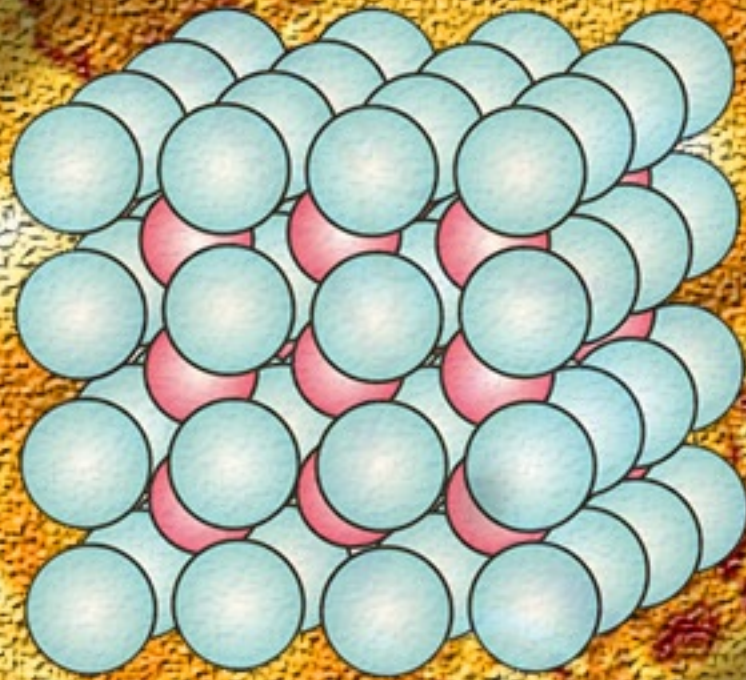


INTERNATIONAL SCIENTIFIC JOURNAL

"MATERIAL SCIENCE"



„NONEQUILIBRIUM PHASE TRANSFORMATIONS“

YEAR X, ISSUE 1/2024

ISSN PRINT 2367-749X

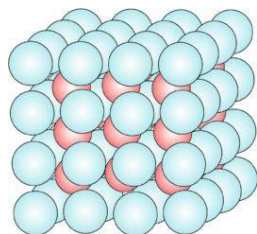
ISSN WEB 2534-8477

PUBLISHER: SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING
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CONTENTS

Increasing Bitrate Speed Using Artificial Intelligence in WDM C-Band Systems Based on Silicon Nitride Waveguide Structures Dror Malka	3
Comparison of gear diagnostic methods used in the space industry Leszek T. Pawlicki	6
Detection of sonochemical hydrogenation effect in the process of hydro-vacuum dispersing of melts and its Significance David Sakhvadze, Gigo Jandieri, Giorgi Sakhvadze, Besik Saralidze	8
Research of the local powder materials permeability Aliaksandr Ilyushchanka, Iryna Charniak, Aliaksei Kusin, Anastasia Astapenka, Ruslan Kusin	14
Experimental measurements of magnetocrystalline anisotropy constants of evaporated cobalt-based thin films Ahmed Kharmouche	18
Optical properties of polymer-CNT thin films Halyna Mykhailova, Mykola. Yakymchuk, Evgen Len	22
On the character of rate primary recrystallization of steels in the zone of laser action Svetlana Gubenko	26
Microstructure and properties of Ti-TiC composite obtained by hot pressing Denys Oryshych, Oleksandr Stasiuk, Dmytro Vedel	30
Deposition of cobalt alloy protective coating on titanium against negative effects of hydrogen environment Volodymyr Dekhtyarenko, Iryna Zagorulko, Oleg Boshko, Tatiana Pryadko, Vasyl Kyrylchuk, Oleksandr Semyrga, Igor Evlash, Denis Stepanov, Vadim Bondarchuk	33
Characterization of self-cleaning coated composite materials for solar cells applications Klodian Dhoska, Ozcan Koysuren, Hafize Nagehan Koysuren	36
Influence of ultrasound in the production of Frass extracts Goda Gudinskaitė, Rasa Paleckienė	39

Increasing Bitrate Speed Using Artificial Intelligence in WDM C-Band Systems Based on Silicon Nitride Waveguide Structures

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Abstract. Back reflection challenges significantly constrain the efficiency of optical communication networks utilizing dense wavelength division multiplexing (DWDM) technology based on silicon multimode interference (MMI) waveguides. To address this issue, we propose an innovative 1×4 optical demultiplexer design based on MMI within a silicon-nitride (SiN) strip waveguide configuration that operates within the C-band spectrum. Our simulation outcomes indicate that the proposed device efficiently transmits four channels with 10 nm spacing in the C-band, exhibiting low power loss ranging from 1.99-2.36 dB, extensive bandwidth of 7.69-8.09 nm, and good crosstalk values between 20.7-23.5 dB. Utilizing the low refractive index of SiN, we achieve exceptionally low back reflection of 40.58 dB without requiring specialized angled MMI designs, typically needed in Si MMI technology. Hence, this SiN-based MMI demultiplexer technology can be effectively employed in DWDM systems to achieve high data transfer rates with minimal back reflection in optical communication systems.

1 Introduction

The rapid advancements in optical communication systems operating over the C-band spectrum necessitate novel and robust waveguide components capable of supporting high-speed light transmission with minimal power losses, broad bandwidth, and low back reflection losses [1-3]. Optical demultiplexers play a critical role in communication networks and can be implemented through various technological approaches: Y-branch devices [4-6], Mach-Zehnder interferometers [7], and multimode interference (MMI) couplers [8-10]. Dense Wavelength division multiplexing (DWDM) technology enhances data transfer rates by reducing the spacing between peak wavelengths, thereby increasing the number of usable channels within a single spectral band [11]. A strip waveguide consists of a narrow high-index region surrounded by a low-index material, facilitating strong light confinement and guidance through total internal reflection [12-13]. MMI couplers are widely used in photonic integrated circuits (PIC) due to their broad optical bandwidth, low losses, and compact structure [14-15]. MMI waveguides operate based on the self-imaging effect, where the entering electric field profile is replicated into multiple images at periodic intervals along the propagation axis [16]. A significant issue affecting transmitter system quality is back reflection, particularly light reflecting back into the laser source. Si MMI couplers often suffer from reflections due to the self-imaging effect and refractive index mismatch between Si and silica (SiO₂) [17]. To mitigate this, we employ Silicon-Nitride (SiN) as a waveguide material due to its lower refractive index, which supports the C-band range with low absorption. Research indicates the potential of SiN strip waveguide-based MMI couplers for designing splitters and wavelength demultiplexers in the C-band, owing to their low back reflection loss and minimal thermal sensitivity, which ensures stable operation across varying temperatures [18-19]. In this paper, we present a design for a 1×4 wavelength demultiplexer based on an MMI coupler within a SiN strip waveguide structure, capable of dividing four channels in the C-band light range at wavelengths of 1530 nm, 1540 nm, 1550 nm, and 1560 nm. The device configuration includes a cascade of 3- 1×2 MMI couplers, input waveguide and tapers, 6- S-bends, and output tapers. We optimized the geometrical dimensions of the strip waveguide and MMI couplers to achieve the self-imaging effect and determine the optimal parameters. Simulations were performed using artificial intelligence (AI), incorporating various optical numerical methods such as the beam propagation method (BPM) [20] in conjunction with AI-enhanced finite difference time domain (FDTD) analysis. The data processing and analysis were conducted using Python scripts to ensure precision and efficiency. In the context of WDM (Wavelength Division Multiplexing) C-band systems based on silicon nitride waveguide structures, AI can play a crucial role in optimizing the design parameters of multimode interference (MMI) couplers. These couplers are integral to ensuring efficient signal splitting and combining in photonic circuits, directly impacting the system's bitrate. AI, particularly machine learning algorithms, can be employed to explore the vast parameter space of MMI coupler design. By training a model on simulated data, AI can predict the optimal width, length, and thickness of the MMI coupler that

minimizes insertion loss and maximizes uniformity across all output channels. The AI model iteratively adjusts these parameters, running simulations or evaluating performance metrics until it converges on an optimal design. This approach significantly reduces the time and computational resources required compared to traditional trial-and-error methods. Additionally, AI can identify complex relationships between the design parameters and the coupler's performance, leading to innovative designs that might not be intuitively obvious. Ultimately, the optimized MMI coupler enhances the overall performance of WDM systems, enabling higher bitrate transmission with improved efficiency and reliability.

2 Demultiplexer design

Figure 1 shows the cross-sectional view in the XZ plane at Y=0, presenting the three cascaded MMI couplers designed for the 1×4 demultiplexer. The MMI coupler width is W_{MMI} , and their lengths are L_{MMI1} , L_{MMI2} , and L_{MMI3} . The input waveguide width is 515 nm with a height of 311 nm. Input taper lengths for MMI1, MMI2, and MMI3 couplers are set to 40.5 μm , with widths varying from 0.55 μm to 0.76 μm . Output taper lengths for MMI1, MMI2, and MMI3 couplers are 35.42 μm , with widths varying from 0.88 μm to 0.515 μm . The gap (G_t) between the output tapers for each MMI coupler is 0.79 μm . In this figure, the blue areas represent SiN, while the white areas indicate SiO₂.

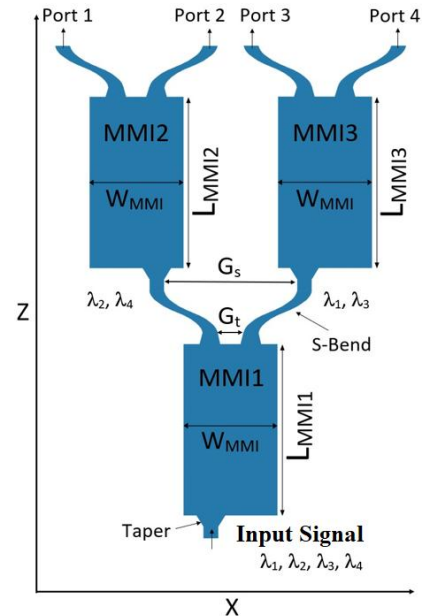


Fig. 1. Schematic diagram of the MMI demultiplexer.

The MMI1 coupler in the three-stage cascade is designed to effectively split four specific wavelengths: 1560 nm (λ_1), 1550 nm (λ_2), 1540 nm (λ_3), and 1530 nm (λ_4). The wavelength pair (λ_2/λ_4) is routed into the MMI2 coupler, while the pair (λ_1/λ_3) is directed into the MMI3 coupler, as depicted in figure 1. The width of the S-Bends was tailored to align with the output width of the taper, set at 0.515 μm , with lengths ranging from 68 μm to 79 μm . The spacing

between the S-Bend outputs (Gs) was set at $15.6 \mu\text{m}$ for MMI1 and $12.6 \mu\text{m}$ for both MMI2 and MMI3. The overall length of the device is 6.73 mm . According to the principle of self-imaging, each wavelength entering the multimode section of the device generates a direct or mirrored replica of itself at regular intervals.

3 Simulation Results

Figure 2 illustrates the TE mode profile solution within the SiN strip waveguide for an operational wavelength of 1560 nm . The strong confinement, indicated by the red color, demonstrates a mode spot size of $2.47 \times 2.33 \mu\text{m}$, which can be enhanced using an adiabatic or special taper for improved light coupling between the device and the input source. Comparable mode profiles were observed for the other operational wavelengths.

The effective refractive index values for the TE mode at each operational wavelength were determined through computational analysis.

Figure 3 illustrates the optimization process for determining the optimal height of the SiN layer, identified as 311 nm . The tolerance range around this optimal value, $\pm 22 \text{ nm}$, yields normalized power efficiencies between 47% and 65%. The highest power is observed at a height of 311 nm . However, considering current fabrication capabilities, maintaining this precision within acceptable fabrication tolerances is challenging.

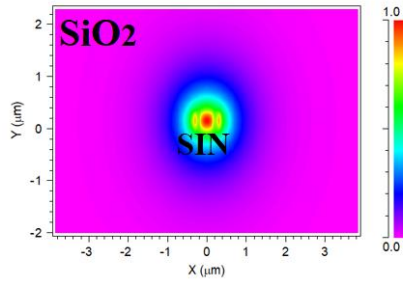


Fig. 2. TE mode solution for 1560 nm .

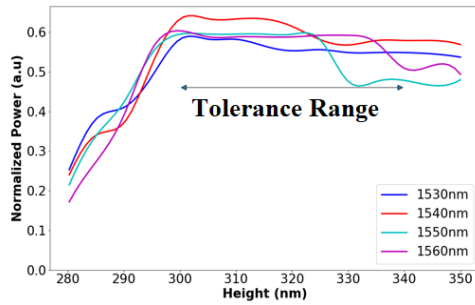


Fig. 3. Optimizations of the SiN height.

Figure 4 illustrates the ideal MMI coupler width, which is $3.51 \mu\text{m}$, along with the tolerance range of $\pm 22 \text{ nm}$ around this optimal value to achieve a normalized power output between 57% and 65%. This tolerance is selected due to the typical fabrication process accuracy, where geometric dimension errors are usually around $\pm 22 \text{ nm}$ from the target value.

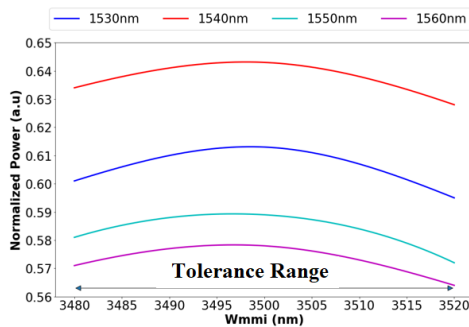


Fig. 4. Optimizations of the MMI width coupler.

Using BPM simulations, the optimal lengths for the MMI couplers were determined. To achieve maximum output power while accommodating fabrication errors, Lmmi1, Lmmi2, and Lmmi3 were selected as $4164 \mu\text{m}$, $2071 \mu\text{m}$, and $2081 \mu\text{m}$, respectively. Figure 5 illustrates a tolerance range of $5.2 \mu\text{m}$ around the optimal length for each MMI, in relation to the corresponding wavelengths, to achieve a normalized power output between 66% and 73%. This wider tolerance range provides significant flexibility in the fabrication process.

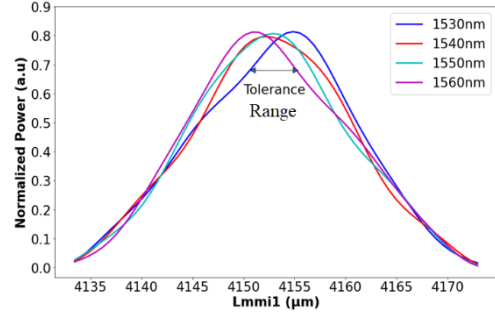


Fig. 5. Optimizations of the MMI1 length coupler.

Figure 6 displays the light intensity profile of the SiN MMI demultiplexer device for the C-band at the XZ plane. The laser light enters the input waveguide at $Z=0$, passing through the input taper into the MMI1 section. The splitting of the four signals into two pairs (λ_2/λ_4 and λ_1/λ_3) occurs at $Z=4253 \mu\text{m}$, which is the output of MMI1. The light then travels through the S-bends into the subsequent MMIs, where further splitting happens at the MMI2 output for 1540 nm (λ_2) (b) and 1560 nm (λ_4) (a) at $Z=6515 \mu\text{m}$, and at the MMI3 output for 1530 nm (λ_1) (c) and 1550 nm (λ_3) (d) at $Z=6531 \mu\text{m}$. Finally, the light continues through the S-bends and reaches the four output channels at $Z=6631 \mu\text{m}$.

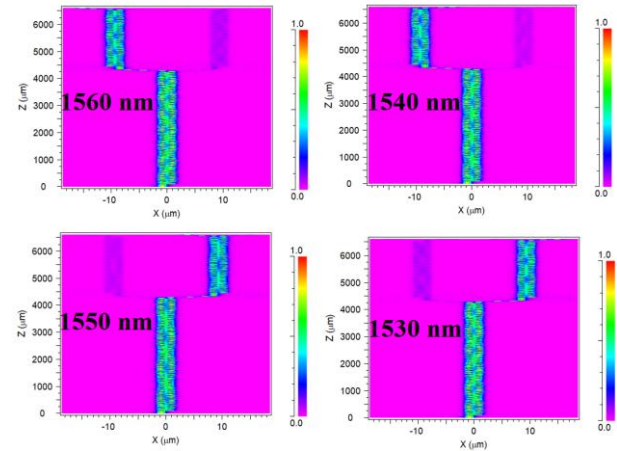


Fig. 6. Power and light intensity profile of the four C-band channels from $1530\text{-}1560 \text{ nm}$.

The spectral transmission for the four channels within the C-band, covering the wavelength range from 1530 nm to 1570 nm , is depicted in Figure 7. The data was obtained by solving the mode for each wavelength within this range, followed by applying these results to the optimized demultiplexer design. The data analysis was carried out using AI-Python scripts. Crosstalk, insertion losses, and spectral bandwidth were evaluated in conjunction with Figure 7, and the outcomes are summarized in Table 1. Another crucial aspect of the MMI coupler is the back-reflection into the input section, which can significantly affect the laser source's performance. In this study, SiN material was employed to reduce the power back-reflection caused by self-imaging within the MMI coupler. To measure the back-reflection, a monitor was positioned in the input waveguide to capture all light reflecting back from the MMI coupler, as illustrated in Figure 8.

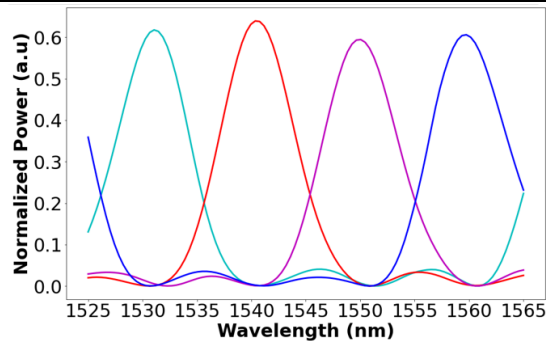


Fig. 7. C-band optical spectrum.

Table 1: Crosstalk, Losses and bandwidth values for each signal.

λ (nm)	1530	1540	1550	1560
Channel	3	2	4	1
Crosstalk (dB)	21.4	23.5	20.7	23.7
Losses (dB)	2.36	1.99	2.22	2.2
Bandwidth (nm)	7.69	7.78	8.01	8.09

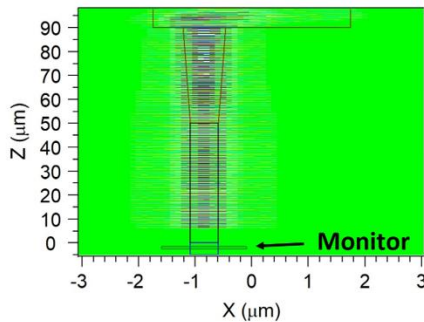


Fig. 8. Back reflection simulation and calculation.

