness of the steel of the plate and the ball were of equal values. The residual impact energy introduced into the sample after the ball bounced was $(5 \dots 30) \times 10^{-3}$ J. The acoustic signal, passing through the sample, was recorded by the PER piezoelectric acoustic pulse receiver (6).

The DES system comprised a metal tube with two optical pairs built into it at a distance of 5×10^{-2} meters, each of which included a light-emitting diode (LED) and a photodiode. The ball, flying through the optical pairs, gave two marks on the PC1 computer monitor (9). These marks were used to calculate the ball raid V_1 and V_2 rebound velocities. The calculated velocities were used to determine the kinetic energy of the acoustic impact, E_{exc} , transmitted to the sample:

$$E_{exc} = \frac{m}{2}(V_1^2 - V_2^2), \quad (1)$$

In this case, the energy losses of the acoustic pulse in the plate were not taken into account. The EMS electrical component generated by the sample during the passage of the acoustic signal was received by a differential capacitive sensor SEM (7) with a built-in power amplifier. The sensor used low and high pass filters, which ensured its operation in the range from 1 to 100 kHz. At the SEM output, the signal was amplified with a factor of 10 or 100. In the measurements, the gain was selected depending on the input EMS amplitude. The SEM input sensitivity is 5×10^{-4} V. Signals from the SEM and PER were transmitted through the NI BNC-2120 multifunctional board (5) to PC1 (9). Subsequently, using a special software program (11), the EMS amplitude was normalized to the amplitude of the acoustic pulse excited by the impact of the ball, and the EMS amplitude-frequency analysis was performed using the fast Fourier transform.

Results and Discussion

Acoustic pulses arise in the destructive zones while the material is cracking. The pulses propagation generate EMS parameters of which are depend on characteristics of the exciting acoustic pulses [2–5, 13]. Thus, the results of numerical simulation of mechanical stresses changing on cracks defects are provided here. The regularities in the EME characteristics under uniaxial compression to the destructive values of the samples were studied experimentally. These studies were carried out to determine the applicability of mechanical-electrical methods when testing the development of destructive zones and destruction in dielectric materials.

For calculations, we analyzed wave propagation in elastic inhomogeneous medium of limited dimensions with given physical and mechanical properties under pulse exposure of part of its surface. The parameters of the stress-strain state (displacement, strain, stress) were calculated. The simplest classical rigid body model was used [16–18].

The problems of wave mechanics are solved by hypotheses conventional for classical elastic medium, such as the approximation of homogeneity and continuity. Any inhomogeneity is caused by defects or inclusions that are considered explicitly, i.e., they are included in the problem statement.

For a given cylindrical magnetite ore sample, this model can be applied with some assumptions. For example, for problems related to wave propagation, it was assumed that the used samples were free of porosity, empty cavities. The study of the sample texture showed that calcite and magnetite minerals are in continuous contact and smoothly mix with each other.

The boundary conditions correspond to the laboratory experiment. Zero displacement was specified at the flat boundaries of the sample since in the laboratory experiment the sample was clamped between the punches. The side faces are free, therefore, the stresses at the boundary equal to zero. For a three-dimensional case, the free boundaries show no components of the stress vector:

$$\sigma_{\tau 1} = \sigma_{\tau 2} = \sigma_n = 0 \quad (2)$$

where σ_n is normal stresses and $\sigma_{\tau 1}, \sigma_{\tau 2}$ are tangential stresses.

In the middle of the vertical dimension of the sample $y = l$ along the normal, load is applied in the form:

$$\begin{aligned} \sigma_n &= T(t) \times F(x, z), \\ \sigma_{\tau 1} &= \sigma_{\tau 2} = 0, \end{aligned} \quad (3)$$

where $T(t)$ is a function that determines the law of load variation with time, $F(x, z)$ is a function that determines the law of load variation over the surface (in a two-dimensional case along the contour line), σ_n is normal stresses and $\sigma_{\tau 1}, \sigma_{\tau 2}$ are tangential stresses, the last components of the load vector are neglected. For calculations, the dependence $T(t)$ was used in the form of a half exponentially decaying sinusoid:

$$T(t) = e^{-\beta t} \sin\left(\frac{2\pi t}{\tau}\right) \times \eta(t),$$

$$\eta(t) = \begin{cases} 1.0 & \leq t \leq \tau \\ 0, & t \geq \tau \end{cases}, \quad (4)$$

where τ is load exposure time that depends on the duration of the deterministic acoustic pulse.

At the face end, the load was specified as a gradually increasing and then gradually decreasing function dependent on temporal and spatial coordinates. Afterpulse exposure, stresses at the upper boundary were set to zero. In calculations, the acoustic excitation pulse was close to the experimental one in shape, amplitude, and duration. In the three-dimensional case, when the load is applied to the surface, the acoustic pulse in the form of a bell-shaped function is represented as:

$$F(x, z) = A \times \exp\left(-\beta \frac{(x - x_0)^2 + (z - z_0)^2}{2d_0^2}\right), \quad (5)$$

where x_0, z_0 are the coordinates of the center of the acoustic pulse source, and d_0 is the value that determines the distance from the pulse center at which the normal stress decreases by a factor of e^β .

In the general case, the system of equations that describes the behavior of a deformable solid body in the spatial case includes the equations of motion

$$\rho \ddot{U}_i = \rho G_i + \sigma_{ij,j}, \quad (6)$$

where ρ is density, U_i is displacement, σ_{ij} is stresses, G_i is mass force vector components, $i, j = 1, 2, 3$.

The dot above the symbol indicates the time derivative, and the comma after the index indicates the derivative of the corresponding coordinate. Summation is performed over the repeated indices, for example:

$$\sigma_{ij,j} = \frac{\partial \sigma_{i1}}{\partial x_1} + \frac{\partial \sigma_{i2}}{\partial x_2} + \frac{\partial \sigma_{i3}}{\partial x_3},$$

the continuity equation

$$\frac{\partial \rho}{\partial t} + \rho \left(\frac{dU_1}{dx_1} + \frac{dU_2}{dx_2} + \frac{dU_3}{dx_3} \right) = 0, \quad (7)$$

where x_i is the coordinate axis.

The relation between the strain tensor components and displacements from the Cauchy relation is represented as

$$\varepsilon_{ij} = 0,5(U_{i,j} + U_{j,i}), \quad (8)$$

and the constitutive relations specify the relations between stress and strain tensor components as:

$$\sigma_{ij} = f(\varepsilon_{ij}). \quad (9)$$

In the elastic case, relations (10) are taken in the form of Hooke's law. In the applied problems of wave mechanics, the processes are described by hyperbolic equations when formulated correctly. Hyperbolic equations and systems make up a significant part of the mathematical models used to solve applied problems. A distinctive feature of hyperbolic equations and systems is that they describe wave processes with the finite rate of disturbance (wave) propagation in the considered region.

For each equation of the form

$$\frac{\partial U}{\partial t} = \frac{\partial F}{\partial x}, \quad (10)$$

the used difference scheme corresponds to the simplest version of McCormack non-central schemes [19, 20].

A volumetric design scheme was used for the equation solution. McCormack's method is a finite-difference predictor-corrector method, which refers to shock-capturing schemes. In accordance with the scheme, the position of the wavefront is not identified, and the computational domain is analyzed for each moment of time, which is needed for subsequent use of the simulation results. McCormack's scheme assumes the use of a rectangular computational grid, which has a number of advantages: simplified mathematical calculations, less computing time, simplified specification of boundary conditions, and simplified pro-

cessing of results without data loss. Results obtained by square-cell grids are best since the hourglass effect – twisting of the grid cells – is minimized. The numerical algorithm of the method is similar to the Runge–Kutta method [20] used to solve ordinary differential equations. To obtain solutions at the next time step $U(t + \Delta t)$ by the Runge-Kutta method using the known $U(t)$, one or several iterations are required.

Before using the method similar to the Runge–Kutta method of the second order of accuracy, spatial derivatives in the equations were replaced by the corresponding ratios of finite differences. Non-central difference operators were used, for example, alternately left or right differences instead of central ones. This approach forms the basis for the effective non-central second-order scheme proposed by McCormack.

Non-central schemes are superior to most conventional central schemes since the program logic is simplified, non-uniform terms are easily included, and generalization to multidimensional problems is performed directly. The advantage of non-central schemes is the absence of half-integer indices, which simplifies realization of the boundary conditions. The scheme has a second order of approximation in both spatial and temporal variables.

Thus, the boundary conditions can be specified by displacements. The size of elements in the finite element model was $(10^{-3} \times 10^{-3})$ m². The calculation involves 237,500 points at a sampling rate of 10^{-6} s. The calculations were performed for an elastic sample of magnetite ore used in the experiments of stepwise compression and subsequent excitation at steps by deterministic acoustic pulse. Cracks specified were of different sizes with a length along the sample axis or along with the acoustic pulse propagation at the point of the ball impact. Numerical simulation was carried out using a special graphics package. The results of numerical simulation are visualized in the form of stress intensity propagation regions [21, 22]. The constructed mathematical model was used to analyze elastic wave propagation in the sample under pulsed mechanical action. This enables detailed distributions of parameters that describe the material behavior in contrast to experimental studies when the measured quantities have predominantly integral meaning. Elastic disturbances were simulated numerically in a cylindrical region, where the lateral surface was exposed to pulse excitation. It is reasonable to consider the problem in flat formulation, namely, with the axial section of the cylinder with dimensions of $(42 \times 80) \times 10^{-6}$ m. Figure 2 shows examples of numerical modeling for this region at the acoustic pulse propagation time of 25×10^{-6} s.

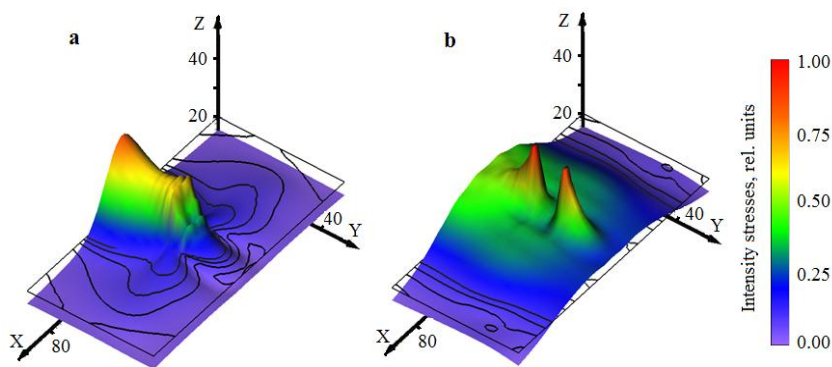


Figure 2. Calculated values of stress intensity in the sample bulk within 25×10^{-6} s from the moment of the acoustic pulse input by the ball impact on the cylindrical surface of the sample: a) crack 10^{-2} m long along the sample axis at a distance of 20×10^{-3} m from the excited cylindrical surface; b) crack 10^{-2} m long across the sample at a distance of 40×10^{-3} m from the face end of the sample under similar external impact.

In numerical modeling, changes in stress intensity over time from zero to 35×10^{-6} s were studied. For example, Figure 2a demonstrates changes in stress intensity in the bulk of the sample on a crack 10^{-2} m long located along the sample axis at a distance of 20×10^{-3} m from the excited cylindrical surface within 25×10^{-6} s from the moment of the acoustic pulse induced by the ball collision with the cylindrical surface. As can be seen in the figure, stresses are concentrated on the crack, and then they drop sharply along the line of AP propagation. As reported in the introduction, the amplitude-frequency spectrum of EMS is directly related to the parameters of the time-varying AP. As a result, the EMS spectrum also changes.

Figure 2b represents changes in stress intensity in the bulk of the sample on the crack 10^{-2} m long located across the sample axis at a distance of 40×10^{-3} m from the sample end face under similar external action from the excited cylindrical surface. The figure also presents the calculation of stresses within 25×10^{-6} s from the moment of the acoustic pulse input after the ball impact on the cylindrical surface. As can be seen in the

figure, stresses are concentrated on the crack, but their shape differs from the previous one (Figure 2a). Therefore, the EMS amplitude-frequency spectrum will be different. The form of the amplitude-frequency spectrum under deterministic acoustic excitation can help to determine the location of existing or emerging cracks during sample fracture propagation caused by different types of strength loading.

Figure 3 shows the results of numerical simulation of the change in the stress intensity in the region of the sample with dimensions $(42 \times 80) \times 10^{-3} \text{ m}^2$ after $30 \times 10^{-6} \text{ s}$ from the moment of injection of a deterministic acoustic pulse in the middle of the surface perpendicular to the direction of uniaxial compression for a crack 10^{-2} meters, for two cracks 20×10^{-3} and 42×10^{-3} meters along the compression axis each at a distance of 10^{-2} meters from the edges of the sample, as well as for several cracks located along the compression axis with dimensions $(2.0, 4.0, 8.0, 16.0, 32.0, 64.0) \times 10^{-3}$ meters, the distance between cracks is $5 \times 10^{-3} \text{ m}$. In the latter case, the cracks are arranged in ascending order from the smallest in length to the largest from the point of application of the impulse.

In Figures 2 and 3, the intensity of the stresses arising in the sample is displayed in color. They show that cracks are stress concentrators. An electromagnetic signal with the highest amplitude will come from the area of such stress concentrations. The Z-axis in Figures 2 and 3 coincides with the direction of the maximum principal stress. Thus, in the process of any type of force action, electromagnetic emission will reflect the appearance of cracks and the development of zones of the destruction of materials.

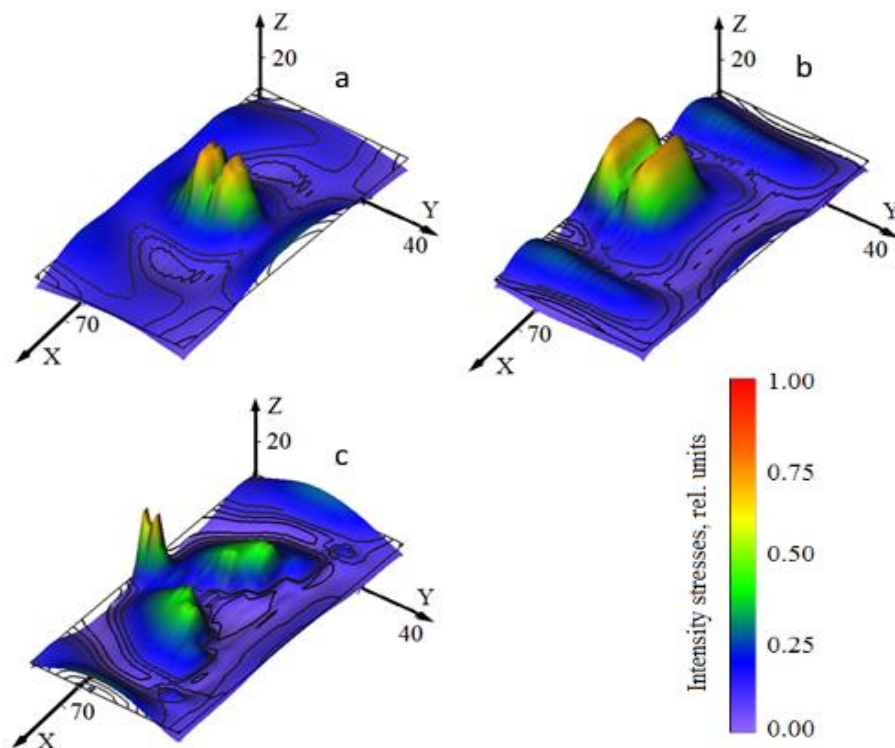


Figure 3. Numerical modeling of the stress intensity dynamic in a sample with dimensions $(42 \times 80) \times 10^{-3} \text{ m}^2$ after $30 \times 10^{-6} \text{ s}$ from the moment of input of a deterministic acoustic pulse in the middle of the surface perpendicular to the direction of uniaxial compression: a) crack 10^{-2} m ; b) two cracks 20×10^{-3} and $42 \times 10^{-3} \text{ m}$ along the compression axis each at a distance of 10^{-2} m from the edges of the sample; c) the area contains several cracks located along the compression axis with dimensions $(2.0, 4.0, 8.0, 16.0, 32.0, 64.0) \times 10^{-3} \text{ m}$, the distance between the cracks is $5 \times 10^{-3} \text{ m}$, the cracks are arranged in ascending order from the smallest to the largest one from the point of application of the impulse.

During the experiments, the electromagnetic emission of rock samples of skarn containing magnetite and magnetite ore of different strengths was investigated when they were loaded along the axis by uniaxial compression. Figure 4a shows the amplitudes of the EME skarn averaged over 1 second in a wide frequency band of 1 ... 100 kHz. The sample contained calcite and magnetite. The EME was recorded continuously with the recording of the current values of the compressive stresses P in the range from zero to destructive loading values P_{lim} . The figure shows the stages of the development of fracture, including the stage of devel-

opment of destruction of the sample material or the growth of primary cracks and their growth in the range of 0.3 ... 0.52 of the relative load.

The relative load is the ratio of the current load to the breaking load P/P_{lim} . Similar changes in the EME amplitude were observed during the development of destructive processes in magnetite ore (Figure 4b). It can be seen from the obtained regularities of the development of destruction at stage 2 that two independent increases in the EME amplitude are observed. This is due to the fact that when the samples are loaded with compressive forces, the resulting stresses are transmitted to their entire volume, including calcite and magnetite. Deformation in brittle materials obeys Hooke's law. As a result of such an impact, the most fragile material will be destroyed first.

Thus, various modifications of calcite, depending on its position and type in the rock, have a strength of $(12-50) \times 10^6$ Pa, while the strength of magnetite ore is significantly higher. In this regard, the zone of destruction in the minerals that make up the rock will develop in different intervals of the relative load P/P_{lim} . This is shown in Figure 4 when loading skarn and magnetite ore samples. Summarizing the results of the study to identify the influence of the mineral composition of rock samples on the EME amplitude, we can say that the least durable inclusions present in the material will always initially undergo destruction.

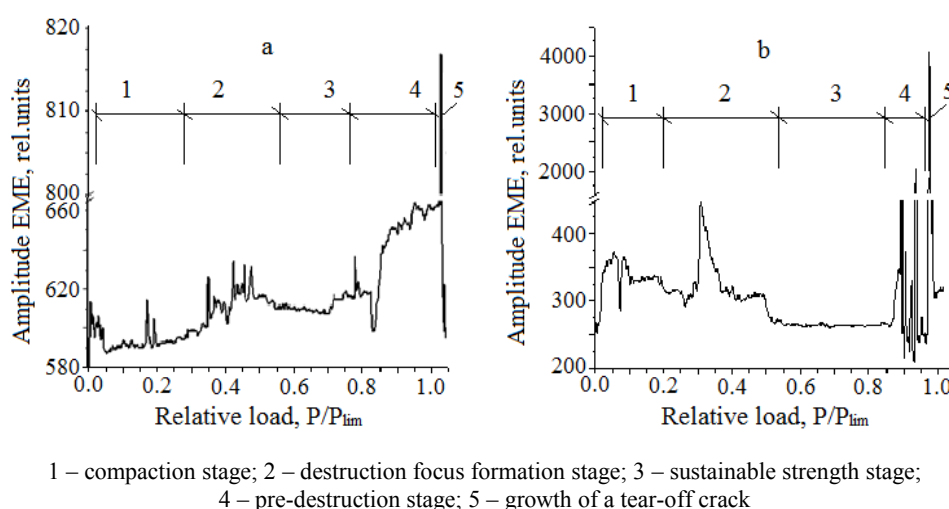


Figure 4. Changes in the EME amplitudes averaged over one second at a frequency of 100 kHz at different values of the relative compressive load on the sample: a) skarn; b) magnetite ore.

Conclusions

Analyzing the numerical calculations of the stress intensity on cracks of different sizes and locations, and the experimental regularities of the EME amplitude and frequency characteristics under uniaxial compression we concluded that some important features can be distinguished during testing the fracture processes development by the method of mechanical and electrical transformations.

Thus, the performed numerical simulation of the stress intensity dynamic in the samples under deterministic acoustic excitation at the middle of the surface perpendicular to the direction of uniaxial compression, revealed that the cracks in the sample volume are stress concentrators. The stress intensity and their type differ significantly with different numbers and sizes of cracks perpendicular to the propagation of the acoustic pulse. EMS with the highest amplitude and with different amplitude-frequency spectra will come from the region of such concentrations because the EMS parameters are related to the characteristics of the arising mechanical stresses.

The experimentally obtained results of EME during the uniaxial compression of skarn and magnetite ore samples of different strengths revealed the stages of preparation for the samples destruction. The emergence and development of destructive zones are in the range from 0.3 to 0.55 of the breaking load. It should be borne in mind that for different materials the interval of this range may vary depending on their strength. This circumstance indicates the depending on the EMS parameters from the samples structure and their dielectric properties under mechanical-electrical conversions.

Thus, the use of the mechanical-electrical method under compression will be useful in testing the processes of the cracks onset and the fracture development in solid dielectric materials and products. In the fu-

ture, the considered method can be used to detect defects in dielectric materials. The prerequisites for such defects testing are the above theoretical studies of changes in mechanical stresses in a model solid on defects in the form of cracks under an external deterministic acoustic effect. Cracks here are stress concentrators during the propagation of acoustic pulses. The same concentrators of mechanical stresses will be the contacts of defects with the material containing them. As a result, in accordance with the defect and the sample impedance ratio, EMS with parameters defining the defects boundaries will appear.

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Диэлектрлік материалдардағы деструктивті процестердің дамуы кезіндегі механикалық және электрлік түрлендірулерді сандық және тәжірибелік зерттеулер

Мақалада диэлектрлік тау жыныстарының үлгілері мысалында кернеулі-деформациялық күйдің өзгеруімен сындың дамуын механикалық және электрлік сынау әдісі талқыланған. Айнымалы электромагниттік өрістердің пайда болу құбылысы қатты дене құрылымдарындағы механикалық және электрлік түрлендірулерге негізделген, олардың кернеулі-деформациялық күйі механикалық жүктеменің әсерінен сыналған материал ішіндегі акустикалық эмиссиямен бірге өзгереді. Авторлар әртүрлі құрамы мен текстурасы бар тау жыныстарының үлгілерінің импульстік детерминирленген акустикалық козуы кезіндегі электромагниттік реакциялардың параметрлерінің өзгеруін сандық және тәжірибелік зерттеулердің нәтижелерін талқылаған. Детерминирленген акустикалық импульстар енгізілген перпендикуляр үлгі осінің бойымен және көлденеңінен орналасқан жарықтардағы кернеу концентраторларының математикалық есептеулерінің нәтижелері берілген. Әр түрлі беріктігі мен электрлік қасиеттері бар кальцит пен магнетит үлгілер жойылғанға дейінгі бірсызғы сығымдау кезіндегі электромагниттік эмиссияны эксперименттік зерттеудің нәтижелері көрсетілген. Үлгі көлеміндегі жарықтар кернеу концентраторлары болып табылады. Акустикалық импульстің таралуына перпендикуляр жарықтардың саны мен мөлшері әр түрлі болған кезде кернеулердің қарқындылығы және олардың сыртқы түрі айтарлықтай өзгереді. Бұл жағдай үлгілердің құрылымының және олардың диэлектрлік қасиеттерінің механикалық және электрлік түрлендірулердің нәтижелерін жазу кезінде электромагниттік сигналдардың параметрлеріне әсерін көрсетеді. Осылайша, сығымдау кезіндегі механикалық-электрлік түрлендірулердің әзірленген әдісін пайдалану қатты денелі диэлектрлік материалдар мен бұйымдарда жарықшақтардың пайда болу және сынулардың даму процестерін сынауда қолданылуы мүмкін.

Кілт сөздер: диэлектриктер, тау жыныстары, сандық модельдеу, акустикалық әсер ету, бірсызғы сығу, электромагниттік эмиссия, механоэлектрлік қайта құру, электромагниттік сигнал.

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Численное и экспериментальное исследования механико-электрических преобразований при развитии деструктивных процессов в диэлектрических материалах

В статье обсужден метод механико-электрического тестирования развития разрушения при изменении напряженно-деформированного состояния на примере диэлектрических образцов горных пород. В основе явления возникновения переменных электромагнитных полей лежат механико-электрические преобразования в твердотельных структурах при изменении их напряженно-деформированного состояния под воздействием механической нагрузки, сопровождающейся акустической эмиссией внутри испытываемого материала. Авторами рассмотрены результаты численных и экспериментальных исследований изменения параметров электромагнитных откликов при импульсном детерминированном акустическом возбуждении образцов горных пород с различным составом и текстурой. Представлены результаты математических расчетов концентрации напряжений на трещинах, расположенных вдоль и поперек оси образца, перпендикулярно которой вводились детерминированные акустические импульсы. Показаны результаты экспериментальных исследований электромагнитной эмиссии при одноосном сжатии до разрушения образцов с содержанием кальцита и магнетита, обладающих разной прочностью и электрическими свойствами. Присутствующие в объеме образца трещины являются концентраторами напряжений. При разном количестве и размерах трещин, перпендикулярных распространению акустического импульса, интенсивность напряжений и их вид существенно различаются. Это обстоятельство указывает на влияние структуры образцов и их диэлектрических свойств на параметры электромагнитных сигналов при регистрации результатов механико-электрических преобразований. Таким образом, использование метода механико-электрических преобразований при сжатии может быть использовано при тестировании процессов начала трещинообразования и развития разрушения в твердотельных диэлектрических материалах и изделиях.

Ключевые слова: диэлектрики, горные породы, численное моделирование, акустическое воздействие, одноосное сжатие, электромагнитная эмиссия, механоэлектрические преобразования, электромагнитный сигнал.

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Influence of the size of iron nanoclusters on their magnetization

The size of iron nanocrystals significantly affects the value of their magnetization. However, an adequate model of the structure of nanocrystalline formations comprising different numbers of iron atoms still does not exist. In this work, spatial models of nanocrystalline iron clusters differing in configuration and the number of their constituent atoms are constructed. Tetrahedrally close-packed cluster assemblies of iron atoms are taken as the basis for the proposed structures of nanocrystals. The spectra of the density of electronic states for the proposed clusters are constructed using the theory of the electron density functional. The calculation was carried out by the method of scattered waves in accordance with the band theory of crystals. The appearance of magnetization in tetrahedral close-packed cluster formations is associated with excited electronic states of atoms located on the surface of the nanocluster. Excited atoms have an increased electron density, that is, electrons are able to transition to states with higher energy, approaching the Fermi energy. In this case, the Stoner criterion necessary for the occurrence of magnetization is fulfilled. The configurations of electrons with spin up and down differ, which is why uncompensated magnetic moments appear. It is shown that the proposed models of iron nanoclusters are in satisfactory agreement with the known experimental data.

Keywords: iron nanocluster, tetrahedrally tightly packed structures, magnetic properties.

Introduction

The nanocrystalline state changes not only the structure but also many physical characteristics of substances [1]. In [2], studies of the magnetic properties of cluster iron particles from different numbers of atoms are presented. It is shown that the ferromagnetic properties of iron clusters depend on the number of atoms in them. For clusters less than 50 atoms in size, the magnetic moments reach 3.1 Bohr magnetons. With an increase in the number of atoms to 500–700 atoms in the cluster, the magnetic moments approach the magnetization of bulk samples, which are 2.2 Bohr magnetons (Fig. 1).

The authors [3] found the presence of magnetization in cluster formations even in the absence of atoms of ferromagnetic substances in them. Hysteresis loops confirming magnetization were obtained for clusters CeO₂, GaN, Al₂O₃, etc. Ferromagnetism is also observed in thin films of HfO₂, TiO₂, and ZnO [4, 5].

Cluster models are the most objective representation of the structure of metals with a small number of atoms [6]. In addition, structures corresponding to cluster structures also occur in the volume of metals, at interfaces, on fracture surfaces, etc. When modeling nanocluster formations, we use sets of dense tetrahedron packages that most adequately correspond to the nanocrystalline state [7].

The purpose of the work is to explain the nature of the increase in the magnetization of iron in nanocluster formations containing different numbers of atoms.

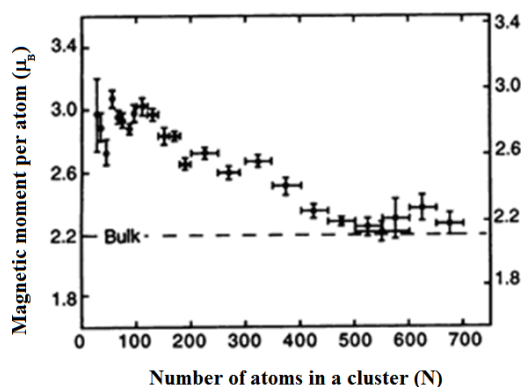


Figure 1. Dependence of the average magnetic moment per atom for iron clusters on the number of atoms in it at 120 K [2]

Tasks of the work:

1. Construction of three-dimensional cluster models of tetrahedral densely packed iron nanoclusters with different numbers of atoms.
2. Construction of density spectra of electronic states of nanoclusters under study.

Experimental

To determine the coordinates of the atoms, spatial models of clusters were constructed using a three-dimensional modeling program. The program has the necessary tools to determine the coordinates of the atoms of the studied clusters. The cluster models were based on the theoretical values of the parameters of iron crystal lattices: $a_{\text{HCC}} = 3.656 \text{ \AA}$, $a_{\text{BCC}} = 2.866 \text{ \AA}$ [8].

The electron state density spectra were constructed within the framework of the electron density functional theory (DFT) [9] using the basis of plane waves and ultra-soft pseudopotentials. The calculation was carried out using the scattered wave (SW) method in accordance with the band theory of crystals – an analogue of the Corringi-Cohn-Roxter method adapted for cluster models. The SW method is based on the formalism of multiple scattering of an electron wave on a system of potentials; it allows calculations for clusters of several atoms and large systems based on the coordinates of atomic nuclei. The interaction of electrons is described by the averaged values of periodic fields described by the MT potential [10]. The software package Quantum Espresso was used for the calculation [11].

Results and Discussion

In the first stage, a model of an octahedral cluster for iron, a face-centered modification of the crystal lattice, including six atoms was constructed (Fig. 2a). Next, a graph of the probability density of electronic states for this cluster was obtained (Fig. 2b).

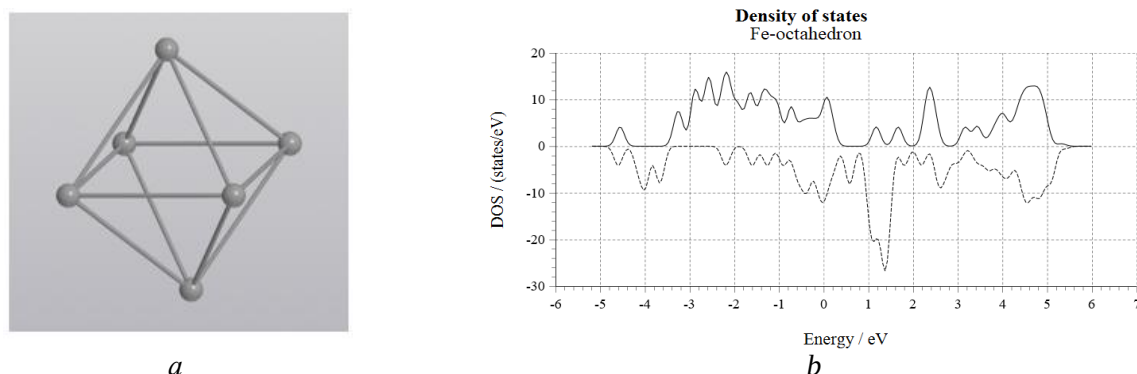


Figure 2. Octahedral cluster of fcc iron of six atoms: *a* – general view; *b* – dependence of the probability density of the distribution of electronic states on the energy of electrons with spin up and down

According to the spectrum data (Fig. 2b), it can be concluded that the electronic moments with dissimilar spins are uncompensated. The calculated average effective magnetic moment per atom was $1.67 \mu_B/\text{atom}$.

This result contradicts the data obtained for the magnetization of austenitic steels having a HCC lattice, which does not exhibit ferromagnetic properties for massive samples [8].

An octahedral cluster of six atoms can be transformed into a cluster formation consisting of densely packed tetrahedra. According to [12], an octahedron can be turned into three connected tetrahedra by switching one chemical bond between two of the six atoms (Fig. 3).

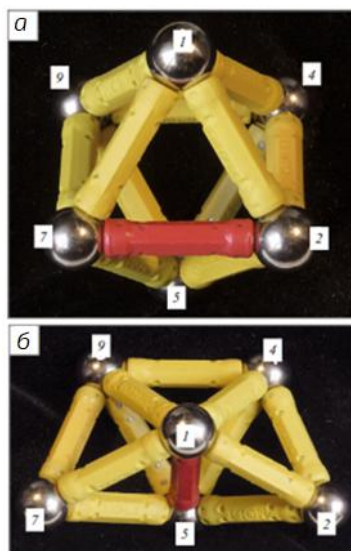


Figure 3. Transformation of nanoclusters: *a* – model of a hexagonal cluster; *b* – model of a cluster of three tetrahedra [12]

Tetrahedral assemblies can be organized in different ways. The most famous example is the Frank-Kasper structure FK-12 [13], which corresponds to an icosahedron. Such an assembly can be constructed from twenty close-packed tetrahedra (Fig. 4a).

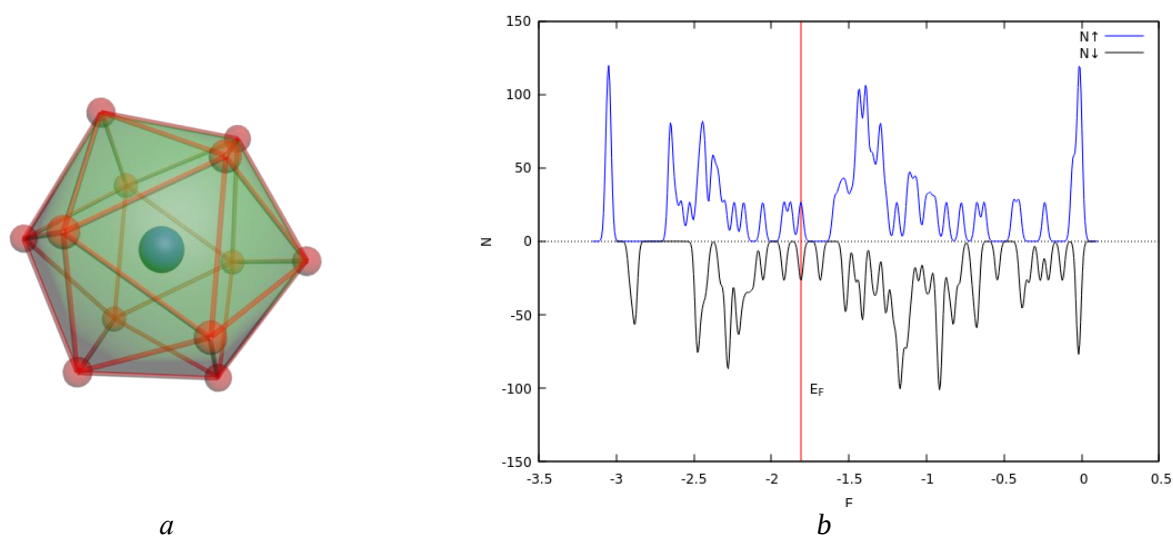


Figure 4. Icosahedral iron cluster of 13 atoms: *a* – general view; *b* – dependence of the probability density of the distribution of electronic states on the energy of electrons with spin up and down; the red line corresponds to the Fermi energy

The calculation of the density of the electronic states of the icosahedral cluster (Fig. 4b) showed that the average magnetic moment is $0.21 \mu_B/\text{atom}$.

The FK-12 structure, along with FK-14, appears in Gadfield steel (110G13L) during plastic deformation on the deformation or fracture surface. Gadfield steel is also austenitic, however, exhibits nonzero magnetization under mechanical action [14].

There are various possibilities for packing tetrahedra in a nanocluster. Thus, the appearance of a cluster in the form of a tetrahedral spiral for compounds Ni_4Ti_3 , Al_4C_3 , and others was shown in [12, 15, 16]. The formation of such a structure is associated with the possibility of the transition of an octahedral cluster into a group of three tetrahedral (see Figure 3). Figure 5a shows a nanocrystalline iron cluster, which is a spiral of seven tetrahedra. For such a tetrahedral assembly, a spin-polarized density of electronic states is constructed (Fig. 5, b), the average magnetic moment per atom was $0.26 \mu_B/\text{atom}$.

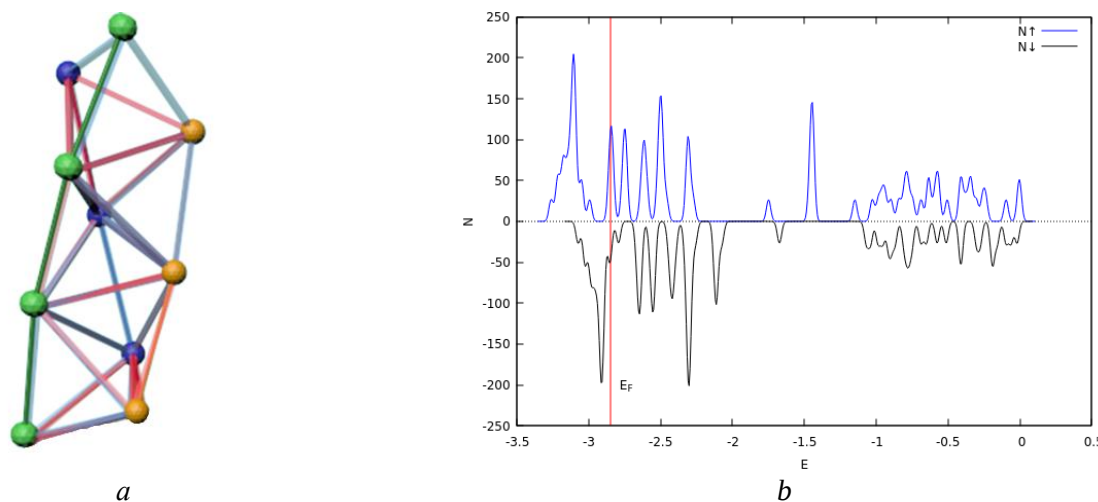


Figure 5. Spiral iron cluster, composed of seven tetrahedra: *a* – general view; *b* – dependence of the probability density of the distribution of electronic states on the energy of electrons with spin up and down

When constructing further coordination spheres (Fig. 6) using tetrahedral clusters, the number of atoms on the surface increases exponentially. The central atom in the center is common to all spirals. The first row of tetrahedra is located on the top and has 12 generalized atoms on the surface. The second row has 20 atoms on the surface, the third has 32 atoms, the fourth has 52 atoms, etc. (Fig. 6). However, according to the Delaunay rule [6], it is impossible to realize in three-dimensional space a densely packed structure of an icosahedron containing over 2 coordination spheres.

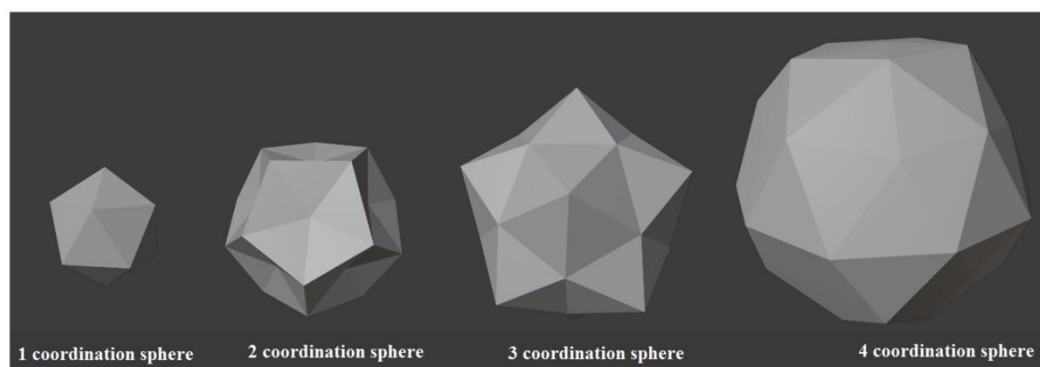


Figure 6. Evolution of coordination spheres from tetrahedral clusters: from the first to the fourth

The next stage of the simulation was a combination of a spiral and an icosahedral cluster. When twenty tetrahedral spirals are tightly packed (Fig. 7), an icosahedron containing 13 atoms is formed in the first coordination sphere. There are 20 atoms in the 2nd coordination sphere. Here, the first 3 tetrahedra from each of the 20 spirals are connected in concert. Further, each spiral grows independently in the direction from the center perpendicular to the faces of the icosahedron of the 1st coordination sphere. Each spiral has 10 atoms, six of which are packed in 3 tetrahedra located in 2 coordination spheres. The remaining 4 atoms of each spiral are packed into “tails” of 4 tetrahedra. The total number of atoms in such positions is $4 \times 20 = 80$. Thus, the total number of atoms in a cluster packed with 20 tetrahedral spirals is $33 + 80 = 113$ atoms (Fig. 6).

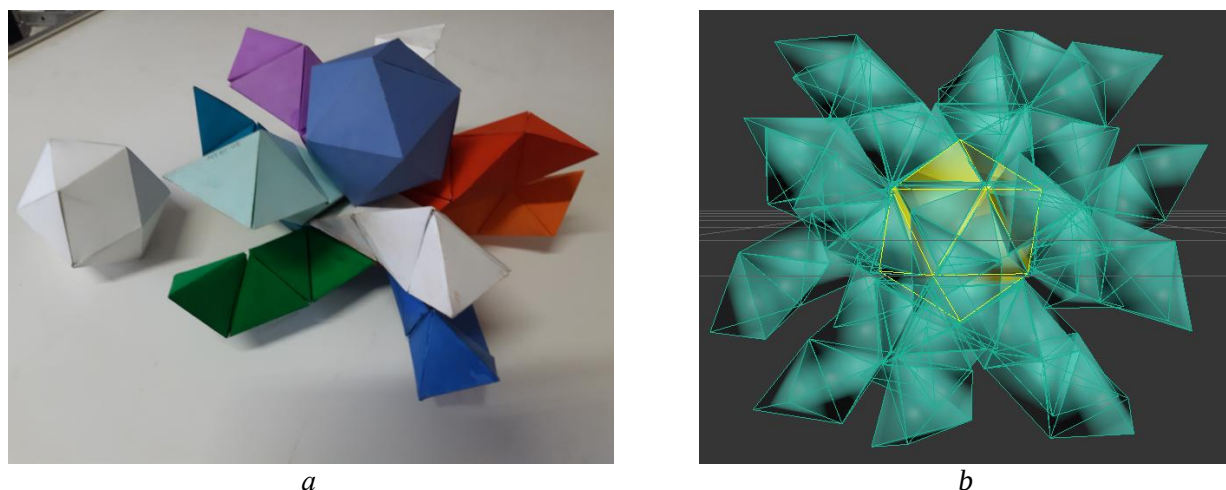


Figure 7. Combination of icosahedral and spiral iron clusters:
a – incomplete paper model; *b* – three-dimensional computer model

Figure 7 presents a structure built of twenty tetrahedral ten-atom spirals with one common atom in the center. In the second coordination sphere, an icosahedron is also formed, containing twenty atoms. This gives 33 atoms in total in the first and second coordination spheres. This structure corresponds to the experimentally obtained result with the maximum magnetization shown in Figure 1.

Conclusions

The appearance of magnetization in cluster formations is associated with the excited electronic states of those atoms that are on the surface of a nanoparticle or nanofilm. Stressed nonequilibrium electronic states arise in such systems. For cluster models of small sizes, most of the atoms are on the surface and have open bonds. Excited atoms have an increased electron density, that is, electrons are able to transition to states with higher energy, approaching the Fermi energy. In this case, the Stoner condition is satisfied, which is necessary for the occurrence of magnetization [17]. The configurations of electrons with spin up and down are different, which gives rise to uncompensated magnetic moments. Thus, the proposed models of iron nanoclusters are in satisfactory agreement with the experimental data of [1].

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Темір нанокластары мөлшеріне олардың магниттелуінің әсері

Нанокристалдардың мөлшері олардың магниттелу мөлшеріне айтарлықтай әсер етеді. Алайда, әр түрлі темір атомдарынан тұратын нанокристалды түзілімдер құрылымының барабар моделі әлі жоқ. Мақалада конфигурация мен оларды құрайтын атомдардың саны бойынша ерекшеленетін нанокристалды темір кластерлерінің кеңістіктік модельдері жасалған. Нанокристалдардың ұсынылған құрылымдарының негізі темір атомдарының тетраэдрлік тығыз оралған кластерлік жинақтары болып табылады. Ұсынылған кластерлер үшін электронды күй тығыздығының спектрлері электронды тығыздық функционалды теориясын қолдана отырып жасалған. Есептеу кристалдардың аймақтық теориясына сәйкес шашыраңқы толқындар әдісімен жүргізілді. Тетраэдрлік тығыз оралған кластерлік түзілімдерде магниттелудің пайда болуы нанокластың бетінде орналасқан атомдардың қозған электронды күйлерімен байланысты екендігі көрсетілген. Қозған атомдардың электронды тығыздығы жоғарылайды, яғни электрондар Ферми энергиясына жақындаған жоғары энергияға ие күйге ауыса алады. Бұл жағдайда магниттелудің пайда болуы үшін қажет тас өлшемі орындалады. Айналдыру жоғары және төмен электрондардың конфигурациясы әр түрлі, сондықтан өтелмеген магниттік моменттер пайда болады. Ұсынылған темір нанокластарының модельдері белгілі тәжірибелік мәліметтерге қанағаттанарлық түрде сәйкес келетіні көрсетілген.

Кілт сөздер: темір нанокластері, тетраэдрлік тығыз оралған құрылымдар, магниттік қасиеттері.

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Влияние размера нанокластеров железа на их намагниченность

Размер нанокристаллов железа существенно влияет на величину их намагниченности. Однако адекватной модели структуры нанокристаллических образований, состоящих из разного числа атомов железа, до сих пор не существует. В статье построены пространственные модели нанокристаллических кластеров железа, различающихся конфигурацией и количеством составляющих их атомов. За основу предлагаемых структур нанокристаллов взяты тетраэдрически плотно упакованные кластерные сборки атомов железа. Спектры плотности электронных состояний для предлагаемых кластеров построены с использованием теории функционала электронной плотности. Расчет проводился методом рассеянных волн в соответствии с зонной теорией кристаллов. Показано, что появление намагниченности в тетраэдрически плотноупакованных кластерных образованиях связано с возбужденными электронными состояниями атомов, расположенных на поверхности нанокластера. Возбужденные атомы имеют повышенную электронную плотность, то есть электроны способны переходить в состояния с более высокой энергией, приближающейся к энергии Ферми. В этом случае выполняется критерий Стоунера, необходимый для возникновения намагниченности. Конфигурации электронов со спином вверх и вниз различаются, поэтому возникают некомпенсированные магнитные моменты. Показано, что пред-

ложенные модели нанокластеров железа удовлетворительно согласуются с известными экспериментальными данными.

Ключевые слова: нанокластер железа, тетраэдрически плотно упакованные структуры, магнитные свойства.

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The investigation of a physical pendulum motion, which move along a horizontal axis

The article presents a study of the physical pendulum, taking into account the force of friction in the kinematic pair, as a result of which oscillations are damped. Graphs of the dependence of the pendulum deflection angle α and the angular velocity on time for different values of the velocity v have been given. It has been established that the speed of the sleeve significantly reduces the amplitude and angular velocity of the pendulum, and the frequency of its oscillations does not depend on the presence of dry friction in the system. The dependences of the change in the amplitude of pendulum oscillations have been given and the results of numerical integration of the differential equation of pendulum motion have been obtained. The graphical dependences of the pendulum deflection angle and the movement of the sleeve x along the horizontal axis from time to time have been obtained at different values of the coefficient of friction. It has been found that during the first five seconds of the system movement, the axial speed of the sleeve is practically independent of the coefficient of friction (at $f = 0.3 \dots 0.5$). To verify the obtained results, an experimental laboratory installation has been designed and manufactured. Theoretical studies are satisfactorily consistent with experimental data, with an error not exceeding 16%. The obtained dependencies can be used in the design and study of various mechanisms, the motion of which is described by similar differential equations. Such mechanisms include inertial conveyors, the gutter of which performs in addition to longitudinal and transverse oscillations. In addition, the proposed technique can be used in the study of the motion of bulk materials in an inclined cylinder, which performs torsional oscillations around the axis of symmetry.

Keywords: physical pendulum, oscillations, speed, amplitude, sleeve, experimental laboratory installation.

Introduction

The study of a mathematical pendulum motion is a classic problem of nonlinear oscillations, the solution of which has an exact analytical solution, especially at small values of the amplitude of oscillations. In contrast to the mathematical pendulum, when studying the operation of a physical pendulum, it is necessary to take into account the force of friction in the kinematic pair, as a result of which the oscillations have been damped.

However, in technology, there are oscillating processes in which dry friction does not reduce the amplitude, but, conversely, sometimes leads to self-oscillations. The motion of a spring-loaded cargo on an infinite moving belt [1, 2], or the motion of a Freud pendulum is an example of such oscillations, that rotates uniformly with some angular velocity [3].

The motion of a mechanical system consisting of a rectilinear rod with a ring passing through an inclined rectilinear guide and a rod oscillating in a vertical plane passing through a guide has been considered in [4]. Therefore, there is a problem of studying the motion of the pendulum when the rod will oscillate in a vertical plane that passes perpendicular to the guide. However, the ring will move along the guide.

This study aims to determine the motion law of a physical pendulum, the suspension point of which moves along the axis relative to which the oscillation occurs.

The theory of linear oscillations in the presence of viscous friction forces has been the most thoroughly developed [5, 6]. Therefore the study of oscillations with dry friction, and especially nonlinear, has been connected with considerable mathematical difficulties, and in some cases, only numerical solutions of the obtained differential equations of the motion or the approximate solution have been possible [7–9].

The averaging method is one of the effective approximate methods of system analysis with nonlinear friction. It allows to study not only the stationary mode of system motion but also the process of establishing the stationary mode [10–15].

Experimental

The motion of a physical pendulum consists of a sleeve 1, which is installed with the ability to slide along a fixed horizontal rod 2, as well as rotate around the axis of the rod. The rod 3 is fixed to the sleeve 1, at the end of which the load 4 is placed (Fig. 1).

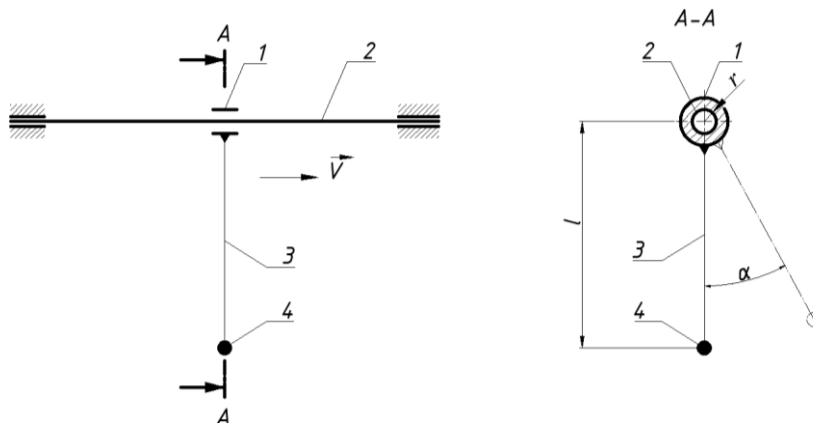


Figure 1. Scheme motion of a physical pendulum

Since the sleeve can move along the horizontal axis, there are two options for this motion:

1. To set the variation speed law $\vec{v}$ of the sleeve relative to the rod $\vec{v}=\vec{v}(t)$;
2. To set the variation law of the horizontal force $\vec{F}$, which is attached to the sleeve $\vec{F}=\vec{F}(t)$.

The first option applies to systems with kinematic transformation of dry friction, and the second — with dynamic transformation.

In the presence of dry friction and the absence of axial movement of the sleeve, the equation of motion will have the form:

$$I \cdot \ddot{\alpha} + mgl \sin \alpha + M_T \operatorname{sgn} \dot{\alpha} = 0, \quad (1)$$

where, M_T – the moment of friction forces

$$M_T = m \cdot g \cdot r \cdot f \cdot \cos \alpha,$$

r – shaft radius; f – consolidated coefficient of friction $f = \frac{4}{\pi} \cdot f_0$ [16]; f_0 – the coefficient of sliding friction between the sleeve and the shaft.

At small values of an angle α : $\sin \alpha = \alpha$; $\cos \alpha = 1$; $M_T = m \cdot g \cdot r \cdot f$.

When the pendulum is deflected at an angle φ_0 the equation of motion (1) will be:

$$I \cdot \ddot{\alpha} + mgl\alpha = mgrf. \quad (2)$$

If the mass of the load is much greater than the mass of the rod and sleeve, it can be assumed that the moment of inertia of the pendulum will be equal to: $I = m \cdot l^2$

Enter the notation $\omega^2 = \frac{g}{l}$; $\frac{rf}{l} = b$.

After replacing the equation (2) takes the form:

$$\alpha + \omega^2 \cdot \ddot{\alpha} = \omega^2 \cdot b. \quad (3)$$

The coefficient b is the pendulum deflection under the action of the maximum moment of friction.

If the pendulum is deflected by a value less than or equal to b , the motion will not occur, because the moment of gravity will be less than the moment of resistance.

The general solution (3) has the form [5]:

$$\alpha = b + c_1 \cos \omega t + c_2 \sin \omega t. \quad (4)$$

Taking into account the sustainable integration ($t = t_0 = 0$; $\alpha = \alpha_0$; $\dot{\alpha} = \dot{\alpha}_0 = 0$), has been get:

$$\alpha = b + (\alpha_0 - b) \cos \omega t. \quad (5)$$

The law of motion will be fair till $\dot{\alpha} < 0$. Because $\dot{\alpha} = -\omega \cdot (\alpha_0 - b) \cdot \sin \omega t$, then the speed will be negative by the time point $t_1 = \frac{\pi}{\omega}$.

At this point, the pendulum will stop:

$$\alpha_1 = b + (\alpha_0 - b) \cdot \cos \pi = -(\alpha_0 - 2b). \quad (6)$$

Consider the first variant of motion, when the sleeve moves relative to the shaft at a constant speed $\vec{v}$.

With simultaneous oscillation of the pendulum and the sleeve motion, the direction of friction between the sleeve and the shaft will depend on the speed $\vec{v}$ of the sleeve motion and speed $\vec{u}$ of the sleeve rotation motion, which occurs due to oscillations of the rod:

$$u = \dot{\alpha} \cdot r, \quad (7)$$

where, $\dot{\alpha} = \frac{d\alpha}{dt}$ – angular velocity of the pendulum; α – the pendulum deflection angle from the vertical.

The normal reaction N of the sleeve surface will be equal:

$$N = m \cdot g \cdot \cos \alpha + m \cdot \dot{\alpha}^2 \cdot l. \quad (8)$$

$$\cos \gamma = \frac{u}{\sqrt{u^2 + v^2}} = \frac{\dot{\alpha} \cdot r}{\sqrt{(\dot{\alpha} \cdot r)^2 + v^2}}. \quad (9)$$

The differential equation of rotational motion of the pendulum relative to the axis should be written:

$$I \cdot \ddot{\alpha} = m \cdot g \cdot l \cdot \sin \alpha - f \cdot (m \cdot g \cdot l \cdot \cos \alpha + m \dot{\alpha}^2 r) \cdot r \cdot \frac{r \cdot \dot{\alpha}}{\sqrt{v^2 + (r \cdot \dot{\alpha})^2}} \quad (10)$$

Consider small oscillations $\sin \alpha = \alpha$; $\cos \alpha = 1$; $r \cdot \dot{\alpha}^2 \ll g$

Taking into account the assumptions, equation (10) will have the form:

$$\ddot{\alpha} = \frac{g}{l} \alpha - f g \frac{r}{l^2} \cdot \frac{r \dot{\alpha}}{\sqrt{v^2 + (r \dot{\alpha})^2}} \quad (11)$$

A replacement should be done: $\frac{g}{l} = \omega^2$; $f g \frac{r}{l^2} = \lambda$.

Then,

$$\ddot{\alpha} = -\omega^2 \alpha - \lambda \cdot \frac{r \dot{\alpha}}{\sqrt{v^2 + (r \dot{\alpha})^2}} \quad (12)$$

The equation (12) is not reduced to quadratures and its solution can be obtained by numerical or approximate method.

Figures 2, 3 are graphs of the dependence of the pendulum deflection angle α and the angular velocity $\dot{\alpha}$ of time to different values of the velocity v , at $r=0,01$ m, $f=0,4$, $l=0,5$ m, $\alpha_0=15^\circ$, $\dot{\alpha}_0=0$ rad/s.

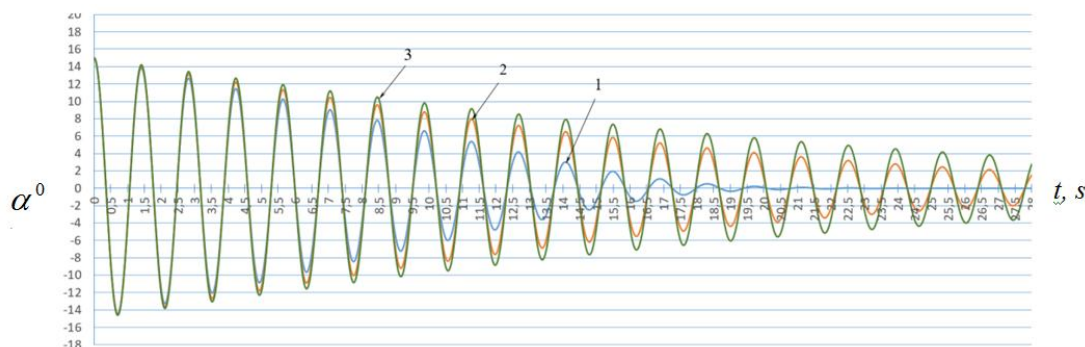


Figure 2. Graph of the pendulum deflection angle α of time for different values of velocity u
1- at $u=0.001$ m/s; 2- at $u=0.006$ m/s; 3- at $u=0.008$ m/s

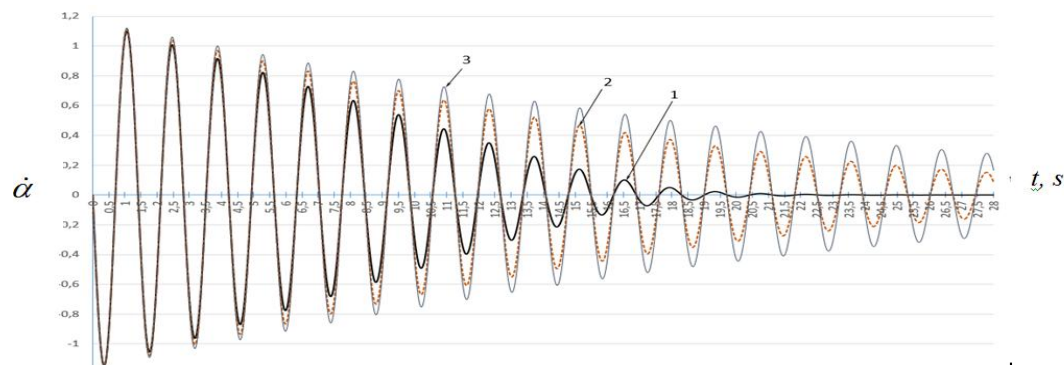


Figure 3. Graph of the dependence of the angular velocity $\dot{\alpha}$ of time for different values of the velocity u
1- at $u=0.001$ m/s; 2- at $u=0.006$ m/s; 3- at $u=0.008$ m/s

The graphs show that the speed of the sleeve significantly affects the reduction of the amplitude and angular velocity of the pendulum, but the frequency of its oscillations does not depend on the presence of dry friction in the system.

Dimensionless quantities should be used to obtain an approximate solution of the equation of pendulum motion:

$$\tau = \omega \cdot t; \xi = \frac{\omega \cdot r \cdot \alpha}{v}; \frac{f g r^2}{l^2 v \omega} = \mu; \dot{\alpha} = \frac{d\alpha}{dt}; \dot{\xi} = \frac{d\xi}{d\tau}; d\tau = \omega \cdot dt.$$

Then, $\frac{d\xi}{d\tau} = \frac{d}{d\tau} \cdot \left(\frac{\omega r \alpha}{v} \right) = \frac{d}{\omega dt} \cdot \left(\frac{\omega r \alpha}{v} \right) = \frac{\dot{\alpha} r}{v}; \ddot{\xi} = \frac{d\dot{\xi}}{d\tau} = \frac{d}{d\tau} \left(\frac{\dot{\alpha} r}{v} \right) = \frac{1}{\omega dt} \left(\frac{\dot{\alpha} r}{v} \right) = \frac{r}{\omega v} \ddot{\alpha}.$

Then the equation (12) takes the form

$$\ddot{\xi} + \xi + \mu \frac{\dot{\xi}}{\sqrt{1+\dot{\xi}^2}} = 0. \quad (13)$$

The μ value has been suggested small and the averaging method has been used [4].

The variables $\xi_1 = \xi; \xi_2 = \dot{\xi}$ has been involved and rewritten (13) in the normal form of Cauchy

$$\xi_1 = \xi_2; \xi_2 = -\xi_1 - \mu \frac{\xi_2}{\sqrt{1+\xi_1^2}} \quad (14)$$

Replace variables

$$\xi_1 = a \sin \varphi; \xi_2 = a \cos \varphi.$$

Turn to the equations in the standard form of the averaging method

$$\dot{a} = -\mu \cdot a \frac{\cos^2 \varphi}{\sqrt{1+a^2 \cos^2 \varphi}} \quad (15)$$

$$\dot{\varphi} = 1 + \mu \frac{\sin \varphi \cos \varphi}{\sqrt{1+a^2 \cos^2 \varphi}} \quad (16)$$

Average the right parts (15) and (16) on the fast variable φ

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{\sin \varphi \cos \varphi}{\sqrt{1+a^2 \cos^2 \varphi}} d\varphi = I_1 \quad (17)$$

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{a \cos^2 \varphi}{\sqrt{1+a^2 \cos^2 \varphi}} d\varphi = I_2 \quad (18)$$

In equation (17) a replacement should be made

$$z = 1 + a \cos^2 \varphi. \quad (19)$$

$$dz = -a2 \cos \varphi \sin \varphi d\varphi. \quad (20)$$

Then

$$I_1 = \frac{1}{2\pi} \int_0^{2\pi} -\frac{dz}{2a\sqrt{z}} = -\frac{1}{4\pi a} \int_0^{2\pi} z^{-\frac{1}{2}} dz = -\frac{1}{4\pi a} \cdot 2z^{\frac{1}{2}}. \quad (21)$$

Returning to (17) it should be:

$$I_1 = -\frac{1}{2\pi a} \sqrt{1+a \cos^2 \varphi} \Big|_0^{2\pi} = -\frac{1}{2\pi a} \left(\sqrt{1+a \cos^2 2\pi} - \sqrt{1+a \cos^2 \varphi} \right) = 0.$$

So,

$$\frac{d\varphi}{d\tau} = 1. \quad (22)$$

In equation (15) a replacement should be made

$$k = \frac{a}{\sqrt{1+a^2}}. \quad (23)$$

where $a^2 = \frac{k^2}{1-k^2}$

Then:

$$\sqrt{1+a^2 \cos^2 \varphi} = \sqrt{\frac{1-k^2+k^2 \cos^2 \varphi}{1-k^2}} = \sqrt{\frac{1-k^2(1-\cos^2 \varphi)}{1-k^2}} = \frac{1}{\sqrt{1-k^2}} \sqrt{1-k^2 \sin^2 \varphi}. \quad (24)$$

$$I_2 = 4 \cdot \frac{1}{2\pi} \int_0^{\frac{\pi}{2}} \frac{k \cos^2 \varphi d\varphi}{\sqrt{1-k^2 \sin^2 \varphi}} = \frac{2k}{\pi} \int_0^{\frac{\pi}{2}} \frac{\cos^2 \varphi d\varphi}{\sqrt{1-k^2 \sin^2 \varphi}} = \frac{2k}{\pi} \left(\frac{1}{k^2} F(k) - \frac{1}{k^2} E(k) \right), \quad (25)$$

where $F(k)$ – the complete elliptic integral has been made with the module k ; $E(k)$ – complete elliptic integral of the second kind [17].

$$\frac{da}{d\tau} = -\frac{2\pi}{\pi} k \cdot B(k), \quad (26)$$

where $B(k) = \frac{1}{k^2} (F(k) - E(k))$

The system of equations (22), (26) can be integrated in quadratures.

Perform differentiation by τ and get:

$$\frac{da}{d\tau} = (1 - k^2)^{-\frac{3}{2}} \frac{dk}{d\tau} \quad (27)$$

Then the equation (26) takes the form

$$\frac{dk}{d\tau} = -\frac{2\mu}{\pi} \cdot k \cdot (1 - k^2)^{\frac{3}{2}} \cdot B(k). \quad (28)$$

Integrate (22) and (28) under initial conditions $\varphi(\tau_0) = \varphi_0$; $k(\tau_0) = k_0$;

$$\varphi = \tau + \varphi_0 - \tau_0. \quad (29)$$

$$\int_{k_0}^k \frac{dk}{k \cdot (1 - k^2)^{\frac{3}{2}} \cdot B(k)} = \int_0^{\tau_0} -\frac{2\pi}{\pi} d\tau. \quad (30)$$

The left part (30) is easily tabulated, because it depends only on the dimensionless value k . Table 1 illustrates the value of $G(k)$ [4].

$$\int_{k_0}^k \frac{dk}{k \cdot (1 - k^2)^{\frac{3}{2}} \cdot B(k)} = G(k) - G(k_0). \quad (31)$$

Table 1

The values free oscillations of the pendulum in the presence of dry friction and axial motion of the sleeve of $G(k)$

k	$G(k)$	k	$G(k)$	k	$G(k)$
0.01	-4.3939	0.3	-0.8268	0.9	2.2917
0.02	-3.9758	0.4	-0.3884	0.92	2.6095
0.03	-3.6380	0.5	0	0.94	3.0267
0.05	-3.1181	0.6	0.3828	0.96	3.6102
0.1	-2.2915	0.7	0.8054	0.98	4.5019
0.2	-1.3903	0.8	1.3510	0.99	5.1568

In Figure 4, the dependences of the change in the amplitude of pendulum oscillations obtained as a result of numerical integration of the differential equation of pendulum motion and the approximate solution are given.

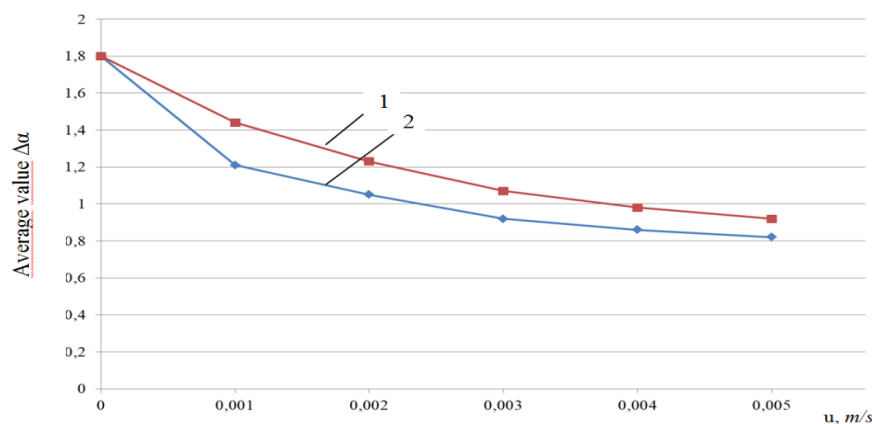


Figure 4. Graph of the dependence of pendulum oscillations amplitude decrease on the speed of the sleeve u

The graphs show that the approximate solution can be used in the study of such mechanical systems, especially when the values of the speed of the sleeve $u > 0.005$ m/s, when the error of the results does not exceed 12%.