4 Conclusions

This study introduces the design of an innovative 1x4 demultiplexer in the C-band, utilizing three cascaded MMI couplers based on a SiN strip waveguide structure. The analysis has identified the optimal parameters for the MMI couplers necessary to efficiently split four specific wavelengths: 1530 nm, 1540 nm, 1550 nm, and 1560 nm. The total propagation length of this device measures 6.63 mm, with insertion losses ranging from 1.99 dB to 2.36 dB. The device also demonstrates excellent crosstalk values between 20.7 dB and 23.5 dB, and an optical bandwidth spectrum ranging from 7.7 nm to 8.1 nm. These findings suggest that this demultiplexer could be highly effective for use in long-haul optical communication networks that employ DWDM technology within the C-band spectrum. Additionally, the proposed device exhibits a low back-reflection loss, between 40 dB and 41 dB, without requiring a specially angled MMI design. This low reflection is primarily attributed to the use of SiN as the core material, which helps to minimize losses and maintain signal integrity. The results underscore the potential of this device to be integrated into DWDM communication systems, enhancing data transmission rates. The design's tolerance range 5.2 μ m for the MMI coupler lengths offers good flexibility, making it compatible with current fabrication processes. Moreover, the simplicity of the design is a key strength. It facilitates the expansion of the number of channels by adding more MMI couplers and fine-tuning their geometrical parameters to suit the desired application. This scalability is particularly valuable for applications that require the handling of multiple wavelengths in optical communication systems. In conclusion, the proposed SiN-based 1x4 demultiplexer offers a promising solution for advanced optical communication systems. Its optimized design, low losses, and excellent crosstalk performance make it well-suited for DWDM

applications in the C-band. The device's compatibility with existing fabrication technologies, combined with its scalability and dual functionality as both a demultiplexer and multiplexer, positions it as a highly adaptable and efficient component for future photonic integration. As the demand for higher data rates continues to grow, such devices will be crucial in supporting the expansion and evolution of optical networks, ensuring that they can meet the increasing needs of data transmission and communication.

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Comparison of gear diagnostic methods used in the space industry

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Abstract: *The basic method for examining the condition of gears is the vibroacoustic method. This method is widely used around the world for diagnostic purposes. However, it is not always possible to use it. This especially applies to mechanisms operating ultimately in space. Harsh working conditions, the presence of the vacuum of space, radiation, reactive oxygen ions and many other factors make diagnostics in this environment much more difficult. This article compares vibroacoustic, electrical, optical and other methods in terms of their potential application for diagnostic purposes of gears used in the space industry.*

KEY WORDS: GEAR, LUBRICANT, DIAGNOSTIC METHODS, SPACE INDUSTRY

1. Introduction

The space industry is an area of engineering that is currently developing very intensively. It provides systems, machines and technologies enabling both space exploration and related scientific research and development of related terrestrial technologies. Due to the specific operation of elements in space and the associated extreme environmental conditions, it is important to constantly monitor the operation of the devices. This is particularly important because in space, not only damage to very expensive equipment but also human life may depend on the proper operation of machines. Due to the need to launch devices into space, replacing parts of damaged machines, repairing them in space or replacing them with a new device requires large financial outlays. For this reason, the development of diagnostic methods in this sector of the economy is particularly important. The diagnostic methods themselves that could be used in space must meet certain conditions specific to this area. Due to the need to transport diagnostic devices into orbit, it is particularly important that such equipment takes up little space and is light. As with any diagnostic device, it is important that such a system is reliable and maximally integrated. It is an advantage if it allows testing of machines without interfering with their structure or dismantling them. It is good if the test can be performed both when the device is running and when it is not. Due to their operation in space, diagnostic devices must be properly protected against radiation and be able to operate on both direct and alternating current power. In the case of diagnostic tests of gears, the analysis of their condition both on Earth and in space comes down to appropriate material tests, which can be divided into characteristic research methods [1-3].

2. Material research methods and the potential of their application in the space industry

Material research methods can be divided into: vibro-acoustic, optical, resonance, ultrasonic, thermodynamic, X-ray, electrical and others.

One of the most popular methods used to analyze the condition of gears are vibro-acoustic methods. During operation of the gear, the gears within it interact mechanically with each other. This causes vibrations and noise. They are then analyzed. In the case of a properly functioning gearbox, both of these parameters maintain a certain regularity and are within specified standards. Irregularity or too high intensity in their case may indicate incorrect operation of the device. The main advantage of this method for gear diagnostics is that it is now widely used on Earth. Therefore, it is a well-known technology in this field. It allows you to diagnose many different threats in the operation of machines and, in many cases, allows you to examine them in a non-invasive way. However, if this method is used in space, its use may be difficult in many cases due to the lack of a sound-transmitting medium (air). Noise and vibrations occur only during mechanical operation of the device. This method does not allow for device diagnostics between cycles of operation. Lack of such diagnostics may result in equipment damage during startup [4-5].

Another type of methods used to analyze the state of materials are resonance methods. They involve placing an appropriate piezoelectric module inside the device. As the material parameters change, e.g. the quality or composition of the lubricant inside the

gear, the characteristic resonance frequency of the piezoelectric changes. Analysis of these changes allows for the assessment of the lubrication condition. The advantage of using this method both on Earth and in space is the small size of the piezoelectric elements that constitute the basis of this research method and their reliability. When such devices operate on Earth, it is necessary to use special technologies to dampen side vibrations that may affect the result of the analysis of the device's operation. Due to the lack of air in space, using this method for machine diagnostics with an appropriate system design may turn out to be easier than on Earth [6].

Another type of potential diagnostic methods are optical methods. Application of a laser light source and a photocell inside the gearbox allow you to measure the speed of the gearbox. Any deviations from the regularity of such operation observed in the light intensity graphs may indicate incorrect operation of the device. If at least partially transparent lubricant is used inside the gear, an analysis of the composition and quality of the lubricant inside the gear can be obtained by optical analysis of its characteristic refractive index. This method is effective both on Earth and in space. However, it usually requires interference in the structure of the machine (introducing a laser and sensors inside) and most often requires disassembling the device [7-8].

Ultrasonic methods can also be used for material analysis of gears. The introduction of a piezoelectric element into the tested system allows for the transmission and reception of ultrasound. As the gear system and the quality and composition of the lubricant change, the time after which the generated sound returns to the source will change. Analysis of such a returning (reflected) signal may allow obtaining information related to the lubrication and structure of the gear. Due to the lack of air in space, the use of this method in orbit may be difficult [9-10].

Thermodynamic methods are commonly used methods for diagnosing various types of devices, including gears. They involve measuring the temperature of the gear and the pressures occurring inside it. Too high friction during gear operation resulting from its incorrect functioning or damage may cause the device to heat up too much or cause too high pressure inside the gear. Thermodynamic methods are simple to use and reliable. They can be used in space without any major problems. However, they usually require dismantling the gear or installing sensors inside it [11-13].

X-ray methods are very precise methods enabling full analysis of structural changes in both gear wheels and lubricants constituting gear elements. However, due to the need for extensive, expensive and heavy diagnostic equipment, the potential for using this type of methods in space is low. However, it is possible to use them in the production of related machines on Earth as part of the space industry [14].

Currently, electrical methods have the greatest potential in the field of gear diagnostics, both in the space industry and in outer space. They require little financial outlay. The devices required are small, light and reliable. They allow you to test the device in a non-invasive way, using the structure of the gear itself. Electrical methods allow for diagnostics both during continuous operation and during breaks between transmission operation. These methods, thanks to the use of several independent material parameters such as specific resistance, electric permeability and magnetic permeability, allow for independent comparative diagnostics [15-21].

3. Summary and conclusions

When comparing various diagnostic methods and the potential of their use in the space industry (including outer space), one can notice a significant advantage of electrical methods, which, unlike vibro-acoustic and ultrasonic methods, do not require an intermediary medium such as air and allow for testing both in both during and outside the device's operation. Unlike thermodynamic, optical and resonance methods, they do not require interference in the structure of the device or penetration into its interior. Unlike X-ray methods, they require only simple and cheap equipment. Electrical methods are simple to use, reliable, cheap and versatile. All this indicates the high potential of electrical methods in the diagnostics of gears in the space industry [1-21].

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Detection of sonochemical hydrogenation effect in the process of hydro-vacuum dispersing of melts and its Significance

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Abstract: The study is devoted to the identification of technological features of the process of hydrovacuum dispersion (atomization) of liquid aluminium, which provides the accompanying self-generation of the effect of sonochemical hydrogenation of the obtained particles. In order to explain this phenomenon, the study reveals the design and functional features of a special, actually developed installation of continuous vertical suction and dispersion of metallurgical melts. Here the graphical scheme-model of influence of ultrafrequency cavitation pulsation generated by shock waves of hydraulic rarefaction, cumulative splitting of water molecules and sonochemical introduction of released hydrogen in solidifying particles of atomized aluminum melt is reconstructed. The results of the revealed sonochemical hydrogenation process are clearly illustrated by both electron microscopy images and X-ray diffractometry and FTIR spectroscopy. It is established that during hydrovacuum atomisation free hydrogen can be dissolved and retained in aluminum microparticles, both with the formation of blown (foamed) clusters of diffusion-amorphous hydrogenation, and - solid solution of embedding, in the form of crystals of face-centred cubic syngony.

KEYWORDS: METALLURGICAL MELT, HYDROVACUUM DISPERSION, SONOCHEMICAL TREATMENT, HYDROGENATED POWDER.

1. Introduction

1.1 Hydrovacuum dispersion of melts: current state and background of the study

The technology of hydrovacuum dispersion of melts (HVD), which is at the stage of industrial implementation at the metallurgical-foundry plant "Geo Enterprise" LLC (Georgia), is a new, progressive direction in the development of the industry of high-performance atomization of metallurgical melts, which is distinguished by its flexibility and multifunctionality. The installation is capable of processing both metal and slag melts with fluidity not lower than 100-150 mm (determined by a standard sample in the form of a channel of a certain length and diameter with a sprue bowl). When atomizing metal melts, the powders obtained in the HVD process are distinguished by a high degree of purification from non-metallic inclusions and increased mechanical activity [1], which is important for its operational properties. And the granules obtained by HV-dispersion of slag melts are distinguished by a high degree of presence of a glassy amorphous hydroactive phase and, without additional activation, can be used as binder additives in the production of construction cement and concrete [2].

HVD technology has been developed and improved for more than 10 years. The copyright for it is protected by Georgian patents: GEP20156384B, GEP20207078B, GEP20247613B [3-5].

In contrast to the traditional methods of production of metallic and non-metallic functional powders for various purposes, the essence of the innovation and superiority of our proposed technology lies in the suction and dispersion of metallurgical melts in the direction opposite to the force of gravity, where the main work is performed by the hydraulic vacuum of the conical profile locally generated as a result of the rapid expansion of the toroidal flow supplied by high pressure and the sharp change in the direction of the flow in a closed space.

The vertically, concentrically directed from the bottom-up forces of a tensile stresses with accompanying rarefaction shock waves influenced on the surface of the melt (cylindrical flow sucked in the vacuum area), is created fundamentally different, hydrodynamically optimized conditions for the melt dispersion. In particular, during hydrovacuum dispersion, the cylindrical flow of molten metal sucked in the device, upon entering the dispersion zone created by the toroidal flow of water, continuously interacts with the high-speed flow of water supplied to an inclined angle as a result, it goes into mode of the intense hydraulic friction, adhesion and capillary disintegration, i.e., a phase of intense disintegration-dispersion is formed. The noted hydraulic-technical scheme of the dispersion process is quite comprehensively described in studies [1,

2], where you can get acquainted with the existing technological differences and advantages of the proposed HVD process.

1.2 Installation design features

The proposed technology is environmentally safe. During operation, no smoke, steam or dust is emitted, because the water circulating in the process system acts as both a wet filter and a steam condenser. The device operates quietly and without vibrations, is compact and easy to install (installation is not related to significant reconstruction of the metallurgical workshop or casting area). The technical water applicable as the work area circulates in its own pipe system and also does not pollute the environment. The technology is energy-resource-saving, eliminates the high-temperature heat treatment of the obtained powders in the regenerating environment. Therefore, it is highly profitable and economically beneficial.

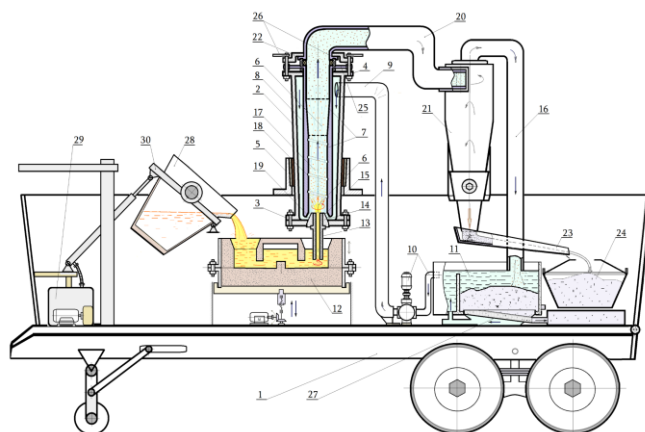


Fig. 1. Portable device for hydro-vacuum dispersion and mechanical activation of metallurgical alloys

The proposed portable device for hydrovacuum dispersing of metallurgical melts presented in Fig. 1, consists an inverted truncated cone-shaped body 2, vertically located on the transport platform 1, with flat toroidal front ends 3-4, a support 5 for the body 2, a melt spraying chamber 6 formed in it with the ability to move vertically, whose internal space has a venture pipe shape 7, the channel 8 formed around the spraying chamber 6, to supply water in it under pressure from top down, the high-pressure pipe 9 connected tangentially to the said channel 8, so that it does not coincide with vertical axis of symmetry of the body 2, which, by means of the water circulation system 10, is connected to the feeding siphon-type tank 11, the horizontal siphon-type casting form for holding the

liquid metal 12, made with the ability to move in the vertical plane, a cylindrical nozzle 13 lowered into the casting form 12 with one end, the other end of which is connected to the lower end 3 of the body 2 with a truncated cone-shaped head 14 in such a way that near the channel 8 formed around the spraying chamber 6 of the body 2, the neck 15 to supply water to the spraying chamber 6, the feed pipe 16 connected to the spraying chamber 6 for supplying loose melt and water suspension (pulp) 17 to the feeding siphon-type tank 11 of the water circulation system 10. In addition, the cylindrical part of the venturi tube-shaped spraying chamber 6 located inside the body 2 is cut according to the principle of Archimedean spiral 18, in the direction coincident with the rotation of the water tangentially supplied in the channel 2 of the body 2. On the inner surface of the lower front-end part of the spraying chamber 6, there is formed a chamfer 19 the surface of which is parallel to the surface of the conical head 13 of the nozzle 13, while the spraying chamber 6 is connected to the feed pipe 16 for supplying the pulp 17 to the feeding siphon-type tank 10 of the water circulation system 11 by means of the output pipe 20 and the hydrocyclone 21, where the output pipe 20 is connected to the spraying chamber 6 in its upper part through a flexible hermetic cover 22. In addition, the feed pipe 16 is connected to the upper part of the hydrocyclone 21, the lower part of which is connected by means of the guide groove 23 to the large fraction collector 24. In addition, the neck 25 of the spraying chamber 6 located in the body 2 with the ability to move vertically from the upper front-end 3 of the body 2 and fixed in the flexible hermetic coupling 22, is equipped on both sides with a symmetrical lifting-lowering screw-lever mechanism 26, and the bottom of the feeding tank 17 of the water circulation system 10 is equipped with an electrodynamic separator 27, while on the transport platform 1, there is placed additionally a driving unit 29 of a ladle 28, which is equipped with a turning mechanism 30 of a ladle 28.

1.3 Technological operating features

The portable device for hydrovacuum dispersion and mechanical activation of metallurgical melts functions as follows:

After filling the device's water circulation system 10 and the feeding siphon-type tank 11 with water, supplying it to the spraying chamber 6 through the channel 2 of the body under high pressure and, accordingly, creating a negative pressure (vacuum of $-0.85 \div -0.95$ bar) in the melt suction nozzle 13 (defined by means of a special vacuum meter), from the ladle 28 located in the hydraulic turning mechanism 30, through the drive node 30, the controlled balanced pouring of melt will begin in the casting form 12, which can be moved in the horizontal plane. The liquid melt, when flowing under the siphon of the casting form 12, is freed from the non-metallic (slag) inclusions embedded in it and in a physically clean state, it goes to the rarefaction formed in the area of the lower front-end of the nozzle 13. The vacuum developed in the nozzle 13 and the suction force generated by it, immediately after contact with the melt, changes its direction by 90 degrees, and at a certain speed, through the inner vertical cylindrical channel of the nozzle 13, it will deliver it to the spraying chamber 6 with a venturi tube-shaped 7 internal space formed in the body shell 2, where it will be captured by a conical vortex of water injected with a flow rate of $0.022\text{--}0.029$ m³/s and a speed of 6–10 m/s from the sloping neck 15 formed between the chamfer 19 of the spraying chamber 6 and the side surface of the truncated cone-shaped head 14 of the nozzle 13. The cylindrical jet of the extracted melt raised vertically in the said vortex, immediately upon contacting the shell of the latter, experiences a powerful 3D (simultaneously twisting and stretching) hydromechanical impact (hydraulic impact), which disintegrates and disperses it in the cylindrical part of chamber 6 in the direction of the upward spiral groove 18 cut according to the Archimedean spiral principle. On average, at this time, a gravitational overload occurs with a value of 140–200g. During the hydromechanical and thermophysical interaction of high-temperature melt with cold water under conditions of increased gravitational overload, cavitation caverns with a core saturated with gases absorbed from the melt particles appear inside the venturi profile pipe chamber 6

along with steam micro-bubbles, which undergo collapse as soon as they pass into the upper expanded zone of the venturi profile pipe 7 and drop the external pressure, which additionally excites high-frequency ultrasonic acoustic waves in the pulp. The said wave impact, in turn, performs additional micromechanical processing of amorphyously solidifying and volumetrically (3D twisting) deformable powder particles weighted in the pulp 17. As a result, the surface area of powder particles increases and the amount of energy accumulated therein increases, resulting in an increased degree of mechanical activation

In order to separate powder particles from the pulp 17 formed in the process, a cyclone 21 rigidly placed parallel to the body 2 is used, in which the said pulp flows through the output pipe 20. The relatively large fractions separated by the cyclone 21 are accumulated in the large fraction collector 24 through the guide groove 23. The lightened pulp from the upper part of the cyclone 21 is supplied through the feed pipe 16 to the feeding siphon-type tank 11 of the water circulation system 10, equipped with an electrodynamic separator 27, where, on the one hand, there occurs the artificial weighting, sedimentation, and dehydration of fine and ultrafine particles of metal. On the other hand, water is purified from suspended particles supplied again into the feeding tank of the high-pressure pump. After low-temperature ($80\text{--}110$ °C) drying, the resulting powdery mass is ready for its intended use.