Consider the second variant of system motion, namely assume that the sleeve moves along the guide under the action of the horizontal force F .

In this case, the differential equations take the form:

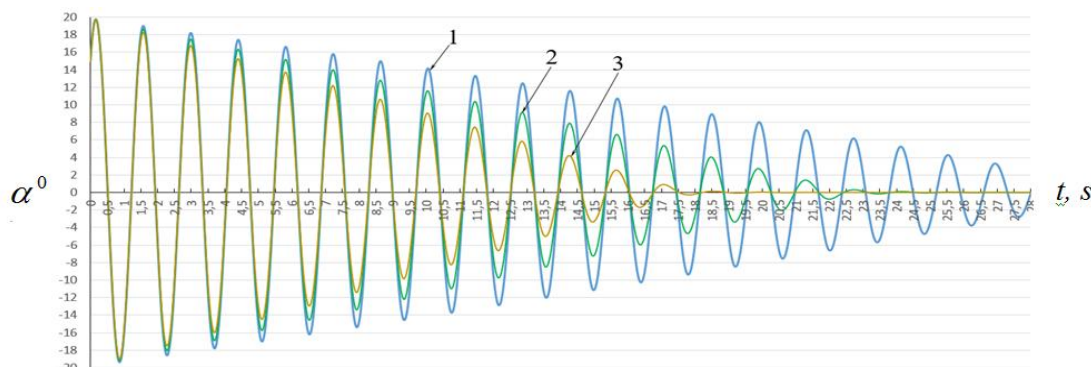
$$\begin{cases} m\ddot{x} = F - fmg \frac{\dot{x}}{\sqrt{\dot{x}^2 + (r\dot{\alpha})^2}} \\ I\ddot{\alpha} = -mgl \sin \alpha - mgfr \frac{r\dot{\alpha}}{\sqrt{\dot{x}^2 + (r\dot{\alpha})^2}} \end{cases} \quad (32)$$

Taking into account the accepted assumptions, the system (32) will be:

$$\begin{cases} \ddot{x} = F_1 - fg \frac{\dot{x}}{\sqrt{\dot{x}^2 + (r\dot{\alpha})^2}} \\ \ddot{\alpha} = -\omega^2 \alpha - \frac{fgr}{l^2} \frac{r\dot{\alpha}}{\sqrt{\dot{x}^2 + (r\dot{\alpha})^2}} \end{cases} \quad (33)$$

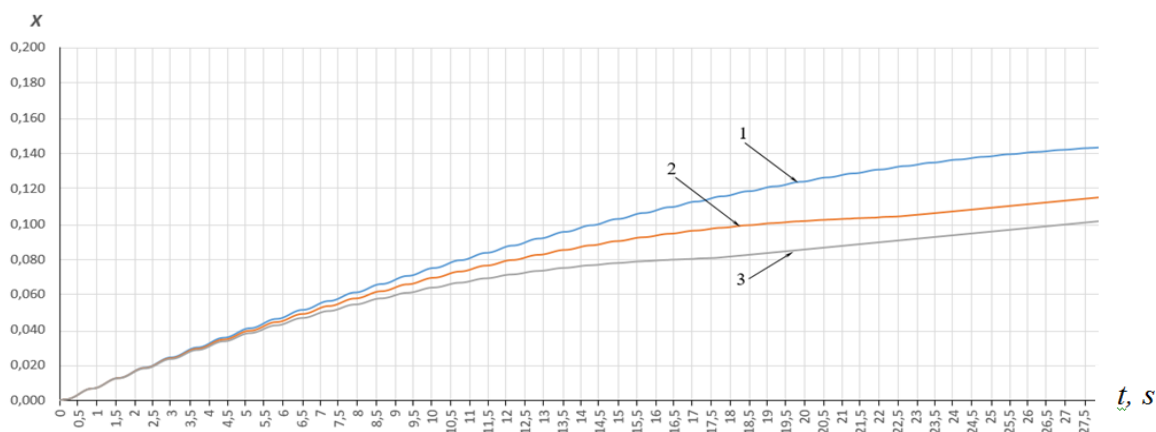
where $F_1 = \frac{F}{m}$.

As a result of the numerical solution of the system (33), obtain the dependences of the pendulum deflection angle α and the movement of the sleeve x along the horizontal axis of time, at different values of the coefficient of friction (Fig. 5- 6)



1- at $f=0.3$; 2- at $f=0.4$; 3- at $f=0.5$

Figure 5. Graph of the pendulum deflection angle α° of time t , at different values of the coefficient of friction f ($r=0.01$ m; $l=0.5$ m; $F_1=2$; $\alpha_0=0^\circ$; $\dot{\alpha}_0=1$ rad/s)



1- at $f=0.3$; 2- at $f=0.4$; 3- at $f=0.5$

Figure 6. Graph of the dependence of the sleeve motion x along the horizontal axis of time, at different values of the coefficient of friction ($r=0.01$ m; $f=0.4$; $l=0.5$ m; $\alpha_0=15^\circ$; $\dot{\alpha}_0=1$ rad/s)

The graphs demonstrate that during the first five seconds of the system motion, the axial speed of the sleeve is practically independent of the coefficient of friction (at $f=0.3 \dots 0.5$). Further, the speed will decrease, and for different values of the coefficient of friction, this change will be different. This is due to the fact that the amplitude of oscillations and the angular velocity of the pendulum will decrease, and, consequently, the axial component of the friction force between the sleeve and the rod will increase.

Since the oscillation frequency of the physical pendulum does not depend on the force of friction, to obtain an approximate solution of the equation of the sleeve motion, assume that at the initial moment of time the motion of the pendulum occurs by law:

$$\dot{\alpha} = \dot{\alpha}_0 \cos \omega t \quad (34)$$

Consider that the pendulum moves from the equilibrium position due to the initial velocity $\dot{\alpha}_0$.

Then the first equation of system (33) takes the form:

$$\ddot{x} = F_1 - fg \frac{\dot{x}}{\sqrt{\dot{x}^2 + (r\dot{\alpha}_0 \cos \omega t)^2}} \quad (35)$$

Proceed to dimensionless quantities:

$$\tau = \omega t, d\tau = \omega dt, \xi = \frac{x\omega}{r\dot{\alpha}_0}, x = \frac{\xi r \alpha_0}{\omega}, \dot{x} = \frac{dx}{dt}, \dot{\xi} = \frac{d\xi}{d\tau}$$

Then,

$$\begin{aligned} \dot{x} &= \frac{d}{dt} \left(\frac{\xi r \alpha_0}{\omega} \right) = \frac{d}{d\tau} \left[\left(\frac{\xi r \alpha_0}{\omega} \right) \cdot \omega \right] = \xi \dot{\alpha}_0 r; \\ \ddot{x} &= \frac{d}{dt} (\xi \dot{\alpha}_0 r) = \ddot{\xi} \dot{\alpha}_0 r \omega \end{aligned}$$

Then equation (35) takes the form:

$$\ddot{\xi} \dot{\alpha}_0 r = F_1 - fg \cdot \frac{\dot{\xi}}{\sqrt{\dot{\xi}^2 + \sin^2 \tau}} \quad (36)$$

or

$$\ddot{\xi} = \mu \left[\gamma - \frac{\dot{\xi}}{\sqrt{\dot{\xi}^2 + \sin^2 \tau}} \right] \quad (37)$$

where, $\gamma = \frac{F}{mfg}$; $\mu = \frac{fg}{\dot{\alpha}_0 r \omega}$.

In our case at $f = 0,4$, $r = 0,01$, $\dot{\alpha}_0 = 1 \text{ rad/s}$, $\alpha_0 = 1,2$, $\omega = 4,92 \text{ c}^{-1}$.

$$\mu = \frac{0,4 \cdot 10}{1,26 \cdot 0,01 \cdot 4,92} = 100 \gg 1.$$

Find the approximate periodic solution of equation (37). To do this, write it as follows:

$$\mu^{-1} \frac{d\dot{\xi}}{d\tau} = \gamma - \frac{\dot{\xi}}{\sqrt{\dot{\xi}^2 + \cos^2 \tau}} \quad (38)$$

The resulting equation is an equation with a small parameter for the derivative. According to Tikhonov's theorem [18], limiting the degenerate approximation and assuming the left-hand side of (38) is zero, obtain:

$$\dot{\xi} = \frac{\gamma}{\sqrt{1-\gamma^2}} [\cos \tau] \quad (39)$$

The obtained dependence determines with accuracy the order of μ^{-1} the main in this problem slow component of the speed of the sleeve motion. Average each part over the period of the pendulum oscillation. Denote the average speed of the sleeve ϑ .

$$\begin{aligned} \vartheta = \langle \dot{\xi} \rangle &= \frac{1}{2\pi} \int_0^{2\pi} \dot{\xi}(\tau) d\tau = \\ \frac{1}{2\pi} \int_0^{2\pi} \frac{\gamma}{\sqrt{1-\gamma^2}} \cos \tau d\tau &= \frac{4\gamma}{2\pi\sqrt{1-\gamma^2}} \int_0^{\frac{\pi}{2}} \cos \tau d\tau = \frac{2\gamma}{\pi\sqrt{1-\gamma^2}} \end{aligned} \quad (40)$$

So,

$$v = \frac{2}{\pi} \cdot \frac{\gamma}{\sqrt{1-\gamma^2}} \quad (41)$$

From equation (40) it is seen that the stationary mode is possible only under the condition $\gamma < 1$, and at $\gamma \geq 1$ the stationary mode will be absent and the sleeve will move with some non-zero acceleration.

Then the average dimensional speed of the sleeve will be equal:

$$v = \vartheta \cdot r \cdot \dot{\alpha}_0 \quad (42)$$

Figure 7 shows graphs of the dependence of the average dimensionless speed of the sleeve along the rod on the coefficient of friction f , and the value of the relative force F_1 .

The experimental laboratory setup has been designed and manufactured to verify the results. Its scheme is shown in Figure 8a, and the general view in Figure 8b.

The horizontal rod 1 is rigidly attached to a fixed base 2. On the rod is a sleeve 3, which is installed with the ability to move along the rod and rotate around its axis. The rod 4 is rigidly attached to the sleeve 3, at the lower end of which is the load 5. At the second end of the rod 1 is a block 6, through which is passed a weightless thread, one end of which is attached to the sleeve 3, and the other to the load 8, the weight of which can be changed. During the experiment, the load 5 is given an initial speed V_0 , while releasing the sleeve 3, which, under the action of gravity of the load 8 begins to slide along the rod.

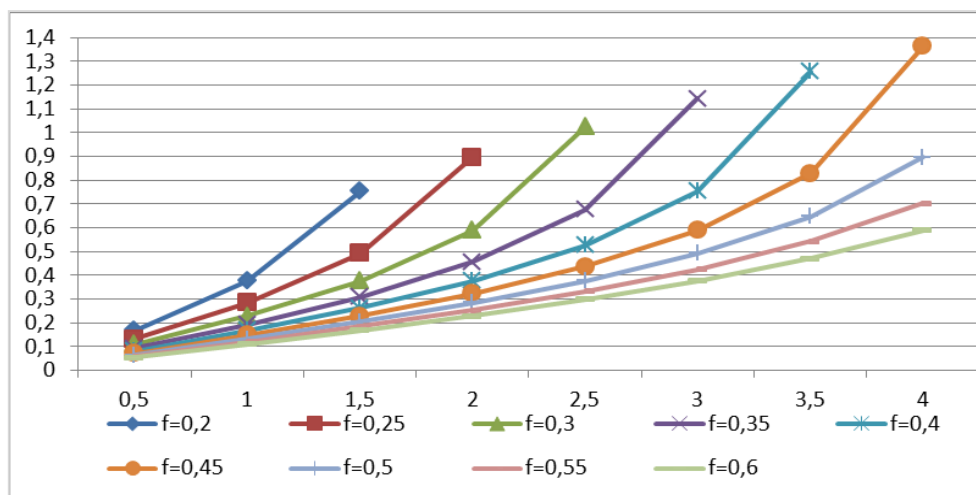


Figure 7. Graphs of the dependence of the average dimensionless speed of the sleeve along the rod on the coefficient of friction f , and the value of the relative force F_l

By measuring the time during which the sleeve will go a certain path, we determined the average speed of the sleeve. Table 2 represents the results of the experiment.

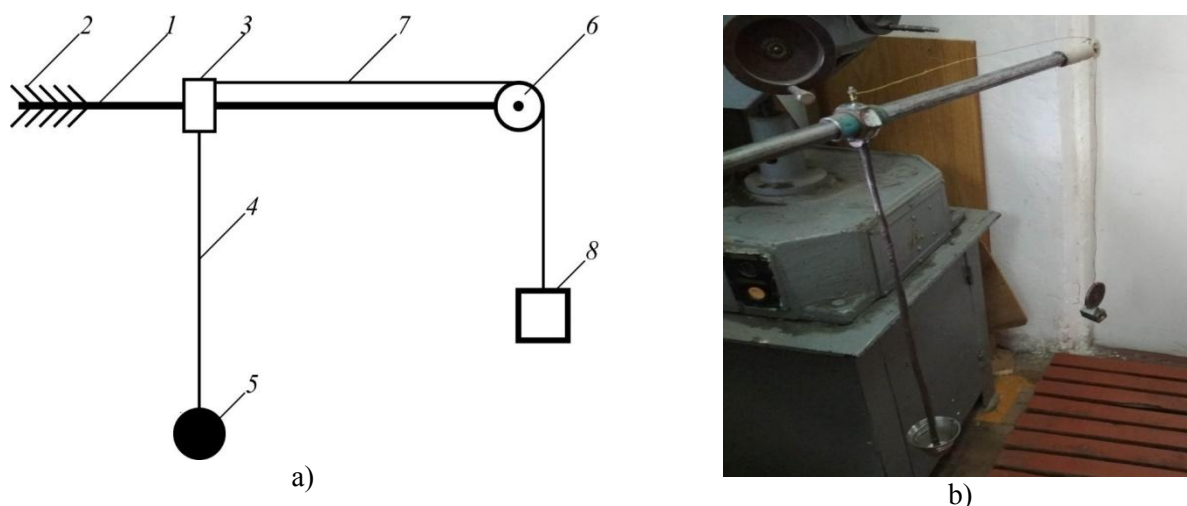


Figure 8. General view: a – constructive scheme; b – the experimental setup

Table 2

The results of the experiment are the average speed of the sleeve

$F_l, \text{ m/s}^2$	$V_T, \text{ m/s}$	$V_E, \text{ m/s}$	$\delta, \%$
1	0.0066	0.0057	15.7
1.5	0.0073	0.0065	12.3
2	0.0078	0.007	11.4
2.5	0.0085	0.0079	8.2
3	0.0092	0.0087	5.7

Conclusions

These graphs show that at the value of $F_l=4$, the maximum value of the dimensionless speed will be at $f=0.45$. At higher values of the coefficient of friction, the dependence of velocity on relative force is less pronounced. Given a constant value of the amplitude of pendulum oscillations, the average speed of the sleeve will be a constant value. As the oscillations of the pendulum fade, the speed of the sleeve will decrease. However, at the beginning of the motion, the error does not exceed 12% at $f < 0.3$ and 18% at $f < 0.45$. As can be seen from Table 2, the results of theoretical studies agree satisfactorily with the experi-

mental data, with an error not exceeding 16%. Similarly, it is possible to determine the speed of the sleeve under the action of gravity, when the rod is inclined at an angle to the horizon that does not exceed the value of the angle of friction. The obtained dependences can be used in the design and study of various mechanisms, the motion of which is described by similar differential equations. The proposed technique can be used in the study of the motion of bulk materials in an inclined cylinder, which performs torsional oscillations around the axis of symmetry.

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Көлденең ось бойымен қозғалатын маятниктің физикалық қозғалысын зерттеу

Мақалада нәтижесінде тербелістердің сөнуіне әкелетін кинематикалық жұптағы үйкеліс күшін ескере отырып, физикалық маятник жұмысының зерттеуі берілген. Маятниктің ауытқу бұрышы мен бұрыштық жылдамдықтың уақытқа тәуелділігінің графиктері v жылдамдықтың әртүрлі мәндері үшін келтірілген. Маятник тербелістерінің амплитудасы мен бұрыштық жылдамдығының төмендеуіне төлкенің жылдамдығы айтарлықтай әсер ететіні анықталды, ал оның тербеліс жиілігі жүйеде құрғақ үйкелістің болуына байланысты емес. Маятниктің тербеліс амплитудасының өзгеруіне және маятник қозғалысының дифференциалдық теңдеуінің сандық интеграциясының нәтижелеріне тәуелділіктер келтірілген. Үйкеліс коэффициентінің әртүрлі мәндері үшін маятниктің ауытқу бұрышының және төлкенің x көлденең ось бойымен уақытқа байланысты орын ауыстыруының графикалық тәуелділігі

алынған. Маятник тербелістерінің амплитудасының өзгеруінің тәуелділіктері және маятник қозғалысының дифференциалдық теңдеуінің сандық интегралдау нәтижелері келтірілген. Маятниктің ауытқу бұрышының графикалық тәуелділігі және үйкеліс коэффициентінің әртүрлі мәндері үшін маятниктің ауытқу бұрышының және төлкенің x көлденең ось бойымен уақытқа орын ауыстыруының қозғалысы алынды. Жүйе қозғалысының алғашқы бес секундында төлкенің осьтік жылдамдығы үйкеліс коэффициентіне тәуелді емес екендігі анықталды ($F=0,3,0,5$ кезінде). Нәтижелерді тексеру үшін эксперименттік зертханалық қондырғы жобаланып, дайындалды. Теориялық зерттеулер эксперименттік деректермен келісілген, бұл ретте қателік 16%-дан аспайды. Алынған тәуелділіктерді қозғалысы ұқсас дифференциалдық теңдеулермен сипатталатын әртүрлі механизмдерді жобалау мен зерттеуде қолдануға болады. Мұндай механизмдерге бойлық және көлденең тербелістерден басқа, науа жасайтын инерциялық конвейерлер жатады. Сонымен қатар, ұсынылған әдісті симметрия осінің айналасында айналмалы тербелістер жасайтын көлбеу цилиндрдегі сусымалы материалдардың қозғалысын зерттеуде қолдануға болады.

Кілт сөздер: физикалық маятник, тербелістер, жылдамдық, амплитуда, төлке, эксперименттік зертханалық қондырғы.

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Исследование физического движения маятника, движущегося вдоль горизонтальной оси

В статье приведены исследования работы физического маятника с учетом силы трения в кинематической паре, в результате которой происходит затухание колебаний. Приведены графики зависимости угла отклонения маятника и угловой скорости от времени для различных значений скорости v . Установлено, что скорость движения втулки оказывает существенное влияние на уменьшение амплитуды и угловой скорости колебаний маятника, при этом частота его колебаний не зависит от наличия сухого трения в системе. Приведены зависимости изменения амплитуды колебаний маятника и результаты численного интегрирования дифференциального уравнения движения маятника. Получены графические зависимости угла отклонения маятника и перемещение втулки x вдоль горизонтальной оси от времени, при разных значениях коэффициента трения. Установлено, что в первые пять секунд движения системы осевая скорость втулки практически не зависит от коэффициента трения (при $f=0,3...0,5$). Для проверки результатов была спроектирована и изготовлена экспериментальная лабораторная установка. Теоретические исследования согласуются с экспериментальными данными, при этом погрешность не превышает 16 %. Полученные зависимости могут быть использованы при проектировании и исследовании различных механизмов, движение которых описывается аналогичными дифференциальными уравнениями. К таким механизмам относятся инерционные конвейеры, желоб которых совершает, помимо продольных, и поперечные колебания. Кроме того предложенную методику можно использовать при исследовании движения сыпучих материалов в наклонном цилиндре, совершающем крутильные колебания вокруг оси симметрии.

Ключевые слова: физический маятник, колебания, скорость, амплитуда, втулка, экспериментальная лабораторная установка.

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The impact of SnO₂ photoelectrode's thickness on photovoltaic properties of the solar cell FTO:SnO₂:PTB7-TH:ITIC/Mo/Ag

The paper reports the results of a study of the morphological, optical and electrophysical parameters of SnO₂ films. SnO₂ films are applied by spin-coating at different revolutions of the centrifuge. The topography of the surface and the thickness of the SnO₂ films are studied using an atomic force microscope. The current-voltage characteristics of solar cells are measured. The optical properties with different thicknesses of SnO₂ films are also investigated. It is shown that an increase in the rotation speed of the substrate leads to a decrease in the surface roughness of the SnO₂ films. It is found that changes in the morphology of SnO₂ films contribute to the rapid transport of injected holes to the external electrode and reduce the probability of reverse recombination. Cells with an electron transport layer of SnO₂ at 2000 revolutions showed a low efficiency of 0.17%. With a decrease in the thickness of the SnO₂ films to a value of 62 nm, there is an increase in the value of the short-circuit current by 2.3 times and a change in the no-load voltage by 1.12 times.

Keywords: Tin(II) oxide (SnO₂) surface morphology, optical and impedance spectroscopy.

Introduction

Tin oxides deserve special attention from materials scientists due to their numerous applications. Recently, tin oxide films have attracted the great attention of scientists and technologists in connection with their possible applications in solid-state gas sensors, electrodes for electroluminescent displays, protective coatings, solar cells, and the transparent field-effect transistors [1]. Currently studying two main tin oxides are SnO and SnO₂.

Due to its efficiency, ease of processing rapid growth of the energy conversion coefficient and flexibility increasing attention has been paid to the development of ESE. After the introduction of highly effective polymer donors with a low bandgap and non-fullerene acceptors research has experienced a renaissance. Now a day, the energy conversion efficiency of polymer solar cells attains 17–18% [2]. It was also established that processing methods and buffer layers also play a crucial role in obtaining better performance parameters except for innovation in the molecular aspects of OSE.

Various n-type metal oxides with a wide bandgap and some polyelectrolytes with a large dipole moment have been successfully used as interfacial electron transport layers in inverted devices [3, 4]. In addition, various forms of nanostructuring of films, surface treatment, and technological additives have been studied to increase the efficiency of charge collection, transportation, and selectivity.

SnO₂ is one of the most promising materials for electron transfer in the ESE due to its good environmental resistance as well as high electron mobility and high transparency in the visible and near-infrared regions. SnO₂ films are produced in various ways, including the sol-gel method. The sol-gel method is a technologically simple process that allows for getting better coatings. It should be noted that the important crystalline properties of thin films depend very much on the growth conditions, growing technique, and substrate [5].

This paper presents the results of the influence of the thickness of SnO₂ films on their structural, optical, and photoelectric properties.

Experimental

The preparation of tin oxide films on the FTO surface was carried out as follows: solution was prepared by dissolving 183 mg of SnCl₂ (Brun New Material Technology Ltd, Purity: 99.99%) in 1 ml of 2-propanol (pure 99.9% Sigma Aldrich). The final solution was stirred at T = 80 °C temperature for 3 hours and then kept at room temperature for 24 hours. SnO₂ films were obtained by centrifugation (SPIN150i, Semiconductor Production System). The rotation rate of the substrate varied from 2000 rpm to 6000 rpm to change the

thickness of the film. Further, the film was annealed for 1 hour at a temperature of 500°C to ensure complete films crystallization after its application. The topography of the film surface was studied using a JSPM-5400 atomic force microscope (AFM) (JEOL, Japan). A special modular program for analyzing scanning probe microscopy data (Win SPMII Data Processing Software) was used to process the images obtained with AFM. From AFM images, the morphology of the surface and the roughness of the SnO₂ films were analyzed. The images of the surface of the film were obtained in the semicontact scanning mode. The absorption spectra of the samples under study were recorded on an AvaSpec-ULS2048CL-EVO spectrometer (Avantes). The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode [6]. The VAC of photosensitive cells was determined by the device Sol3A Class AAA Solar Simulators (Newport) with PVIV-1A I-V Test Station [7, 8].

Results and Discussion

Figure 1 shows images of the surface morphology of SnO₂ films obtained by using AFM. It can be seen that the solution at different revolutions of the centrifuge affects the surface morphology.

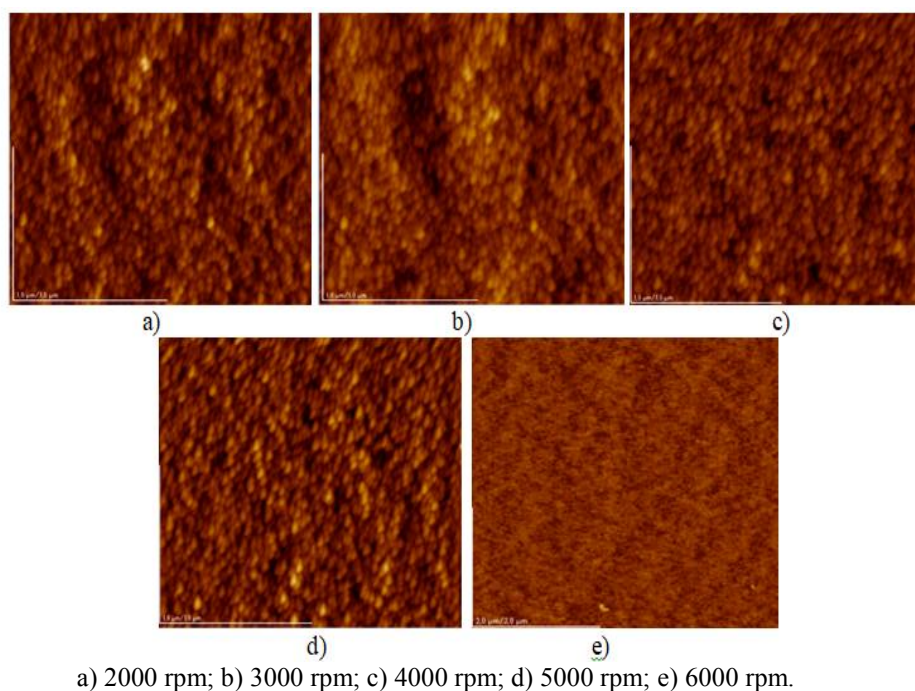


Figure 1. Images of surface morphology of SnO₂ films obtained at different speeds of rotation

The roughness of film is an important factor in the characteristics of the surface film. Reducing the surface roughness of the SnO₂ improves the quality of the SnO/photoactive layer interface, which contributes to the effective injection of photoinduced electrons from the acceptor and reduces the probability of recombination of charge carriers at the interface. In the process of obtaining the film, increasing the rotation speed of the substrate leads to the smoothing of the SnO₂ surface; the roughness of the film begins to decrease. Respectively, the morphology of the SnO₂ films obtained at the rotation speed of the centrifuge 2000–4000 rpm has a surface roughness of 4.8–2.7 nm. With an increase in the rotation speed of the centrifuge to 5000–6000 rpm, the surface roughness decreases to 1.6 nm.

Figure 2 illustrates AFM images of the ETL thickness of the SnO₂ layer. Table 1 represents the obtained parameters of the surface morphology and thickness of SnO₂ films. The thickness of the SnO₂ film was studied by the depth of the scratch on the surface of SnO₂.

To do this, a scratch was formed with thin tweezers to the entire depth of the sample, the most suitable area was located on the optical microscope, and then this area was scanned using an atomic force microscope.

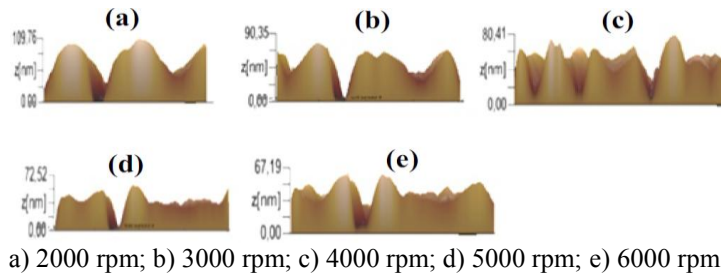


Figure 2. Images of the thickness of SnO₂ films obtained at different rotational speeds

Table 1

Parameters of surface morphology and thickness of SnO₂ films

Sample	R _q , nm	Thickness, nm
SnO ₂ – 2000 rpm	4,8	102
SnO ₂ – 3000 rpm	3,9	88
SnO ₂ – 4000 rpm	2,7	76
SnO ₂ – 5000 rpm	2,1	62
SnO ₂ – 6000 rpm	1,6	58

Figure 3 demonstrates the absorption spectra ETL at different thicknesses of the SnO₂ layer. The absorption spectrum is typical of the absorption spectrum of wide-band semiconductors. The measured absorption spectra of semiconductor films show that the edge of the absorption band of SnO₂ films is located at about 350 nm. At measuring the absorption spectra, it can be seen that the optical density of the films increases with increasing thickness. At the same time, the position of the maximum of the absorption spectrum does not change.

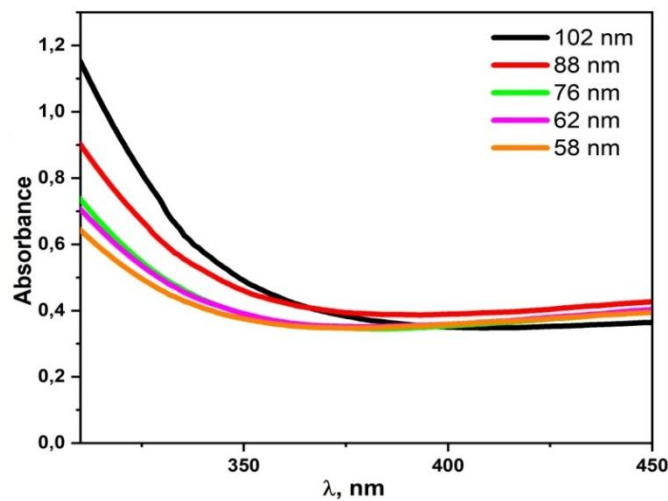


Figure 3. Absorption spectra of SnO₂ films with different thickness

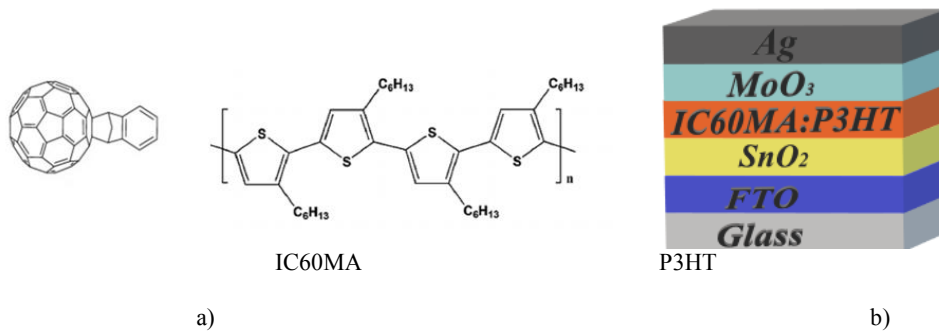


Figure 4. Chemical structures of BHJ compounds (a) and the architecture of the inverted PSC (b)

Further, based on the obtained SnO₂ films, solar cells were constructed and the effect of thickness on the photovoltaic parameters of the cells was studied (Figure 4).

Figure 5 shows the current-voltage characteristics of organic solar cells based on a photoactive PTB7-Th: ITIC layer with different thicknesses of SnO₂ films.

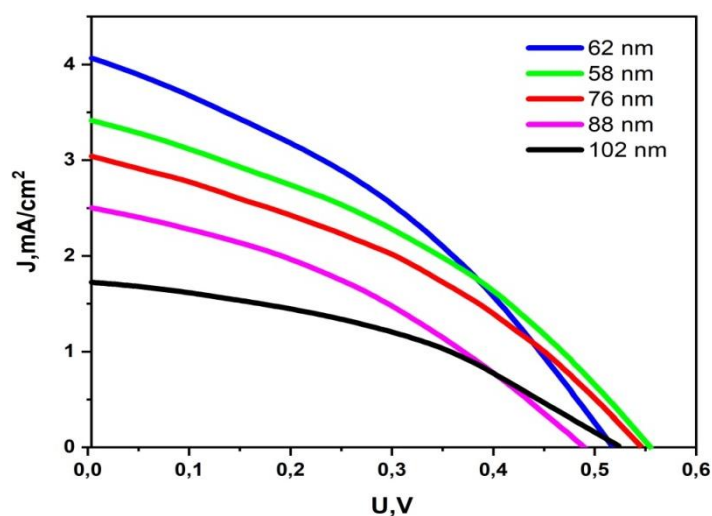


Figure 5. Current-voltage characteristic of a polymer solar cell depending on the thickness of SnO₂ films

Table 2

Photovoltaic characteristics of organic solar cells

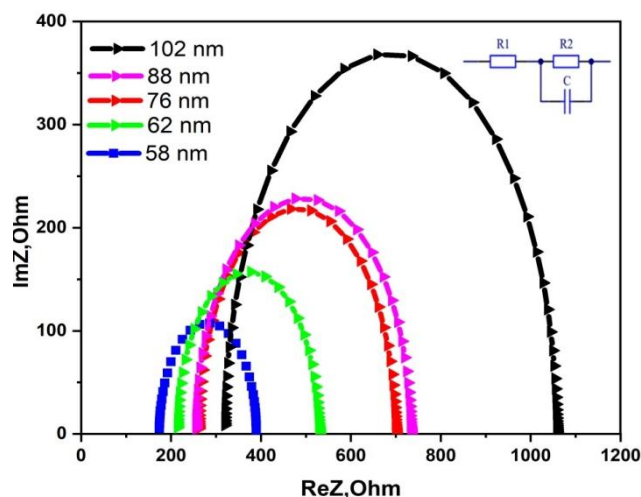
SnO film thickness, nm	J_{sc} mA/cm ²	U_{oc} V	J_{max} mA/cm ²	U_{max} V	FF %	η %
58	3.4	0.28	2.0	0.18	0.38	0.29
62	4.0	0.25	2.4	0.16	0.38	0.38
76	3.0	0.27	1.8	0.17	0.37	0.26
88	2.5	0.24	1.7	0.15	0.43	0.23
102	1.7	0.25	1.1	0.16	0.41	0.17

When the thickness of the SnO₂ films was reduced to 62 nm, an increase in short-circuit current density by 2.3 times and a change in the no-load voltage by 1.12 times were observed (Table 2). Moreover, it can be seen that with a further decrease in the thickness of SnO₂, a decrease in the value of the short-circuit current was observed. The decrease in the current value was because the film becomes so thin that gaps appear in it, through which current leakage occurs.

With a film thickness of 62 nm, the efficiency of the cell was 0.38%. When the film thickness was reduced to 58 nm, the efficiency of the cell decreased to 0.17%.

By impedance spectroscopy, the mechanisms of transport and recombination of charge carriers in thin films of a mixture of PTB7-TH:ITIC polymers with different thicknesses SnO₂ were studied. Figure 6 shows the impedance spectra in Nyquist coordinates based on thin films. Table 3 presents the main electric transport properties. An equivalent electrical circuit was used to interpret the impedance spectra. The fitting of the impedance spectra was calculated using the software package EIS-analyzer. Using the method of impedance spectroscopy the analysis of the electric transport characteristics of solar cells was carried out. The analysis of the hodographs indicated that a change in the thickness of the SnO₂ films leads to a change in the electric transport characteristics of the polymer solar cell.

To interpret the impedance spectra, an equivalent electrical circuit of a photovoltaic cell was used, where R₁ (R_w) is the equivalent resistance of a multilayer film, R₂ (R_{rec}) is the resistance characterizing the recombination of localized electrons with holes (Figure 6).

Figure 6. Impedance spectra of PSCs with different SnO₂ films thickness.

As the spin-coater rotation speed increases, the thickness of the SnO₂ films decreases; this should contribute to a decrease in the resistance (R_w) of the film. It can be seen from Table 3 that with a decrease in the thickness of the films, the resistance R_w also decreases, which in general should improve the injection of electrons into the FTO. However, a decrease in the thickness of the photoactive layer also leads to a decrease in the resistance of R_{rec} , which ensures increased recombination of electrons at the interface. On the one hand, the decrease in R_w contributes to the rapid transport of electrons, but on the other hand, there is a competing recombination process through the resistances of R_{rec} , which also decreases, which increases the recombination rate.

We assume that there is an optimal thickness of SnO₂ films, at which there is a balance between injection efficiency and recombination of charge carriers. In this case, the electrons in the photoactive layer have the maximum lifetime of charge carriers and a low probability of recombination. From the analysis of the impedance spectra, it follows that the thickness of 58 nm is optimal, at which the lifetime of the charge carriers was $\tau_{eff} = 0.9$ ms (Table 3).

Table 3

The value of the electrophysical parameters of SnO₂ films

Film thickness, rpm	R_w , (Ohm)	R_{rec} , (Ohm)	R_{rec}/R_w	τ_{eff} , (ms)	k_{eff} , (s^{-1})
58	174	215	1.2	0.9	10704
62	214	314	1.4	0.8	12221
76	245	458	1.8	0.5	18190
88	262	437	1.6	0.4	20768
102	320	738	2.3	0.4	23711

Conclusions

As a result of the research, a method for the synthesis of SnO₂ films was developed. The results demonstrated that with an increase in the rotation speed of the substrate, a decrease in the surface roughness of SnO₂ films was observed. It was found that the edge of the absorption band of SnO₂ films is located at about 350 nm. When the thickness of the SnO₂ films was reduced to 62 nm, there was also an increase in the value of the short-circuit current by 2.3 times and a change in the no-load voltage by 1.12 times. With a further decrease in the thickness of SnO₂, a decrease in the value of the short-circuit current was observed. With a film thickness of 62 nm, the efficiency of the cell was 0.38%. When the film thickness was reduced to 58 nm, the efficiency of the cell decreased to 0.17%. The decrease in the current value for SnO₂ films was because the film becomes so thin that gaps appear in it, through which current leakage occurs.

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SnO фотоэлектроды қалыңдығының FTO:SnO:PTB7-TH:ITIC/Mo/Ag күн ұяшығының фотоэлектрлік параметрлеріне әсері

Мақалада SnO₂ пленкаларының морфологиялық, оптикалық және электрофизикалық параметрлерінің зерттеу нәтижелері берілген. SnO₂ пленкаларын центрифуганың әр түрлі айналу жылдамдығында айналдыру *spin-coating* әдісі арқылы жасалды. Эксперименттік зерттеулер оптикалық спектроскопия, вольтамперометрия және импедансты өлшеу әдістерімен жүргізілді. Атомдық күш микроскопының көмегімен SnO₂ бетінің топографиясы мен пленкаларының қалыңдығы зерттелді. Қалыңдығы әр түрлі SnO₂ пленкаларының оптикалық қасиеттері анықталды. Айналу жылдамдығының артуы SnO₂ пленкаларының бетінің кедір-бұдырының төмендеуіне әкелетіні көрсетілді. SnO₂ пленкаларының морфологиясының өзгеруі инжекциялық тесіктердің сыртқы электродқа тез тасымалдануына және кері рекомбинация ықтималдығын азайтуға ықпал ететіні анықталды. Электронды тасымалдау қабаты бар SnO₂ ұяшығы 2000 айналымда 0,17% төмен тиімділікті көрсетті. SnO₂ пленкаларының қалыңдығының 62 нм мәніне дейін төмендеуімен қысқа тұйықталу тогының мәні 2,3 есе және бос жүріс кернеуі 1,12 есе артады.

Кілт сөздер: қалайы (II) тотығының (SnO₂) беттік морфологиясы, оптикалық және импеданс спектроскопиясы.

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Влияние толщины фотоэлектрода SnO на фотоэлектрические параметры солнечной ячейки FTO:SnO:PTB7-TH:ITIC/Mo/Ag

В статье представлены результаты исследования морфологических, оптических и электрофизических параметров пленок SnO₂. Пленки SnO₂ наносились методом *spin-coating* при различных оборотах вращения центрифуги. Экспериментальные исследования проводились методами оптической спектроскопии, вольтамперометрии и измерения импеданса. С помощью атомно-силового микроскопа исследовались топография поверхности и толщина пленок SnO₂. Исследованы оптические свойства пленок SnO₂ с различной толщиной. Показано что увеличение скорости вращения подложки приводит к уменьшению шероховатости поверхности пленок SnO₂. Установлено, что изменение морфологии пленок SnO₂ способствует быстрому транспорту инжектированных дырок к внешнему электроду и уменьшению вероятности обратной рекомбинации. Ячейки с электрон-транспортным слоем SnO₂ в 2000 оборотах показали низкую эффективность (0,17 %). С уменьшением толщины пленок SnO₂ до значения 62 нм наблюдается возрастание значения тока короткого замыкания в 2,3 раза и изменения напряжения холостого хода в 1,12 раз.

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Physical and Chemical Processes of Structure Formation of (BeO+TiO₂)-Ceramics with the Addition of TiO₂ Nanoparticles

This paper describes in detail the solid-phase sintering mechanism of BeO + TiO₂^{μm} + TiO₂^{nano} ceramics in the 1520–1550 °C temperature range. It is shown that the structural elements are formed due to the processes of pore disappearance and grain growth in the process of ceramic shrinkage during sintering. It is found that under the influence of TiO₂ nanoparticles it is possible to increase the sintering temperature of such ceramics by 30 °C, which promotes the transformation of the crystal structure of TiO₂ into a more conductive Ti₃O₅ with an orthorhombic structure. The mechanism of the slowing down of the grain boundary movement by the second phase impurity as the segregation of nano impurities on the grain boundary is described. The calculation of binding energy of spontaneous chemical reactions during sintering of ceramics is performed, chemical elements and compounds related to conductive phase in ceramics of BeO + TiO₂^{μm} + TiO₂^{nano} composition at sintering temperature 1550 °C are determined. It is shown that the specific conductivity of the synthesized nanocomposite material increases in comparison with the ceramics consisting of micropowders in the frequency range of 100 Hz–100 MHz, at a sintering temperature of 1550 °C.

Keywords: (BeO+TiO₂)-ceramics, nanoparticles, solid-phase sintering, microstructure, mechanical mixture, specific conductivity, phase diagram.

Introduction

At present, due to the wide development of radio-electronic equipment, devices, and wireless communication equipment, much attention is paid to the creation of small-sized receiving and transmitting devices, containing in composition shielding and absorbing bulk materials that retain their properties in a wide range of frequencies and temperatures [1]. One of the most perspective materials for the creation of absorbers of microwave energy is ceramics based on BeO with the addition of TiO₂ to 30 wt.% [2]. Electrophysical and other properties of such ceramics can be essentially improved by introducing into structure of micro- and nano-powders TiO₂ [3]. Because sintering of ceramics is a physical and chemical process of production of dense workpieces under the influence of heat treatment, the study of the processes occurring at this is the most relevant task [4]. In particular, in the semiconductor industry, many products are produced by sintering: capacitors, resistors, substrates, bulk microwave energy absorbers, ferroelectrics, etc. [5].

The possibility of increasing the sintering temperature of BeO-based ceramics with the addition of TiO₂ micro-powders by adding a small amount of TiO₂ nanoparticles is one of the directions of research to improve the electrodynamic properties of such ceramics [6]. Theoretically, it will allow for achieving an increase in the density of ceramic samples and, consequently, higher values of electrophysical and absorption characteristics of the investigated material [7].

Information about the change in the electrophysical characteristics of ceramics based on BeO with the addition of micro- and nano-powder TiO₂ at a change in sintering temperature in the literature at the present time is absent. In this scientific article, the studies of physical and chemical processes occurring during the formation of the structure of ceramics based on (BeO+TiO₂)_{μm} with the addition of nanoparticles TiO₂, under the influence of temperature are presented.

Experimental

Microstructure, granulometric composition, and phase analysis of powders and sintered samples were studied on a scanning electron microscope with energy dispersive microanalysis attachment JSM-6390LV, 2007, with resolution in high vacuum until 3nm and the ability to image in secondary and reflected electrons. The microscope has a magnification from 5x to 300,000x at accelerating voltages from 0.5 kV to 30 kV.

Evaluation of the primary data on the powder material and the sintered product crystal size, analysis, and measurement of micropores, cracks, inclusions, and other defects were performed using an optical microscope MBS-10, at 16x magnification, with a measuring scale with a division value of 0.05 mm.

The AgilentE5061B Spectrum Analyzer technique is designed to measure the total complex resistance (impedance) of composite samples in the frequency range 1 Hz–100 MHz. The “frequency variation” method allows measuring the frequency dependence of such electrophysical characteristics as complex conductivity, dielectric permittivity, and contact resistance.

The essence of the method is to determine the electro-physical characteristics of composite materials depending on the frequency of the alternating voltage applied to the electrodes mounted on the sample, based on Ohm's law to determine the instantaneous values of alternating current and measure the phase shift between current and voltage. As a result, the total complex resistance (impedance modulus $|Z|$) is calculated as the ratio of the effective alternating voltage to the effective alternating current.

Results and Discussion

Beryllium oxide in relation to TiO_2 is an inert compound, that is, there is no chemical potential of interaction between them. Figure 1 shows phase diagram of beryllium oxide interaction with titanium dioxide.

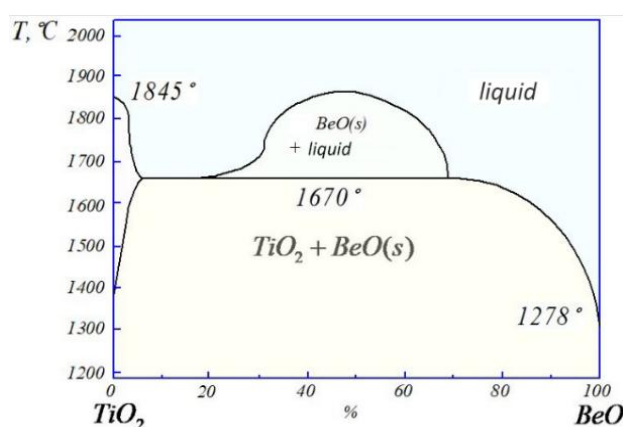


Figure 1. Phase diagram of TiO_2 — BeO interaction [8]

As can be seen from Figure 1, the content of titanium dioxide is from 20 to 70 mol. %wt., above the temperature of 1670 °C, titanium dioxide passes into the liquid phase. Therefore, in order not to “lose” mechanical properties due to crystal growth, the sintering temperature of ($\text{BeO} + \text{TiO}_2$)-ceramics should not exceed this temperature. In turn, the optimum sintering temperature for serial ceramics ($\text{BeO} + 30 \text{ wt}\% \text{TiO}_2^{\mu m}$) is 1520–1530 °C, above this temperature starts crystal growth, the sample loses density, mechanical strength, geometric parameters (bloated).

Depending on the sintering mechanism, the microstructure of the ceramic is also determined. In the case of the solid-phase sintering mechanism, individual grains are formed due to the pore disappearance and grain growth processes. Both of these processes are accompanied by a change in the shape of the crystals, which tend to take the form of polyhedrons capable of filling the existing volume of the sample (Figure 2).

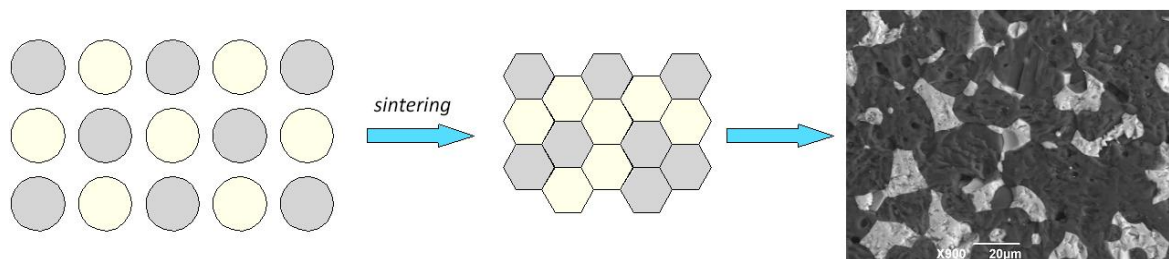


Figure 2. Solid-phase sintering mechanism of ceramics. In the inset on the right microstructure of ceramics of $\text{BeO} + 29.0 \text{ wt}\% \text{TiO}_2^{\mu m} + 1.0 \text{ wt}\% \text{TiO}_2^{\text{nano}}$ sintered at $T = 1550 \text{ °C}$

The free energy in this sintering mechanism changes because of changes in the total surface area of all grains and changes in the specific surface energy when the solid-gas interface is replaced by a solid-solid interface. These changes can be represented as summations:

$$dG = \gamma dA + A d\gamma$$

where A — area; γ — surface energy. These two summands are also expressed accordingly in the change in the microstructure of ceramics during sintering (Figure 3).

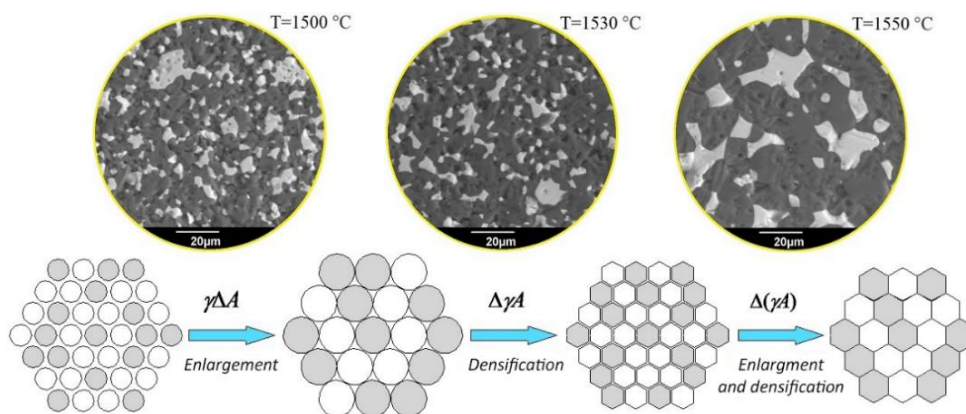


Figure 3. Scheme of mechanisms of enlargement and densification of ceramic structure during sintering. On the inserts on top the microstructure of ceramics of composition $\text{BeO} + 28,5 \text{ wt\% TiO}_2^{\mu m} + 1,5 \text{ wt\% TiO}_2^{\text{nano}}$

In practice, during the sintering of ceramics the processes occur simultaneously — “enlargement of particles”, accompanied by reduction of the total surface area of grains, and compaction, as a result of which the grain-gas interface is replaced by the grain-grain interface. This replacement can be accompanied by a decrease in the specific surface energy.

In turn, the chemical potential of the phase depends on the curvature of the surface, since the properties of the atoms on the surface of the particle are different from the properties of the atoms inside it.

The intergranular boundary is formed as a result of particle sintering, on which the change of direction of crystallographic grain axes takes place, characterized by the value of specific surface energy γ_b . In the case of two-phase ceramic composition (BeO , TiO_2) at the grain boundary with the second phase, a region is formed, which is represented in Figure 4.

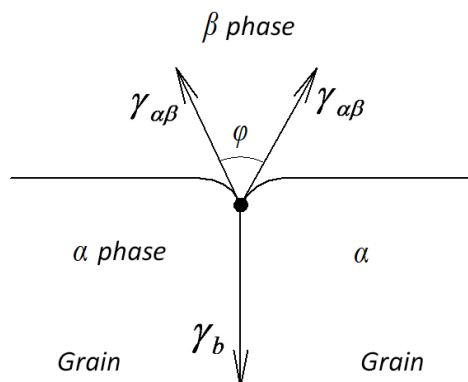


Figure 4. Schematic of the intergranular region in contact with the second phase

For an equilibrium boundary, there must be a relationship between the values of surface energy at the crystal-vapor and crystal-crystal boundary:

$$\gamma_b = 2\gamma_{\alpha\beta} \cos \frac{\phi}{2}.$$

The angle ϕ is called the dihedral angle. Its value does not depend on gas pressure, but only on the ratio between $\gamma_{\alpha\beta}$ and γ_b . If the β phase is gaseous, the relationship $\gamma_{\alpha\beta} \gg \gamma_b$ is true and the dihedral angle takes on

a value greater than 120° . The surface energy γ_b changes when the crystallographic orientation of the grains relative to each other changes. In real structures, this is the reason for the presence of different values of the dihedral angle that can be detected in ceramics at the initial moment when the porosity is high enough. The variation of angles in real samples is also observed because of the system's non-equilibrium. One of the options for bringing the system to an equilibrium state is to expose the system to a temperature at which liquid-phase sintering will take place under the action of the flow of one of the phases.

Thus, to describe the sintering process it is necessary to understand to what state a polycrystalline material consisting of grains and pores will tend to. As a result of the disappearance of pores during the sintering process, a polycrystal is formed in which the surface energy of the grain boundaries takes on a minimum value for a given number of grains and the grains form a dense, non-porous packing. Eventually, in the equilibrium state, all grains will have the same shape and size.

Ceramic samples of $\text{BeO} + 5 \text{ wt\% } \text{TiO}_2^{\text{nano}}$ composition representing a two-phase system were subjected to a sintering temperature of 1800°C (above transition to liquid-phase sintering — 1670°C (Figure 1)) to achieve a liquid-phase sintering mechanism. We will consider BeO beryllium oxide as the first phase, and TiO_2 nanoparticles, which should tend to occupy the grain contact area near the tops of the BeO crystal, as the second phase with lower temperature. In a structure close to equilibrium, the values of contact angles tend to be values given by the ratio of surface energies at the interfaces. In such a case, the shape of the ternary intersection in the two-dimensional microstructure will be different, as well as the values of the dihedral angles (Figure 5).

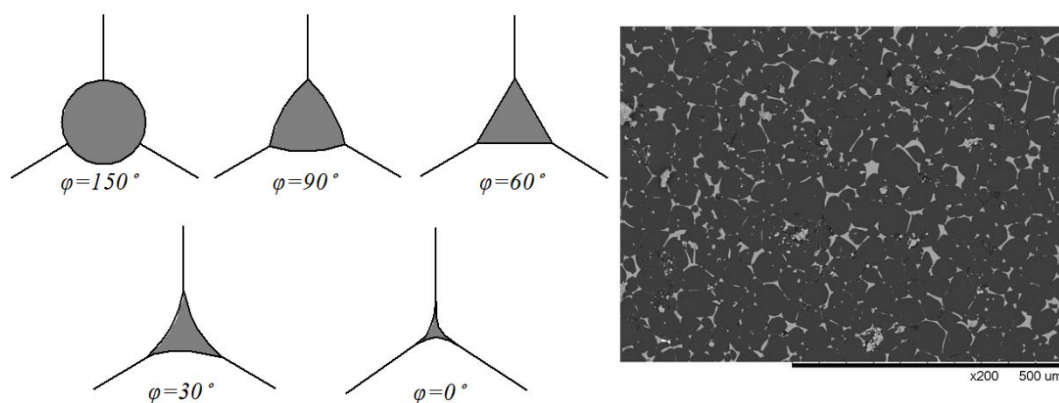


Figure 5. The shape of the triple crossing in the two-dimensional microstructure. In the inset on the right microstructure of ceramics of $\text{BeO} + 5.0 \text{ wt. \%}$ sintered by the mechanism of liquid-phase sintering at $T = 1800^\circ\text{C}$

Figure 5 points out that the contact area between grains decreases with decreasing dihedral angle value, while the contact area of grains with the second phase increases. For the investigated sample, the dihedral angle is $0\text{--}30^\circ$. Based on the analysis of the macrostructure, grains during sintering of ceramics tend to take the shape characterized by a minimum of free energy. To achieve the minimum interfacial surface energy of the two-phase system, the minimum value of the dihedral angle is necessary, which tends to decrease at a temperature of 1800°C .

Thus, the possibility of increasing the sintering temperature of ceramics by adding nanoparticles TiO_2 will reduce the interfacial surface energy, hence increasing the density, hardness, mechanical strength and possibly other physical and chemical properties, provided that the growth of the crystal size of BeO is contained.

The observed discrepancies in the theoretical calculations of the grain growth rate and the experimental data are due to the influence of impurities. In turn, if the impurity forms the second phase, its very presence slows down the movement of the grain boundary, as shown in Figure 6.

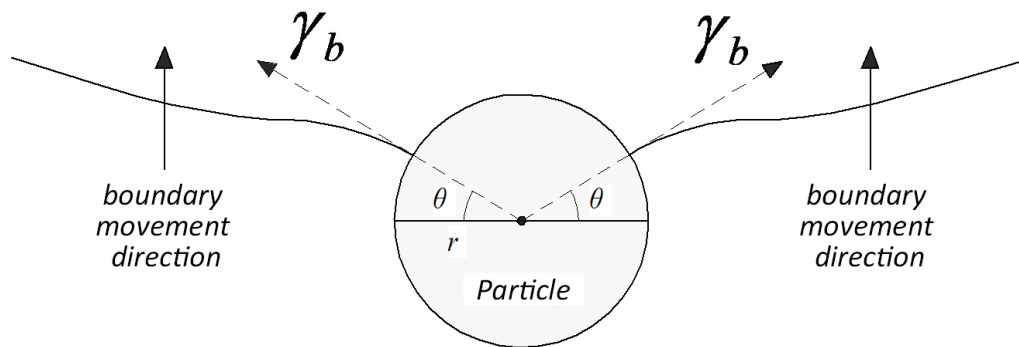


Figure 6. Illustration of the slowing down of the grain boundary movement by the second phase impurity

In ceramics of $\text{BeO} + \text{TiO}_2^{\mu m} + \text{TiO}_2^{\text{nano}}$, the impurity $\text{TiO}_2^{\text{nano}}$ is soluble in the phase $\text{TiO}_2^{\mu m}$, whose concentration in the volume and at the grain boundary differ from each other. If the energy of impurity atoms at the grain boundary is lower than in its volume, the segregation of impurity at the grain boundary is observed. To assess the influence of impurity atoms on the segregation processes we consider the distribution P atoms of impurity on N available positions in the crystal lattice of the main substance and p atoms of impurity distributed on n available positions in the area of the grain boundary. When an atom of the main component is replaced by an atom of the impurity in the volume of the grain, the internal energy E increases, which is accompanied by the change in energy e at the replacement of the atom at the grain boundary. Due to the dissolution of impurity atoms, the change in free energy G can be expressed in the form that is typical for solutions:

$$G = pe + PE - kT[\ln N! - \ln(n-p)!p!(N-P)!P!]$$

Under the conditions of equilibrium $\frac{dG}{dp} = 0$ and $\frac{dG}{dP} = 0$. Given the large value of N , in the presence of nanoscale impurities, the Stirling approximation is valid:

$$\ln N! \approx N \ln N - N.$$

Considering these circumstances, the equilibrium distribution of atoms at different locations is described by the equation:

$$\frac{n}{n-p} = \frac{P}{N-P} \exp\left(-\frac{e-E}{kT}\right).$$

This equation takes a simpler form if instead of the number of atoms and distribution sites we use their mole fractions. Thus, we obtain that the impurity atoms B , replace the atoms of the main substance A . Accordingly, the molar fractions of the atoms in the volume of the grain and at the boundary: X_A , X_B , X_A^b , X_B^b . In this case, the equation takes the form:

$$\frac{X_B^b}{X_A^b} = \frac{X_B}{X_A} \exp\left(-\frac{\Delta E}{kT}\right),$$

where $\Delta E = e - E$ is the change in energy due to the segregation of impurities at the grain boundary.

To calculate the ΔE values, the model of a regular solution of paired atom interactions is applied, ignoring the interactions between impurity atoms. If we assume that the impurity atom is a solid nondeformable sphere, the lattice distortion energy W is equal:

$$W = \frac{4\pi Y r_0^3}{1+\nu} \left(\frac{r_1-r_0}{r_0}\right)^2,$$

where Y — Young's modulus, ν — Poisson's ratio, r_0, r_1 — radius of atom of the main substance and impurity, respectively. Because of the difference in the Young's modulus in the volume of a grain and at its boundary with another grain, the elastic strain energy at the introduction of an impurity atom into the lattice may be different — $\Delta E \neq 0$.

In the case of nanoscale particles as an impurity phase, impurity segregation and internal energy changes can occur by completely different mechanisms. Beryllium oxide belongs to the group of “insulating oxides” derived from metals of the left and right parts of the D.I. Mendeleev table. Titanium dioxide refers to

semiconductors or metallic oxides located in the middle of the table. Sintered mechanical mixture (ceramics) of such oxides with the addition of nanoparticles can show anomalous physical and chemical properties. In the size range from 2 to 10 nm classical laws and laws of quantum chemistry are not acceptable. In nanoparticles of spherical shape sized 3 nm, half of the atoms or ions are located on the surface. This position allows the volumetric properties to change due to surface effects in the region of reaction chemistry near the stoichiometric composition. The presence of a strong chemical bond can lead to changes in chemical and physical properties. When particles become smaller in size, different morphologies are formed, which affect changes in surface chemistry and adsorption properties due to an increase in their specific surface area.

During the study of the interaction of BeO and TiO₂ in a wide range of temperatures, it was found that titanium practically does not form solid replacement solutions with BeO. However, weak chemical interaction between them, along the interface surfaces, is not excluded in the process of sintering ceramics containing TiO₂^{nano} where other impurities can be concentrated. In turn, titanium (Ti) with oxygen (O) forms a large number of oxides: TiO₂, Ti₂O₃, Ti₃O₅, homologous series of oxides Ti_nO_{2n-1} and possibly others. Increasing the sintering temperature, due to the presence of TiO₂ nanoparticles contributes to more effective recovery of TiO. When sintering (BeO+TiO₂)-ceramics in furnaces with carbon heaters in a reducing environment (in a carbon monoxide atmosphere) carbon penetrates the inner region of ceramic samples, which leads to a uniform chemical interaction and distribution of phases both inside and on the surface of the sample.

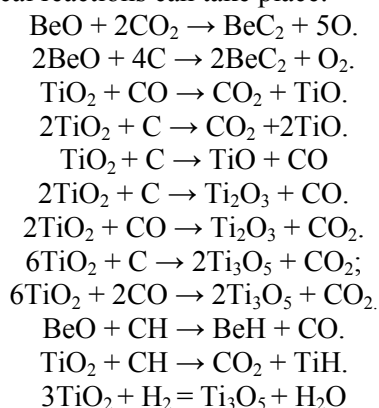
After analyzing the main chemical elements and compounds involved in the manufacturing process of conducting ceramics of the composition of BeO + TiO₂, Table 1 was compiled.

Table 1

Conductivity of chemical elements and compounds involved in the technological process of making (BeO + TiO₂)-ceramics

Conductor	Dielectric
Be	
C	
Ti	BeO
BeH	Be ₂ C
BeC ₂	TiO ₂
TiO	Be(OH) ₂
Ti ₂ O ₃	TiC
Ti ₃ O ₅	
TiH	

The conductivity of each element depends on the sintering temperature, for example, when TiO₂ is heated at 750–1000 °C in hydrogen environment, the compound Ti₂O₃ is formed. At hydrogen pressure of 13–15 MPa and temperature 2000 °C — TiO₂ is reducing to TiO, the only compound that gives a maximum of three free electrons (Ti⁺³) is TiH. During sintering of such ceramics in weakly reducing environment of carbon monoxide the following chemical reactions can take place:



To determine the possibility of interaction between BeO and TiO₂ at an increased sintering temperature, due to the presence of TiO₂ nanoparticles, we use the entropic method of calculating the equilibrium con-

starts, — $\Delta G_T^\circ = \Delta H_{298}^\circ - T\Delta S_{298}^\circ$, where $T = 1550^\circ\text{C}$ [9]. The data of this calculation allow us to identify four main chemical reactions that can occur at this temperature (Table 2).

Table 2

Calculation of the change of Gibbs energy, which determines the possibility of spontaneous reaction at $T = 1550^\circ\text{C}$

№	Chemical reactions	ΔG , kJ/mol
1	$\text{TiO}_2 + \text{C} \rightarrow \text{TiO} + \text{CO}$	$\Delta G_T^\circ < 0$
2	$2\text{TiO}_2 + \text{C} \rightarrow \text{Ti}_2\text{O}_3 + \text{CO}$	
3	$3\text{TiO}_2 + \text{H}_2 \rightarrow \text{Ti}_3\text{O}_5 + \text{H}_2\text{O}$	
4	$\text{TiO}_2 + \text{CH} \rightarrow \text{CO}_2 + \text{TiH}$	

According to the results of calculation of possible electrically conductive phases responsible for the conductivity of ceramic composition ($\text{BeO} + \text{TiO}_2^{\mu m} + \text{TiO}_2^{\text{nano}}$), sintered at $T = 1550^\circ\text{C}$, the main electrically conductive phases are TiO, Ti_2O_3 , Ti_3O_5 and TiH.

To describe the electrical conductivity of composite materials, we commonly refer to a conductive cluster of particles of any phase. After the percolation threshold, a conductive cluster can be called percolation, considering its limited size and the possibility of binding conductive phase clusters by dielectric layers that have local resistances comparable to those of particles in micro- and nano-clusters.

Figure 7 represents the results of the study of the frequency dependence of the real and imaginary components of the specific conductivity of serial ceramics of $\text{BeO} + 30\text{ wt\% TiO}_2$.

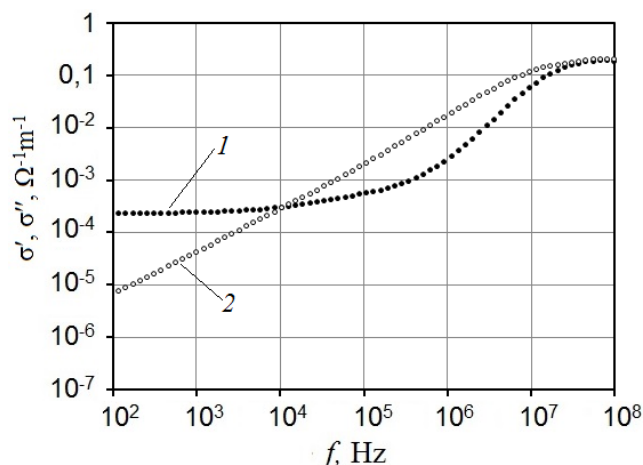


Figure 7. Frequency dependence of real σ' (1) and imaginary σ'' (2) components of specific conductivity of serial ceramics of $\text{BeO} + \text{TiO}_2^{\mu m}$ at $T = 1530^\circ\text{C}$

Figure 7 shows that the real component of conductivity at low frequencies up to 104 Hz remains at the level of $2.4 \cdot 10^{-4} \Omega^{-1}\text{m}^{-1}$. With further frequency increase conductivity stepwise increases up to the value of $0.15 \Omega^{-1}\text{m}^{-1}$. The imaginary component of specific conductivity increases linearly over the whole range of frequencies understudy, coinciding with the real component at frequencies higher than $3 \cdot 10^7 \text{ Hz}$.

Figure 8 displays the dependence of the specific conductivity on the concentration of TiO_2 nanoparticles of composition $\text{BeO} + (28.0 - 29.9 \text{ wt\% TiO}_2^{\mu m}, \Sigma \text{TiO}_2^{\mu m} + \text{TiO}_2^{\text{nano}} = 30 \text{ wt\%})$ at the sintering temperature of ceramics 1550°C .