Under conditions of variations in operation and technological characteristics of dispersible melts (overheating temperature, composition, gas concentration, flowability, the latent heat of melting and crystallization, volume shrinkage, etc.), which are operatively controlled or imitatively modeled during the process, the height of a neck 15 is optimized, that is, the area (cross-section) of the ring-shaped jet generating the conical vortex that is formed in the spraying chamber 6. The regulation is carried out by means of a screw-lever mechanism 26 hermetically connected to a flexible hydraulic coupling 22, which in turn is equipped with a venturi profile pipe 7 formed in the body 2 of the spraying chamber 6 with an identity reader of the actual lowering depth. An accelerometer digital gyroscope is used to record the micro-oscillations and vibrations generated in the spraying chamber 6 during the dispersion process, and an acoustic chamber (digital microphone) recording the ultrasonic audio spectrum is used to assess the effect of cavitation. All sensors serving the device are connected to the main metrology controller, which in turn is connected to a pre-programmed operating computer/laptop (not shown). Through operational control of the granulometric composition of the obtained powder, which is carried out by means of a special portable express-analyzer integrated with the above-said controller, based on the computer program MATLAB simulation modeling database, a decision is made automatically/operationally on controlling the dispersion process, in particular on the rational regulation of the size of the water injection neck 15 or the pressure of the water tangentially entering the channel 8 of the body 2 flowing from the pipe 9, and as a result, the vacuum developed in the nozzle 13 (melt suction speed). The technical-technological solution described above, along with the decision to place the device on the vehicle platform 1, lends the function of inter-enterprise portability and universality to the latter.



Fig. 2. Pilot installation for hydrovacuum dispersion of metallurgical melts, implemented in "Geo Enterprise" LLC

2. Significance of Hydrogenation and methods of its implementation

Hydrogenated metal powders (abbreviation – MeH_n) belong to a series of solid energy materials of the hybrid type. Their production is associated with high technologies and the comprehensive use of areas of basic science such as inorganic chemistry, physical chemistry, solid-state physics, thermal physics, hydrodynamics, acoustics, mechanics, materials science, metallurgy, etc. [6, 7]. The hydrogenation of metal materials, which is manifested in obtaining a solid-phase binary compound of metal and atomic hydrogen, is considered the most energy-efficient way of hydrogen storage (accumulation), transportation, controlled emission, and its intended use in normal conditions [8]. Hydrogen, in the modern world, is considered an environmentally friendly, renewable source of promising fuel. It has the potential to make modern internal combustion engines completely environmentally safe [9, 10]. When using hydrogen fuel, the combustion product is an environmentally harmless water vapor. In addition, hydrogen is the most active ore-reducing chemical component that can eliminate the need for harmful carbon reducing agents in traditional blast furnace or electrocarbothermal processes for the production of steel, pig iron and ferroalloys [11]. Hydrogen is also an indispensable component in the production of modern dry electric accumulators [12]. Hydrogen-saturated metal hydride materials are the best resource-rich cathode materials for Ni-MH type electric accumulators, while they are cheaper and environmentally safe, unlike traditional Li-Ion and Li-Pol type accumulators. Based on the goals and objectives set in the EU strategic program [13] on ensuring climate neutrality in the potential of hydrogen as a self-renewable natural resource should be maximally exploited and used for the decarbonization of the world economy and, accordingly, for the elimination of environmental pollution with greenhouse gases.

The solubility of hydrogen, as the lightest chemical element (0.089 kg/m^3), in metals, especially in aluminium, is so high that this method of its accumulation and transportation ($\approx 10 \text{ wt.}\%$) is much more effective than the method of cryogenic ($70\text{--}100 \text{ K}$) liquefaction at high pressures ($600\text{--}700 \text{ bar}$) and storage-transportation in metal-organic ball tanks reinforced with special cryolite or carbon fibers [14]. Moreover, in contrast to the latter, the transportation of metal hydrides and the operation of heating up to $120\text{--}160^\circ\text{C}$ for hydrogen reverse-emission are not associated with any kind of risks and dangers. The reverse-emission of hydrogen proceeds slowly, and increases in proportion to the increase in the heating temperature of the hydrogenated metal. It was found that hydrogen in metal hydrides, due to the low ionization of the latter, binds its electron to the band of generalized (free) electrons of the metal, thereby establishing a metallic bond with it. Along with that, metal hydrides, whose composition is often non-stoichiometric, are formed with almost all transition metals that react reversibly with hydrogen. That is, they can bind, release, and bind again hydrogen multiple times, that is, they function as rechargeable batteries. It is known that the most stable compound of metal hydrides is aluminum hydride (AlH_3) of the α allotropic modification called "Alan". In addition, due to its cheapness, as well as its chemical and thermophysical properties, aluminum is in high demand in the fields of metallurgy and machine-building, such as direct, non-carbon (aluminothermal) recovery and refining of machine-building and construction materials (iron, manganese, chromium, nickel, etc.), thermal welding, etc. Recent studies prove that it is with the consistent use of these two elements (intermediate solid-phase reducing of metal oxides with hydrogen + liquid-phase finishing recovery with aluminum) that one of the most energy- and carbon-intensive metallurgical industry of the world industry can be fundamentally transformed and taken to a completely new level of development [15].

Among the known methods of obtaining the α allotropic modification AlH_3 compound, the plasmachemical synthesis method based on the placement of trimethylaluminum ($\text{Al}(\text{CH}_3)_3$) and/or aluminum chloride (AlCl_3) in gaseous hydrogen environment and ionization with the DC electric arc is considered to be one of

the most productive methods of processing [16]. The desired chemical transformations are achieved by artificially increasing the partial pressure of hydrogen under conditions of high pressure and temperature and the forced embedding (clamping) in crystal lattices of aluminum. It should be noted that the use of aluminum hydride obtained in this way, due to its high cost, is justified only as a solid rocket fuel. According to modern studies, the sonochemistry (ultrasonic acoustic synthesis) method is considered one of the most promising methods of hydrogen extraction and metal hydrogenation [17]. The method is carried out by artificially initiating unsteady cavitation foci on the surface of metal particles (ultrasonic irradiation), providing conditions of cumulative collapse of formed caverns saturated with water vapour, and subsequent micropulse impact (penetration) by hydrogen atoms generated in the aftermath of high-temperature ($3000\text{--}5000^\circ\text{C}$) dissociation of water molecules. Hydrogen atoms, which are released during the collapse of the noted caverns, in the aftermath of the directed shock-wave impact on the metal surfaces are embedded in its crystal lattices, i.e. - leads to its diffusion-adsorption saturation with hydrogen. The average duration of one operation of sonochemical hydrogenation is $160\text{--}180$ minutes. Despite the progressiveness of the method, the hydrogenation process is quite inertial, costly, and difficult to scale in practice, requiring a portioned, intermittent supply of pre-prepared powdered metal materials to a specially screened sonothermal bath for the safety of the service personnel, where the hydrogenation process continues until the water starts boiling. In addition, the quality of the final purity of the powders depends on the quality and purity of the electrode of the ultrasonic generator immersed in water, because during the sonosynthesis process, there is an intense erosion of the latter and contamination of the target powder particles with foreign bodies.

3. Phenomenon of sonochemical hydrogenation during hydrovacuum dispersion of melts

It is noteworthy that traces of sonochemical hydrogenation of powdered metallic particles were unplanned discovered during research work, at the stage of studying the morphological and operational characteristics of powders obtained as a result of hydrovacuum dispersion of liquid aluminum, carried out within the framework of a scientific grant from Shota Rustaveli National Science Foundation of Georgia No. AR-22-1495.

As a result of special observations and studies, it was established that during certain modes of hydrovacuum dispersion, hydromechanical (shock) waves acting on a vertically raised melt jet due to hydraulic rarefaction created in the disperser, stimulated the effect of cavitation pseudo-boiling. Caverns concentrated near the surfaces of metallic particles experienced cumulative collapse upon transition from the hydraulic rarefaction zone to the injection area and compression. The variable, (pulsating) high-temperature, microcumulative pneumo-shocks generated during the collapse of the caverns, in turn, generated ultrasonic acoustic waves (frequency $\geq 20\text{--}25 \text{ kHz}$) directed toward the points of contact with the particles [18]. The sonopulsation generated at this time provided directional acceleration of elementary hydrogen atoms, released during sonothermal dissociation of water vapor molecules, to the surface of metallic aluminum particles, which led to adsorption-diffusion saturation (condensation) and embedding of hydrogen into the crystal lattices of powdered metallic particles (forming a metallic bond). As a result of our subsequent observations, it was found that the molecular hydrogen " H_2 " released during the collapse of caverns led to foaming of the particle structure, with the formation of so-called blown clusters, and the embedding of atomic hydrogen " H " occurred without appreciable expansion of the particle volume, as it penetrated deeper and embedded directly in the aluminum crystal lattice. There was also a partial dissolution of free hydroxide radical " OH " in the surface layers of solidifying particles of atomized aluminum melt. In general, the process of dynamic pulsation-sonochemical hydrogenation during hydrovacuum suction and dispersion of metallurgical melts can be represented according to the diagram illustrated in Fig. 3.

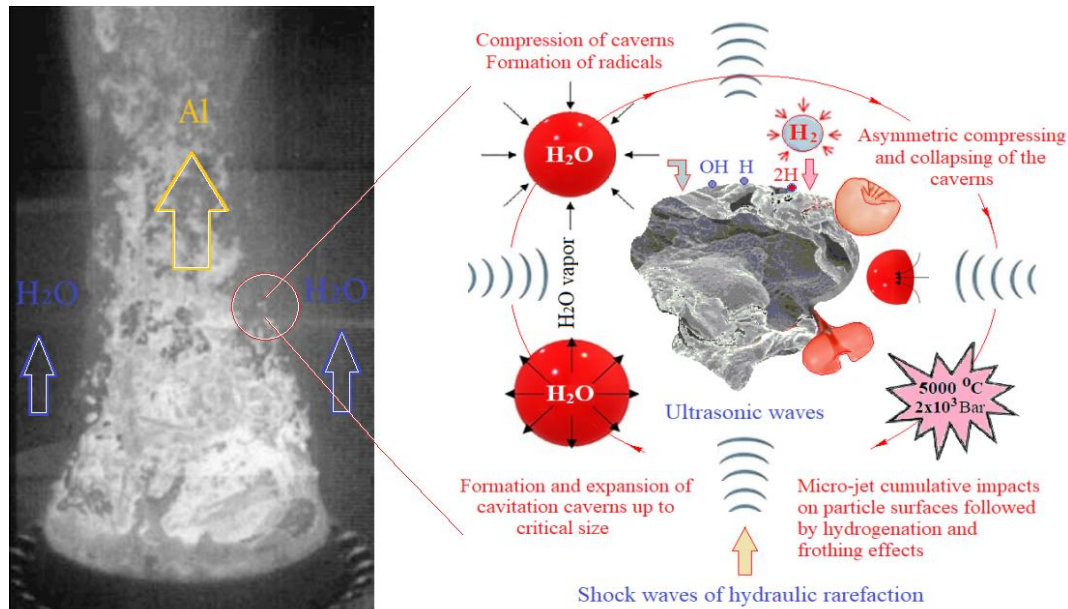


Fig. 3. Schematic diagram of the effect of sonochemical hydrogenation of a particle formed during hydrovacuum dispersion of an aluminum melt

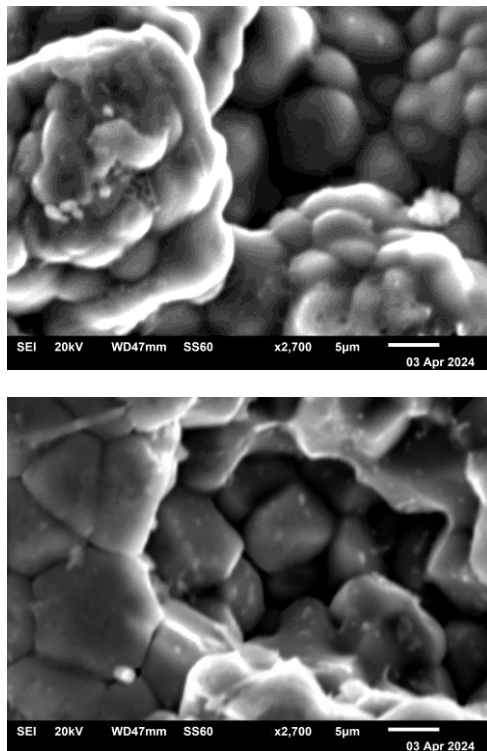


Fig. 4. a) bloated areas with AlH_2 and b) crystalline formations of hexagonal syngony of AlH_3 binary compound

It was established by microscopic-morphological studies that in the obtained aluminum particles Fig. 4, there were appeared the so-called „swollen” (bloated) zones AlH_2 characteristic of diffusion-adsorption hydrogenation appeared, as well as crystalline formations of hexagonal syngony of AlH_3 binary compound called the „Alan”. This is also confirmed by X-ray spectral analysis, illustrated in Fig. 5. The result of X-ray diffraction analysis, illustrated in Fig. 5 showed that the crystal lattice of hydrogenated powder aluminum grains in general is cubic, face-centered with hydrogen atoms embedded in it.

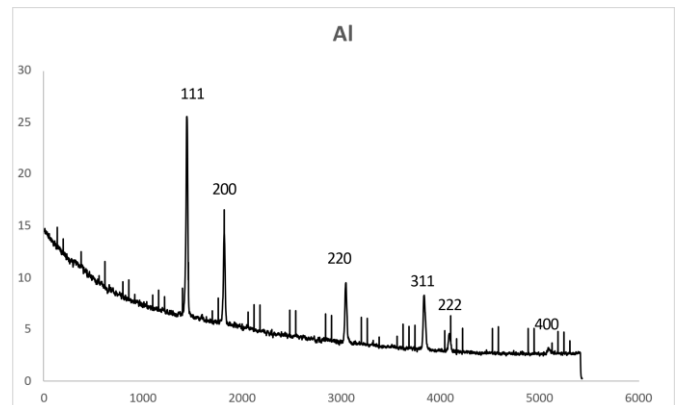


Fig. 5. X-ray diffraction pattern of hydrogenated aluminum powder

In contrast to the stationary sonochemical method of hydrogenation implemented by a periodic process, in our case, the process is carried out continuously, in the form of a duplex operation, which is manifested in the provision of the hydration of powder particles directly at the stage of hydrovacuum dispersion of metals, that is, the stage of re-filling the obtained powders into the water reservoir and long-term treatment with an ultrasonic generator is excluded. This effect can be considered one of the most important scientific-practical values of the proposed method because no information about the theory or practice of the combined implementation of these operations can be found in the world scientific literature. Meanwhile, in our case, the hydrogenation process proceeds much more intensely, since gaseous hydrogen interacts directly with the liquid metal. The solubility of hydrogen in liquid metal is significantly higher than its solubility in a cold state [19, 20].

The primary results that we obtained, some of which have already been already reflected in the research [21] indicate the immeasurably high potential of the hydrovacuum-sonopulsation method of hydrogenation of metals, because there were observed highly hydrogenated aluminum powder particles obtained by this process. There the content of hydrogen from 1 to 5% was measured, which is 10-50% of the theoretical volume of solubility-diffusion of hydrogen in aluminum. This effect, as an already existing result, on the one hand, and the possibility of doubling it as an achievable

goal, on the other hand, render the need for fundamental research of the complex physico-chemical phenomenon of hydro-vacuum sonopulsation particularly topical.

The scientific-practical value of the proposed hydrogenation approach is also clearly confirmed by the results obtained by FT-IR spectrometry of aluminum powder dried under natural room conditions, without the use of special forcing drying units. The spectrogram recorded by the Agilent Cary 630 model IR spectrograph, which is shown in Fig. 6 shows the presence of peaks with vibrational frequencies corresponding to compounds/molecules: H-O-H, Al-OH, Al-OH, Al-H and Al-O. At the same time, the presence of water molecules is explained by its capillary presence in the small micropores located between the

granular space of powder particles. In its turn, aluminum hydroxide compound AlOH is predominantly fixed in the surface layers of the noted particles up to the depth of 0.2-0.5 microns, - aluminum hydrides AlH₂ and AlH₃ are predominantly concentrated in foamed areas and crystals of hexagonal syngony, packed compactly and located relatively in the deep layers of particles, and aluminum monoxides AlO are found in the form of small spherical formations of white colour, scattered as satellite microparticles on the surfaces of the main particles of the obtained powder. Such spherical white particles can be clearly seen in the microrelief shown in Fig. 4, they are located next to or directly on the outer surfaces, foamed or prism-shaped grains of the investigated samples.

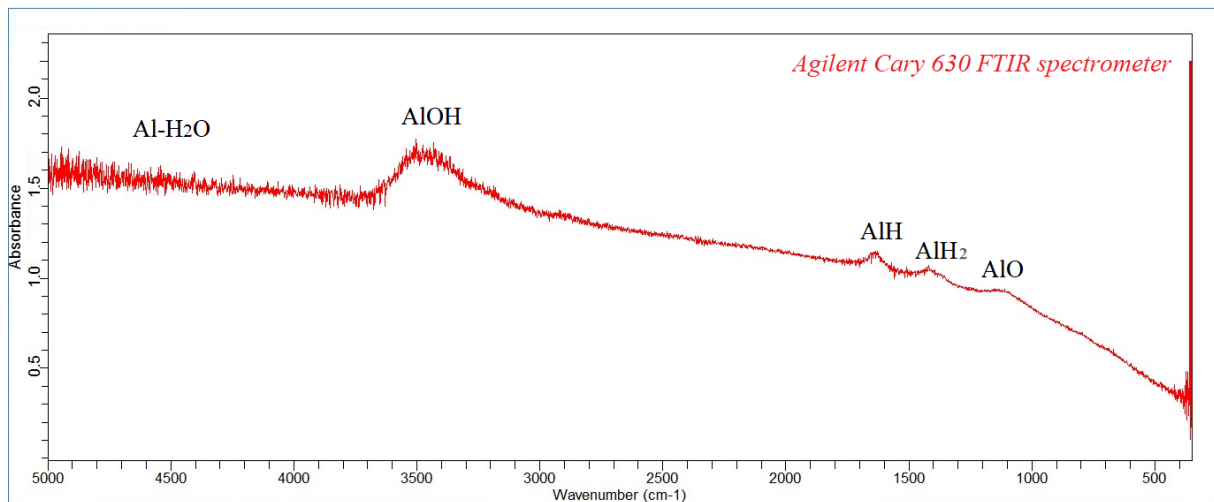


Fig. 6. The result of FT-IR spectrometry of hydrogen containing compounds in powder produced by Hydrovacuum dispersion of aluminum melt.

Hydrogenation of aluminum powder gives it both increased resistance to long-term storage and oxidation, and improved reactivity when used in pyrometallurgical ore-reduction processes, while achieving higher recovery index of target metals.

4. Conclusions

- the main physical and technological factor of origin of the effect of sonochemical hydrogenation of powder particles in the process of hydrovacuum suction and dispersion of metallic melts is the volumetric sound-capillary shock effect on the liquid, vertically drawn melt jet by ultrafrequency waves of hydraulic rarefaction, formed in the zone of forced vacuum diffusion of the melt jet with energy-carrying flow of high-speed cavitating water;

- established that the degree of sonochemical hydrogenation of the obtained powder particles is the dependency on the intensity of cavitation pulsation and hence - the frequency of ultrasonic action on the dispersed melt droplets, regulated in turn, from the speed (pressure) supplied to the dispersing chamber of technical water and the specific volume of melt suctioned by it;

- in case of dispersion of liquid aluminium of technical purity (Al - 99.5%), in order to create a stable condition of continuous sonochemical hydrogenation of the obtained powder particles it is necessary to maintain the ultrasonic range of generated rarefaction shock waves in the range of 20-25 kHz and higher, which is achieved at a water pressure of 12-14 bar, with a weight ratio of water to metal at the level of 25:1 - 20:1;

- detection of the sonochemical effect of hydrogenation of metals during their hydrovacuum dispersion in liquid state is important, as it expands the technological capabilities of the developed unit and gives it the function of an industrial sonochemical semi-reactor of continuous operation;

- the hydrogenated powders obtained by the proposed method will have a reduced cost price, since there is no need for their additional high-energy-intensive physical and chemical treatment.

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Funding:

The authors acknowledge funding support from the Shota Rustaveli National Science Foundation of Georgia, Grant no. **AR-22-1495**.

Acknowledge:

For the technical support provided, the authors also express their gratitude to the management of the Nalbandyan Institute of Chemical Physics, (Armenia) represented by its director, Dr. Seyran Minasyan.

Research of the local powder materials permeability

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Abstract: A method for determining the local permeability of powder filtering materials (PFM) based on the measurement of gas-flows sequentially passing through the measuring head and different areas of the measured object (sample, product), and a device for its implementation are described. The device is characterised by simplicity of execution and can be used both in laboratory and production conditions. By the average value of localised flow rates the throughput capacity of the whole product can be estimated.

KEYWORDS: POWDER FILTERING MATERIALS, PERMEABILITY DISTRIBUTION UNIFORMITY, LOCAL PERMEABILITY, DEVICE FOR DETERMINING LOCAL PERMEABILITY.

1. Introduction/Введение

An important characteristic of powder filtering materials is the uniformity of permeability distribution over the filtration area [1-3]. It presents a particular interest in those cases when the application of PFM products isn't associated with the capture of impurities in the process of operation, but is aimed at providing a uniform supply of a certain amount of gas or liquid from the working surface of the product. Examples of successful application of such products are aeration of air flow for the purpose of oxygenation of air saturation of culture liquid during cultivation of aerobic microorganisms in bioreactors, dispersion of ozone-containing air mixture flow for disinfection of fish habitat (including fry) in closed water supply systems and uniform distribution of steam flow over the volume of heat carrier (water) for temperature regulation in working vessels during heat treatment of milk, milk mixtures and technological means, used in the process of heat treatment of milk and milk products [4-6].

The permeability distribution uniformity over the filtration area is determined by various methods. The simplest one consists in cutting out control samples from separate sections of porous sheet and blowing or pouring them at the same pressure drops [7, 8]. The main method disadvantage is the need to destroy the sample (product). Other methods make it possible to measure the flow of liquid or gases in separate areas of the sample (product) using thermoanemometers or special devices [7]. However, devices for measuring local flows using thermoanemometers [9, 10] are complicated in hardware design, require additional calibration and adjustment work, cannot be operated in draughts and outdoors. Special devices, as a rule, are also complicated in hardware design and construction [11, 12] and are limited by the standard sizes of measured samples (products). Among special devices, the simplicity of design execution stands out. Their operation is based on the measurement of local air flows passing through different samples sections with the help of special measuring heads [13, 14]; the heads are pressed to the surface of the investigated objects manually. However, these devices don't allow determining local permeability on cylindrical surfaces, since the accuracy of measurements deteriorates with decreasing radius of curvature, and in case of attempting to produce long tubular samples, it may be impossible to carry out measurements due to the need to provide large flow rates to uniformly load the entire permeable surface. The need to seal the object under investigation requires the use of special tooling and creates additional difficulties in the measurement process. The disadvantages also include the negative influence on the measurement accuracy of the subjective factor during manual pressing of the measuring head.

It seems that changing the direction of air flow through the measuring head to the sample (product) will eliminate the impossibility of studying large-sized and long products, as the value of air flow rate in this case is determined by the cross-section of the air supplying tubular head element; when studying the product of cylindrical shape, the end of the head contact element, which provides sealing at the interface between the head and the product under the action of pressure forces, to improve the accuracy

of measurements can be made as follows besides, the necessity of sealing of the investigated sample (product) is eliminated.

The aim of the work is to approbate the method of determining the local permeability of porous products using the measuring head in manual mode, when the air flow is directed through the measuring head to the sample.

2. Research materials and methods

The device for determining local permeability is schematically shown in Figure 1 and includes a pressure vessel 1, a flow meter 2, flexible hoses 3, a pressure gauge 4, a measuring head 5, a device for fixing samples or goods 6. The fixture for fixing samples can be any device fixing the sample.

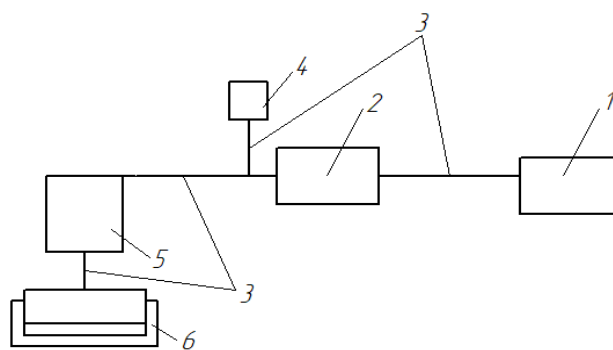


Fig.1. Scheme of the device for determination of local permeability: 1 - pressure vessel, 2 - flow meter, 3 - flexible hoses, 4 - pressure gauge, 5 - measuring head, 6 - attachment for fixing samples or products.

Before starting work, an impenetrable standard is installed in the fixture for fixing samples for the operator to practise the skill of pressing the measuring head. In the process of work the sample or product is fixed in the holder 6. With the help of a reducing valve from the pressure vessel 1 (which, depending on the measurement place (laboratory, production site, etc.) can be a compressor receiver, compressed gas cylinder, other technological container) through flexible hoses 3 compressed air is supplied to the measuring head 5, the free end of which is tightly pressed to the sample or product. With a gradual increase in pressure, the pressure gauge 4 establishes the required pressure drop and records the gas flow rate on the flow meter 2. Moving the tip of the measuring head over the surface of the sample, the local permeability is measured at all required points.

Measurement results are the basis for porous material permeability properties analysing: calculation of local permeability coefficients, construction of histograms of local permeability distribution by relative frequencies or distribution density, etc.

The measuring drawing and 3D- model of the head is shown in Figure 2, a, the external view with a removable tip - in Figure 3, a, the measurement process - in Figure 4.

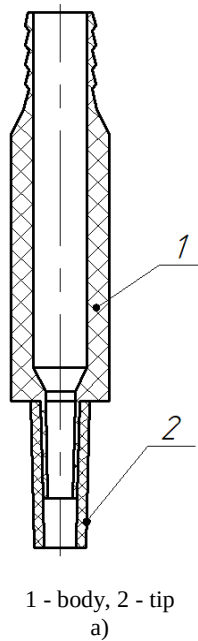


Fig. 2. Schematic(a) and 3-D model (b) of the measuring head.



Fig. 3. External head view of the measuring head.



Fig. 4. Local permeability measurement process.

The measuring head was manufactured by 3-D printing on the printer Z - BOLT S300 (country of origin - Russia); for manufacturing of the head body we used polymer PET - G UMKA (country of origin - Belarus), for manufacturing of the tip - polymer TRU FLEX (country of origin - Russia).

For the device approbation for determination of local permeability we used samples with diameter 30 and thickness 3 mm made of powders of tin-phosphoric bronze of the brand Br O10F1 of fractions (minus 0,4 + 0,315), (minus 0,2 + 0,1) and (minus 0,1 + 0,063) mm and titanium of fractions (minus 0,63+0,306) mm, (minus 0.306+0.16) and less than 0.16 mm. The scheme of the measured areas on the samples was chosen arbitrarily and is shown in Figure 5.

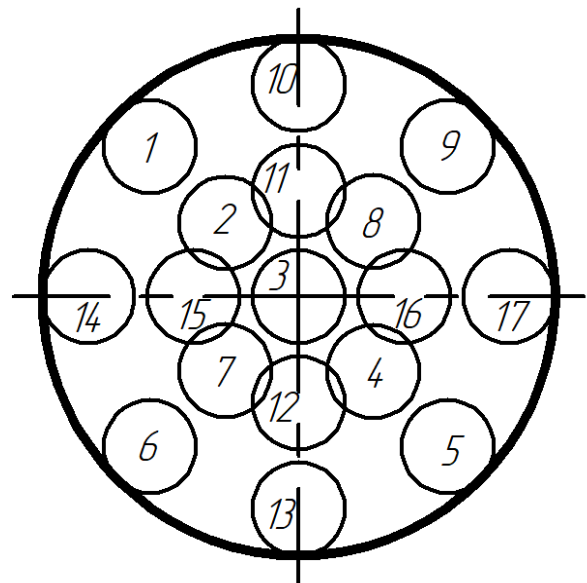


Fig. 5. Schematic layout of the sample sections selected for local flow rate measurements

Permeability coefficients were determined according to the recommendations of work [15].

3. The results of experiment and their discussion

Local permeability coefficients and their coefficients of variation were calculated on the basis of measured values of local flow rates. In addition, permeability coefficients and samples pore sizes were

determined (pore sizes were determined by the method of liquid (ethyl alcohol) displacement in accordance with the recommendations of [16]). The samples research results are presented in the Table 1.

Table.1. Results of sample studies.

Samples material	Defined parameter	Site number	Particle size, mm		
			minus 0,4+0,315	minus 0,2+0,1	minus 0,1+0,063
Br O10F1	Local permeability coefficient, m^2 , $\times 10^{13}$	1	1414,2	200,6	82,3
		2	1563,1	280,8	96,0
		3	1579,7	255,3	120,0
		4	1499,9	255,3	110,7
		5	1448,7	200,6	90,0
		6	1381,3	187,2	92,9
		7	1434,7	255,3	110,7
		8	1588,2	255,3	106,6
		9	1387,8	200,6	92,9
		10	1337,8	216,0	92,9
		11	1470,2	244,2	106,6
		12	1477,5	234,0	110,7
		13	1381,3	216,0	87,2
		14	1374,9	187,2	82,3
		15	1349,9	255,3	110,7
		16	1515,2	234,0	108,6
		17	1400,9	200,6	84,7
	Average value		1447,4	228,1	99,2
	Mean squared deviation		77,45	28,15	11,65
	Variations coefficient		0,05	0,12	0,12
	Permeability coefficient m^2 , $\times 10^{13}$		1147,78	140,00	62,45
	d_{max} , μm		145,04	48,35	36,26
	d_{avg} , μm		131,51	44,83	32,23
Samples material	Defined parameter	Site number	Particle size, mm		
			minus 0,63+0,306	minus 0,306+0,16	minus 0,16
Titanium	Local permeability coefficient, m^2 , $\times 10^{13}$	1	191,3	67,1	47,0
		2	221,8	79,0	60,5
		3	212,1	81,7	57,5
		4	226,9	75,4	50,6
		5	187,7	66,2	48,0
		6	180,7	67,1	48,5
		7	212,1	75,4	54,1
		8	212,1	87,5	56,1
		9	187,7	68,0	49,0
		10	187,7	67,1	51,7
		11	212,1	84,5	65,6
		12	212,1	84,5	56,1
		13	195,2	69,0	48,5
		14	191,3	68,0	53,5
		15	216,8	82,3	63,8
		16	221,8	83,0	51,2
		17	180,7	66,2	47,5
	Average value		203,0	74,8	53,5
	Mean squared deviation		15,19	7,62	5,56
	Variations coefficient		0,07	0,10	0,10
	Permeability coefficient m^2 , $\times 10^{13}$		151,57	49,98	28,79
	d_{max} , μm		78,9	38,98	25,29
	d_{avg} , μm		69,95	36,16	23,43

The analysis of the obtained results shows that all the samples studied have high uniformity of permeability distribution over the material area: the coefficient of variation of the local permeability coefficient for samples from tin-phosphor bronze powders doesn't exceed 0.12, titanium - 0.1. At the same time for all samples the average value of local permeability coefficient essentially differs from permeability coefficient; so for samples from tin-phosphor bronze powders the average value of local permeability coefficient is 1,26 - 1,63 times more than permeability coefficient, so for samples from titanium powders - 1,34 - 1,86 times. This can be explained by redistribution of an air flow part along the directions of lower hydraulic resistance. Nevertheless, using predetermined correction factors, this method can be used as an express method of permeability assessment of products. The disadvantages of the method include the negative influence on the measurements accuracy of the subjective factor at manual pressing of the measuring head.

4. Conclusion

A method for determining the local permeability of powder filtering materials based on measuring gas-flows sequentially passing through a measuring head and different measured product areas, and a device for its implementation are described. The device is characterised by simplicity of execution and can be used both in laboratory and production conditions. By the average value of the localised flow rates, the flow capacity of the entire product can be estimated, but in this case it's necessary to use predetermined correction factors. This is due to the significant difference between the average value of the local permeability coefficient and the value of the permeability coefficient, which can be mitigated by improving the measuring head design.

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Experimental measurements of magnetocrystalline anisotropy constants of evaporated cobalt-based thin films

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Abstract. Under a base pressure of 10^{-7} mbar, we used physical vapor deposition process to fabricate cobalt-based thin films onto monocrystalline silicon Si (100) substrates. The incident atomic beam reaches the substrates under normal incidence within a home-made evaporation chamber. The thickness of the synthesized films ranges from 50 to 400 nm. From X-ray diffraction measurements we infer that the samples are polycrystalline, through a hexagonal close packed structure and display a $\langle 0001 \rangle$ preferred orientation. The crystallite sizes increase with the magnetic layer thickness increase. The films are subject to a compressive stress. Magnetic force microscopy images exhibit stripe patterns for the thickest films and hysteresis loops infer that the easy magnetization vector lies in the film plane. We used Brillouin light scattering tool to measure magnetic anisotropy factor. Values of K_u higher than 10^6 erg.cm $^{-3}$ have been measured.

KEYWORDS: X-RAY DIFFRACTION; THIN FILMS; HYSTERESIS; MAGNETIC ANISOTROPY; BRILLOUIN LIGHT SCATTERING.

1. Introduction

Cobalt-based ferromagnetic thin films have been largely studied in the last years due to the progress of novel and elaborated synthesized methods and procedures of investigations [1-8]. Several materials exhibit a desirable perpendicular magnetic anisotropy and may be then good candidates for high density storage media; their magnetic properties depend closely on the methods and conditions of preparation and are influenced by the structural properties. In this work, we report structural, static and dynamic magnetic studies of Co/Si (100) thin films, synthesized using thermal evaporation method under vacuum. The main varying parameter is the thickness of the magnetic layer. To characterize these films, a lot of techniques were performed: X-ray diffraction, Alternating Gradient Field Magnetometer, Brillouin Light Scattering, Magnetic Force Microscopy.

2. Experimental procedures

We used thermal heating process under vacuum in a homemade chamber to evaporate series of Co thin films onto Si (100). The base pressure inside the glass bell was around 10^{-7} mbar; and the working pressure was lower than 10^{-6} mbar, and the electric current intensity was fixed at 285 A. The deposition rate was around 2 Å/s. The series consists of samples with thickness ranging from 50 to 400 nm, measured using a 'Taylor-Hobson' Talystep apparatus. The structural characterizations were done by X-ray diffraction, using a Siemens D-500 diffractometer with wavelength $\lambda = 1.789$ Å, in the " θ - 2θ " scan mode of the Bragg-Brentano geometry. We used a Veeco 3100 Atomic Force Microscope to explore the morphology structure of the thin films and measure the surface roughness. The hysteresis loops were carried out by AGFM measurements, with the external magnetic field H applied perpendicular (polar configuration) and in the film plane (longitudinal configuration), and the zero-field magnetic structure has been investigated by Magnetic Force Microscopy. Finally, the magnetic anisotropy was investigated by means of Brillouin Light Scattering tools, using a (2×3) -pass tandem Fabry-Perot interferometer. The films were illuminated by a single-mode Ar $^{+}$ ion laser at $\lambda = 5145$ Å, with an incident power of 100 mW. The transferred in-plane wave vector $q_{||}$ value is linked to θ as $q_{||} = (4\pi/\lambda)\sin\theta$. The experiments were done in the 0–5 kOe range of the applied magnetic field intensity.