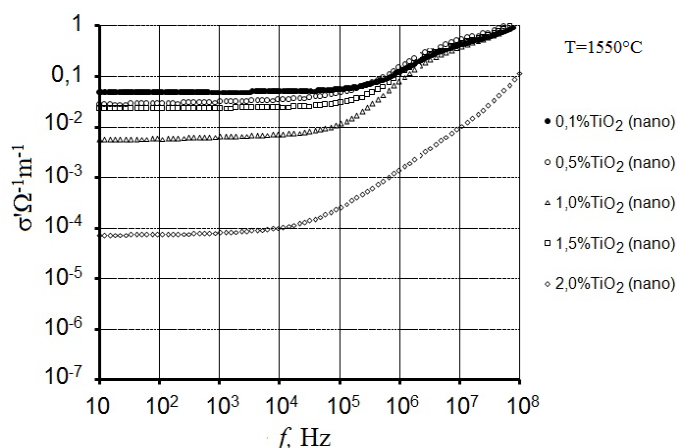


Figure 8. Frequency dependence of the real σ' component of specific conductivity on the content of TiO_2 nanoparticles, at $T = 1550^\circ\text{C}$

The conductivity curves, depending on the content of TiO_2 nanoparticles, are parallel to each other in the frequency range from 10 to 10^5 Hz. The minimum conductivity value in this range, is $\sigma'_{(1.0\%)} = 5.5 \cdot 10^{-3} \Omega^{-1}\text{m}^{-1}$, the maximum $\sigma'_{(0.1\%)} = 4.8 \cdot 10^{-2} \Omega^{-1}\text{m}^{-1}$. With the increasing frequency of electric field, specific conductivity on all samples increases sharply, at a maximum frequency of 10^8 Hz conductivity curves practically coincide, maximum value $\sigma'_{(0.5\%)} = 1.36 \Omega^{-1}\text{m}^{-1}$.

The conductivity mechanism can be explained by the fact that during sintering of ceramics TiO_2 nanoparticles are pushed to the surface of micron crystals (i.e., to the intercrystalline interlayers). Thus, conduction follows by a random grid of interlayers between the crystals. Some interlayers of adjacent crystals may not interact, therefore, there is a finite resistance and a hopping mechanism of conductivity from one layer to another (between the interlayers). As the concentration of titanium dioxide nanoparticles increases up to 2.0 wt%, they begin to stick together with each other or with titanium oxide microparticles inside the crystal and do not go into the intercrystalline interlayers, so the material becomes a dielectric.

Conclusions

The solid-phase sintering mechanism, the schemes of the mechanisms of enlargement and densification of the ceramic structure of $\text{BeO} + \text{TiO}_2^{\mu\text{m}} + \text{TiO}_2^{\text{nano}}$, during sintering, confirmed by real photographs of the microstructure in the temperature range $1500\text{--}1550^\circ\text{C}$, were described. According to the results of the study of the dihedral angle during liquid-phase sintering of ceramics containing $\text{BeO} + 5 \text{ wt}\% \text{TiO}_2^{\text{nano}}$, $T = 1800^\circ\text{C}$, the angle values are within $0\text{--}30^\circ$, which characterizes the presence of a minimum interphase surface energy of the two-phase system.

The slowing mechanism of the grain boundary movement by the second phase impurity was described as the segregation of nano-impurities on the grain boundary, provided that the energy of the impurity atoms on the grain boundary is lower than in its volume.

Chemical elements and compounds related to the conducting phase in the ceramics of $\text{BeO} + \text{TiO}_2^{\mu\text{m}} + \text{TiO}_2^{\text{nano}}$ composition were determined by calculating the binding energy of possible chemical reactions. The reactions with the formation of the conducting compound TiO , Ti_2O_3 , Ti_3O_5 , and TiH were established.

It was established that the specific conductivity of the synthesized ceramics of composition $\text{BeO} + (28.0\text{--}29.9 \text{ wt}\% \text{TiO}_2^{\mu\text{m}}, \Sigma \text{TiO}_2^{\mu\text{m}} + \text{TiO}_2^{\text{nano}} = 30 \text{ wt}\%)$ at sintering temperature of ceramics 1550°C significantly increases in comparison with the serial sample.

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TiO₂ нанобөлшектері қосылған (BeO + TiO₂)- керамиканың құрылымын қалыптастырудың физика-химиялық процестері

Мақалада 1520–1550 °C температура аралығында BeO + TiO₂^{um} + TiO₂^{nano} құрамындағы керамиканы қатты фазалық біріктіру механизмінің сипаттамасы берілген. Құрылымдық элементтер біріктіру кезінде керамиканың шөгу процесінде кеуектердің жоғалуы және түйіршіктердің өсуі нәтижесінде пайда болатындығы көрсетілген. TiO₂ нанобөлшектерінің әсерінен мұндай керамиканың балку температурасын 30 °C-қа көтеру мүмкіндігі бар екендігі анықталды, бұл TiO₂ кристалды құрылымын орторомбалық құрылымы бар Ti₃O₅ өткізгіш құрылымына айналдыруға ықпал етеді. Түйіршік шекарасындағы нанокоспалардың сегрегациясы ретінде екінші фазалық қоспамен түйіршік шекарасының қозғалысын баяулату механизмі сипатталған. Керамиканы біріктіру процесінде өздігінен жүретін химиялық реакциялардың байланыс энергиясы есептелді, 1550 °C температурада BeO + TiO₂^{um} + TiO₂^{nano} құрамындағы керамикада өткізгіштік фазаға жататын химиялық элементтер мен қосылыстар анықталды. Синтезделген нанокompозиттік материалдың меншікті өткізгіштігі микроұнтақтардан тұратын керамикамен салыстырғанда 1550 °C температурада 100 Гц–100 МГц жиілік диапазонында өсетіні көрсетілген.

Кілт сөздер: (BeO+TiO₂)-керамика, нанобөлшектер, сұйық фазалық біріктіру, микроқұрылым, механикалық қоспа, меншікті өткізгіштік, фазалық диаграмма, байланыс энергиясы.

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Физико-химические процессы формирования структуры (BeO+TiO₂)-керамики с добавкой наночастиц TiO₂

В статье приведено подробное описание твердофазного механизма спекания керамики состава BeO + TiO₂^{um} + TiO₂^{nano} в интервале температур 1520–1550 °C. Показано, что структурные элементы формируются за счет процессов исчезновения пор и роста зерен в процессе усадки керамики при спекании. Установлено, что под действием влияния наночастиц TiO₂ представляется возможность повысить температуру спекания такой керамики на 30°C, что способствует трансформации кристаллической структуры TiO₂ в более проводящую Ti₃O₅ с орторомбической структурой. Описан механизм замедления движения границы зерна примесью второй фазы как сегрегация нанопримесей на границе зерен. Произведен расчет энергии связи самопроизвольно протекающих химических реакций в процессе спекания керамики, определены химические элементы и соединения, относящиеся к проводящей фазе в керамике состава BeO + TiO₂^{um} + TiO₂^{nano} при температуре спекания 1550 C. Показано, что удельная проводимость синтезированного нанокompозитного материала возрастает в сравнении с керамикой, состоящей из микропорошков, в диапазоне частот 100 Гц–100 МГц, при температуре спекания 1550 °C.

Ключевые слова: (BeO+TiO₂)-керамика, наночастицы, жидкофазное спекание, микроструктура, механическая смесь, удельная проводимость, фазовая диаграмма, энергия связи.

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Photocatalytic activity of zinc oxide – graphene oxide composites

Recently, the use of various dyes in the cellulose, textile, plastics and rubber industries has resulted in severe toxic and dye contamination of wastewater. These toxic dyes are not biodegradable and have a detrimental effect on the environment, blocking sunlight and reducing photosynthesis. Consequently, there is an urgent need to develop a low-cost effective technology for purifying wastewater from harmful organic pollutants. In this context, photocatalysis is an advanced, environmentally friendly oxidation process for wastewater treatment. Recent studies have shown that the use of semiconductor photocatalytically active materials with a wide band gap is an effective method for the decomposition of organic pollutants in aqueous solutions. In this work, a low-cost technology for the synthesis of composite semiconductor zinc oxide / graphene oxide (ZnO / GO) materials by chemical deposition from an aqueous solution has been developed. The morphology, structural and photoluminescent properties of the synthesized ZnO/GO samples with different graphene oxide concentration have been studied. The research of the photocatalytic activity of synthesized zinc oxide – graphene oxide composite materials is carried out by observing an aqueous solution of rhodamine B dye degradation under ultraviolet illumination.

Keywords: chemical deposition, zinc oxide, graphene oxide, composites, optical and structural properties, photocatalytic activity, rhodamine B.

Introduction

In recent years, as a result of environmental changes associated with the ineffective use of water resources, the problem of purifying wastewater from industrial and agricultural waste has become urgent [1, 2]. Numerous waste dyes used in various industries, such as the production of cosmetics, textiles, and food end up in water bodies in the form of wastewater [3–5]. Due to that, emerged the urgent task to develop effective and economical methods for eliminating organic pollution [6, 7]. Various types of biological, physical, and chemical methods, such as chemical precipitation, separation, coagulation, removal, adsorption of activated carbon, chlorination and ozonation, are used for industrial wastewater treatment [8–10]. Chemical methods of chlorination and ozonation are slow processes and as consequence, they are not economically feasible; therefore, the use of these approaches is limited [11]. Traditional filtration methods do not have high efficiency and cause only phase changes in pollutants. In recent decades, photocatalytic decomposition processes have been actively considered successors to the previous methods, since they can significantly accelerate the degradation of organic pollutants [12–14]. Photocatalysis is a reaction in which light is used to activate a substance that changes the rate of a chemical reaction. Under the illumination of semiconductor, photocatalyst electrons move to the conduction band, a hole appears in the valence band, thus an electron-hole pair is generated. The generated electron-hole pairs cause a complex series of secondary reactions with dye molecules, which leads to the complete degradation of dye contaminants adsorbed on the semiconductor surface [15].

Zinc oxide (ZnO) is one of the most studied photocatalytically active materials due to its low toxicity, wide band gap (3.37 eV), long-term stability, high photostability, and high efficiency [16, 17]. Usually, oxide semiconductors have relatively low charge mobility and a high degree of electron-hole recombination, which reduces the efficiency of the photocatalytic reaction and prevents their widespread use as practical photocatalysts [18].

The photocatalytic characteristics of ZnO can be improved by synthesizing composites based on it in combination with other components, such as noble metals [19], carbon materials [20, 21], and by doping [22]. In particular, nanocomposites with graphene and graphene oxide (GO) have attracted the attention of researchers in recent years. ZnO is a good electron donor with high optical activity and stability. Moreover, graphene is a good electron acceptor with high conductivity. Thus, the hybrid system can act conjointly by

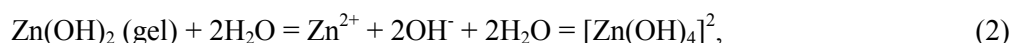
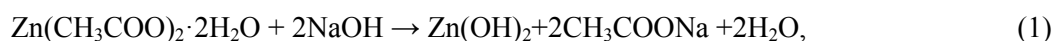
increasing the migration efficiency of photo-generated electrons and decreasing recombination. H. Fan et al. synthesized a series of composites of graphene and ZnO by a simple hydrothermal method [23]. The effect of the graphene inclusion in ZnO structure on the photocatalytic degradation of an aqueous dye solution was noted in the article [24]. In most of these works, ZnO / graphene oxide composites were synthesized either at a higher temperature or with complex equipment and a complex reaction procedure with the participation of intermediate products of the growth of zinc oxide particles on reduced graphene oxide sheets is required.

In this regard, the task of improving photocatalytic characteristics by the efficient, low-cost synthesis methods of composite materials based on ZnO is urgent.

Experimental

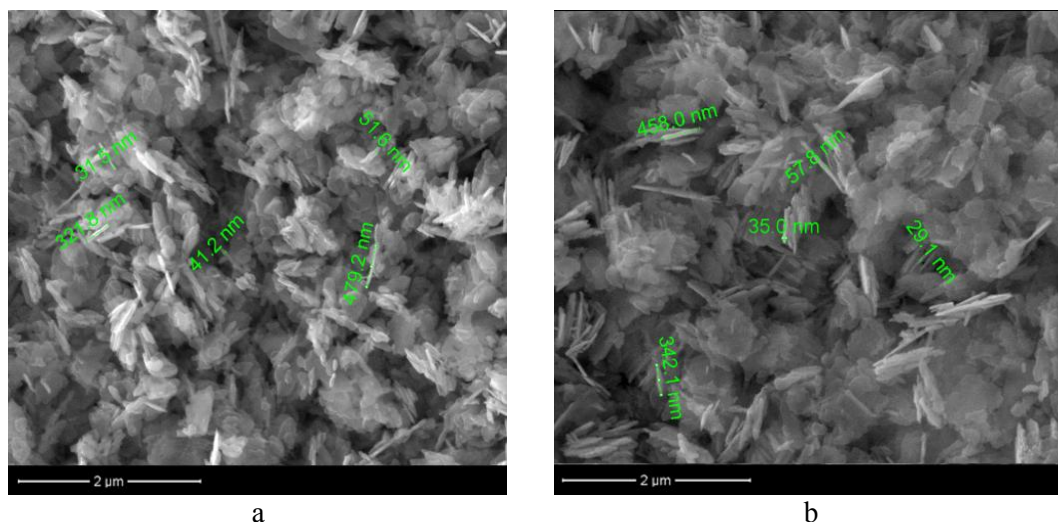
Composite materials based on zinc oxide and graphene oxide were synthesized by low-temperature chemical deposition from an aqueous solution. For the synthesis of ZnO / GO composites, we used ready graphene oxide obtained by the Hammers method [25]. Graphene oxide was dissolved in distilled water for half an hour using an ultrasonic bath. In a separate glass, zinc acetate dihydrate ($(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$, Sigma-Aldrich) was dissolved in distilled water. Then both solutions were mixed on a magnetic stirrer. Then, to form zinc oxide nanoparticles, an aqueous solution of sodium hydroxide (NaOH, Sigma-Aldrich) was added dropwise to a glass beaker with an aqueous solution of zinc acetate and graphene oxide. Then the entire solution was thoroughly mixed on a magnetic stirrer for another 15 minutes. The whole process of synthesis of ZnO composites - GO was carried out at room temperature.

The NaOH concentration was 0.7M with a zinc acetate concentration of 50mM. The graphene oxide concentration was varied from 0.01 to 0.7 mm wt% (samples: ZGP 2 – 0.01 wt% GO, ZGP 4 – 0.025 wt%, ZGP 5 – 0,14 wt% GO, ZGP 7 – 0,7 wt%). The resulting precipitate was washed with distilled water, separated by centrifugation, and then dried in an oven at 125 °C for 12 hours. The formation of zinc oxide in this process can be described by the following chemical reactions [26]:



Results and Discussion

The results of electron microscopy studies carried out on a Quanta 200i 3D scanning electron microscope (FEI Company) with a directly heated tungsten cathode showed that the ZnO / GO composites synthesized by this growth technique are two-dimensional structures in the form of 2D thin petals about 30 nm thick (Figure 1). It was noted that an increase in the concentration of GO in the growth solution of ZnO / GO leads to the decrease in the thickness of ZnO petals. As a result, the 2D structures become thinner, the amount of the flocculent structure increases. It allows increasing their working specific surface to equal weight.



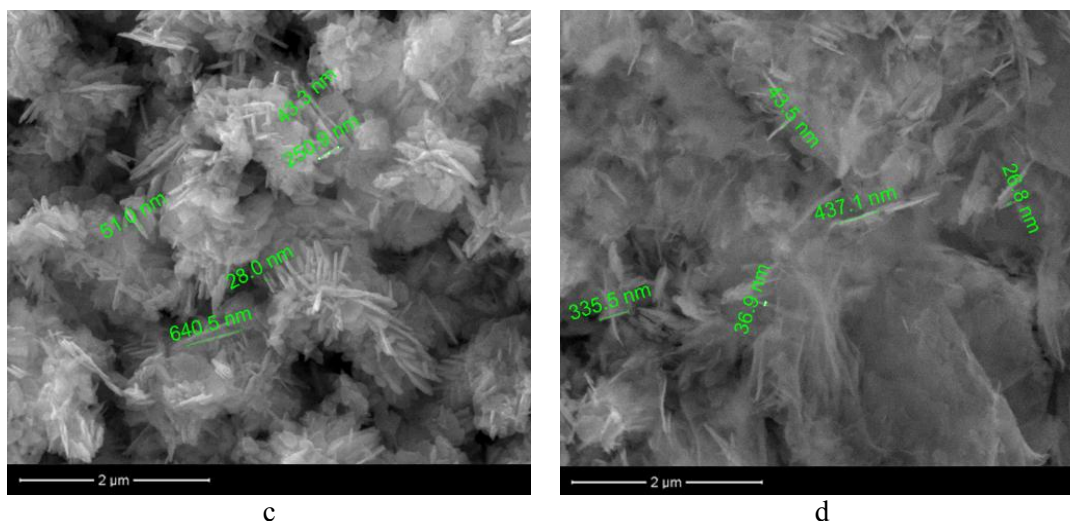


Figure 1. Morphology of ZnO / GO samples: a – ZGP 2 – 0.01 wt% GO, b – ZGP 4 – 0.025 wt% GO, c – ZGP 5 – 0,14 wt% GO, d – ZGP 7 – 0.7 wt% GO.

The structural properties of the synthesized ZnO / GO samples were studied by X-ray diffraction analysis. X-ray diffractometry measurements were performed under the same conditions for all synthesized samples. Figures 2, 3 show diffractograms of the samples ZGP 2 and ZGP 7 with the lowest and highest concentration of graphene oxide, respectively, in considered series of ZnO / GO samples.

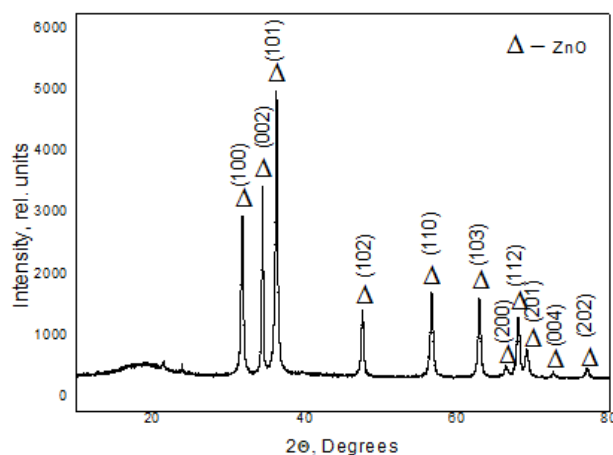


Figure 2. X-ray diffraction of ZGP 2 sample

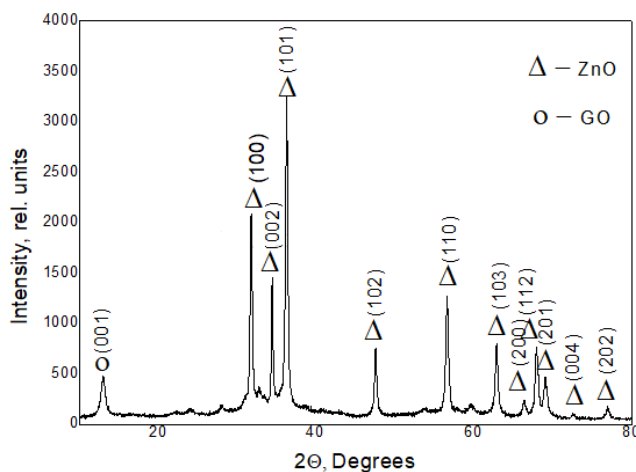


Figure 3. X-ray diffraction of ZGP 7 sample

All ZnO / GO samples exhibit the hexagonal structure of zinc oxide wurtzite (JCPDS card # 01-080-3004). The diffractogram of the ZGP 7 sample with the highest GO concentration contains (001) reflex, corresponding to GO sheets.

Changes in the structural properties of ZnO / GO composites depending on the concentration of graphene oxide in the growth solution were also studied using Raman spectroscopy (Figure 4).

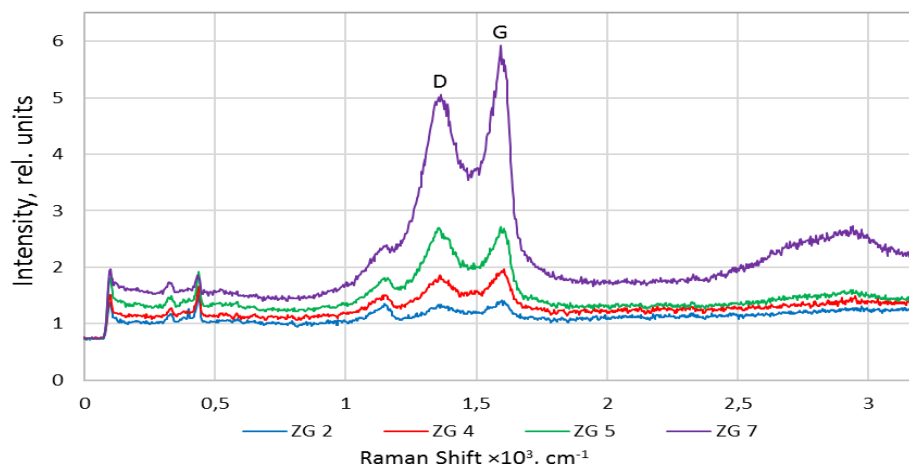


Figure 4. Raman spectra of ZnO / GO samples: ZGP 2 – 0.01 wt% GO, ZGP 4 – 0.025 wt% GO, ZGP 5 – 0,14 wt% GO, ZGP 7 – 0.7 wt% GO.

Raman spectra allow one to take into account conjugated and double carbon-carbon bonds, which leads to high-intensity peaks in the Raman spectrum. A typical GO Raman spectrum is characterized by a G band at a displacement of the 1605 cm^{-1} , which corresponds to the E_{2g} phonon of sp^2 carbon atoms, and a D band at 1353 cm^{-1} , which corresponds to the breathing mode of point phonons with A_{1g} symmetry.

The Raman spectra of synthesized ZnO / GO composites show that the D peaks for these samples appear at 1370 cm^{-1} . G peaks at 1600 cm^{-1} characterize lattice distortions. A shift in the D band indicates a change that can occur due to certain defects, such as vacancies, grain boundaries [27] and amorphous forms of carbon [28]. The intensity ratio I_D/I_G was $0.9 / 1$. The study [29] demonstrated that an increase in the I_D/I_G ratio of graphene oxide indicates an increase in the number of defects in the structure. The lowest ratio $I_D/I_G = 0.85$ was observed for ZGP 7 sample, which indicates the quality of this sample.

Graphene, a two-dimensional planar monolayer of carbon, whose atoms are connected in a honeycomb lattice structure, possesses such electronic properties as a zero band gap and high conductivity, which in combination with photocatalytically active ZnO should help to reduce the recombination of photogenerated electron-hole pairs and lead to an increase in the efficiency of photoconversion. Thus, graphene oxide in ZnO / GO composites acts as a fast electron transfer channel. In addition, the presence of oxygen-containing functional groups of graphene oxide makes it an excellent support material for anchoring metal oxide particles during synthesis. Figure 5 illustrates a diagram of a possible illustration of the degradation process of the RhB dye under the influence of ultraviolet radiation in the presence of ZnO / GO samples.

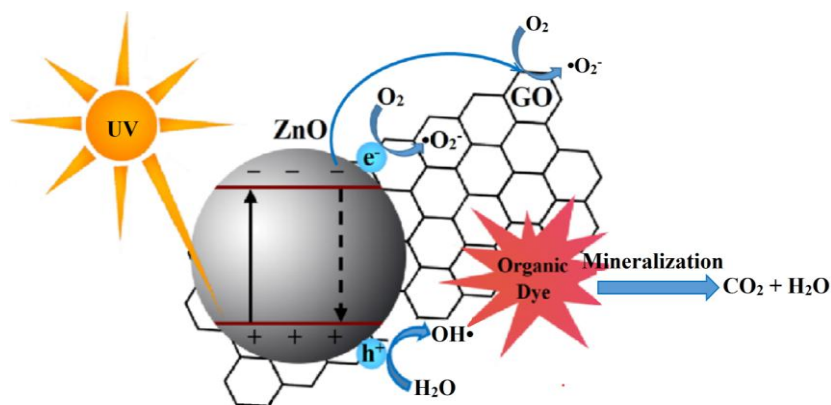


Figure 5. Possible charge transfer circuit in the ZnO / GO samples

Under the influence of UV radiation, electrons e^- move from the upper levels of the valence band (VB) of semiconductor materials to the conduction band (CB). These photogenerated electrons are absorbed by oxygen O_2 , resulting in the superoxide anion O_2^- . At the same time, as a result of protonation, $HOO^\bullet$ radicals are obtained. Holes h^+ , located in the valence band, move to the surface of ZnO and GO, and interact with either water (H_2O) or OH^- , which leads to the production of such active hydroxyl substances as $OH^\bullet$, which, together with $HOO^\bullet$ radicals, decompose the dye into components. Thus, the process of photogeneration of e^- - h^+ electron-hole pairs on the surface of ZnO / GO composites with a large specific surface area leads to degradation of the rhodamine B (RhB) dye.

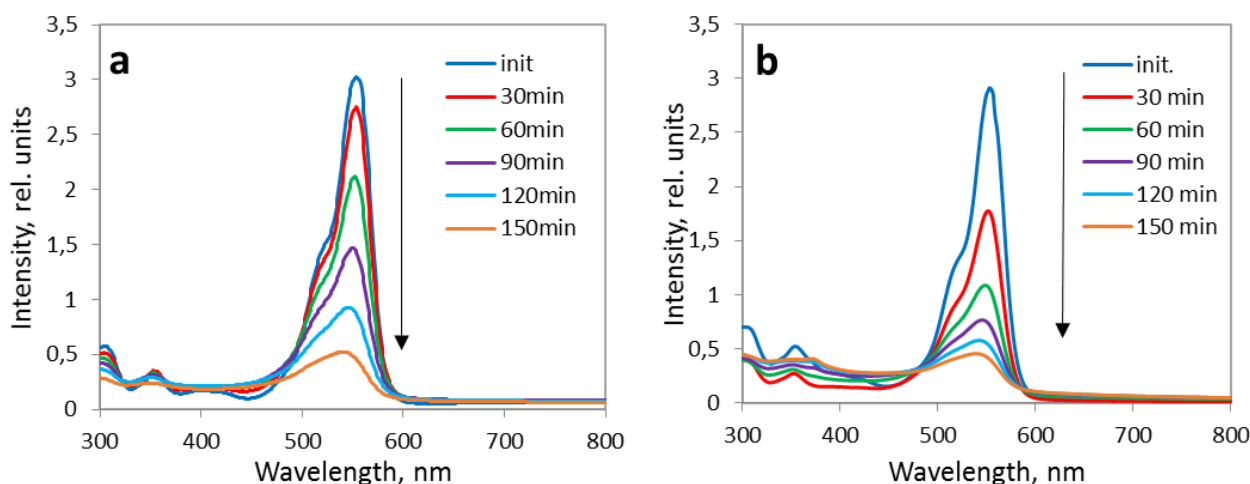
To study the photocatalytic activity of the synthesized ZnO / GO composites, we used an aqueous solution of rhodamine B, containing 8 ml of the dye dissolved in 500 ml of distilled water on a magnetic stirrer for 30 minutes. Then, 9 mg of the obtained ZnO / GO composites were added to 112.5 ml of the solution, followed by thorough mixing. The measurement of photocatalytic degradation was carried out in a glass reactor. The source of UV illumination was a mercury lamp (LIH Germany, power 14 W), which was located inside the reactor with the solution.

The photocatalytic activity of the synthesized ZnO / GO composites was evaluated by observing the change in the optical density spectra of the RhB dye solution in the presence of ZnO / GO samples exposed to UV radiation for 150 minutes. The solution was sampled every 30 minutes (Figure 6).



Figure 6. Photo of the RhB solution in the presence of the ZGP 7 sample subjected to UV illumination

Figure 7 represents optical density spectra during the degradation of an aqueous solution of a dye in the presence of ZnO / GO composites under ultraviolet illumination. The results showed that the maximum value of the absorption intensity for the initial dye solution with ZnO / GO composites is at 555 nm. It is noted that, with an increase in the UV exposure time, the absorption intensity of rhodamine B in the presence of ZnO / GO samples decreases, which indicates a decrease in the concentration of RhB in the solution.



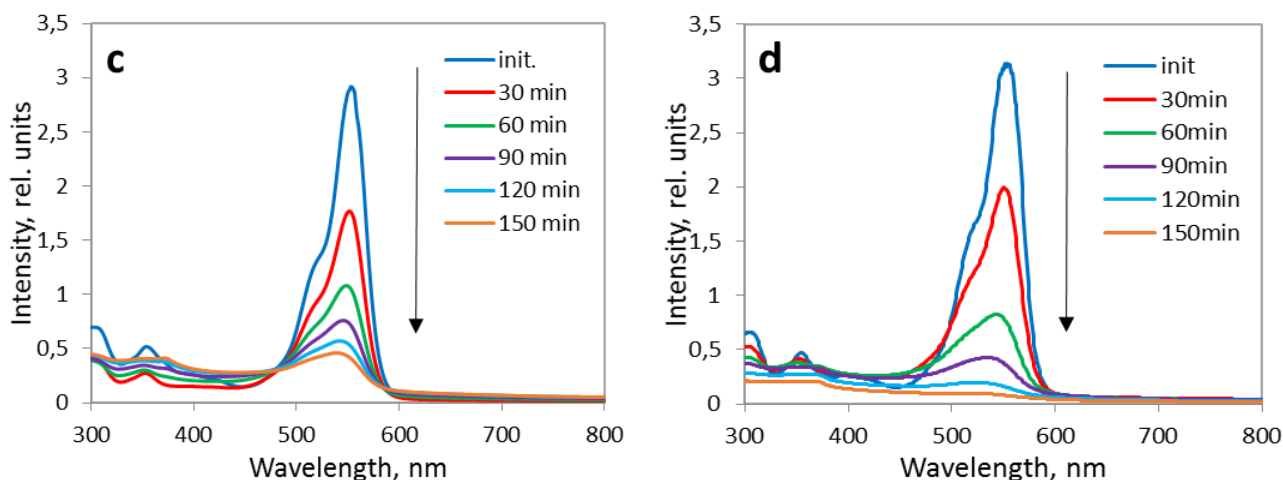


Figure 7. Optical density spectra of an aqueous solution of RhB in the presence of samples: a – ZGP 2, b – ZGP 4, c – ZGP 5, d – ZGP 7.

To compare the photocatalytic activity of ZnO / GO powders with different GO concentration in the growth solution under degradation of an aqueous dye solution, kinetic curves were presented in Figure 8.

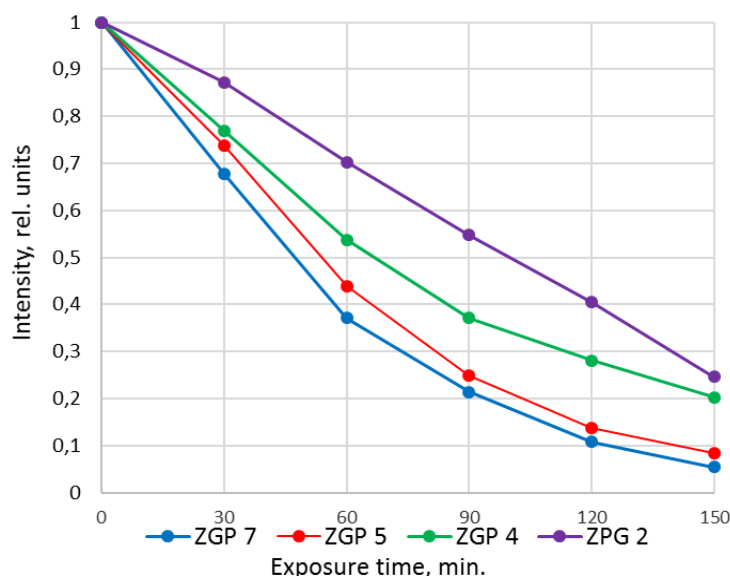


Figure 8. Kinetic curves of RhB degradation in the presence of ZnO / GO composites with different concentrations of GO: ZGP 2 – 0.01 wt% GO, ZGP 4 – 0.025 wt% GO, ZGP 5 – 0.14 wt% GO, ZGP 7 – 0.7 wt% GO.

It was noted that an increase in the concentration of GO in the growth solution makes it possible to obtain more photocatalytically active composites ZnO-GO because an increase in the GO concentration in the growth solution provides an increase in the specific surface area of the composites. Moreover, this increase promotes a decrease in the recombination of photogenerated electrons, which leads to an increase in active $\text{HOO}\cdot$ radicals in solution under UV radiation and accelerates the decomposition of the organic dye.

For ZnO / GO samples with different GO concentrations, photoluminescence spectra were investigated (Figure 9). Data on the photoluminescent properties of photocatalytically active zinc oxide were published in a paper [30]. The PL spectra of all the samples consisted of a narrow (~ 0.25 eV) NBE at ~ 380 nm, and broad deep-level emission (DLE) in the range from 450 to 750 nm with a maximum of around 555 nm. It is suggested that the origin of the violet emission at $\lambda \sim 420$ nm (2.96 eV) is due to the transitions from the conduction band (CB) to the holes localized at the defect level associated with zinc vacancy (VZn) [31].

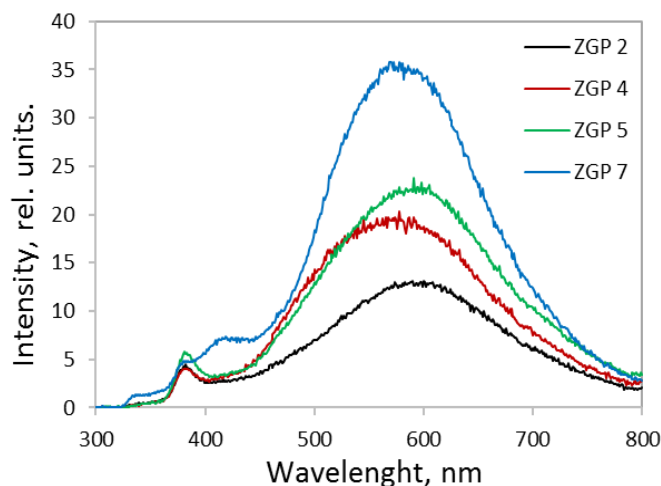


Figure 9. Photoluminescence of ZnO / GO samples with different GO concentration: ZGP 2 – 0.01 wt% GO, ZGP 4 – 0.025 wt% GO, ZGP 5 – 0.14 wt% GO, ZGP 7 – 0.7 wt% GO.