3. Results and discussion

3.1. Structural study

Figure 1 displays examples of XRD spectra recorded for 200 nm Co/Si(100) film. From this spectrum we can assume that the prepared Co samples are polycrystalline and exhibit a hexagonal phase mainly due to the presence of the diffraction peaks with Bravais-Miller indices $(10\bar{1}0)$ and $(10\bar{1}1)$ with moderate intensity, and a high intensity peak (0002), situated respectively at 2θ equal to 48.8° , 55.8° and 52.4° . The films are polycrystalline with $\langle 0001 \rangle$ texture. These planes are a little broad and their intensity

increases with increasing thickness. This behavior conforms to the Van der Drift evolutionary model which specifies that texture is more pronounced as the film thickness increases [9,10]. Also, we measured the crystallite size, for they carry information about the thin films' conditions of production and their electrical

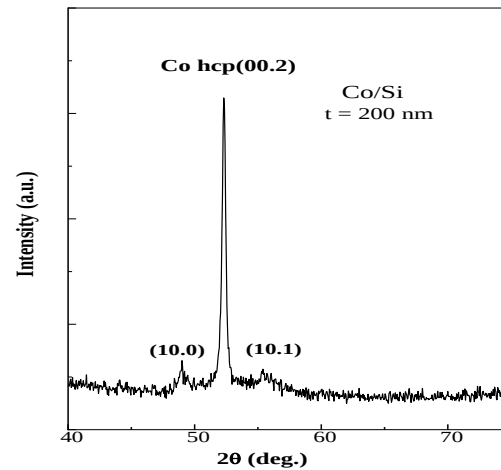


Fig.1 Specimen of diffraction spectrum for 200 nm Co thin film and magnetic properties [11]. In order to examine the crystallinity of the films, we computed the typical crystallite size D , using the broadening of the highest (0002) diffraction Bragg peak and the widely used Scherrer equation [12, 13]:

$$\langle D \rangle = k \lambda / \beta \cos \theta \quad (1)$$

where k is Scherrer's constant, whose value is close to 0.9; λ is the monochromatic wavelength, whose value in the present work is $\lambda = 1.789$ Å. β is the full angular width at half maximum corresponding to the most intense (0002) diffraction peak. θ is the Bragg diffraction angle at the top of this peak. Table1 exhibits the average crystallite size of our Co thin films. D values display a monotonous increase with thickness, from 18.40 to 79.46 nm, as the Co thickness increases from 50 to 400 nm. Obviously, large crystallite size is a signature of good crystallinity and texture. Films with large crystallite size are suitable for application in magnetic sensors. This evolution of the crystallite size with thickness is expectable. Zhenyuan Li *et al.* reported an increasing of the crystallite size from 36.10 to 47.78 nm with increasing Bi concentration in their synthesized ZnO nanoparticles [14]. Cherrad *et al.* measured crystallite size increasing from 8.6 to 19.6 nm as the thickness increases from 132 to 277 nm in their synthesized permalloy thin films onto monocrystalline silicone [15]. Further, the lattice parameters have been measured using the X-ray diffraction spectra and the Bragg equation

$$2 d_{hkl} \sin \theta = n \lambda \quad (2)$$

And the quadratic form

$$Q(hkl) = \frac{n^2}{[d(hkl)]^2} = \frac{4 \sin^2 \theta}{\lambda^2} \quad (3)$$

d is the inter planar distance, and h , k and l are the Miller indices of the crystalline planes.

For hcp structure $Q(hkl) = \frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}$ (4)

And hence $\frac{4 \sin^2 \theta}{\lambda^2} = \frac{4}{3} \frac{h^2 + k^2 + hk}{a^2} + \frac{l^2}{c^2}$ (5)

The a and c parameters are determined respectively by reflections of type $(h\ k\ 0)$ and $(0\ 0\ l)$, because by this type of reflections there remains only one parameter to be determined.

Then, $a = \frac{\lambda \sqrt{h^2 + k^2 + hk}}{\sqrt{3} \sin \theta}$ (6)

And $c = \frac{\lambda l}{2 \sin \theta}$ (7)

The values of a , c and c/a , determined for different thicknesses and crystallographic orientations, are presented in Table1. The average computed values are ranging from 2.52 to 2.62 Å, for a , and from 4.17 to 4.42 Å for c , the ratio c/a increases from 1.655 to 1.688, as the Co thin film increases from 50 to 400 nm. Related to the bulk parameters [16,17], our Co films are under a *tensile* stress, probably due to the film's growth mode, a Stranski-Krastanov growing mode. Table1 displays also the progress of c/a as a function of crystallite size, D . We can see that c/a increases monotonously with the increase of D . This increase of the lattice parameter has been observed by other authors [18]. In addition, we computed the values of the microstrain $\varepsilon(\%)$:

$$\varepsilon(\%) = \frac{c/a - c/a_{bulk}}{c/a_{bulk}} \quad (8)$$

These values are exhibited in Table1; they are positive and increase from 1.53 to 3.56 %, as the film thickness increases from 50 to 400 nm, which infer that the films are subject to a low *tensile* stress due probably to the mismatch lattice parameter between Co thin film and Si substrate.

Table1 Crystallite size, D ; lattice parameters a , c , and c/a ratio; microstrain, ε , and rms, w , as functions of Co layer thickness

t (nm)	50	100	150	200	300	400
D (nm)	18.40	26.62	36.82	47.46	63.28	79.46
a (Å)	2.52	2.54	2.57	2.58	2.60	2.62
c (Å)	4.17	4.21	4.28	4.31	4.37	4.42
c/a	1.655	1.658	1.665	1.670	1.682	1.688
$\varepsilon(\%)$	1.53	1.72	2.15	2.45	3.19	3.56
w (nm)	0.20	0.35	0.60	0.80	1.10	1.50

This tensile microstrain is allied to the morphological properties and topography of the thin films. We used Atomic Force Microscopy technique [19] to observe the morphology and measure the roughness. Figure 2 represents a specimen of representative 2D and 3D AFM images. These images exhibit very smooth surfaces. All the samples exhibit quasi-identical homogeneous surfaces reflecting a good crystallinity. Table1 displays the average root mean square (rms) roughness values, measured for all the Co thin films. The rms values, w , increases with increasing thickness, from 0.2 to 1.5 nm. Other authors measured higher rms values for cobalt-based thin films. Tinouche *et al.* measured rms roughness up to 2.1 nm for Co thin films synthesized on GaAs substrate [20]. Anup Kumar Bera *et al.* reported rms roughness values ranging from 0.5 and 1.6 nm for their cobalt ultra-thin films grown on Si (100) [21].

3.2. Static magnetic study

3.2.1. Hysteresis curves

In figure 3, we present examples of hysteresis curves, obtained for the 100 nm Co film, in the longitudinal and the polar configurations. It is easy to saturate the films in the longitudinal configuration,

whereas for the polar configuration, we have to apply a very high magnetic field to reach saturation and this is typical to in-plane magnetic anisotropy. From the shape of the magnetic loops in the two configurations, we deduce that the easy magnetization axis lies in the film plane, for all samples.

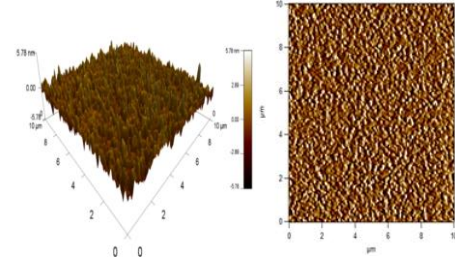


Fig.2 Specimen of 2D and 3D surface topographic images for 200 nm Co thin film. Scan area is $10 \times 10 \mu\text{m}^2$

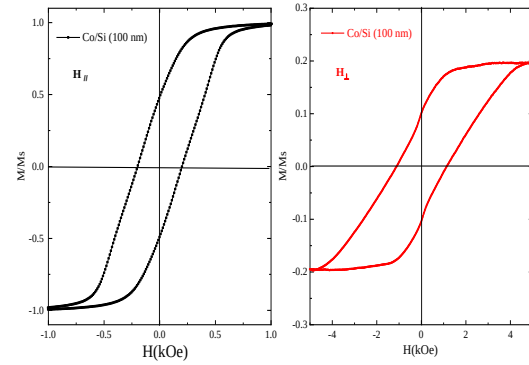


Fig.3 Specimen of hysteresis loops, recorded in the longitudinal and polar configurations. Indications inside the figure

3.2.2. MFM observations

With the aim to scrutinize the domain configurations of our evaporated Co thin films, we utilized the magnetic force microscope to observe the images. Figure 4 is an image of stripes domains, recorded for the 400 nm Co thicker sample. Obtained with a lift scan of 50 nm, the MFM image shows plainly the presence of magnetic domains. The light and dark areas correspond to the sites of up and down domains. These weak stripes patterns are evidence of the presence of an out-of-plane component of the magnetization vector M in the thickest samples where the magnetocrystalline anisotropy is dominant.

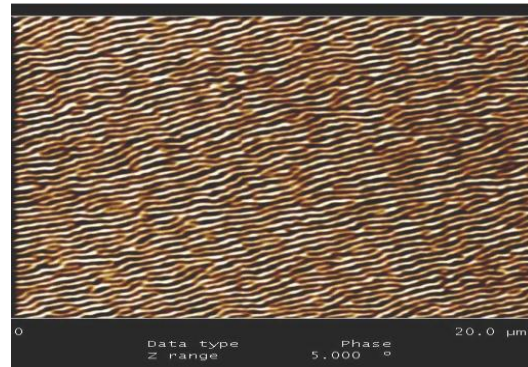


Fig.4 Specimen of MFM images of Co (400 nm) thin film with stripe domain structure. Scan area is $20 \times 20 \mu\text{m}^2$

3.3 Dynamic magnetic study

In the recent years, Brillouin Light Scattering tool has been used to investigate the magnetic anisotropy of materials [22–24]. BLS experiments were done under the conditions defined in Section 2. Figure 5 shows specimens of BLS spectra obtained with $H = 5$ kOe for the 200 nm sample. These spectra reveal two highly asymmetric structures in frequency and intensity: several standing modes are present in the anti-Stokes part, while the intense peak in the Stokes part is the Damon-Eshbach surface mode [25,26]. As can be seen on this figure, the agreement between the experimental and the calculated spectra is good, thanks to the fitting the magneto-crystalline anisotropy field H_a (assumed to be uniaxial $H_a = 2Ku/Ms$, with Ku the uniaxial anisotropy constant).

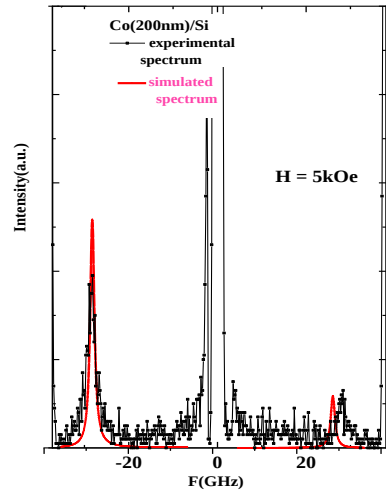


Fig.5 Specimen of Brillouin Light Scattering spectra for 200 nm Co thin film. Indications inside the figure

In Figure 6, we display frequency shift as a function of applied magnetic field H curves for the representative 200 nm Co /Si film. The experimental data for the DE mode are the points and the simulated predictions are the solid lines; here too, the fit is very satisfactory. Table 2 presents the computed magnetic anisotropy factors as a function of the thickness t of the magnetic layer, for the Co/Si thin films. As can be observed in Table 2, Ku considerably decreases, from 8.4×10^6 erg.cm⁻³ as the magnetic layer thickness increases from 50 to 400 nm. Numerous phenomena play a crucial role in the magnetic anisotropy in thin films, specifically the magnetocrystalline structure and the two-dimensional shape of the material. In the thinnest 50 nm Co thin film, the demagnetizing field is important; this will lead to a preponderant shape anisotropy, and thus, gives rise to a high value of Ku . On the contrary, in the thickest 400 nm Co thin film, the demagnetizing field is lower; this will lead to a reduced shape anisotropy and infers a relatively low value of Ku , due principally to the magnetocrystalline anisotropy.

Table2 Anisotropy magnetic field and constant as a function of Co film thickness

$t(\text{nm})$	50	100	150	200	300	400
H_a (kOe)	12.0	8.0	6.9	6.2	5.8	4.7
K_u (erg.cm ⁻³)	8.4	5.6	4.8	4.3	4.1	3.3

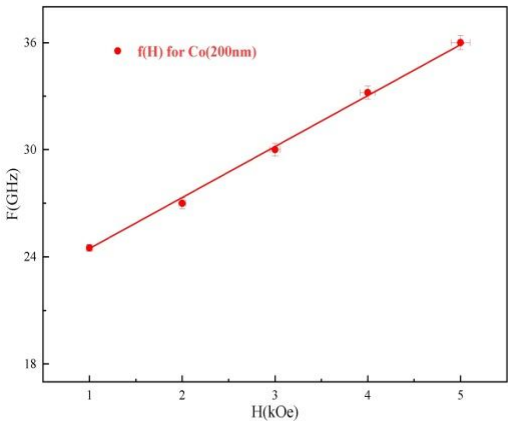


Fig.6 Damon-Eshbach mode frequency shift as a function of the applied magnetic field. Indications inside the figure

4. Conclusion

We produced series of Co thin films, deposited onto Si (100) substrate. All the samples are polycrystalline exhibiting hexagonal close packed structure with a $\langle 0001 \rangle$ preferred orientation. The hysteresis curves infer that the easy magnetic axis is lying in the plane of the film. For the thicker films, we observe well-defined stripes patterns. Using the dynamic Brillouin Light Scattering tools, we computed the magnetic anisotropy factors and found values as high as 8.4×10^6 erg.cm⁻³ and decreasing to 3.3×10^6 erg.cm⁻³ as the magnetic thickness increases from 50 to 400 nm.

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Optical properties of polymer-CNT thin films

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Abstract: The influence of external factors (heat treatment, high pressure) on the optical properties of the samples was analyzed. It was established that samples of pure PTFE4 after the specified external influence increase their throughput, while the largest increase in throughput is observed for samples that were obtained under high pressure, and for samples that were subjected to heat treatment during synthesis, an increase in throughput is characteristic ability with increasing synthesis temperature. For PTFE-4 composites from 5 wt. % CNT (film thickness $h=200\ \mu\text{m}$) samples become opaque in the wavelength range $\lambda=320\text{-}1000\ \text{nm}$ and regardless of the method of their production, which indicates the possibility of using such materials as absorbing coatings.

KEY WORDS: CARBON NANOTUBES, ELECTRICAL PROPERTIES, COMPOSITE, MECHANICAL PROPERTIES

Introduction

New areas of nanotechnology are actively developing based on the use of composite polymer materials. This creates conditions for the development and implementation of new methods and technologies, in particular in the direction of coatings. When moving to the nanoscale, new properties are observed in substances that are not inherent in the macro range, this is intensively used to expand the spectrum of materials applications. When one or more elements of the system have dimensions of a few nanometers, the main role in the formation of physical characteristics is played by the increased contribution of the surface (compared to the volume), quantum-size effects and, under certain conditions, many-particle effects can dominate in low-dimensional systems. Another way to significantly change the physical properties of a substance is the creation of non-equilibrium states in systems, as well as the synthesis of heterogeneous systems, for example, composite materials that acquire properties different from the properties of the individual components of the composite and their averaged characteristics. Carbon nanotubes (CNTs) can be sources of intense self-electron emission. The unique properties of carbon nanotubes (small size, huge specific surface, chemical and thermal stability, high strength, emission properties and high electrical conductivity) contribute to their effective use in various fields of science and technology [1]. The deformation of CNT affects its electronic structure, in particular, the width of the band gap and the concentration of charge carriers [2]. The high length-to-diameter ratio characteristic of nanotubes leads to anisotropy of properties [3] and provides them with additional advantages, which are manifested in achieving percolation in composites at concentrations below 5 wt. %, at which the specific electrical conductivity increases sharply due to the formation of a three-dimensional network of nanotubes - paths of electrical conductivity. Nanocomposite materials have a significantly more developed (by many orders of magnitude) surface area of filler particles compared to conventional materials. This contributes to the increase in surface energy and the dependence of the properties of nanocomposites on the morphology of the filler and the nature of the interaction of components in the interface of phases.

The inclusion of nanotubes in the amorphous-crystalline structure of polymers fixes their orientation, protects against the negative influence of the surrounding environment, and can transfer the polymer to an electrically conductive state with a jump of 8 orders of magnitude during the percolation transition. In addition, it is known that the deformation of nanotubes changes its electronic structure and electrical conductivity by several orders of magnitude and leads to nonlinear current-current characteristics. When the above factors are combined, it is possible to ensure extremely high sensitivity of the composite to the action of deformations, radiation, electrons, etc. The presence of conduction electrons in nanotubes, which are introduced into the polymer, as well as nanopores in the composite can lead to more efficient absorption of electromagnetic radiation in a wide range of frequencies due to the excitation of electron vibrations, electron-phonon interactions and thermal conductivity, which is important for the creation of film absorbing materials.

Polymer-carbon nanotube composite materials retain the advantages of the polymer matrix and additionally acquire the characteristics of a stronger and electrically conductive carbon filler. In such composites, it is possible to use simultaneously several of the specified methods of radically changing the properties of materials. Thus, after adding electrically conductive CNTs to the polytetrafluoroethylene (PTFE) dielectric matrix in an amount exceeding a certain critical value (percolation threshold), a conductive network of CNTs is formed and a dielectric-conductor transition occurs. The specific values of the conductivity of such systems will be determined by the electronic structure and conductivity of individual CNTs, their linear dimensions and aspect ratio, the degree of ordering of polymer molecules and filler particles, the homogeneity of the composite (including CNT aggregation), the type and number of contacts of the filler particles with each other and with matrix material, the presence of defects in both components (in particular, free volumes in the polymer and Stone-Wells defects in CNTs), redistribution of charges between the components of the composite, etc. The presence of a filler significantly changes not only the electrical properties of polymer-based composites, but also their mechanical, thermal, optical and other properties. The large surface area of the carbon filler leads to an increase in the filler-polymer interaction, which improves the load transfer between the filler and the matrix, and the contacts between the filler particles provide electrical and thermal conductivity and increase the absorption of electromagnetic waves of a wide range, weakening their intensity by several orders of magnitude. These properties, as well as low density and high stability in aggressive environments, provide polymer-nanocarbon composites with a promising future as protective and absorbing coatings in a wide range of wavelengths.

Therefore, the study of the nature and mechanisms of the absorptive capacity of these composite materials, as well as their relationship with structural features, are an important and urgent task. The project envisages the creation of new materials based on stochastic leading networks for strategic needs.

Experiment

Multilayer carbon nanotubes with a diameter of $18\pm 6\ \text{nm}$ obtained by the CVD method with a propylene precursor on an $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-MoO}_3$ catalyst and PTFE-4 granules were used to create polytetrafluoroethylene-carbon nanotubes (PTFE-CNT) nanocomposites. Also, for nanocomposites, the indicated CNTs were used, which were subjected to radiation irradiation with γ -quanta with an energy of 1.2 MeV and a dose of $4,51\cdot 10^{16}\ \gamma_{\text{kb}}/\text{cm}^2$.

Also, thin films were made on the basis of a PTFE-CNT nanocomposite, made on the basis of a PTFE emulsion of type SFN-1 ($d=1.51\ \text{g/cm}^3$, mass fraction of dry residue 55.25 %) and purified, as well as purified and dispersed by the cavitation method of multilayer CNT. To obtain experimental samples of composites, PTFE powders (4PN20) were mixed with multilayer CNTs in the presence of surfactants, coagulation of the PTFE emulsion on CNTs, and subsequent hot pressing.

Initial samples of carbon nanotubes for the study of electrophysical properties were placed in a dielectric cylinder under a piston, which, together with the bottom of the cylinder, served as electrodes.

During the lowering of the piston, contact is established between the electrodes and the sample, and the sample goes into a conductive state, corresponding to the fixation of electrical conductivity. At the same time, conductive bridges are created between the components of the composite and the electrodes, which is confirmed by a sharp increase (by several orders of magnitude) in electrical conductivity. The compression was carried out to the maximum hardware permissible value, after which the reverse process was carried out - unloading: the piston is gradually raised, while, due to elastic relaxation, the electrical contact between the particles and the electrodes is maintained, which allows measuring the electromechanical characteristics of the studied samples. Completion of the elastic relaxation process leads to a sharp drop in electrical conductivity and leads to the opening of the electrical circuit [4].

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Results

Chaotically oriented carbon nanotubes can form a network of conducting channels in the polymer matrix with sufficiently high resistance and capacity due to ohmic and tunnel contacts between CNTs. Systems of a large number of such channels of various lengths and orientations should be characterized by a large attenuation decrement and, accordingly, effective absorption of electromagnetic radiation, which provides a high-quality masking effect during active and passive control of space with the help of radars and IR light sensors. The presence of defects in carbon nanostructures can change the absorption parameters, so it is important to investigate the original components that are added to the polymer.

The influence of defects that arise during γ -irradiation on the properties of multilayer carbon nanotubes

Defects in CNTs can be formed during the synthesis process, as well as under external influence, for example, radiation exposure [5]. Since CNTs are characterized by a strong anisotropy of properties, which increases with the presence of defects, such structures are interesting for research with the aim of further application in various industries.

It is known that γ -irradiation can cause the displacement of carbon atoms due to the Compton effect, with the formation of not only vacancies and adsorbed atoms (analogous to Frenkel pairs), but also Stone-Wells type defects (5-7), which lead to topological disorder and CNT distortion [6]. Therefore, the CNT array was irradiated with γ -quanta with an energy of 1.2 MeV in order to increase the concentration of defects. Thus, for the next introduction into the polymer, CNTs irradiated with γ -quanta with a dose of $4,51 \cdot 10^{16} \gamma_{\text{KB}}/\text{cm}^2$ were used.

Microscopic images of used CNTs after irradiation are shown in Fig. 1. It can be seen that irradiation contributes to the formation of tangled bundles of nanotubes, tube bends, and a complex tangled structure is formed. Usually, this behavior is characteristic of carbon nanotubes saturated with defects of various types, in particular defect type 5-7, which is accompanied by bending of the framework structure of the tubes. In some areas, the formation of column-shaped associations and cross-connections is observed.

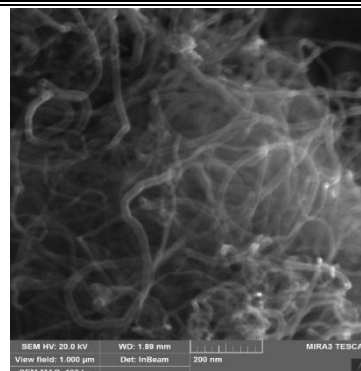


Fig 1 – CNTs irradiated with γ -quanta with a dose of $4,51 \cdot 10^{16} \gamma_{\text{KB}}/\text{cm}^2$

Irradiation with a dose of $4,51 \cdot 10^{16} \gamma_{\text{KB}}/\text{cm}^2$ is accompanied by a decrease in the density of the transition to the conducting state by almost two times, compared to the original CNTs (Fig. 2). The density of the transition to the conducting state ρ_0 depends on the degree of deviation of the shape of the CNT in the array from the ideal straight line characteristic of a defect-free nanotube. The maximum value of electrical conductivity $\sigma = 0.46 (\Omega \cdot \text{cm})^{-1}$ is observed at a density of 0.16 g/cm^3 . At the same time, the load curve has a different appearance than that of CNTs before irradiation. After irradiation with γ -quanta, elastic relaxation is observed up to the density $\rho_{\text{rel}} = 0.34 \text{ g/cm}^3$. The change in the shape of the $\sigma(\rho)$ curves for irradiated samples during the forward and reverse strokes of the piston shows that the contribution of inelastic processes to the electrical conductivity of the material appears almost immediately after the start of unloading (Fig. 3). Also, this behavior is caused by the interaction of the formation of new and healing of existing defects in CNTs and their interaction.

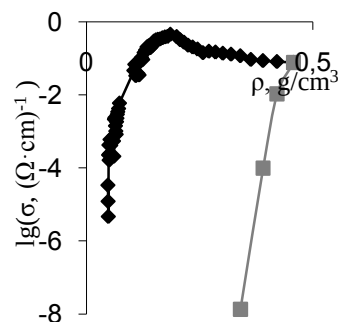


Fig. 3 – Dependence of $\lg \sigma$ of the CNT array on the density ρ during compression and unloading for irradiated γ -quanta with $E = 1.2 \text{ MeV}$ and dose $D = 4,51 \cdot 10^{16} \gamma_{\text{KB}}/\text{cm}^2$. $\blacklozenge$ - loading, $\blacksquare$ - unloading

For CNTs, the value of the Seebeck coefficient (α) is $38 \mu\text{V/K}$ for the original CNT sample and $44.61 \mu\text{V/K}$ for the irradiated sample. Such an increase in the coefficient α is associated with the appearance of radiation defects of the acceptor type under the action of high-energy irradiation with γ -quanta.

The calculation of the coefficients of the transverse limit of elasticity ϵ of the CNT array and the irradiated sample is 80% and 26% , respectively. γ -irradiation has a strong influence on the defective structure of CNTs. Such a change in the electrophysical properties of the investigated CNT arrays is due to the complex nature of the interaction of primary (a minimal concentration of defects is always present in the CNT array after synthesis) and radiation defects: primary defects compensate for the effect of radiation defects on the electrical properties of the array, but do not change their effect on elasticity.

Therefore, controlled changes in the concentration of primary defects in CNTs with the help of thermal and mechanical processing can compensate for the effect of radiation exposure on the electrical conductivity of the CNT array, which is important for their practical application.

Absorption of light with a wavelength of $\lambda=320 - 1000$ nm by PTFE-4 nanocomposites + 5 wt. % CNT

Obtaining materials with predetermined properties is one of the tasks of the development of modern materials science. Thus, to create new functional materials, polymers are modified with carbon nanostructures (more often nanotubes). At the same time, the strength, thermal stability, gas permeability, electrical conductivity and other important operational properties of polymers can change significantly [7]. Carbon nanotubes are introduced into the polymer composition by mixing and uniform dispersion at the micron level. Such methods of introduction of such structures primarily affect thermo-deformation and other physical and mechanical characteristics of polymers.

Both multilayer and single-layer nanotubes synthesized either by the electric arc method, or by the laser ablation method, or by the chemical vapor deposition method are used as additives to the polymer material. If the interaction of the CNT surface with the polymer molecules is van der Waals in nature, the nanotube, when a mechanical load is imposed on the material, moves almost freely through the volume of the polymer and has little effect on the latter's mechanical properties. A real improvement of the mechanical parameters of the polymer material as a result of the introduction of CNTs into it can be achieved if the surface of the nanotube is connected to the polymer molecules by a chemical interaction, the characteristic energy of which is ten times higher than the corresponding value of the van der Waals interaction energy. Thus, the problem of increasing the strength properties of composite materials by adding CNTs is reduced to the problem of combining the surface of CNTs with polymer molecules in order to ensure the most effective chemical interaction between them. In the case of introducing multilayered CNTs into the polymer, a problem arises related to the relatively weak van der Waals interaction between adjacent layers of the nanotube. Due to this circumstance, the real interaction of CNTs with the polymer occurs only at the expense of the outer layer of the multilayer nanotube, and only if its surface interacts well with the polymer matrix. The degree of homogeneity of the composite material containing nanotubes depends significantly on their concentration.

The most interesting properties of carbon nanostructures, important from the point of view of both fundamental research and applied development, are related to their abnormally high mechanical characteristics. Thus, the results of numerous experiments show that the value of the Young's modulus of a single-layer CNT exceeds the record value of 1 TPa. Such high stiffness of nanotubes in combination with their flexibility, low specific weight and chemical stability allows treating this object as the basis of future materials with unique mechanical properties. One of the most possible structures of such a material is a polymer-based composite with the addition of some CNTs. The problem standing in the way of developing such materials is related to the need to ensure the transfer of mechanical force from the nanotube to the polymer matrix. This requires a strong chemical bond with the CNT surface. Thus, a record absorption of electromagnetic radiation is observed for composites based on polymers with carbon nanotubes [8]. Thus, CNTs are characterized by a record high value of Young's modulus (~1 Tpa) [9]. Developed technology for obtaining ultra-strong fibers, yarns, fabrics from nanotubes. These products stand out from the competition in terms of their mechanical characteristics. Currently, the efforts of many researchers are aimed at obtaining composite materials, which are polymers with the addition of CNTs. If the problem of connecting the surfaces of the polymer and the nanotube, which ensures effective load transfer from the polymer matrix to the nanotube, will be solved, then such materials, which combine the plasticity and low cost of polymers with good electrical conductivity and high strength of CNTs, will be unique in their absorption properties.

Optical properties were studied on samples of PTFE-4 and PTFE-4 with CNTs, which were dispersed by the cavitation method, and CNTs, which were irradiated with γ -quanta with an

energy of 1.2 MeV. The thickness of the obtained films was 170-200 μm .

In fig. 4 shows the dependence of the light transmission coefficient in the range of 320-1000 nm for the obtained films under different conditions. For films obtained using a press with a pressure of 2 t and a thickness of 400 μm , the highest transmittance (18%) is observed at $\lambda=1000$ nm. At a reduced wavelength, the light transmittance monotonically decreases to the values of 1.5% at $\lambda=320$ nm. For samples of pure PTFE with a thickness of 200 μm , obtained by compression and rolling at different temperatures (Fig. 5), a change in the transmission coefficient is observed from 0.1% to 0.2% for rolling at room temperatures, 0.3-0.5% - at rolling at a temperature of 70° C, 0.4-0.6% - rolling at a temperature of 80° C. At the same time, the samples obtained by rolling at different temperatures are visually opaque.

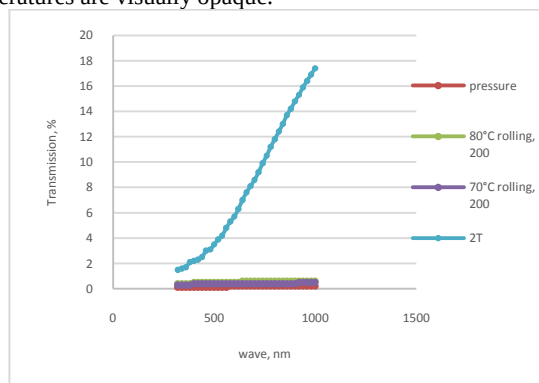


Fig. 4 – Transmittance spectrum of PTFE films obtained under different conditions

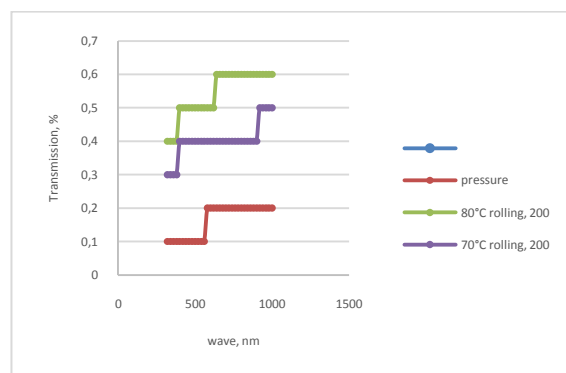


Fig. 5 – Transmission spectrum of PTFE films obtained by rolling at different temperatures (compression – room temperature)

Adding to the Teflon matrix 5 wt. % CNTs followed by the formation of a 200- μm -thick film is accompanied by sample opacity in the wavelength range $\lambda=320$ -1000 nm, i.e., samples of the specified composition are opaque regardless of the conditions of their synthesis (pressure, high-temperature rolling).

Conclusions

External influence (heat treatment, high pressure) on samples of pure PTFE4 helps to increase its throughput, and in the case of its composites from 5 wt. % CNT ($h=200$ μm) samples become opaque in the range $\lambda=320$ -1000 nm and regardless of the method of their production, which indicates the possibility of using such materials as absorbent coatings.

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On the character of rate primary recrystallization of steels in the zone of laser action

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Abstract. The features of high-speed primary recrystallization of the cold-worked steels with different chemical composition and structure in the laser impact zone are studied. It has been established that during laser heating of the cold-formed steels, either polygonization or primary recrystallization occurs, which has a dynamic character. It is shown that the range of degrees of cold rolling, at which the character of structure recovery changes from polygonization to recrystallization, increases from 25...30 to 50...60%. The effect of heredity of the cold deformation substructure is revealed. It has been found that the density of dislocations in the surface layer after laser exposure increases by more than an order of magnitude due to plastic shears that introduce forest dislocations. It is shown that in the zone of laser treatment there are signs of columnarity of recrystallized grains and subboundaries, as well as a crystallographic texture.

KEYWORDS: STEEL, PRIMARY RECRYSTALLIZATION, POLYGONIZATION, LASER ACTION, MICROSTRUCTURE, HEREDITY, STRESSES, HIGH SPEED RELAXATION

1. Introduction.

During laser treatment of the steels, complex structural and phase transformations occur, which determine the effect of laser strengthening of the surface layer [1–5]. These transformations in steels proceed at a very high rate. Numerous studies have established that the effect of strengthening steels under laser irradiation is achieved by high-temperature strengthening, martensitic transformation, obtaining an ultrafine structure, dissolution of carbides and non-metallic inclusions, saturation of the matrix with their components, microchemical inhomogeneity, an increase in the number of defects in the crystal structure and plastic shears [1–8]. Among the many factors that determine the effect of laser strengthening, processes leading to softening should be singled out, for example, recrystallization, which occurs under conditions of short-term exposure to high temperatures and stresses [6, 9]. The goal of the work was to study the features of high-speed

recrystallization in cold-deformed steels with different chemical composition and type of crystal lattice under laser action.

2. Materials and Procedures.

Cold-rolled sheet steels 08kp, 08Yu, E3, 08Kh18N10T were studied (Table 1). The samples were subjected to laser irradiation on the Kvant-16 and GOS-30 installations according to the regime: pulse energy 18 J, radiation power density $6 \times 10^4 \text{ W / cm}^2$, pulse exposure time 10^{-3} s , heating rate 10^5 °C / s , cooling rate $- 10^6 \text{ °C/s}$. The microstructure of steels in the laser impact zone was studied using light microscope Neophot-21 and electron microscope Tesla. The dislocation density and texture in the surface layer were evaluated on a DRON-2.0 X-ray diffractometer. Microhardness was determined on a PMT-3 instrument. Some samples after cold rolling were subjected to annealing according to the standard regime used for sheet steels (680 °C).

Table 1. Chemical composition of the steels

Steel	Element content, %									
	C	Mn	Si	Cu	Cr	Al	Ti	Ni	S	P
08Kp	0,09	0,32	0,01	0,22	0,05	0,01	-	0,05	0,025	0,009
08Yu	0,07	0,29	0,01	0,07	0,03	0,04	-	0,05	0,022	0,007
E3	0,035	0,10	3,1	0,09	0,05	0,013	-	0,09	0,005	0,005
08H18N10T	0,08	1,2	0,80	0,07	18,0	-	0,6	10,1	0,021	0,006

3. Results and discussion.

Under shock compression pressure in the laser impact zone, the normal stresses in the steel exceed the yield point, and the shear stresses become higher than the critical value, and the material flows [10]. As a result, there is a multiplication of dislocations, the movement of which is associated with the relaxation of thermoplastic stresses arising during irradiation, which contributes to the implementation of anomalous mass transfer [11–13], which has a wave character [14]. Stress relaxation in the zone of laser action is carried out by means of plastic shifts and rotations [6, 9, 15]. Laser exposure is essentially thermal shock. During abrupt heating to high temperatures, high pressures develop in shock waves, which create thermal and deformation stresses, for the relaxation of which there is an extremely short time of shock compression [14]. The described conditions provoke avalanche stress relaxation. The main mechanism of stress relaxation is a high-speed plastic deformation. At the same time, high-temperature high-speed heating contributes to the manifestation of recrystallization processes in the laser impact zone.

The structure of cold-rolled steels in the initial state is characterized by highly elongated grains, the dislocation density reaches $10^{10} \dots 10^{11} \text{ cm}^{-2}$. After laser irradiation, the structure of the surface layer of cold-rolled specimens changes. In 08kp steel, the grains become equiaxed, and wavy grain boundaries appear perpendicular to the sample surface (Fig. 1, a). From the point of

view of the shape of the grains, it can be said that primary recrystallization has taken place.

In steel 08Yu, in the zone of laser impact, the grains also changed their shape from elongated to equiaxed (Fig. 1, b), however, some grains retained their elongated shape. Primary recrystallization in this steel can be considered not complete, but partial, since the influence of AlN particles was manifested, which, located along slip planes and at grain boundaries, inhibit grain growth and recrystallization (Fig. 1, c). Wide grain boundaries are visible in the steel structure, perpendicular to the surface of the sample.

In the ferritic steel E3, after laser irradiation, the elongated grains turned into equiaxed ones, and there is a tendency to the presence of broadened boundaries perpendicular to the sample surface (Fig. 1, d). The defectiveness of recrystallized grains is extremely high. Austenitic steel 08Kh18N10T is also characterized by the appearance of fine equiaxed grains with a high degree of defectiveness in the zone of laser action (Fig. 1, e).

A comparative analysis of cold-rolled steels of various compositions and structures showed that, after laser exposure, the grain shape changed from elongated to equiaxed. This indicates the passage of primary recrystallization (in steels 08kp, E3, 08Kh18N10T – it is the complete, in steel 08Yu – it is the partial).