As can be seen from Figure 9, the highest DLE photoluminescence is observed for the ZGP 7 sample, which contains the largest amount of graphene oxide in the growth solution (0.7 wt % GO). It is noted that a decrease in the GO concentration leads to a decrease in the DLE photoluminescence.

Conclusions

Low-cost synthesis of ZnO / GO nanocomposites by chemical deposition from the solution was developed. The photocatalytic activity, morphology, structural and photoluminescent properties of the synthesized samples were studied. The results of electron microscopy studies have shown that the obtained composites consist of 2D petals about 30 nm thick. At the same time, an increase in the concentration of GO in the growth solution of ZnO / GO does not significantly change their morphology. A study of the structural properties of the synthesized ZnO / GO composites showed that the Raman spectra contain D peaks at displacement of the 1370 cm^{-1} , and G peaks at 1600 cm^{-1} . The intensity ratio I_D / I_G was 0.9 / 1. The smallest ratio $I_D / I_G = 0.85$ for the ZGP 7 sample, which contains the largest amount of graphene oxide in the growth solution (0.7 wt% GO), indicates the quality of this sample. It is noted that the highest DLE photoluminescence is observed for the ZGP 7 sample. In addition, an increase in the GO concentration leads to an increase in DLE photoluminescence. When studying the photocatalytic activity of the obtained samples regarding the decomposition of the dye rhodamine B (RhB), it was noted that an increase in the concentration of GO in the growth solution makes it possible to obtain more photocatalytically active composites ZnO-GO.

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Мырыш оксиді–графен оксиді композиттердің фотокаталитикалық белсенділігі

Соңғы кездері целлюлоза, тоқыма, пластмасса және резеңке өнеркәсібінде әр түрлі бояғыштарды қолдану ағынды сулардың улы заттармен және бояғыштармен қатты ластануына әкелді. Бұл улы бояғыштар күн сәулесін бөгең, фотосинтезді азайтып, қоршаған ортаға зиянды әсер етеді. Сондықтан ағынды суларды зиянды органикалық ластаушы заттардан тазартудың аз шығынды тиімді технологиясын тез арада әзірлеу қажет. Осы тұрғыда фотокатализ ағынды суларды тазартуға арналған жетілдірілген, экологиялық таза тотығу процесі болып табылады. Соңғы зерттеулер көрсеткендей, кең шектеу аймағы бар жартылай өткізгішті фотокаталитикалық белсенді материалдарды қолдану сулы ерітінділердегі органикалық ластаушы заттардың ыдырауының тиімді әдісі болып табылады. Осы мақалада композициялық жартылай өткізгіш материалдарды сулы ерітіндіден химиялық тұндыру арқылы мырыш оксиді/графен оксидін (ZnO/GO) синтездеудің арзан әдісі әзірленген. Графен оксидінің әр түрлі концентрациясы бар синтезделген ZnO/GO үлгілерінің морфологиясы, құрылымдық және фотолуминесценттік қасиеттері зерттелді. Синтезделген композициялық материалдардың фотокаталитикалық белсенділігін зерттеу ультракүлгін сәулелену кезінде родамин Б бояғышының сулы ерітіндісінің ыдырауын бақылау арқылы жүзеге асырылды.

Кілт сөздер: химиялық тұндыру, мырыш оксиді, графен оксиді, композиттер, оптикалық және құрылымдық қасиеттері, фотокаталитикалық белсенділік, родамин Б.

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Фотокаталитическая активность композитов оксида цинка–оксида графена

В последнее время использование различных красителей в целлюлозной, текстильной, пластмассовой и резиновой промышленности привело к сильному загрязнению сточных вод токсичными веществами и красителями. Эти токсичные красители не поддаются биологическому разложению и оказывают пагубное воздействие на окружающую среду, блокируя солнечный свет и снижая фотосинтез. Следовательно, существует острая необходимость в разработке малозатратной эффективной технологии очистки сточных вод от вредных органических загрязнителей. В этом контексте фотокатализ является передовым, экологически безопасным процессом окисления для очистки сточных вод. Недавние исследования показали, что применение полупроводниковых фотокаталитически активных материалов с широкой запрещенной зоной является эффективным методом разложения органических загрязнителей в водных растворах. В настоящей статье разработана малозатратная технология синтеза композиционных полупроводниковых материалов оксид цинка/оксид графена (ZnO/GO) методом химического осаждения из водного раствора. Исследованы морфология, структурные и фотолуминесцентные свойства синтезированных образцов ZnO/GO с различной концентрацией оксида графена. Исследование фотокаталитической активности синтезированных композиционных материалов оксид цинка–оксид графена проводили путем наблюдения за деградацией водного раствора красителя родамин Б при ультрафиолетовом освещении.

Ключевые слова: химическое осаждение, оксид цинка, оксид графена, композиты, оптические и структурные свойства, фотокаталитическая активность, родамин Б.

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Longitudinal magnetoresistance of uniaxially deformed n-type silicon

The study of Galvano-magnetic effects (as well as tenseffects) in silicon under extreme conditions allows not only to identify the mechanisms of these effects but also to identify the possibility of creating gaussmeters, infrared detectors, sensitive strain gauges, amplifiers and generators of a wide frequency range. The reliability of the mechanism of negative magnetoresistance was verified using uniaxial elastic deformation of the studied crystals. Uniaxial deformation excludes interline transitions of electrons, as a result of which negative magnetoresistance disappears with an increase in uniaxial pressure. When cubic symmetry is violated, anisotropic phenomena occur in such crystals. The multipath of the isoenergetic surface of the bottom of the silicon conduction band causes anisotropies of the effective mass and relaxation time, which are associated with the features of the transfer phenomenon. In particular, magnetoresistance (piezoresistance), which is the most sensitive to the anisotropy of the iso energy surface. The influence of the latter on magnetoresistance is most clearly revealed in the region of strong magnetic fields, where the magnetoresistance is saturated since the longitudinal magnetoresistance is entirely due to the anisotropy of electron mobility.

Keywords: galvano-magnetic effects, piezoresistance, negative magnetoresistance, uniaxial pressure, isoenergetic, multivalley model, valley crossing, silicon magnetoresistance.

Introduction

The longitudinal magnetoresistance of n-type silicon on crystals is investigated $d = n_e = 3,1 \cdot 10^{12} \text{ cm}^{-2}$ in the temperature range 77–300K and the observed negative magnetoresistance due to interband transitions of electrons in $J \parallel H \parallel [110]$.

The reliability of the mechanism of negative magnetoresistance was verified using uniaxial elastic deformation of the studied crystals.

Uniaxial deformation excludes interline transitions of electrons, as a result of which negative magnetoresistance disappears with an increase in uniaxial pressure.

According to the classical theory, the magnetoresistance should be saturated in strong magnetic fields when $\mu H \gg 1$, where (μ – electron mobility, H – magnetic field strength). To test this theory, we investigated the longitudinal magnetoresistance of n-type silicon in the case of $J \parallel H \parallel [110]$.

The isoenergetic surface of the bottom of the silicon conduction band consists of six ellipsoids of rotation (energy minima) located along the axis of type $[100]$ at a distance of $k = 0,85k_{\text{max}}$ (k_{max} is the value of the wave vector corresponding to the boundary of the Brillouin zone) from the center of the Brillouin zone. These energy minima in silicon crystals at six equivalent points are sometimes called valleys [1].

The energy in the vicinity of the extreme point is related to the wave vector by the following relation:

$$\varepsilon = \frac{\hbar^2}{2} \left\{ \frac{(k_x + k_{ox})^2}{m_{\parallel}} + \frac{(k_y - k_{oy})^2}{m_{\perp}} + \frac{(k_z - k_{oz})^2}{m_{\perp}} \right\}$$

where $m_{\parallel}, m_{\perp}$ – longitudinal and transverse effective masses of electrons, k_{ox}, k_{oy}, k_{oz} – coordinates of the center of the ellipsoid, $T = 77,4\text{K} : m_{\parallel} = 0,911m_0, m_{\perp} = 0,191m_0$ m_0 – free electron mass, and the

attitude $\frac{m_{\parallel}}{m_{\perp}} = 4,72$ characterizes the anisotropy of isoenergetic surfaces. Thus, in silicon, the total electric current comprises currents caused by carriers located in different valleys and, consequently, the total conductivity of the crystal is the sum of the conductivities of individual valleys.

If there are no external influences that violate the cubic symmetry of the crystal (for example, uniaxial deformation, heating electric field, quantizing magnetic field), then the electrons are evenly distributed across the valleys. In this case, the total conductivity of the crystal is an isotropic value, despite the anisotropic nature of the conductivity of each valley separately.

Experimental and Results and Discussion

The saturation of the longitudinal magnetoresistance of silicon in a classically strong magnetic field ($\mu H \gg 1$), in the case of $J \parallel H \parallel [110]$ is determined by the formula [2].

$$\left[\frac{\rho_H}{\rho_0} \right]_{sat} = \frac{(2k+1)(k+1)}{k(k+5)} \quad (1)$$

where ρ_H – resistivity silicon crystal in a magnetic field, ρ_0 – specific resistance of the crystal in the absence of magnetic field, $k = \frac{m_{\parallel} \prec \tau_{\parallel} \succ}{m_{\perp} \prec \tau_{\perp} \succ}$ is the parameter of anisotropy ($\tau_{\parallel}, \tau_{\perp}$ – longitudinal and transverse relaxation time, respectively).

Taking $k=4.72$, we make numerical estimates of magneto resistance

$$\left[\frac{\Delta \rho_H}{\rho_0} \right]_{sat} = 1,315$$

which gives a good agreement with the experimental values in the temperature range of 150–300 K obtained on a sample with a concentration of current carriers $n_e = 4,1 \cdot 10^{12} \text{ cm}^{-3}$.

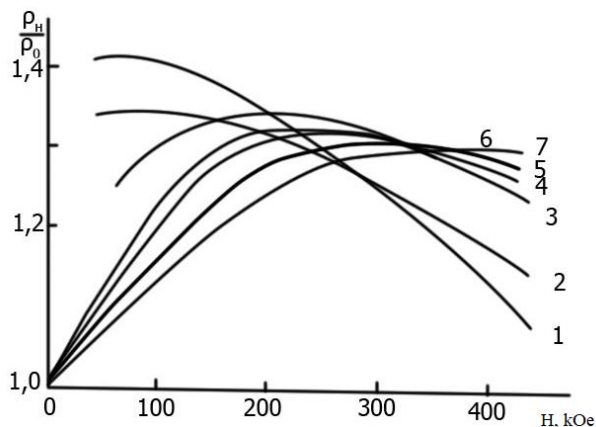


Figure 1. Temperature dependence of the longitudinal magnetoresistance of n-type silicon for a sample with $\rho_{300K} = 150 \text{ Ohm} \cdot \text{cm}$ $\text{ЛПН} [110] T^0 \text{ K}$ 1 – 77, 2 – 102, 3 – 150, 4 – 204, 5 – 240, 6 – 270, 7 – 300

$$\left[\frac{\rho_H}{\rho_0} \right]_{sat} = 1,31$$

This indicates that in this temperature range $k_{\tau} = \frac{\prec \tau_{\perp} \succ}{\prec \tau_{\parallel} \succ} = 1$ the interline scattering mechanism dominates.

However, with a decrease in temperature, the discrepancy between the experimental results and the calculated ones increases, so, for example, for $T = 77,4\text{K}$, it reaches

$$\left| \frac{\rho_H}{\rho_0} \right|_{sat} = 1,4.$$

This is due to the contribution of the anisotropy of the scattering mechanism (in this case, acoustic phonons, for which $k_r = 0,76$) [3].

As can be seen from Fig. 1, in strong magnetic fields, in addition to saturation of magnetoresistance, the manifestation of quantum effects is also observed. The latter, in turn, are associated with a number of features, in particular, the redistribution of electrons between valleys having effective electron masses of $0,26m_0$ and $0,422m_0$ respectively, leading to the appearance of negative magnetoresistance. This phenomenon was first experimentally observed in [3] in Germany when studying the longitudinal magnetoresistance at 20, 4 K, and its theoretical interpretation was given in the work [4].

We observed this effect on n-type silicon when studying both longitudinal and transverse magnetoresistance (at 77.4 K) in the following cases $H \parallel [001]$, $H \parallel [110]$, which is caused by the redistribution of electrons between valleys, that is, interline transitions of electrons.

Fig.1 (Curves 1 and 2) shows that the magnetoresistance after saturation has a decline area, which is associated with a multi-valley model of the isoenergetic surface of the silicon conduction band, and it can be easily understood from the following.

In the quantum limit, due to the nonequivalence of different valleys relative to the magnetic field, their bottoms in the magnetic field rise differently due to the different effective mass in these valleys and the migration of electrons from the upper valley to the lower ones begins, as a result of which the conductivity increases, that is, the resistance decreases and a decrease in the magnetoresistance curves is observed.

The complete migration of electrons from the upper valley to the lower ones is carried out only in the ultra-quantum region (when $\hbar\omega_H \leq 3k_B T$),

where $\hbar$ – is the Planck constant of division by 2π , $\omega_H = \frac{e \cdot H}{m \cdot c}$, e – is the electron charge, H – is the magnetic field strength, m is the effective mass of the electron, c – is the speed of light, k_B – is the Boltzmann constant, T – is the absolute temperature) only a part of the electrons moves.

Electron migration between valleys at $H=400$ kOe reaches

$$\frac{n_i}{n_j} = 0,51.$$

Thus, the results of the experiment in n-type silicon clearly demonstrate the reliability of the mechanism of negative magnetoresistance caused by the actual pumping of current carriers between the valleys of the conduction band, shifting along the energy scale in a quantizing magnetic field at different “speeds”.

Note that with the help of uniaxial elastic deformation, the energy gap between the valleys can be changed to a wider range than is achieved in quantizing magnetic fields and thereby verify the validity of this interpretation of the observed negative magnetoresistance of n-type silicon at orientation $J \parallel H \parallel [110]$.

The results of such experiments are shown in Figure 2. The data obtained on a uniaxially deformed n-type silicon crystal proves that the decline in magnetoresistance (Fig.2, curve 1) is due to the interline transition of electrons, which gradually disappears with an increase in mechanical stress (Fig.2, curves 4,6). In this case, the magnetoresistance is doubled in magnitude and the negative part of the curve disappears completely. A low-amplitude magnetic resonance is observed on these crystals.

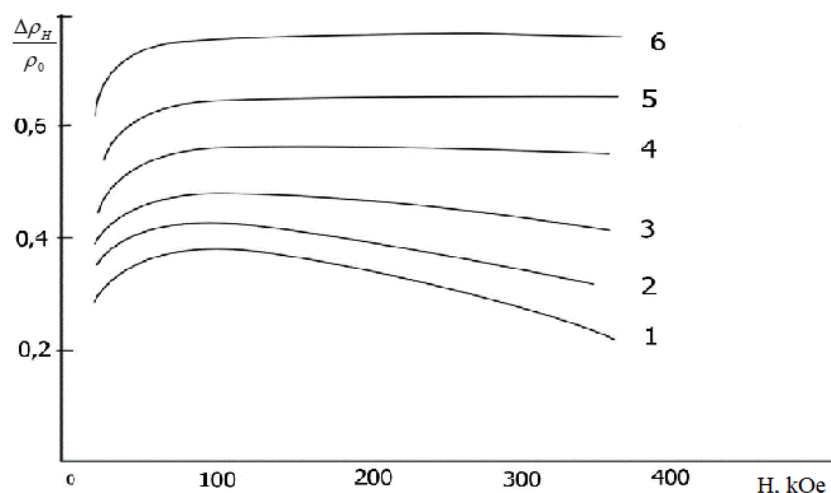


Fig.2 Effect of uniaxial pressure X on the negative part of the magnetoresistance of n-type silicon at $X \parallel J \parallel H \parallel [110]$ ($n_e = 4,1 \cdot 10^{13} \text{ sm}^{-3}$, $T = 77,4 \text{ K}$); $X \cdot 10^{-3} \frac{\text{Pa}}{\text{sm}^2}$: 1 – $X = 0$; 2 – 1; 3 – 2; 4 – 3; 5 – 4; 6 – 5

Conclusions

The increase in the magnetoresistance of silicon with uniaxial pressure is explained as follows. The saturation of the longitudinal piezoelectric resistance of n-type silicon in the case of $XJ \parallel [110]$ is determined by the formula derived by one of the authors [5–7]:

$$\left[\frac{\rho_X}{\rho_0} \right]_{\text{sat}} = \frac{2(2k+1)}{3(k+1)} \quad (2)$$

Using this formula, $\left[\frac{\rho_X}{\rho_0} \right]_{\text{sat}} = 1,35$ was calculated, which is in good agreement with the experimental value of magnetoresistance $\left[\frac{\rho_X}{\rho_0} \right]_{\text{sat}} = 1,354$ (Figure 2, curve 1)

Combining the ratio (1) and (2), we obtain an expression that allows us to calculate the longitudinal magnetoresistance in saturation by the magnetic field according to the measurement data of the longitudinal piezoresistance at strong single-bearing deformations [8, 9]:

$$\frac{\rho_{H \rightarrow \infty}}{\rho_{X \rightarrow \infty}} = \frac{3(k+1)^2(k+2)}{2k(2k+1)(k+5)} \quad (3)$$

The calculated value according to the formula (3) $\frac{\rho_{H \rightarrow \infty}}{\rho_{X \rightarrow \infty}} = 0,73$, which gives a good agreement with the experimental value – 0.732, shown in Fig.2 (curve 5,6). This proves the increase in magnetoresistance with uniaxial pressure.

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Деформацияланған бір осьті п-типте кремнийдің бойлық магниттік кедергісі

Төтенше жағдайларда кремнийдегі гальваномагниттік әсерлерді (сонымен қатар тензоәсерлерді) зерттеу бұл әсерлердің механизмдерін анықтап қана қоймай, гауссметрлерді, инфрақызыл детекторларды, сезімтал тензобергішті, күшейткіштерді және кең жиілік диапазонының генераторларын құруға мүмкіндік береді. Теріс магниттік кедергі механизмінің беріктілігі зерттелетін кристалдардың бір осьті серпінді деформациясы арқылы тексерілді. Бір осьті деформация электрондардың аңғарарлық ауысуын болдырмайды, нәтижесінде теріс магниттік кедергісі бір осьті қысымның жоғарылауымен жойылады. Мұндай кристалдардың кубтық симметриясы бұзылған жағдайда анизотропия құбылыстар пайда болады. Кремнийдің өткізгіштік зонасынан изоэнергиялық беттің көп аңғарлы сипаты тиімді массасы мен релаксация уақытының анизотропиясын анықтайды, бұл тасымалдау құбылысының ерекшеліктерімен байланысты. Атап айтқанда, магниттік кедергі (пъезокедергі) изоэнергетикалық беттің анизотропиясына ең сезімтал болып табылады. Соңғысының магниттік кедергіге әсері магниттік кедергі қаныққан күшті магниттік өрістер аймағында айқын көрінеді, өйткені бойлық магниттік кедергісі толығымен электрон қозғалтқышының анизотропиясына байланысты.

Кілт сөздер: гальваномагниттік эффекттер, пьезокедергісі, теріс магниттік кедергісі, бір осьті қысым, изоэнергетикалық аймақаралық өтулер, аймақтық қиылысулар, кремнийлі магниттік кедергі.

О.Д. Бигожа, А.Ж. Сейтмуратов, Л.У. Таймуратова, Б.К. Казбекова, З.К. Аймаганбетова

Продольное магнитосопротивление одноосно-деформированного кремния n-типа

Изучение гальваномагнитных эффектов (а также тензоэффектов) в кремнии в экстремальных условиях позволяет не только выявить механизмы этих эффектов, но и возможность создания гауссметров, инфракрасных детекторов, чувствительных тензодатчиков, усилителей и генераторов широкого частотного диапазона. Надежность механизма отрицательного магнетосопротивления проверена с помощью одноосного упругого деформирования исследуемых кристаллов. Одноосная деформация исключает междолинные переходы электронов, вследствие чего исчезает отрицательное магнетосопротивление с увеличением одноосного давления. При нарушении кубической симметрии в таких кристаллах возникают анизотропные явления. Многодолинность изоэнергетической поверхности дна зоны проводимости кремния обуславливает анизотропии эффективной массы и времени релаксации, с которой связаны особенности явления переноса. В частности, магнетосопротивление (пьезосопротивление), которое является наиболее чувствительным к анизотропии изоэнергетической поверхности. Влияние последней на магнетосопротивление наиболее отчетливо выявляется в области сильных магнитных полей, где магнетосопротивление насыщается, так как продольное магнетосопротивление всецело обусловлено анизотропией подвижности электронов.

Ключевые слова: гальваномагнитные эффекты, пьезосопротивление, отрицательное магнитосопротивления, одноосное давление, изоэнергетические междолинные переходы, пересечение долины, кремниевое магнитосопротивление.

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Influence of the environment on the morphology, optical and electrical characteristics of the PEDOT:PSS polymer

The paper presents the results of studying the influence of the environment on the surface structure, optical and electrical characteristics of the PEDOT:PSS film. The studies have been carried out in three different types of atmosphere under the same conditions of thermal annealing of the films. It has been established that the modification of the surface of a polymer film with ethanol and isopropanol in vacuum, in a nitrogen atmosphere, and in the air atmosphere leads to a change in the surface morphology and the optical electric transport properties of the polymer. Depending on the environment, when the PEDOT:PSS film is modified with a certain concentration of ethyl and isopropyl alcohols, the absorption spectra show a shift in the absorption maximum responsible for PEDOT to the short-wavelength region of the spectrum, as well as a decrease in the absorption peak of the part of the spectrum responsible for the absorption of the aromatic fragment PSS. It is identified that the structural features of the PEDOT:PSS surface morphology affect the electrical transport parameters of the films: R_h is the resistance of the PEDOT:PSS polymer film, R_{ext} is the charge carrier transfer resistance at the PEDOT:PSS/electrode interface, k_{eff} is the effective charge carrier extraction rate and τ_{eff} is the effective transit time of charge carriers. The optimal technological parameters for film production have been determined, at which the electrical transport properties of PEDOT:PSS polymer films are increased.

Keywords: PEDOT:PSS, isopropanol, ethanol, vacuum, nitrogen atmosphere, air atmosphere, surface morphology, optical spectroscopy, impedance spectroscopy.

Introduction

Currently, global manufacturers of electronic devices and components for solar energy pay special attention to elements based on organic semiconductor materials (OPV) [1–3]. The photoelectric characteristics of OPV devices are strongly influenced by the structural features and surface morphology of the organic material of the films they are made of [4, 5].

The most common organic semiconductor polymer used PEDOT:PSS as a hole transport layer (HTL) in OPV devices [6]. The electrical transport properties of PEDOT:PSS directly depend on the surface morphology, which, in turn, depends on the type of dopants, solvents, annealing temperature, and environment. Alcohols are suitable and effective additives in PEDOT:PSS due to their low cost, non-toxicity, and good polymer solubility in it [7, 8]. The addition of alcohol solvents to the PEDOT:PSS polymer leads to a significant increase in conductivity [9, 10]. In addition, due to low boiling points, alcohols are easily removed during heat treatment, and alcohol-treated PEDOT:PSS films are smooth, which makes them well-suited for use as an HTL layer in organic photoconverters [11].

It should be noted that the heat treatment of PEDOT:PSS films leads to an increase in the crystallinity of the polymer and a change in the surface morphology [12–16]. At the same time, the combined influence of the environment and annealing of PEDOT:PSS films on the surface structure, optical and electrical characteristics of the PEDOT:PSS film have not been practically studied [17–20].

In this regard, in this paper, we carried out studies on the influence of the environment on the structural, optical, and electrical transport parameters of the films. To change the surface morphology, PEDOT:PSS films were obtained in a vacuum, nitrogen, and air atmosphere, with the addition of a certain concentration of alcohols. The obtained results were analyzed by comparing the surface morphology, optical and impedance spectra of PEDOT:PSS films.

Experimental

Films were obtained in three different environments: in vacuum, in nitrogen and air atmosphere. To change the surface morphology, the polymer with hole conductivity PEDOT:PSS was extended with a certain concentration of alcohol (ethyl, isopropyl) and placed in the test environment. A comparative analysis of the modified PEDOT:PSS film was carried out by comparing the structure of the surface morphology, optical and electrical transport properties, depending on the preparation environment.

Figure 1 shows the structural formulas of the compounds. The preparation of the substrates was carried out according to the procedure [21]. We used PEDOT:PSS (1%, Ossila A14083), Isopropanol, Ethanol (pure 99.9% Sigma Aldrich). Before starting the experiments, the PEDOT:PSS solution was filtered through a 0.45-micrometer filter. PEDOT:PSS films were obtained on the surface of quartz glass by centrifugation (on a SPIN150i centrifuge manufactured by Semiconductor Production System) at a rotation speed of 5000 rpm. The choice of the concentration of alcohol solvents was determined based on the studies of the authors [22]. They proved that the optimal proportion of alcohol in the polymer is 50% by weight.

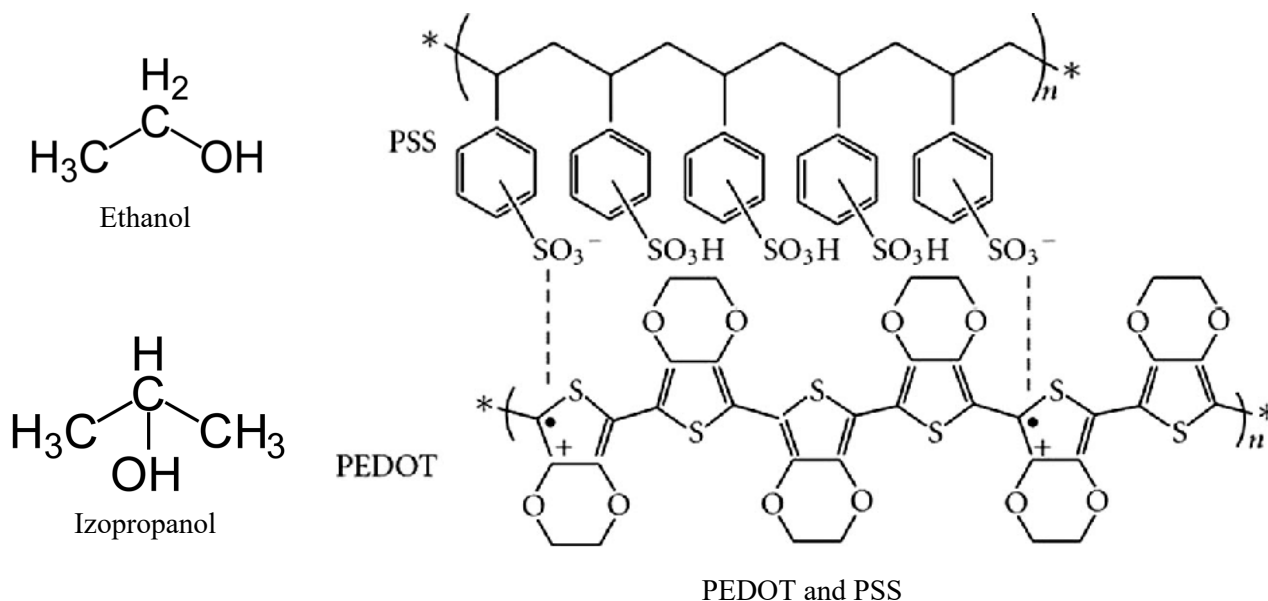


Figure 1. Chemical structure of Ethanol, Isopropanol, PEDOT and PSS

For experiments in a vacuum, the samples were placed in a vacuum furnace (YHCHEM, Shanghai Yuanhuai Industrial Co.) and annealed at 120°C for 10 minutes. For experiments in a nitrogen atmosphere, the samples were deposited and annealed at 120°C for 10 minutes in a specialized two-chamber inert atmosphere glove box (CY-VGB-6-II-LD, Shanghai Yuanhuai Industrial Co.). To carry out experiments in air, the samples were deposited at room temperature and annealed at 120°C for 10 minutes.

The surface topography of the samples was studied using an atomic force microscope (AFM) JSPM-5400 (JEOL, Japan). The AFM images were processed using a special modular program for analyzing scanning probe microscopy data (Win SPMII Data-Processing Software). Surface morphology, roughness of PEDOT:PSS thin films were analyzed from AFM images. The images of the surface of the PEDOT:PSS films were obtained in the mode of the semi-contact scanning method. The absorption spectra of the studied samples in the range of 200–1100 nm were recorded on an AvaSpec-ULS2048CL-EVO spectrometer (Avantes). The impedance spectra were measured using a P-45X potentiostat (Elins) with an additionally installed FRA-24M frequency analyzer module. Fitting and analysis of the spectrum parameters were carried out using the EIS-analyzer software package, according to the procedure [23].

Results and Discussion

Figure 2 illustrates images of the surface morphology of PEDOT:PSS films in a vacuum with different ratios of ethyl and isopropyl alcohols. Table 1 shows the roughness values of PEDOT:PSS films. Figure 2 shows that the PEDOT:PSS film without the addition of alcohols after thermal annealing has a rather

pronounced relief. At the same time, the surface morphology has a pronounced heterogeneity; the surface roughness is 0.64 nm.

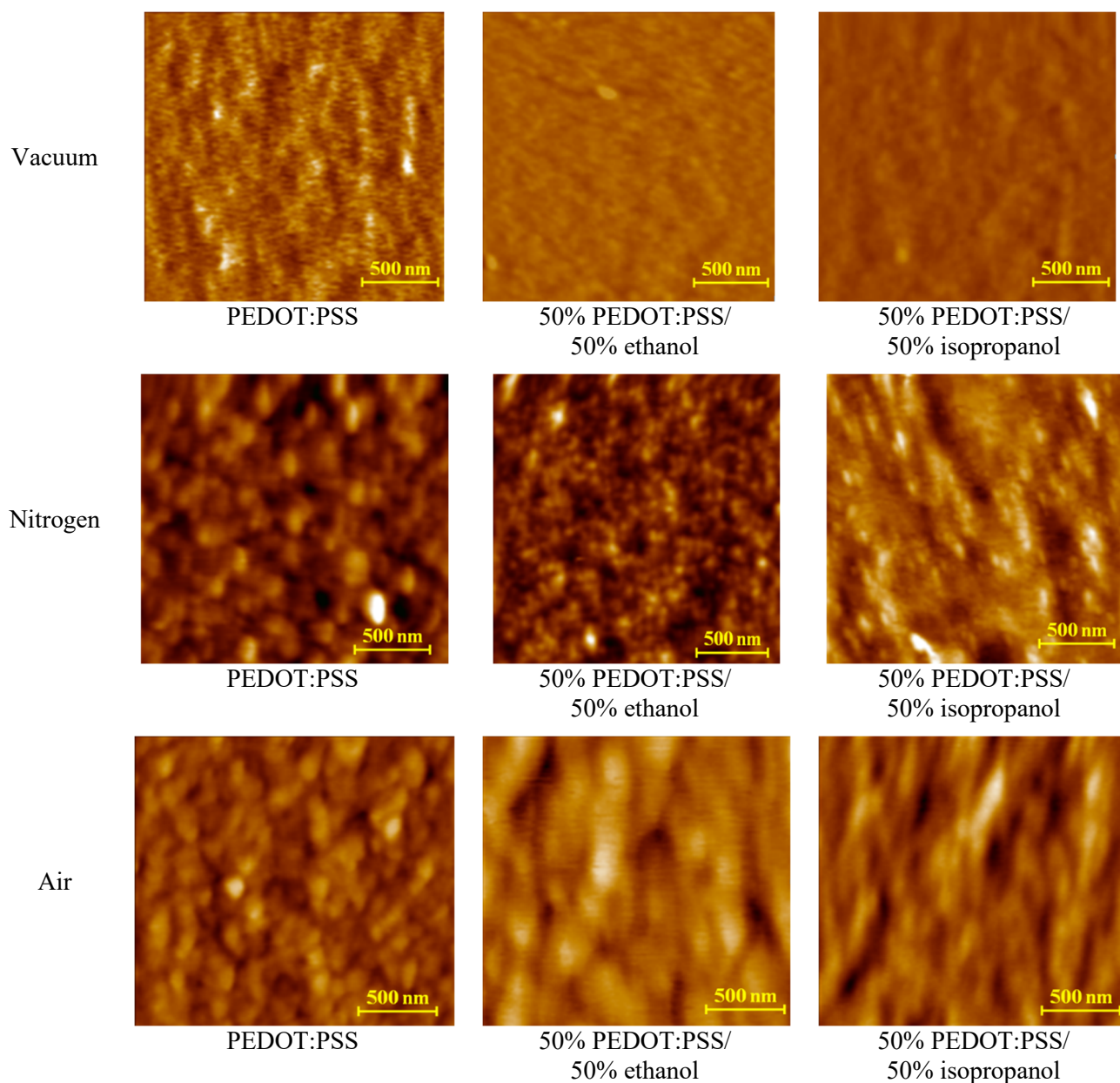


Figure 2. Surface morphology images of PEDOT:PSS films

In PEDOT:PSS film prepared in 50/50 ethyl alcohol, the surface roughness of PEDOT:PSS film is reduced to 0.45 nm. The addition of 50/50 isopropyl alcohol to the PEDOT:PSS film resulted in smoothing of the film surface with a roughness of 0.43 nm. Comparative analysis of changes in surface roughness showed that in the process of film preparation with the addition of ethyl alcohol, the surface roughness decreases by 1.4 times, and isopropyl alcohol – by 1.5 times.

Figure 2 also demonstrates images of the surface morphology of PEDOT:PSS films prepared in a nitrogen atmosphere after exposure to ethyl and isopropyl alcohol vapors in a ratio of 50/50%. The PEDOT:PSS film has an inhomogeneous surface structure with a roughness of 0.65 nm (Table 1).