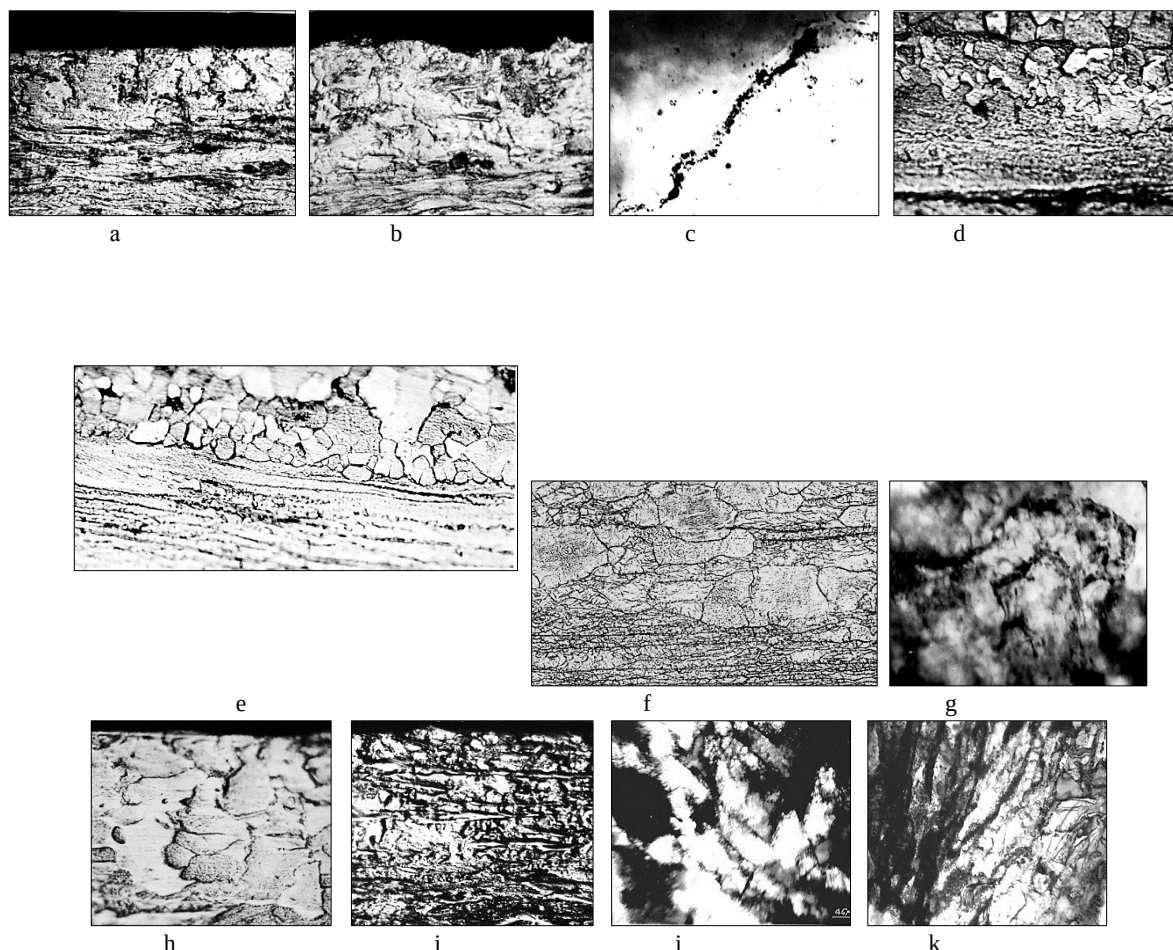


Fig. 1. Microstructure of cold-worked steels 08kp (a), 08Yu (b, c, g - k), E3 (d, f), 08Kh18N10T (e) in the laser impact zone: a, b, f, i - $\times 500$, h - $\times 700$, c - $\times 20000$, j, k - $\times 50000$

To reveal the fine structure of steel, a special etching of E3 steel was used. An analysis of the microstructure showed that the degree of imperfection of the original deformed and recrystallized structures is approximately at the same level. In the grains of the laser impact zone, an increased density of defects in the crystalline structure is observed, compared with grains after conventional annealing (Fig. 1, f). In many grains, the substructure of the laser irradiation zone is identical to the substructure of cold deformation, which makes it possible to assume substructural heredity that manifests itself under laser irradiation, just as austenite inherits the substructure of the initial martensite during shear polymorphic transformation.

An electron microscopic study of the structure of steel 08Yu showed that in the zone of laser exposure over the entire area of the samples, the original cellular substructure of cold deformation is preserved (Fig. 1, g), however, inside many cells, an increased density of forest dislocations and dislocation coils introduced by plastic shifts is observed occurring in shock waves. Apparently, the short duration of exposure to laser irradiation, as well as strong pressure in shock waves, make it possible to maintain the density of defects in the crystalline structure introduced by cold deformation.

An analysis of the fine structure indicates that the primary recrystallization takes place under dynamic conditions and is accompanied by the inheritance of the original cellular substructure of cold deformation and the introduction of new dislocations. The density of dislocations in the zone of laser exposure during the analysis of 100 fields of view was 10^{11} cm^{-2} - 10% and 10^{12} cm^{-2} - 90% of the studied area, while in the initial state it was at the level of 10^{10} cm^{-2} - 10% and 10^{11} cm^{-2} - 85%. Thus, during laser treatment of cold-rolled steels, the dislocation density increased by almost an order of magnitude. Microdistortions in the crystal lattice increased after laser treatment, and the size of the blocks decreased from 11.6×10^{-5} to $0.72 \times 10^{-5} \text{ cm}$.

The influence of the degree of cold deformation ε on the change in the structure of steel 08Yu upon laser heating was studied. At ε from 10 to 33%, the grain structure of the steel remained practically unchanged after laser exposure (Fig. 1, h), wavy boundaries appeared, perpendicular to the sample surface. At ε 43 and 50%, a similar picture was observed. An increase in ε to 60 and 66% led to a change in the steel structure after laser irradiation. Most of the grains changed their shape from elongated to equiaxed, although grains remained, the shape of which corresponds to the cold-rolled state (Fig. 1, i). In the zone of laser impact, many wavy boundaries are seen, perpendicular to the surface of the sample. At ε 75%, most of the steel grains in the laser impact zone changed their shape from prolate to equiaxed, although some of the prolate grains were preserved. These elongated grains differ from the so-called fritter-like grains, which are formed during conventional annealing of 08Yu steel, both in shape and in the degree of pickling. Obviously, these grains are inherited by the laser recrystallization structure from the cold-deformed state, which is associated with the presence of dispersed AlN particles in the steel, which block the grain boundaries.

When analyzing the fine structure of steel 08Yu in the laser treatment zone, one should take into account the initial state of the dislocation structure, which depends on the degree of deformation. In the range of ε less than 20%, the presence of randomly distributed dislocations and dislocation coils is typical; at ε 20%, a cellular structure with thin cell boundaries is formed. An increase in ε to 40...50% leads to a slight thickening of the cell boundaries; at higher degrees of deformation, a significant accumulation of dislocations occurs in the cell boundaries. The dislocation density depends on the degree of cold deformation ε . It increased in comparison with the initial state for all ε by almost an order of magnitude and significantly differs from the value after conventional annealing (Table 2).

Table 2. Change in dislocation density ρ after cold rolling (1), laser exposure (2), and conventional annealing (3) of steel 08Yu

ϵ , %	ρ , cm^{-2}		
	1	2	3
10	$1,91 \cdot 10^{10}$	$1,41 \cdot 10^{11}$	$1,21 \cdot 10^6$
20	$6,92 \cdot 10^{10}$	$2,21 \cdot 10^{11}$	$1,84 \cdot 10^7$
33	$1,3 \cdot 10^{11}$	$4,93 \cdot 10^{11}$	$2,52 \cdot 10^7$
43	$1,61 \cdot 10^{11}$	$6,46 \cdot 10^{11}$	$4,31 \cdot 10^7$
50	$1,92 \cdot 10^{11}$	$8,17 \cdot 10^{11}$	$1,83 \cdot 10^8$
60	$2,27 \cdot 10^{11}$	$6,41 \cdot 10^{12}$	$2,17 \cdot 10^8$
66	$2,60 \cdot 10^{11}$	$7,61 \cdot 10^{12}$	$3,02 \cdot 10^8$
75	$2,7 \cdot 10^{11}$	$9,23 \cdot 10^{12}$	$4,61 \cdot 10^8$

After laser exposure, the nature of the dislocation structure of steel also depends on the degree of preliminary deformation ϵ . At ϵ up to 20%, along with dislocation coils, fragments of subboundaries appeared, and the density of randomly distributed dislocations increased. At ϵ from 20 to 50%, the walls of the cell boundaries thinned, but a large number of dislocations appeared inside the cells (Fig. 1, j). At ϵ 60...75%, the cellular structure was preserved, but the density of dislocations sharply increased in the cells (Fig. 1, k). Thus, under laser irradiation, the cold deformation substructure is generally inherited; in addition, plastic shears introduce new dislocations, which are randomly distributed in the cells according to the type of forest dislocations. The nature of the fine structure after laser treatment differs from that after conventional annealing.

According to the effect of the degree of preliminary cold deformation ϵ on laser recrystallization, it can be divided into two intervals. After ϵ below or equal to 50%, the shape of the grains in the steel does not change, the steel does not undergo primary recrystallization, although the presence of wavy boundaries indicates their attempts to migrate. The appearance of new wavy subboundaries indicates the passage of polygonization processes. Since plastic shifts occur in the surface layer under the action of a shock wave, it should be assumed that, at ϵ below 50%, dynamic polygonization develops in the laser impact zone, and recrystallization does not have time to occur. After ϵ above 50%, primary recrystallization takes place in the laser impact zone, since the shape of most grains changes from elongated to equiaxed. Recrystallization is dynamic. Due to the incomplete dissolution of the AlN particles, it partially passes.

The degree of preliminary cold rolling ϵ affects not only the mechanism of dynamic structure recovery, but also the parameters of the laser impact zone (Fig. 2). The higher ϵ , the smaller the depth of the laser impact zone h and the fraction of the dynamically recrystallized volume V_p (the number of grains that have changed from an elongated shape to an equiaxed one). The microhardness of the laser impact zone H increases with an increase in the degree of preliminary deformation, and at all ϵ it is significantly higher than the microhardness of 08Yu steel after conventional recrystallization annealing, which is associated with the inheritance of the cold rolling substructure and an increased dislocation density after laser exposure compared to annealed steel. The nature of the curves of changes in the microhardness of steel 08Yu after laser exposure and after cold rolling is identical, which is associated with the succession of the substructure and indirectly confirms the fact that the steel inherits a cellular structure.

The features of the structure of the zone of laser exposure of cold-rolled steel include the presence of wavy boundaries perpendicular to the surface of the sample, and the appearance of a crystallographic texture (110) α , revealed in X-ray studies. The direction of the grain boundaries perpendicular to the surface of the sample is due to the direction of the effect of heat removal, which entailed the formation of signs of a columnar structure. The waviness of these boundaries is associated with their migration at the time of laser exposure due to high pressure and temperature. The specific conditions of laser exposure, mainly its short duration and localized powerful energy, ensured the processes of restoring the structure of a dynamic nature (polygonization and primary recrystallization).

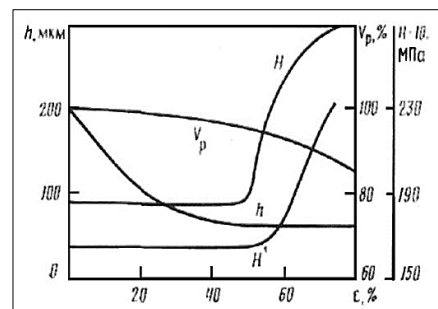


Fig. 2. Dependence of the volume fraction of recrystallized grains (V_p), the depth of the zone of structural changes (h), and the microhardness of the laser impact zone (H) on the degree of cold rolling ϵ of 08Yu steel (H' is the microhardness of 08Yu steel after rolling).

4. Conclusions.

During laser heating of cold-formed steels, polygonization or primary recrystallization takes place, which has a dynamic character. The range of degrees of cold rolling ϵ , at which the character of structure recovery changes from polygonization to recrystallization, increases from 25...30 to 50...60%. In the zone of laser impact, the effect of the heredity of the cold deformation substructure is manifested, while the density of dislocations increases by more than an order of magnitude due to plastic shears that introduce forest dislocations. In the laser treatment zone, there are signs of columnarity of recrystallized grains and subboundaries, as well as a crystallographic texture.

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Microstructure and properties of Ti-TiC composite obtained by hot pressing

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Abstract: Direct Metal Laser Sintering (DMLS) is a revolutionary technology that allows a production of fully functional metal parts directly from a 3D CAD data, eliminating the investment to production tools and technologies which brings considerable cost and time savings. Metal parts made by DMLS technology are fully comparable with casted or machined parts. A range of application of DMLS technologies is very wide – from prototypes, through short-run production to final products. Advantages of DMLS technology are arising along with complexity of parts – more complex geometry of parts (in terms of shape and occurrence of the detail) make DMLS technology even more economically effective.

Keywords: TITANIUM ALLOY, DMLS, LASER SINTERING, 3D PRINTING, MICROSTRUCTURE

1. Introduction

Titanium alloys play a crucial role in modern aerospace, automotive, shipbuilding, and military technologies due to their high specific strength, fracture toughness, fatigue strength, corrosion resistance, non-magnetic properties, and other specialized physical-mechanical characteristics [1-3]. However, traditional titanium alloys, which are alloyed with various elements typically categorized as α - or β -phase stabilizers, often fall short in meeting the desired combination of physical and mechanical properties. For example, these alloys tend to have low wear resistance, susceptibility to fretting corrosion, and relatively low hardness [4, 5]. These limitations can be addressed by developing titanium-based Metal Matrix Composites (MMC) that incorporate fine hard particles such as carbides or borides [6, 7].

Blended Elemental Powder Metallurgy (BEPM) manufacturing method offers significant advantages over ingot metallurgy for various alloys, providing opportunities for smaller grain sizes, improved chemical and structural uniformity, and greater economic efficiency. [8-10].

The hot-pressing (HP) method is widely used for densification of ceramic and metal-ceramic composite. The main advantage of HP is the obtaining the fully dense materials by applying pressure and temperature during sintering. Technology of hot pressing in air using graphite layers led to significantly decrease the price of the proses in comparison with other technologies (HP in vacuum or spark plasma sintering). Another advantage is the speed of densification, which allows the save fine microstructure. Preservation of the fine microstructure leads to an increase mechanical properties of metal matrix composites.

2. Materials and experimental procedure

Production of Metal Matrix Composite Ti+40TiC (vol.%) was investigated. This MMC is promising for products that require very high strength [25, 26, 27]. It was used titanium hydride and TiC powder as starting materials. This blend was compacted at pressure of 650 MPa, room temperature. The powder compact was heated in vacuum at rate of 10 °C / min to 1250°C and exposed at this temperature for 4 hours. During the heating cycle the hydrogen is removed of from the powders. Also, it causes, sintering and homogenization of powder blends thus transforming them in bulk alloys.

In order to reduce material porosity and to improve mechanical properties it was applied hot deformation. using various powders.

Hot pressing was carried out in an SPD-120 apparatus (Frantsevich Institute for Problems in Materials Sciences, Ukraine (IPMS)). The as-sintered specimen was placed in graphite die with diameter of 25 mm. All walls of the die were covered with graphite paper to prevent interaction between the material and the die. An induction-heating with heat rate 100 °C/ min was set to achieve the sintering temperature of 1300°C, 1400°C, and 1500°C defined according to the piston movement during shrinkage. The initial load was 8 MPa and, once achieved the peak temperature, the load was

increased to 32 MPa. After dwell at the maximum temperature for 30 min, the furnace was slowly cooled down to 600°C to avoid crack formation. The temperature was monitored by a pyrometer.

3. Results and discussion

The morphology of starting particles of titanium hydride and titanium carbide was investigated. It is shown on fig.1 that during grinding, titanium hydride particles have a size of less than 100 micrometers. In contrast to the relatively equiaxed particles of titanium carbide, small hydride particles can be irregularly shaped.

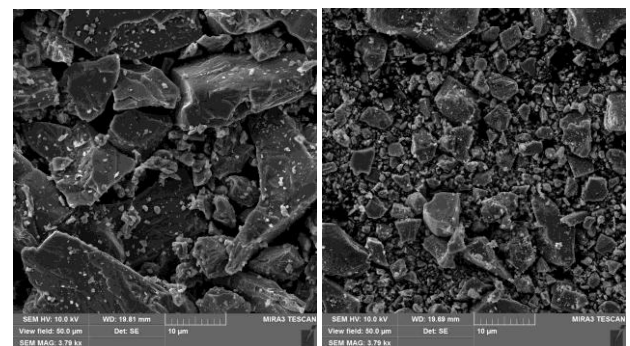
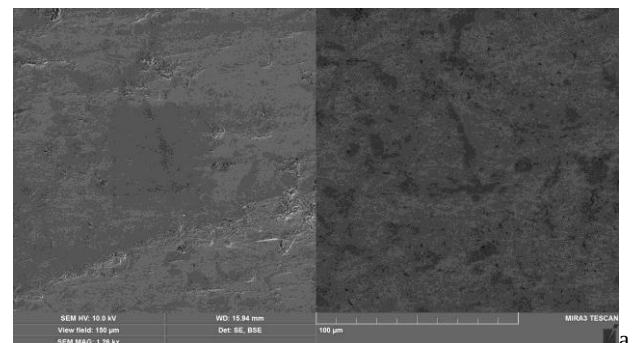


Fig. 1. Morphology of starting powders.

In fig. 2 shows the microstructure of the material after sintering. As you can see, after sintering, a certain residual porosity remains in the material, which negatively affects the mechanical properties. In addition, it was observed that most of the pores are concentrated around TiC particles. This may be due to the fact that the reinforcing phase forms a kind of carcass that prevents the metal matrix from shrinking during sintering. Therefore, hot pressing of the material was carried out to heal the residual porosity. For comparison, temperatures of 1300 °C, 1400 °C and 1500 °C were taken



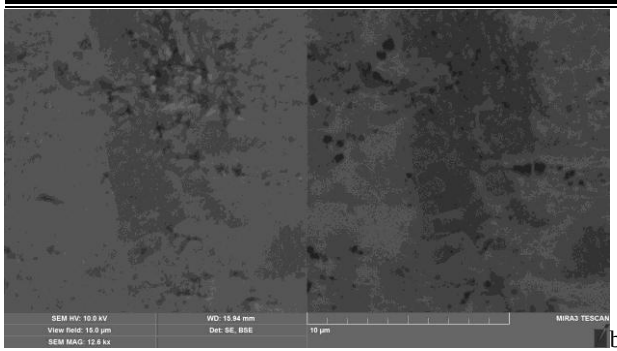


Fig. 2. Microstructure of as-sintered MMC

Figure 3 presents the microstructure of a hot-pressed metal matrix composite that was processed at a temperature of 1300 °C. It reveals the presence of some local residual pores, which healing was incomplete. Additionally, the examination of the composite's microstructure highlights the occurrence of cracks within the carbide particles. These cracks may result from thermal stresses during the hot-pressing process. The presence of such defects could potentially impact the mechanical properties of the composite, such as its strength and durability, by serving as initiation points for further cracking under stress.