When the PEDOT:PSS polymer film is kept in ethanol vapor in an inert atmosphere, the surface is smoothed. The film roughness decreased and amounted to 0.58 nm (Table 1). When keeping the film in vapors of isopropyl alcohol, the roughness of the PEDOT:PSS film was 0.43 nm. Thus, the obtained results indicate that the smallest film surface roughness is obtained upon annealing in isopropanol vapor.

To study the effect of the air atmosphere on the polymer surface morphology, the film was kept in vapors with a certain concentration of ethyl and isopropyl alcohols. It can be seen from Figure 2 that the PEDOT:PSS film has a grain structure. At the same time, against the background of a fine grain structure, large particles are observed; the surface roughness is 0.63 nm (Table 1).

After treatment with alcohol vapors for 10 minutes, the proportion of large particles decreases significantly, the roughness becomes 0.48 nm for ethyl alcohol and 0.45 nm for isopropyl alcohol. The addition of alcohol solvents to the film causes a smoothing of the film surface.

Table 1

Surface roughness of PEDOT:PSS films at different concentrations of alcohols in the volume during annealing in vacuum, nitrogen and air atmosphere

Sample	R _a , nm
Vacuum	
PEDOT:PSS	0.64
50% PEDOT:PSS/50% ethanol	0.45
50% PEDOT:PSS/50% isopropanol	0.43
Nitrogen	
PEDOT:PSS	0.65
50% PEDOT:PSS/50% ethanol	0.58
50% PEDOT:PSS/50% isopropanol	0.43
Air	
PEDOT:PSS	0.63
50% PEDOT:PSS/50% ethanol	0.48
50% PEDOT:PSS/50% isopropanol	0.45

Figure 3a shows the absorption spectra of PEDOT:PSS films prepared in a vacuum, annealed at $T=120^{\circ}\text{C}$ with 50% ethanol and isopropyl alcohol. It can be noted that the original PEDOT:PSS film has a maximum at a wavelength of $\lambda_1 = 216$ nm with a spectral half-width of 10.2 nm (Table 2). In the absorption spectra of all films, a shoulder λ_2 is observed with a maximum at 224 nm (Fig. 3a). The absorption bands with a maximum at 224 nm are associated with the absorption of the polymer PSS – poly(styrenesulfonate) [24].

When ethyl alcohol is added to the film during preparation, the positions of the maxima in the absorption spectra do not change, only a decrease in the optical density and a decrease in the half-width of the spectrum are observed. The value of the maximum at a wavelength of 216 nm decreased by 1.2 times, and at a wavelength of 224 nm – by 1.3 times.

A comparison of the shapes and positions of the absorption spectra maxima of films with isopropyl and ethyl alcohol showed no visible changes. The half-width of the absorption spectrum remained within the same range as for ethyl alcohol. The values of the optical density at the absorption maxima decrease. The value of the maximum at a wavelength of 216 nm decreased by 1.8 times, and at a wavelength of 224 nm – by 2.3 times.

Figure 3b presents the absorption spectra of PEDOT:PSS films prepared in a nitrogen atmosphere. Table 2 indicates the absorption spectra parameters. The absorption maximum of the original PEDOT:PSS film is 216 nm with a half-width of 9 nm. It can be seen from Figure 3b that the absorption spectra of the PEDOT:PSS films treated with alcohol vapors in an inert gas atmosphere show a change in shape. Thus, in addition to the short-wavelength narrow band, a rather broad long-wavelength band with a maximum of 230 nm is observed in the spectrum. Also, when the film is treated in alcohol vapors, the absorption spectrum of the final film shows a shift of the absorption maximum relative to the initial film to the short-wavelength region of the spectrum. Moreover, a shift is observed for the short-wavelength maximum, which is responsible for the PEDOT component, while the position of the long-wavelength maximum remains constant. The values of optical densities decrease at the absorption maximum. For the film treated with ethyl alcohol vapor, the optical density decreased to a value of 0.53, and for isopropyl alcohol – to 0.48 (Table 2). The half-width of the spectra does not change.

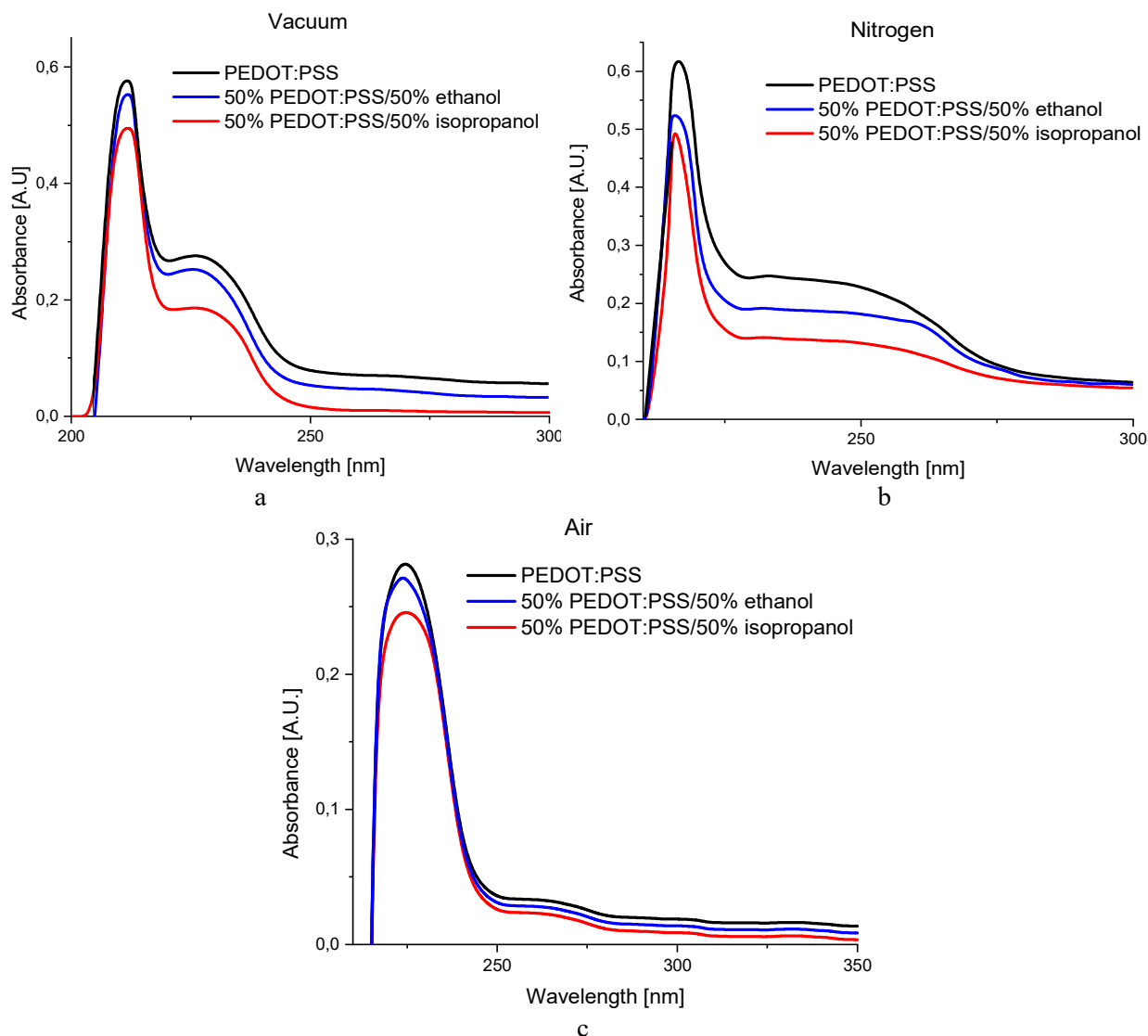


Figure 3. Absorption spectra of PEDOT:PSS films in vacuum (a), nitrogen atmosphere (b) and air atmosphere (c)

Figure 3c shows the absorption spectra of the original PEDOT:PSS film and PEDOT:PSS films treated in alcohol vapor prepared in air. It can be seen that the initial PEDOT:PSS film has a maximum at a wavelength of $\lambda_I = 224$ nm with a spectral half-width of 28 nm (Figure 3c). In the absorption spectra of all films, a shoulder with a maximum of 260 nm is observed, which is associated with the absorption of the PSS aromatic fragment [24]. The position of the absorption maxima of the films obtained by preparing PEDOT:PSS solutions with alcohol solvents does not change, the half-width of the spectra increases (Table 2).

The value of the optical density at the absorption maximum does not undergo significant changes. Treatment with ethanol vapor leads to a change in the value of optical density at the maximum of short-wavelength absorption by 0.1, and the value of the long-wavelength shoulder practically does not change. When treated with isopropyl alcohol vapor, a similar picture is observed.

It should be noted that a comparative analysis of the change in the optical density values at the absorption maxima of the films shows that for isopropyl alcohol a greater decrease in absorption is observed than for ethyl alcohol.

Table 2 lists the characteristics of the absorption spectra of PEDOT:PSS films in various types of atmosphere.

Table 2

Characteristics of absorption spectra of PEDOT:PSS films

Sample	Absorption Peaks		D ₁	D ₂	FWHM, nm
	λ ₁ , nm	λ ₂ , nm			
Vacuum					
PEDOT:PSS	216	224	0.58	0.28	10
50% PEDOT:PSS/50% ethanol	216	224	0.55	0.25	9.5
50% PEDOT:PSS/50% isopropanol	216	224	0.49	0.18	8.5
Nitrogen					
PEDOT:PSS	216	230	0.61	0.24	9
50% PEDOT:PSS/50% ethanol	215	230	0.53	0.19	9
50% PEDOT:PSS/50% isopropanol	214	230	0.48	0.14	9
Air					
PEDOT:PSS	224	260	0.28	0.03	28
50% PEDOT:PSS/50% ethanol	224	260	0.27	0.03	29
50% PEDOT:PSS/50% isopropanol	224	260	0.25	0.02	32

Next, we studied the effect of modification of the PEDOT:PSS structure on the transport of charge carriers in the cells of the FTO/PEDOT:PSS/Al structure using the method of impedance spectroscopy. The analysis of the impedance measurement results was carried out according to the diffusion-recombination model and the equivalent circuit shown in Figure 4a was used for the fitting, where CPE is a constant phase element, which is an equivalent component of an electrical circuit that simulates the behavior of a double layer but is an imperfect capacitor. The main electrical transport parameters were calculated from the spectra (Table 3), where: k_{eff} is the effective charge carrier extraction rate from PEDOT:PSS, τ_{eff} effective transit time through PEDOT:PSS, R_h is the resistance of the PEDOT:PSS film, R_{ext} is the resistance of charge carrier transfer at the PEDOT:PSS/electrode interface. Figure 4b designates the diagram of the movement of charges in the cell.

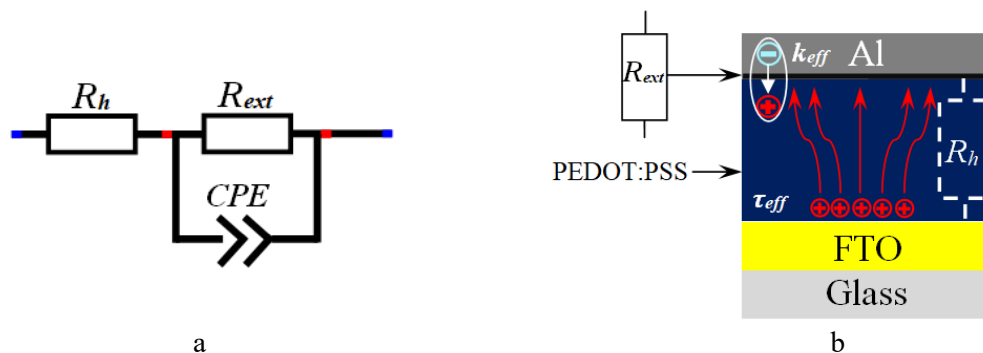


Figure 4. Equivalent electrical circuit (a) and scheme of charges transport in the cell (b)

Figure 5 indicates the impedance spectra of PEDOT:PSS films in vacuum, nitrogen and air atmospheres. Table 3 shows the values of the electrical physical parameters of the films. As can be seen from the Table 3, the modification of PEDOT:PSS with organic solvents in various types of atmosphere affects the transport of charge carriers in PEDOT:PSS. Cells based on films obtained from solutions with organic solvents (ethanol, isopropanol) have better electrical transport properties (Table 3). In all types of atmosphere, the addition of ethanol reduces the resistance of the PEDOT:PSS (R_h) film and the resistance of the PEDOT:PSS/Al (R_{ext}) interface, which increases the efficiency of hole transport from FTO to Al through PEDOT:PSS. When using isopropyl alcohol, the decrease in R_h and R_{ext} is more significant: in a vacuum, R_h decreased by 2.6 times, while R_{ext} decreased by 3.9 times compared to the original PEDOT:PSS, in a nitrogen atmosphere, the film resistance decreased by 2 times, and the resistance the interface decreased by 2.4 times compared to PEDOT:PSS, and in air atmosphere, the resistances R_h and R_{ext} decreased by 2.3 and 3.1 times, respectively.

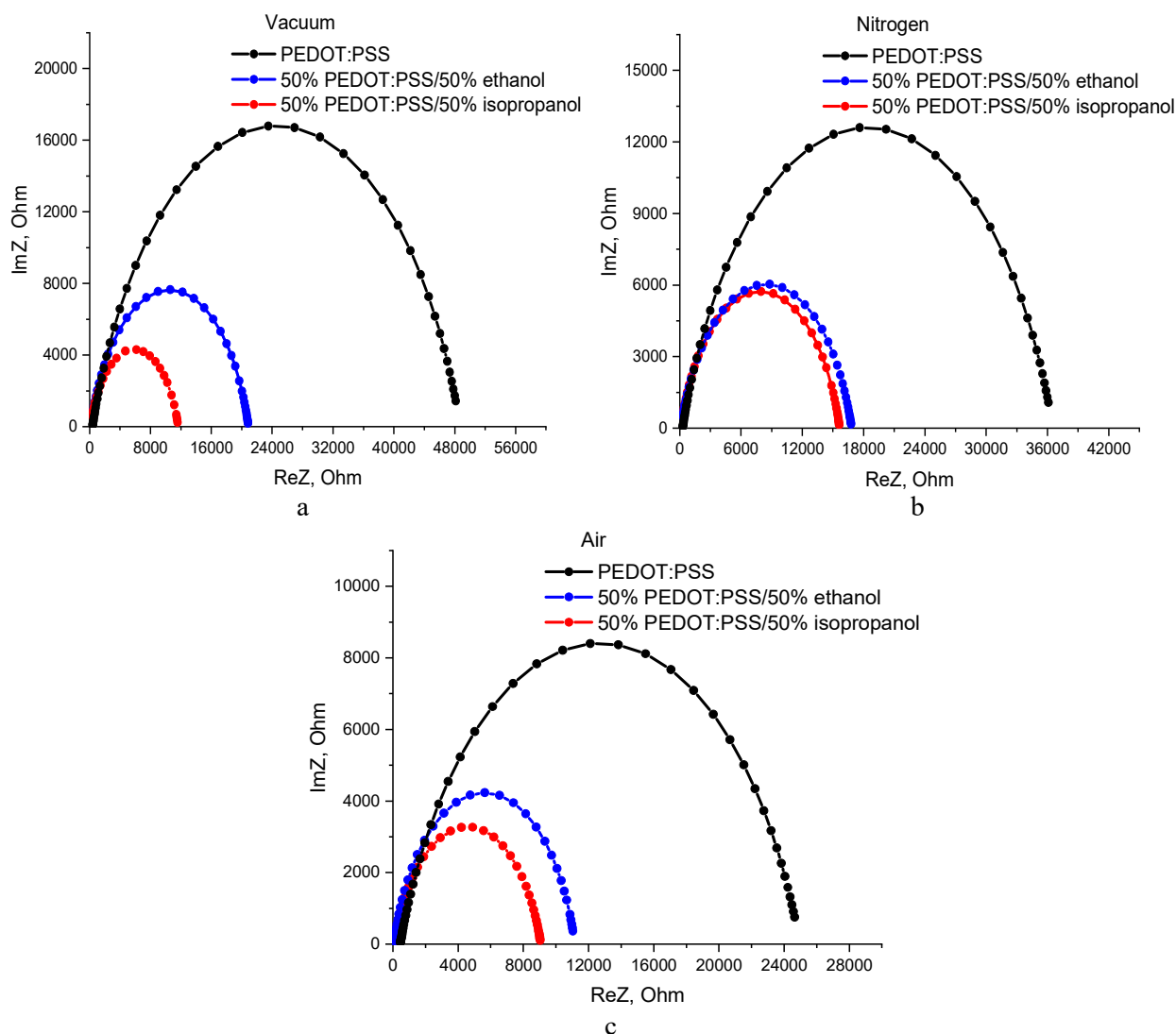


Figure 5. Impedance spectra of PEDOT:PSS films in vacuum (a), in nitrogen atmosphere (b) and in air atmosphere (c)

The values k_{eff} and τ_{eff} characterize the effective charge carrier extraction rate from PEDOT:PSS and the effective transit time through PEDOT:PSS. As can be seen from Table 3, the addition of ethyl and isopropyl alcohol to PEDOT:PSS has a noticeably positive dynamic in k_{eff} and τ_{eff} . The atmosphere in which the films are prepared also influences these parameters. When ethyl alcohol is added to the film, a positive dynamics is observed. However, the best results are shown by films prepared with the addition of isopropyl alcohol. The effective charge carrier extraction rate from PEDOT:PSS films obtained from a solution with isopropyl alcohol more than doubled, and the effective transit time of charge carriers decreased inversely. The highest value of τ_{eff} is observed in films prepared in the air atmosphere (Table 3). This means that the lifetime of charge carriers in films prepared in air is longer than in films prepared in a vacuum and a nitrogen atmosphere. Holes injected into PEDOT:PSS diffuse to the electrode, where they recombine with electrons. Fast transport of injected holes to the outer electrode is paramount since this reduces the probability of their reverse recombination. In our case, fast hole transport is provided by improving the structure of PEDOT:PSS after adding isopropyl alcohol to the initial solution, which leads to an improvement in the quality of the PEDOT:PSS/FTO interface [25, 26].

Table 3

The value of the electrical physical parameters of the films

Sample	R_h, Ω	R_{ext}, Ω	k_{eff}, s^{-1}	τ_{eff}, ms
Vacuum				
PEDOT:PSS	268.7	48745	157.5	6.4
50% PEDOT:PSS/50% ethanol	148.5	21054	259.4	3.9
50% PEDOT:PSS/50% isopropanol	104.7	12487	348.1	2.9
Nitrogen				
PEDOT:PSS	197.8	36748	74.8	13.4
50% PEDOT:PSS/50% ethanol	104.2	16874	110.8	9.1
50% PEDOT:PSS/50% isopropanol	98.5	15478	154.5	6.5
Air				
PEDOT:PSS	145.9	28876	48.5	20.6
50% PEDOT:PSS/50% ethanol	65.5	13564	53.7	18.6
50% PEDOT:PSS/50% isopropanol	63.7	9456	92,1	10.9

Conclusions

An analysis of the experiments showed that changing the film preparation environment and adding an alcohol solvent affects the surface structure of PEDOT:PSS films, which, in turn, affects the process of charge carrier transport. It has been established that the addition of alcohol to the PEDOT:PSS polymer in all types of studied atmospheres leads to a decrease in surface roughness. When the PEDOT:PSS surface is modified in different types of atmosphere, the absorption spectra show shifts in the maximum of the absorption spectra responsible for PEDOT in the short-wavelength region, as well as a decrease in the absorption of the PSS aromatic fragment. Changes in the structure and morphology of the PEDOT:PSS surface affects the electrical transport parameters of the films. It has been established that the surface of the PEDOT:PSS film modified in the volume of isopropyl alcohol and prepared in air atmosphere has the lowest resistance parameters R_h and R_{ext} , and the highest value of τ_{eff} , at which, due to the change in the structure of the PEDOT:PSS surface, the fastest transport of charge carriers is ensured.

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PEDOT: PSS полимерінің морфологиясына, оптикалық және электрофизикалық сипаттамаларына қоршаған ортаның әсері

Мақалада PEDOT: PSS пленкасының беттік құрылымына, оптикалық және электрофизикалық сипаттамаларына ортаның әсерін зерттеу нәтижелері берілген. Зерттеулер атмосфераның үш түрлі түрінде пленкаларды термиялық өндеудің тең жағдайында жүргізілді. Вакуумда, азот ортасында және атмосферада этил және изопропил спирттерімен полимерлі пленканың бетін өзгерту беттік морфологияның, полимердің оптикалық электрлік қасиеттерінің өзгеруіне әкелетіні анықталды. PEDOT: PSS пленкасын модификациялау кезінде ортаға байланысты этил және изопропил спирттерінің белгілі бір концентрациясымен жұтылу спектрінде PEDOT жауап беретін жұтылу максимумының спектрдің қысқа толқындық аймағына ауысуы, сондай-ақ PSS хош иісті фрагменті жұтылуға жауап беретін спектрдің бір бөлігінің жұтылу шыңының төмендеуі байқалады. PEDOT: PSS беттік морфологиясының құрылымдық ерекшеліктері электрлік тасымалдау пленкасының параметрлеріне әсер етеді, мысалы: R_h - PEDOT: PSS полимерлі пленкасының кедергісі, R_{ext} - PEDOT: PSS / электрод интерфейсындағы заряд тасымалдаушылардың тасымалдау кедергісі, k_{eff} - заряд

тасымалдаушыларды алудың тиімді жылдамдығы және τ_{eff} - заряд тасымалдаушылардың тиімді ұшу уақыты. PEDOT: PSS полимерлі пленкалардың электрлік тасымалдау қасиеттері жоғарылайтын пленкаларды алудың оңтайлы технологиялық параметрлері анықталды.

Кілт сөздер: PEDOT: PSS, Izopropanol, Ethanol, вакуум, азот атмосферасы, ауа атмосферасы, беттік морфология, оптикалық спектроскопия, импеданс спектроскопиясы.

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Влияние среды на морфологию, оптические и электрофизические характеристики полимера PEDOT: PSS

В работе представлены результаты исследования влияния среды на структуру поверхности, оптические и электрофизические характеристики пленки PEDOT: PSS. Исследования проводились в трех разных типах атмосферы при равных условиях термического отжига пленок. Установлено, что модификация поверхности полимерной пленки этиловым и изопропиловым спиртами в вакууме, в среде азота и на атмосфере приводит к изменению морфологии поверхности, оптических электротранспортных свойств полимера. Показано, что, в зависимости от среды при модификации пленки PEDOT: PSS определенной концентрации этилового и изопропилового спиртов, в спектрах поглощения наблюдается сдвиг максимума поглощения, отвечающего за PEDOT, в коротковолновую область спектра, а также уменьшение пика поглощения части спектра, отвечающего за поглощение ароматического фрагмента PSS. Показано, что структурные особенности морфологии поверхности PEDOT: PSS оказывают влияние на электротранспортные параметры пленок, такие как R_h — сопротивление полимерной пленки PEDOT:PSS; R_{ext} — сопротивление переноса носителей заряда на границе раздела PEDOT: PSS/электрод; k_{eff} — эффективная скорость извлечения носителей заряда и τ_{eff} — эффективное время пролета носителей заряда. Определены оптимальные технологические параметры получения пленок, при которых повышаются электротранспортные свойства полимерных пленок PEDOT: PSS.

Ключевые слова: PEDOT:PSS, Izopropanol, Ethanol, вакуум, атмосфера азота, атмосфера воздуха, морфология поверхности, оптическая спектроскопия, импедансная спектроскопия.

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The study of carbon nanomaterials by IR-Fourier spectroscopy, obtained by the action of an ultrasonic field on graphite

In this work, the absorption lines corresponding to nanomaterials (nanotubes, nanofibers, graphene), as well as vibrational spectra in the studied samples of graphene structures obtained by processing an ultrasonic field on an aromatic hydrocarbon and pure graphite, are studied by IR-Fourier spectroscopy. With an increase in time in the studied spectra of ultrasonic treatment on pure graphite, absorption bands are observed in the frequency range of $\nu = 2967,7 \text{ cm}^{-1}$, $2926,1 \text{ cm}^{-1}$, 2853 cm^{-1} , 1449 cm^{-1} , related to stretching and deformation vibrations of the bond C-H of saturated aromatic hydrocarbons. The spectra of carbonyl (carbon) compounds of the C-C bond are also noted in the regions of the absorption bands: $1449,9 \text{ cm}^{-1}$ – $1652,6 \text{ cm}^{-1}$. This means that in the IR spectra, with an increase in the time of sonication, the carbon formations of asymmetric stretching vibrations of C-C bonds increase. In these frequency ranges, the absorption bands corresponding to adsorbed benzene are not observed. With an increase in the processing time of the samples, the absorption band of OH hydroxyl groups is not observed. In the samples under study, numerous aromatic carbon-carbon bonds are observed, due to the collective groups of vibrations of carbon nanomaterials (graphene structures, nanofibers, single-layer and multilayer carbon nanotubes, etc.).

Keywords: carbon nanosystems, polyaromatic condensed systems, aromatic hydrocarbon, carbonate-carboxylate compounds, absorption lines, by IR-Fourier spectroscopy, stretching and deformation vibrations, ultrasonic treatment.

Introduction

Carbon nanomaterials (fullerene, nanotubes, graphene) are topical materials in modern materials science. The introduction of small additives of carbon nanoparticles with a developed and active surface makes it possible to provide new properties of materials such as sorption capacity with respect to heavy metals [1].

Multilayer (technical) graphene is of great interest for studying its properties and applications in modern materials science. Such graphite nanoplanes are obtained as a result of its oxidation and subsequent destruction by ultrasound by the Hammer method [2].

Due to the fact that this method (Hammer method) is due to the release of toxic reaction products, the method of combined action of ultrasound and surfactant has received wide practical application. The advantage of the method is that the substances used are non-toxic, but the power and duration of ultrasonic interaction are increased [1].

The authors of [3] studied intense bands in the region of $1700\text{--}1450 \text{ cm}^{-1}$, which correspond to stretching vibrations of the carbon plane of graphene. In the region of $1450\text{--}1000 \text{ cm}^{-1}$ the most intense vibrations correspond to deformation vibrations of the graphene plane and deformation vibrations of terminal C–H bonds [3]. The most intense band (about 900 cm^{-1}) corresponds to the out-of-plane vibrations of C–H bonds [3]. It should be noted that the ratio of the intensities of carbon plane stretching vibrations C–H bonds out-of-plane vibrations can be used to estimate the size of graphene fragments [3, 4].

The spectra of the initial graphite powder and graphene are well described by the authors of [1]. Two absorption maxima were obtained by IR spectroscopy at 1273 and 2373 cm^{-1} , which we attributed to the C–O–C and C–O₂ bonds in accordance with the data of [5]. The formation of these bonds is due to the oxidation of graphite and the formation of broken carbon-carbon bonds, which increases the reactivity of the resulting graphene. Graphene which does not have OH groups on the surface is hydrophobic, which makes it difficult to introduce it into binders [1].

Experimental

In this work, samples obtained by ultrasonic treatment of pure graphite and aromatic carbon (benzene) were studied by the IR-Fourier spectroscopy. The absorption lines corresponding to carbon nanosystems (nanotubes, graphene structures, etc.) and carbonate-carboxylate compounds and polyaromatic condensed systems in the studied samples have been studied and analyzed. With an increase in the time of sonication, numerous single carbon-carbon bonds are formed due to the collective modes of carbon nanostructures, including carbon nanotubes [5, 6].

According to [1], during ultrasonic interaction with graphite and the preparation of graphene nanoplanes, two absorption maxima appear at 1273 and 2373 cm^{-1} . As mentioned above, such absorption peaks signify the formation of symmetrical C–O–C and C–O₂ bonds [7]. These values allow us to conclude that the formation of bonds reflects the oxidation of graphite at broken C–C bonds. The presence of –OH groups chemically bonded on the surface confirms the value of the spectrum at 3414 cm^{-1} [1].

Results and Discussion

Carbonate-carboxylate compounds and polyaromatic condensed systems in the studied graphene-containing structures obtained by processing an ultrasonic field on an aromatic hydrocarbon (benzene) and pure graphite have been studied and interpreted by IR-Fourier spectroscopy.

In the IR spectrum of the original sample there are absorption bands of OH hydroxyl groups in the region of absorption bands $\nu=3440.6 \text{ cm}^{-1}$ (Figure 1).

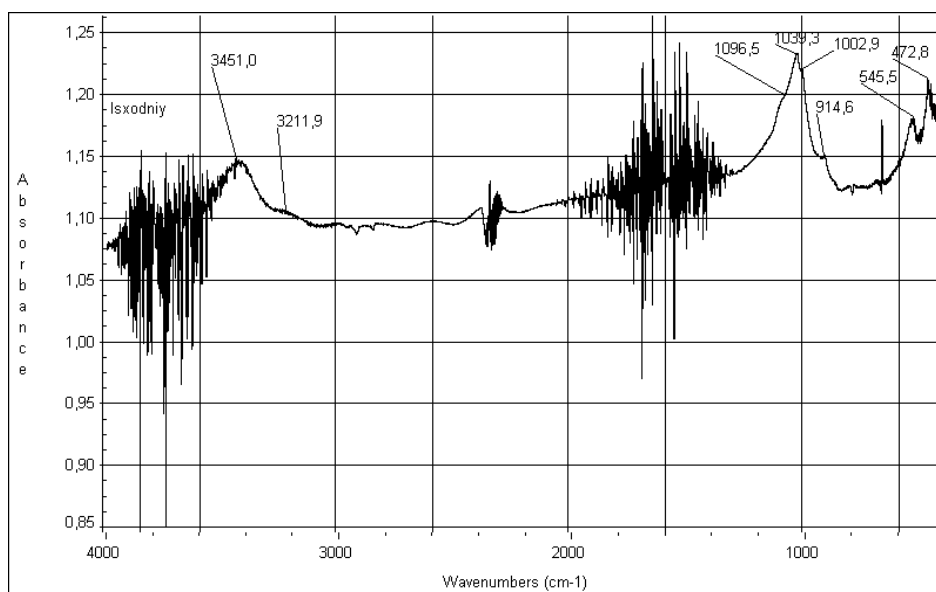


Figure 1. IR-Fourier spectrum of the original sample

In the range $\nu=2000\text{--}4000 \text{ cm}^{-1}$ there are intense absorption bands, $\nu=1075.7$ and 602.7 cm^{-1} . These ranges contain absorption bands related to the stretching and bending vibrations of silicon, aluminum, and iron oxide groups. According to the literature data [8], graphite contains ash containing oxides of silicon, aluminium, and iron with a content of 5–20%.

Since the absorption bands of metals in the IR spectra are in the range $\nu=700 - 50 \text{ cm}^{-1}$, the marked absorption bands belong to oxides of silicon, aluminium, and iron.

Figure 2 shows the IR spectrum of a sample treated for 10 minutes. This spectrum contains very weak absorption bands at 1039 and 1008 cm^{-1} of silicon, aluminium, and iron oxides; this is due to the washing out of ash impurities from graphite during sonication. There are no signs of benzene adsorption, since there are no absorption bands in the range $\nu=3100 - 3000 \text{ cm}^{-1}$, as well as at $\nu=1600$ and 685 cm^{-1} .

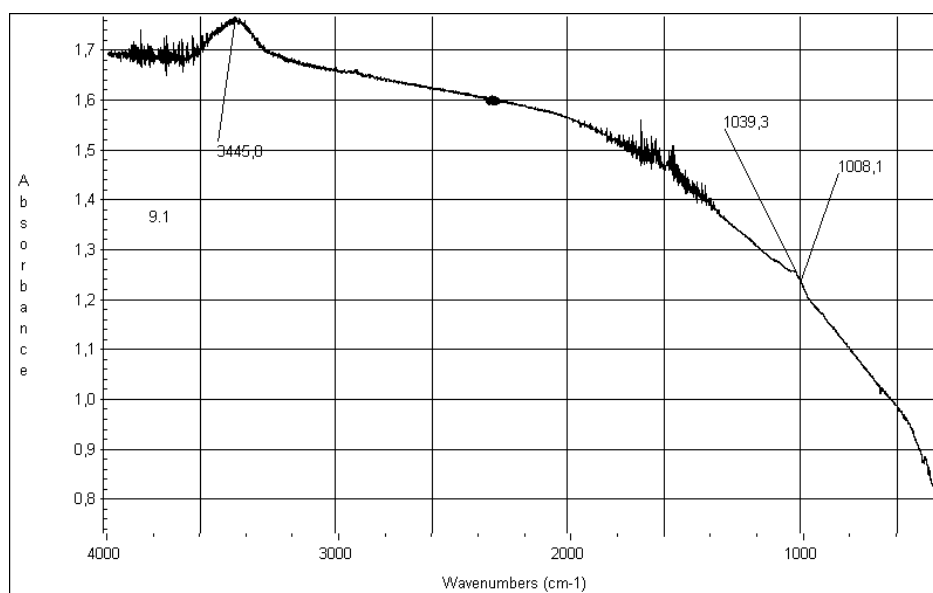


Figure 2. IR-Fourier spectrum of a sample treated for 10 minutes

Stretching vibrations of the C-C bond are present in the ranges of absorption bands $\nu=1100 - 900 \text{ cm}^{-1}$.

Figure 3 illustrates the IR spectrum of a sample treated for 20 minutes. The spectrum shows stretching vibrations of the C-C bond in the range $\nu=1100 - 900 \text{ cm}^{-1}$, as well as stretching and deformation vibrations of the C-H group in the region of absorption bands $\nu=1449 \text{ cm}^{-1}$, 2967, 2926, 2853. Benzene adsorption is not observed.

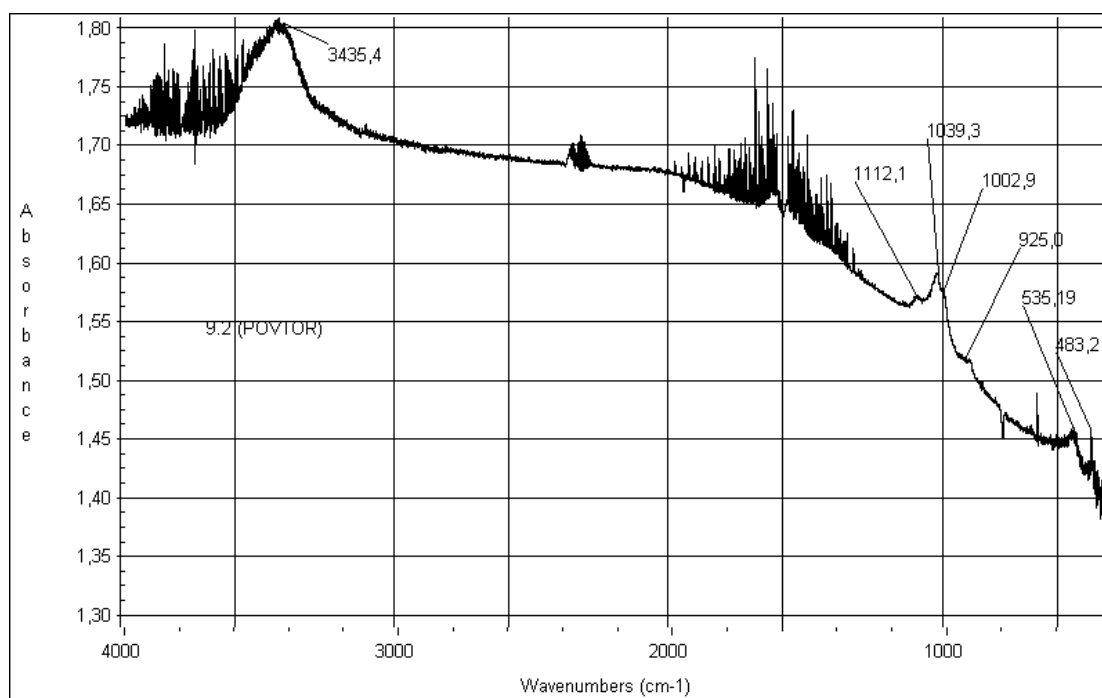


Figure 3. IR-Fourier spectrum of a sample treated for 20 minutes

In the IR spectrum of the sample treated with ultrasound for 120 minutes, there are new absorption bands $\nu=2967.7$, 2926.1, 2853, 1449 cm^{-1} , related to the stretching and deformation vibrations of the C-H bond of saturated aromatic hydrocarbons (Figure 4).

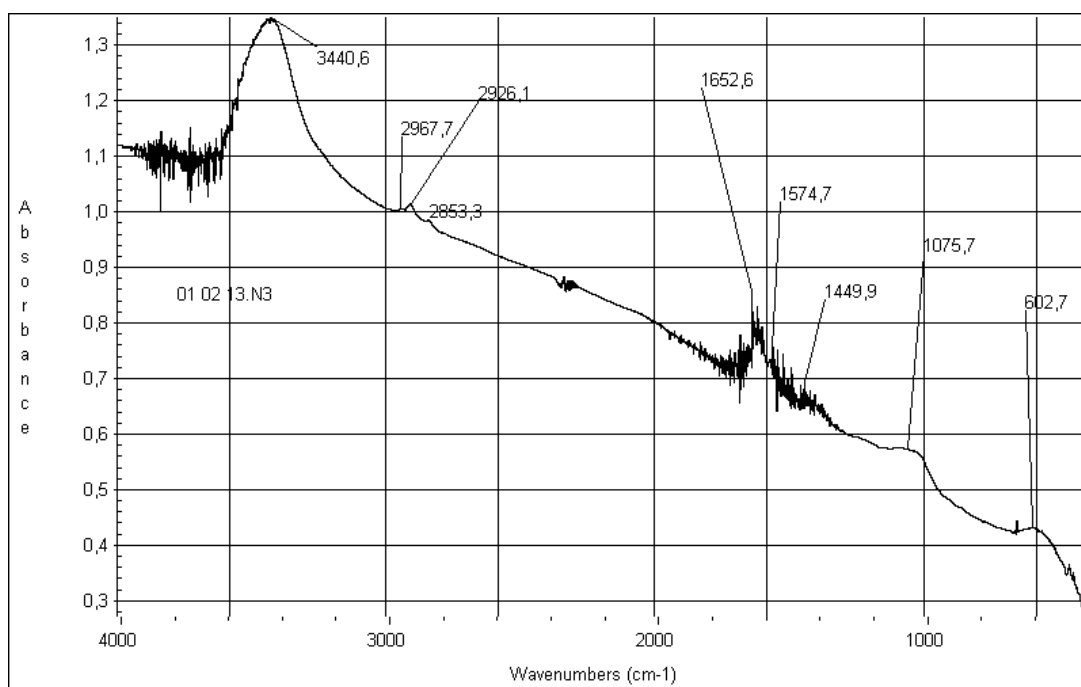


Figure 4. IR-Fourier spectrum of a sample sonicated for 120 minutes

There are also stretching vibrations of the C-C bond in the region of the absorption bands 1449.9 - 1652.6 cm^{-1} .

In the region of absorption of bonds (metal – oxygen) Me–O ($700 - 50 \text{ cm}^{-1}$), one band is observed at 602.7 cm^{-1} , with an increase in the time of ultrasonic treatment of benzene and graphite. No absorption bands corresponding to adsorbed benzene (in the range of absorption bands $\nu=3440.6\text{--}2967.7 \text{ cm}^{-1}$, 1547.7 cm^{-1} and 602.7 cm^{-1}) were found. As a result of studies carried out on an IR-Fourier spectrometer, a decrease in the ash content of graphite with the time of sonication was established. It is noted that an increase in carbon formations of stretching vibrations of C-C bonds.

Conclusions

As a result of the studies carried out by the method of IR spectroscopy, a decrease in the ash content of graphite with the time of sonication was established. It is shown that an increase in carbon formation of stretching vibrations of carbon-carbon bonds with an increase in the processing of the ultrasonic field.

Based on these data, it can be concluded that vibrations of single carbon-carbon bonds of carbon nano-systems are observed in the ranges of $1320\text{--}1652.2 \text{ cm}^{-1}$ [5, 6].

IR-Fourier studies show that the absorption bands in the ranges of 1652.2, 1574.7 and 1449.9 cm^{-1} are due to the absorption of collective modes of carbon nanosystems (multilayer nanotubes, graphenes, fullerenes and nanofibers). In terms of their structure, carbon nanosystems can be considered three-dimensional analogues of aromatic compounds [4, 5]. Thus, IR spectroscopic studies confirm the formation of carbon nanosystems in the samples under study, which is in good agreement with literature data [5, 6, 9, 10].

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Графитке ультрадыбыстық өріс әсер еткен кезде алынатын көміртікті наноматериалдарды ИК-Фурье спектроскоп әдісімен зерттеу

Жұмыста спектроскопияның ИК-Фурье әдісімен тиісті наноматериалдардың (нанотүтікшелер, наноталшық, графен) жұтылу сызықтары, сонымен қатар ультрадыбыстық өрісті хош иісті көмірсутек пен таза графитке өңдеу кезінде алынған графен құрылымдарының зерттелетін үлгілеріндегі тербелмелі спектрлері зерттелген. Зерттелетін ультрадыбыстық өңдеу спектрлерінде таза графитке уақыттың жоғарылауымен қаныққан хош иісті көмірсутектердің С-Н байланысының валенттік және деформациялық ауытқуларына жататын $\nu=2967,7 \text{ см}^{-1}$, $2926,1 \text{ см}^{-1}$, 2853 см^{-1} , 1449 см^{-1} жиіліктер аймағында сіңіру жолақтары байқалады. Сондай-ақ, $1449,9 \text{ см}^{-1} \div 1652,6 \text{ см}^{-1}$ сіңіру жолақтары аймағында С-С байланысының карбонилді (көміртекті) қосылыстарының спектрлері көрінді. Бұл ИК спектрлерінде ультрадыбыспен уақыт жоғарылаған сайын С-С байланыстарының асимметриялық валентті тербелістерінің көміртегі түзілімдері артады дегенді білдіреді. Осы жиілік диапазондарында адсорбцияланған бензолға сәйкес келетін сіңіру жолақтары байқалмайды. Үлгілерді өңдеу уақытының ұлғаюымен ОН гидроксил топтарының сіңіру жолақтары белгіленбейді. Зерттелетін үлгілерде көміртекті наноматериалдардың (графен құрылымдары, наноталшықтар, бірқабатты және көпқабатты көміртекті нанотүтікшелер және т.б.) тербелістерінің ұжымдық топтарына байланысты көптеген хош иісті көміртегі-көміртекті байланыстары көрсетілген.

Кілт сөздер: көміртекті наножүйелер, полиароматикалық конденсатты жүйелер, хош иісті көмірсутектер, карбонат-карбоксилат қосылыстары, сіңіру желілері, ИК-Фурье-спектроскопия әдісі, валенттік-деформациялық тербелістер, ультрадыбыстық өңдеу.

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Изучение углеродных наноматериалов методом ИК-Фурье спектроскопии, полученных при воздействии ультразвукового поля на графит

В работе методом ИК-Фурье спектроскопии исследованы линии поглощения соответствующих наноматериалов (нанотрубок, нановолокна, графен), а также колебательные спектры в исследуемых образцах графеновых структур, полученных при обработке ультразвукового поля на ароматический углеводород и чистый графит. С повышением времени в исследуемых спектрах ультразвуковой обработки на чистый графит наблюдаются полосы поглощения в области частот $\nu=2967,7 \text{ см}^{-1}$, $2926,1 \text{ см}^{-1}$, 2853 см^{-1} , 1449 см^{-1} , относящиеся к валентным и деформационным колебаниям связи С-Н насыщенных ароматических углеводородов. Также отмечаются спектры карбонильных (углеродных) соединений С-С связи в областях полос поглощения $1449,9 \text{ см}^{-1} \div 1652,6 \text{ см}^{-1}$. Это означает, что в ИК спектрах с повышением времени обработки ультразвуком увеличиваются углеродные образования асимметричных валентных колебаний С-С связей. В этих диапазонах частот полос поглощения, соответствующих адсорбированному бензолу, не наблюдается. С увеличением времени обработки образцов полосы поглощения гидроксильных групп ОН не намечаются. В исследуемых образцах образуются многочисленные ароматические углерод-углеродные связи, обусловленные коллективными группами колеба-

ний углеродных наноматериалов (графеновых структуры, нановолокна, однослойные и многослойные углеродные нанотрубки и др.).

Ключевые слова: углеродные наносистемы, полиароматические конденсированные системы, ароматический углеводород, карбонатно-карбоксилатные соединения, линии поглощения, метод ИК-Фурье спектроскопии, валентно-деформационные колебания, ультразвуковая обработка.

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Numerical research of characteristic mixing times of isothermal three-component steam-gas systems

Multicomponent diffusion in gases is characterized by a number of effects that are not observed in binary diffusion. Analysis of existing works shows that convective instability may occur in some systems with significantly different diffusion coefficients with certain geometric and thermophysical characteristics. Stability analysis allows determining the spectrum of parameters at which a transition from a diffusive state to a convective is possible. However, this approach does not allow the researchers to investigate the dynamics of the process. Therefore, this work aims to describe emergence and evolution of convective flows in three-component systems and assess the influence of the initial composition on the occurrence of concentration gravitational convection. The main part of the work presents a mathematical model describing the occurrence of convective flows based on the splitting scheme according to physical parameters. Numerical data on the concentration fields of the gas with the highest molecular weight at various time points is obtained. It is established that curvature of the isoconcentration lines of the diffusing components can be associated with instability of the mechanical equilibrium of the system. Degree of curvature is determined by the initial concentration of components of the mixture. The obtained data can be used to determine the main characteristics of mass transfer used in calculations related to combined heat and mass transfer in a wide range of thermophysical parameters.

Keywords: gas mixtures, diffusion, convection, instability, initial composition, numerical calculation, isothermal mixing, formic acid vapors.

Introduction

Rayleigh-Benard convection is one of the few classical problems of heat and mass transfer to which there is increased attention at the present time [1]. Interest in this problem is associated with the study of the variety of flows arising in channels from a given geometry and the properties of the studied liquid or gas medium. Generalization of studies on the occurrence of gravitational convection in an inhomogeneous temperature field made it possible to develop recommendations for determining the main parameters of heat and mass transfer associated with properties of the substance under research. These recommendations allow for specific conditions to predict mixing modes. At the same time, the occurrence of instability of mechanical equilibrium and the subsequent development of convective formations depend on the direction of the vectors of density gradients and gravity [2, 3]. Occurrence and further evolution of convective perturbances are fixed, in the case when directions of the corresponding gradients do not coincide. Opposite situation assumes a stable stratification of medium and absence of convective motion.

However, for multicomponent mixtures in which several concentration flows interfere, the spread of approaches [2, 3] to describe the behavior of system can lead to distortion of the expected results associated

with mass transfer, since the features, that are absent in binary systems are unconsidered. These include, first of all, the fact of the destabilizing effect of diffusion on the development of convective flows in mixtures [4, 5]. Convective flows that arise in this case form a synergistic mixing mechanism, leading to the selective transfer of a component with specified thermophysical properties.

Experimental studies [6, 7] have shown that even in the extreme case of isothermal multicomponent mixing, convective separation effects associated with differences in the diffusion coefficients of components, pressure, and composition occur. Distinctive feature of the studies conducted in [6,7] was the condition for the implementation of multicomponent mixing, which assumed that density of the medium in the upper part of the diffusion channel was less than density of the gas localized in the lower part of the channel. Physical meaning, emergence of the convection instability and subsequent development of hydrodynamic perturbances are described in detail in [2, 3]. However, using the formalism of the Rayleigh thermal problem to describe isothermal multicomponent mixing under conditions of initial stable stratification of the mixture observed in [4–7] requires consideration of the influence of several partial concentration gradients. Importance of such an adjustment was shown in [8, 9], in which it was found that in ternary systems with different molecular weights M_i and different diffusion coefficients D_{ij} [10] there are areas of damping and increasing convective perturbances. Extreme perturbances can be the reason of structured flows in multicomponent diffusion. However, the approach developed in [8, 9] defines only the boundary of the “diffusion–convection” regime change in the area of specified thermophysical and geometric parameters. Process of the emergence of structured convective flows and their subsequent evolution has not been considered. In this regard, it is relevant to study the dynamics of the emergence of structural formations at the boundary of the “diffusion – convection” regime change during isothermal multicomponent mixing. This work presents the results of numerical studies on the mixing of triple gas mixtures in vertical diffusion channels with different initial compositions. The comparative analysis presented with obtained and experimental data.

Problem statement and numerical method

The diffusion transfer of a triple gas mixture in a flat (or cylindrical) channel is studied. The problem statement is shown in Figure 1.

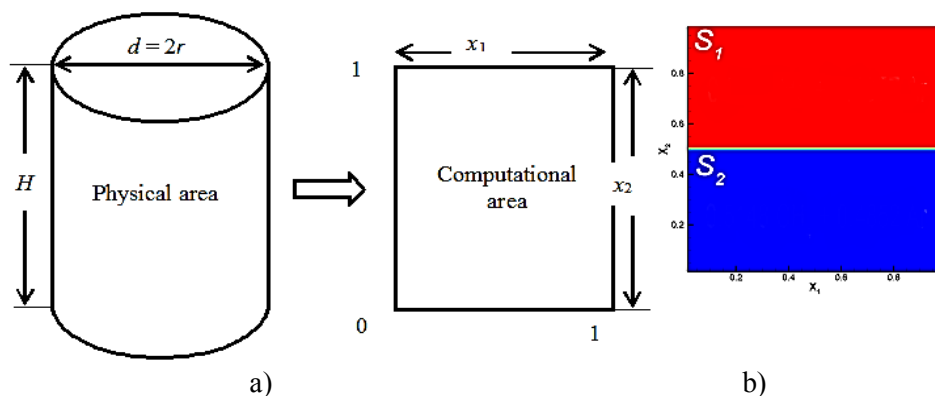


Figure 1. Model of multicomponent mass transfer:
a) mixing areas; b) placement of three-component mixtures in the diffusion cell.

The upper part of the channel S_1 contains a mixture of gases with the M_1 and M_3 molecular weights, mixture diffuses into a gas with a molecular weight M_2 , which is located at the bottom of the channel S_2 . At the same time, the following assumptions occur:

1. For the molecular weights of the components M_i , the condition is accepted: $M_3 > M_2 > M_1$.
2. The condition of independent diffusion assumes:

$$\sum_{i=1}^3 j_i = 0 \text{ and } \sum_{i=1}^3 c_i = 1$$

Multicomponent mixing is studied near the boundary of the “diffusion–convection” regime change, total transfer of components can be described by a system of hydrodynamic equations for perturbed quantities written in the Boussinesq approximation [11, 12].

$$\begin{aligned}\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \nabla) \mathbf{u} &= -\frac{1}{\rho_0} \nabla p + \nu \nabla^2 \mathbf{u} + g(\beta_1 c_1 + \beta_2 c_2) \gamma, \\ \frac{\partial c_1}{\partial t} + \mathbf{v} \nabla \langle c_1 \rangle &= D_{11}^* \nabla^2 c_1 + D_{12}^* \nabla^2 c_2, \\ \frac{\partial c_2}{\partial t} + \mathbf{v} \nabla \langle c_2 \rangle &= D_{21}^* \nabla^2 c_1 + D_{22}^* \nabla^2 c_2, \\ \operatorname{div} \mathbf{v} &= 0,\end{aligned}\tag{1}$$

where $\langle c_i \rangle$ – constant average concentration value, taken as the starting point, $\vec{\gamma}$ – the unit vector, ν – coefficient of kinematic viscosity, ρ_0 – average density of the mixture. The dependence of the density mixture on the concentration is determined as follows:

$$\beta_i = \frac{1}{\rho_0} \left(\frac{\partial \rho}{\partial c_i} \right)_{p,T,c_j}, \quad \rho = \rho_0 (1 - \beta_1 c_1 - \beta_2 c_2),$$

Diffusion complexes D_{ij}^* related to the coefficients of mutual diffusion D_{ij} by the relations:

$$\begin{aligned}D_{11}^* &= \frac{D_{13}[c_1 D_{32} + (c_2 + c_3) D_{12}]}{D}, \quad D_{12}^* = \frac{c_1 D_{23} + (D_{12} + D_{13})}{D}, \\ D_{22}^* &= \frac{D_{23}[c_2 D_{13} + (c_1 + c_2) D_{12}]}{D}, \quad D_{21}^* = \frac{c_2 D_{13} + (D_{12} + D_{23})}{D}, \\ D &= c_1 D_{23} + c_2 D_{13} + c_3 D_{12}.\end{aligned}$$

Perturbations of the average mass and average numerical velocities are of the same order, therefore, in further relations, we will replace the perturbed quantities $\mathbf{v}$ with $\mathbf{u}$ [8]. Let us choose the characteristic measurement scales: H – linear size of the cavity, H^2/ν – time, D_{22}^*/H – velocity, $A_1 H$ – concentration, $\rho_0 \nu D_{22}^*/H^2$ – pressure. System of equations (1) in dimensionless quantities has the form:

$$\begin{aligned}\frac{\partial c_1}{\partial t} + \frac{1}{\operatorname{Pr}_{22}} \mathbf{u} \nabla c_1 &= \frac{1}{\operatorname{Pr}_{11}} \Delta c_1 + \frac{1}{\operatorname{Pr}_{22}} \tau_{12} \Delta c_2, \\ \frac{\partial c_2}{\partial t} + \frac{1}{\operatorname{Pr}_{22}} \mathbf{v} \nabla c_2 &= \frac{A_1}{A_2} \frac{1}{\operatorname{Pr}_{22}} \tau_{21} \Delta c_1 + \frac{1}{\operatorname{Pr}_{22}} \Delta c_2, \\ \frac{\partial \mathbf{u}}{\partial t} + \frac{1}{\operatorname{Pr}_{22}} \nabla (\mathbf{u} \cdot \mathbf{u}) &= -\nabla p + \Delta \mathbf{u} + (\operatorname{Ra}_1 \tau_{11} c_1 + \operatorname{Ra}_2 c_2) \gamma, \\ \operatorname{div} \mathbf{u} &= 0,\end{aligned}\tag{2}$$

where $\operatorname{Pr}_{ii} = \nu/D_{ii}^*$ – the diffusion Prandtl number, $\operatorname{Ra}_i = g\beta_i A_1 H^4/D_{22}^* \nu$ – partial Rayleigh number, where A_1 – dimensionless initial gradient, $\tau_{ij} = D_{ij}^*/D_{22}^*$ – parameter, which determines the relationship between the practical diffusion coefficients.

Next, we will use the algorithm written in [12]. The system of equations (2) is solved numerically by the splitting scheme according to physical parameters [13]. The two-dimensional cross-sectional area of the

cylinder area $H \times d$ in the Cartesian coordinate system is considered (Fig. 1a). Calculations were carried out in a dimensionless grid with dimensions of 128×128 .

The first stage of the calculation assumes, that transfer of the quantity of motion is carried out only by convection and diffusion. The intermediate velocity field is found according to the Adams-Bashforth and Crank-Nicholson schemes [14].

$$\frac{\hat{\mathbf{u}}^n - \mathbf{u}^n}{\Delta t} = -\frac{1}{2}(3H^n - H^{n-1}) + \frac{1}{2}\Delta(\hat{\mathbf{u}}^n + \mathbf{u}^n) + (\text{Ra}_1\tau_{11}c_1 + \text{Ra}_2c_2)\gamma, \quad (3)$$

where $H^n = -\nabla(\mathbf{u} \cdot \mathbf{u})^n$ – convective members, $\hat{\mathbf{u}}$ – intermediate velocity field, Δt – time step, n – is the iteration number at time t^n .

The second stage of the calculation determines the relationship of pressure with the velocity value:

$$\Delta p = \frac{\nabla \cdot \hat{\mathbf{u}}^n}{\Delta t}. \quad (4)$$

The third stage assumes recalculation of the velocity field exceptionally due to the pressure drop:

$$\frac{\mathbf{u}^{n+1} - \hat{\mathbf{u}}^n}{\Delta t} = -\nabla p. \quad (5)$$

At the fourth stage, the concentration of the mixture components is calculated:

$$\frac{c_1^{n+1} - c_1^n}{\Delta t} = \frac{1}{2}(F^{n+1} - F^n) + \frac{1}{\text{Pr}_{11}}\Delta c_1^n + \frac{1}{\text{Pr}_{12}}\Delta c_2^n, \quad (6)$$

$$\frac{c_2^{n+1} - c_2^n}{\Delta t} = \frac{1}{2}(F^{n+1} - F^n) + \frac{1}{\text{Pr}_{21}}\Delta c_1^n + \frac{1}{\text{Pr}_{22}}\Delta c_2^n,$$

$$c_3^{n+1} = 1 - c_1^{n+1} - c_2^{n+1},$$

where $F^n = -\nabla(\mathbf{u}^{n+1} \cdot \mathbf{c}^n)$ – convective terms.

The boundary conditions are set as follows:

$$\mathbf{u}(\mathbf{x}_B, \tau) = 0, \quad \frac{\partial c_i}{\partial \mathbf{n}} = 0, \quad i = 1-3, \quad (7)$$

where $\mathbf{n} = (n_1, n_2)$ – external normal to the boundary of the computational area.

The initial conditions are written as follows:

$$\begin{aligned} \mathbf{u}(\mathbf{x}, \tau) &= 0, \\ c_1(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_1} &= X_1, \quad c_1(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_2} = 0, \\ c_2(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_1} &= X_2, \quad c_2(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_2} = 0, \\ c_3(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_1} &= 0, \quad c_3(\mathbf{x}, \tau = 0)|_{\mathbf{x} \in S_2} = X_3. \end{aligned} \quad (8)$$

where X_i – concentrations of components in the upper S_1 and lower S_2 areas.

Numerical calculation results

The numerical results (Fig. 2) illustrate the dependence of concentration on time for the heaviest component in terms of density in a triple system of formic acid vapors and water diffusing into argon at $p=0.1$ MPa, $T=298.0$ K experimentally studied in [15]. Several mixing modes are clearly visible. At the initial stage (Fig. 2a), diffusion takes place. After 0.93 s, a violation of monotony in the distribution of isoconcentration lines (Fig. 2b) is recorded. This behavior is not typical for diffusion mixing. It can be assumed that starting from this time, an instability of mechanical equilibrium occurs in the system under study.

In this case, instability is the reason of convection formation. Fig. 2c presents a convective cell formed 1.4 seconds after the start of mixing. At the final stage (Fig. 2d), the convective formation begins to move in the gravity field relative to the diffusion interface. Then, under different initial conditions (Fig. 2c), the process of structural formation begins again, i.e., in a steam-gas system, a drip mixing mode may occur.

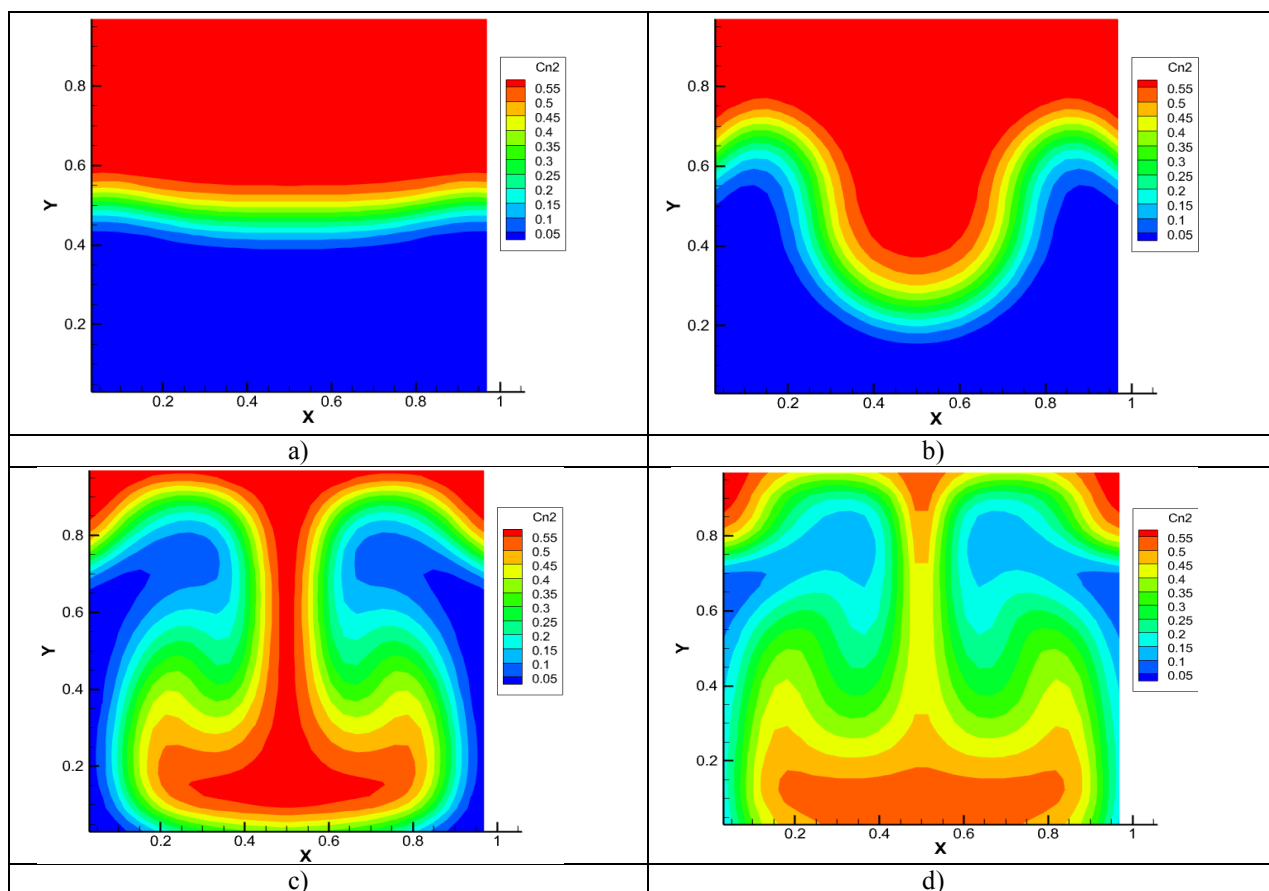


Figure 2. Isoconcentration lines of formic acid vapors for the system $0.6H_2O(1) + 0.4CH_2O_2(3) - Ar(2)$ at $p = 0.1\text{ MPa}$, $T = 298.0\text{ K}$, $L = 0.257\text{ m}$, $r = 11.2 \cdot 10^{-3}\text{ m}$. a) $t = 0.47\text{ s}$ b) $t = 0.93\text{ s}$; c) $t = 1.4\text{ s}$; d) $t = 1.86\text{ s}$.

In Table 1, for different compositions of formic acid vapors in a triple mixture $H_2O + CH_2O_2 - Ar$ the characteristic mixing times describing the diffusion (t_1), the occurrence of instability of mechanical equilibrium (t_2), formation of a structural formation (t_3) and the initial displacement in the channel due to gravity (t_4) are provided.

Table 1

Characteristic mixing times for different vapor compositions of formic acid at $P = 0.1\text{ MPa}$, $T = 298.0\text{ K}$.

Molar composition CH_2O_2 , mol.fraction	$t_1, \text{ s}$	$t_2, \text{ s}$	$t_3, \text{ s}$	$t_4, \text{ s}$
0.89	0.47	0.93	1.4	1.86
0.60	0.47	0.93	1.4	1.86
0.40	0.44	0.88	1.32	1.76
0.30	diffusion			

Table 1 data indicates weak dependence characteristic times of occurrence of the convection formation on the initial composition of the mixture.

Conclusions

Numerical study of the occurrence of instability of mechanical equilibrium and subsequent structure formation in the $H_2O + CH_2O_2 - Ar$ parabolic system with different CH_2O_2 composition in the mixture can be carried out based on a splitting scheme according to physical parameters. Mathematical model allows describing the process of a convective structure formation for different values of the composition of a triple mixture. Definition of convective instability may be associated with a significant curvature of the isoconcentration distributions, which are absent during diffusion. Degree of curvature of concentration distributions depends on the content of the component with the highest molecular weight in the system. With certain compositions, curvature disappears and diffusion is realized in the system. It was found that when vapor content of formic acid is less than 0.3 mole fractions in the mixture corresponds to the diffusion mode of mixing.

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Үшкомпонентті бугаз жүйелерінің изотермиялық араласуының сипаттамалық уақыттарын сандық зерттеу

Газдардағы көп компонентті диффузия бинарлық диффузияда байқалмайтын бірқатар әсерлермен сипатталады. Қолданыстағы жұмыстарды талдау белгілі бір геометриялық және жылуфизикалық сипаттамалары бар диффузия коэффициенттері айтарлықтай ерекшеленетін кейбір жүйелерде конвективті тұрақсыздық орын алуы мүмкін екенін көрсетеді. Тұрақтылықты талдау диффузиялық күйден конвективке ауысуға болатын параметрлер спектрін анықтауға мүмкіндік береді. Алайда, бұл тәсіл процестің динамикасын зерттеуге мүмкіндік бермейді. Сондықтан жұмыстың мақсаты үшкомпонентті жүйелердегі конвективті ағындардың пайда болуы мен эволюциясын сипаттау және концентрациялық гравитациялық конвекцияның пайда болуына бастапқы құрамның әсерін бағалау болып табылады. Жұмыстың негізгі бөлімінде физикалық параметрлер бойынша бөліну схемасы негізінде конвективті ағындардың пайда болуын сипаттайтын математикалық модель ұсынылған. Әр түрлі уақыт аралықтарында ең жоғары молекулалық салмағы бар газ концентрациясының өрістері туралы сандық мәліметтер алынды. Диффузияланушы компоненттердің изоконцентрлік сызықтарының қисықтығы жүйенің механикалық тепе-теңдігінің тұрақсыздығымен байланысты болуы мүмкін екендігі көрсетілген, ал қисықтық дәрежесі коспа компоненттерінің бастапқы концентрациясына байланысты. Алынған мәліметтер жылуфизикалық параметрлердің кең диапозонындағы аралас жылумасса тасымалымен байланысты есептеулерде қолданылатын масса алмасудың негізгі сипаттамаларын анықтау үшін пайдаланылуы мүмкін.

Кілт сөздер: газ коспалары, диффузия, конвекция, орныксыздық, бастапқы құрам, сандық есептеу, изотермиялық араласу, құмырсқа қышқылының буы.

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Численное исследование характерных времен смешения изотермических трехкомпонентных парогазовых систем

Многокомпонентная диффузия в газах характеризуется рядом эффектов, которые не наблюдаются при бинарной диффузии. Анализ существующих работ показывает, что в некоторых системах с существенно отличающимися коэффициентами диффузии при определенных геометрических и теплофизических характеристиках может иметь место конвективная неустойчивость. Анализ на устойчивость позволяет определить спектр параметров, при которых возможен переход из диффузионного состояния в конвективное. Однако этот подход не позволяет исследовать динамику процесса. Поэтому целью работы является описание возникновения и эволюции конвективных течений в трехкомпонентных системах и оценка влияния исходного состава на возникновение концентрационной гравитационной конвекции. В основной части работы представлена математическая модель, описывающая возникновение конвективных течений на основе схемы расщепления по физическим параметрам. Получены численные данные о полях концентрации газа с наибольшим молекулярным весом в различные моменты времени. Показано, что искривление изоконцентрационных линий диффундирующих компонентов может быть связано с неустойчивостью механического равновесия системы, а степень искривления обусловлена начальной концентрацией компонентов смеси.

Ключевые слова: газовые смеси, диффузия, конвекция, неустойчивость, исходный состав, численный расчет, изотермическое смешение, пары муравьиной кислоты.

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