Fig.3. Hot-pressed MMC at temperature 1300 °C

Figure 4 shows that further increasing the hot-pressing temperature results in more effective healing of porosity within the metal matrix composite. This enhanced densification helps to strengthen the composite by minimizing potential weak points within its structure. However, despite this improvement, some macropores still remain, indicating that complete elimination of larger voids may not be achievable at this point of temperature. Additionally, an increase in the density of the reinforcing phase within the material is observed (fig. 4 b). As the hot-pressing temperature increases, the distribution and integration of the reinforcing particles, such as carbides or other hard phases, become more uniform and compact. This results in a higher density of the reinforcing phase, which can enhance the mechanical properties of the composite, such as its stiffness, strength, and wear resistance. The improved distribution of the reinforcing phase contributes to a more robust and homogeneous composite material, capable of withstanding greater mechanical stresses and extending its application potential.

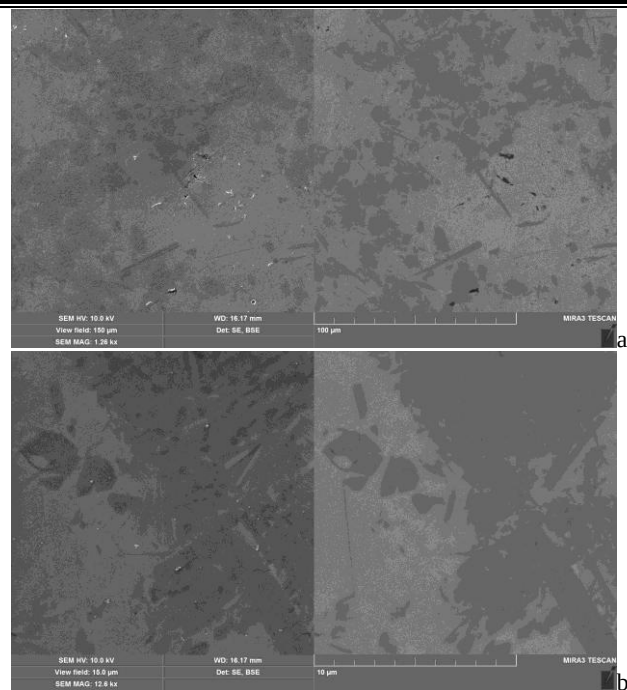


Fig.4. Hot-pressed MMC at temperature 1400 °C

On figure 5 can be observed that further temperature increasing leads to almost complete porosity healing. It was observed that at this temperature macropores was also close unlike during processing at lower temperatures (figure 6).

Figure 5 illustrates that further increasing the hot-pressing temperature leads to almost complete healing of porosity in the metal matrix composite. At this elevated temperature, the material's ability to flow and consolidate is significantly enhanced, resulting in the near elimination of both micro and macropores.

Unlike processing at lower temperatures (1300 °C), as shown in Figure 6, where macropores remain visible, the elevated temperature (1500 °C), facilitates the closure of these larger voids. The reduction in porosity, particularly the closure of macropores, contributes to the overall strength and integrity of the composite by minimizing structural weaknesses and potential failure points.

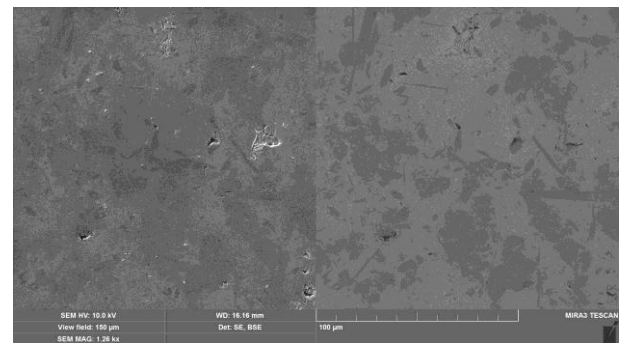


Fig.5. Hot-pressed MMC at temperature 1500 °C

This advancement in processing conditions underscores the importance of temperature control in achieving optimal material properties. By effectively reducing porosity and enhancing the distribution of reinforcing phases, the composite becomes more robust and suitable for applications requiring high mechanical performance and durability. The findings highlight the potential of temperature optimization in the manufacturing process to significantly improve the quality and reliability of metal matrix composites.

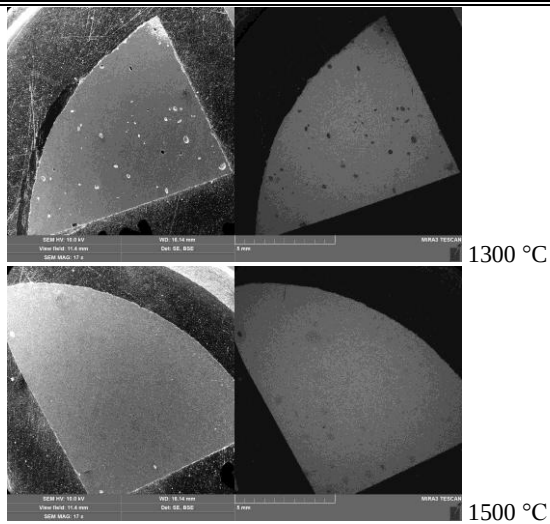


Fig. 6. Macrostructure comparison of hot-pressed samples at different temperatures.

The mechanical properties of these materials were investigated using a three-point flexural test. The stress-strain curves obtained from these tests, as shown in Figure 7, highlight the differences in mechanical behavior based on the hot-pressing temperatures used during processing. The material hot-pressed at 1300 °C exhibits the lowest mechanical properties. This can be attributed to the presence of residual porosity in both the metal matrix and the reinforcing phase, which act as stress concentrators and potential points of failure under load. The incomplete densification at this temperature leaves behind voids that weaken the overall structure.

Conversely, materials processed at higher temperatures (1400 °C) demonstrate significantly improved strength values. This improvement is due to an increase in the density of the reinforcing phase within the material and more effective healing of porosity. As the hot-pressing temperature rises, the material undergoes better densification, resulting in a more uniform and compact microstructure. The enhanced bonding between the matrix and the reinforcing particles further contributes to the material's mechanical performance. At a temperature of 1500 °C, the almost complete closure of pores leads to even higher levels of strength and plasticity. This results in a composite that not only withstands greater loads but also exhibits increased ductility, allowing it to deform more before failure.

These findings highlight the critical role of temperature in optimizing the mechanical properties of metal matrix composites. By carefully controlling the processing conditions, it is possible to tailor the microstructure to achieve the desired balance of strength and ductility, making these materials suitable for a wide range of demanding applications.

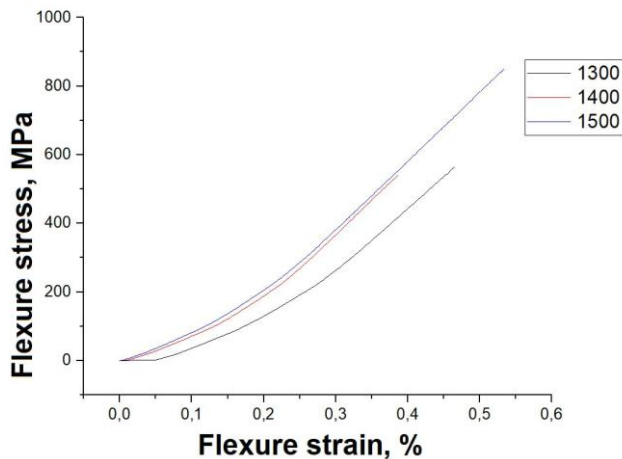


Fig. 7. Stress-strain curves of three-point flex test.

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Deposition of cobalt alloy protective coating on titanium against negative effects of hydrogen environment

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Abstract: The protective coating on a cubic-shaped titanium sample was deposited by the plasma method in an argon atmosphere in several stages, in order to form a continuous barrier on all surfaces of the sample. It was shown that, when the protective coating was deposited by the specified method, partial or complete melting of the powders occurred, and subsequently, when they were deposited on the surface of the substrate, active interaction occurred. This made it possible to form a sufficiently continuous layer on the surface of titanium due to mutual diffusion. It is found out that the deposited protective coating allows titanium to be heated up to 400 ± 10 °C in a hydrogen atmosphere (hydrogen pressure 0.6 ± 0.2 MPa) without interaction with the gas.

KEYWORDS: TITANIUM, HYDROGEN, POWDER, SOLID SOLUTION BASED ON COBALT, NIOBIUM CARBIDE, PROTECTIVE COATING.

1. Introduction

Hydrogen dissolves in almost all metals and causes significant changes in their physical and mechanical properties [1,2]. This issue is particularly important for titanium and Ti-based alloys [3,4]. Prevention of interaction of various parts and structures with hydrogen during service is complicated by the fact that the forms of this interaction are very diverse, so it is not easy to predict all possible negative effects. Besides, hydrogen in metals is very mobile and easily redistributes under the influence of stresses and temperatures, which can lead to dangerous local zones enriched with hydrogen. The penetration of hydrogen into metals is controlled by phenomena occurring on the surface [5]; the intensity of this process is determined by the catalytic activity of the surface, solubility and diffusion. In this regard, it is important to passivate the surface and form a barrier against the penetration of hydrogen into the volume to protect metal products [6].

Protective coatings are widely used in industry, and their use gives a great economic effect [7-10]. The techniques of deposition of these coatings are very diverse: electrolytic deposition of metals and alloys, gas transport reactions, ion implantation, chemical and thermal treatment, etc. The compositions of protective coatings are also very diverse: oxides, borides, nitrides, carbides, silicides.

Among the existing variety of protective coatings, Al_2O_3 coatings are most widely used as protective barrier layers to reduce hydrogen permeability due to their excellent properties [11,12]. However, it was found out in [13] that an Al_2O_3 layer prevented the penetration of hydrogen into titanium when the exposure time in a hydrogen atmosphere did not exceed 3 hours at 400 °C and a pressure of 0.2 MPa. When the exposure time was increased to 4 hours, the amount of absorbed hydrogen drastically increased, which was associated with the difference in the coefficients of thermal expansion of the metallic substrate and the coating. This led to the formation of high thermal stresses in the coating, and as a result, cracks and delamination were observed. Constantly increasing requirements for the service conditions of Ti-based products require a continuous search for materials to protect bulk material from the negative effects of the hydrogen environment.

Wear-resistant alloys of the HTN family designed for operation at high temperatures in friction nodes of power equipment have been developed at the G.V. Kurdyumov Institute for Metal Physics of the NAS of Ukraine. These alloys are based on the Co–NbC eutectic system (HTN-62) [14,15]; they are used as a material to protect the airfoil shroud platforms in the high-pressure gas turbines from wear. These alloys can work for quite a long time in an aggressive environment at high temperatures and alternating loads. In addition, the alloys of this type are resistant to hydrogen environment.

The purpose of this work was to determine the kinetic parameters of the physico-chemical interaction with hydrogen of titanium samples with protective coatings based on cobalt alloy (alloy of the HTN family), in order to achieve maximum protection

of the material against the penetration of hydrogen. The composition of the HTN-62 alloy [14] (Table 1.) was taken as a reference. The contents of the main components of the alloy were varied, and boron was added to improve the melt spinning process.

Table 1. Compositions of alloys.

	Elements, mass. %							
	Co	Cr	Nb	W	Fe	Al	C	B
HTN-62 [14]	48.2	20	15.5	9.5	3	2	1.8	-
Investigated alloy	55.18	17.66	12.18	7.45	3.07	1.88	1.5	1.59

2. Materials and methods

The phase compositions and lattice constants of the materials in initial state, as well as after heat treatment in a hydrogen atmosphere, were determined by X-ray phase analysis at a DRON-3M diffractometer. Metallographic investigations were carried out using a VEGA3 TESCAN scanning electron microscope with an EDX detector XFlash610M (Bruker).

The stability of the original powder and the deposited protective coatings in a hydrogen atmosphere was investigated by the Sieverts technique at a IVGM-2M unit at room temperature and during heating at pressures 0.5–3.0 MPa, according to the method described in detail in [16,17]. The amount of adsorbed hydrogen was determined by the change in pressure in a closed volume (volumetric method), and was additionally controlled by weighing with an accuracy of $1.5 \cdot 10^{-5}$ g (gravimetric method).

3. Results and discussion

The manufacturing process of forming Co-based alloy protective coatings included: production of the cobalt alloy by induction melting; spinning of the melt (production of a tape); annealing the tape; grinding of annealed tape in order to produce powder of the required fraction (Fig. 1); sieving of the powder of the required fraction; application of the powder on the surface of titanium by the plasma technique.

SEM investigations showed that the powder contained particles of Co-based solid solution and niobium carbide (Table 2). X-ray phase analysis confirmed that the phase composition of the powder contained Co-based solid solution with an FCC lattice ($a=0.3630 \pm 0.0009$ (nm)), and niobium carbide with an FCC lattice ($a=0.4406 \pm 0.0009$ (nm)). In addition to these phases, the third phase $\text{Cr}_{0.7}\text{Fe}_{0.3}$ with a BCC lattice ($a=0.2841 \pm 0.0009$ (nm)) was revealed.

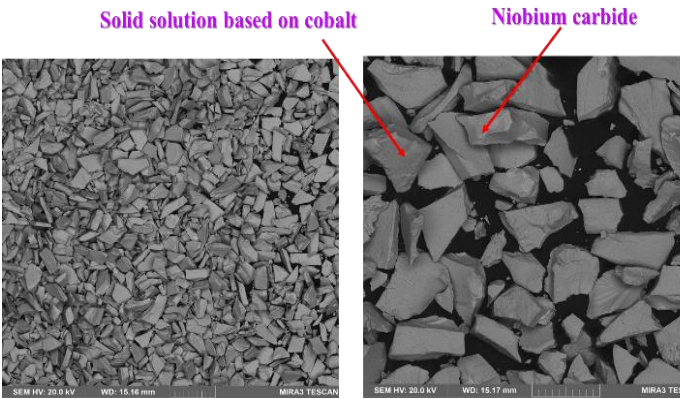


Fig. 1. Appearance of produced powder.

Table 2. Compositions of phases in powder.

	Phase	Elements, mass. %								
		Co	Cr	Nb	W	Fe	Al	C	B	
Initial state	Solid solution based on cobalt	51.55	15.78	.92	4.73	.11	1.06	10.21	5.63	
	Niobium carbide	8.69	2.95	61.79	1.96	.45	0.23	20.19	3.75	
After annealing in hydrogen	Solid solution based on cobalt	51.76	15.72	9.26	5.65	.27	1.26	8.05	5.04	
	Niobium carbide	5.58	1.95	63.56	1.77	.24	0.16	22.76	3.98	

The composition chosen for the study differed from the convenient HTN-62 alloy by an increased cobalt content (Table 1). According to the literature data [4,18], this element, as well as chromium and niobium [19], can interact rather actively with hydrogen. Therefore, it was important to investigate the stability of the powder in a hydrogen atmosphere. The stability of the powder in an atmosphere of gaseous hydrogen was studied in rather severe conditions according to a specially developed method: the powder was kept at room temperature and a hydrogen pressure of 0.2 MPa for 20 hours, then the pressure in the chamber was increased to 2.0 MPa; the powder was heated up to 630 ± 10 °C and then cooled to room temperature – during the heating, the hydrogen pressure in the chamber varied from 2.0 to 3.0 MPa; after the heating, the sample was additionally kept in the chamber for 140 hours at room temperature and at a hydrogen pressure of 2.0 MPa.

The microstructure of the powders after heat treatment in a hydrogen atmosphere was investigated by scanning electron microscopy (Fig. 2). It was found out that this treatment did not affect the size and shape of the initial powder (Fig. 2). There were no particles joining into conglomerates (sticking together) or increasing the area of separate coarse particles at the expense of significantly finer ones. No changes in the shape and size of the carbide component were observed (Fig. 2). The X-ray phase analysis confirmed the above conclusion regarding the lack of interaction between the powder and hydrogen. The Co-based solid solution, niobium carbide (Table 2.), as well as the third phase $\text{Cr}_{0.7}\text{Fe}_{0.3}$ remained in the powder structure. The lattice constants of the phases corresponded to the nominal values within the measurement error.

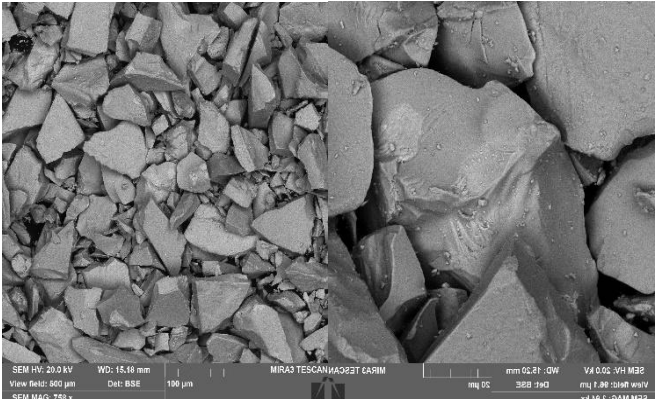


Fig. 2. Appearance of powder after annealing in hydrogen atmosphere.

In order to achieve high adhesion between the coating and substrate material, powder with an average size of 65 μm was sieved. The protective coating was deposited on a cubic titanium sample using a plasmatron in several stages in order to form a continuous barrier on the entire surface of the sample. The design feature of the plasmatron was a removable water-cooled copper anode working in laminar plasma jet generation mode, which provided better conditions for powder melting. Argon with a total flow rate of 0.2 m^3/h was used as the plasma-forming, transporting and pressing gas. The operating current was set in a range of 80–100 A, the arc voltage was 35–45 V, the consumption of plasma-forming and shielding gas was 4–5 l/min. Argon simultaneously performed two functions: protection of the fused and/or completely melted powder from the negative effects of the environment (oxygen, nitrogen), and powder transport to the substrate surface.

According to the results of scanning electron microscopy, the surface of the powder melted and subsequently, when it was deposited on the surface of the substrate, the powder particles interacted with each other when the protective coating was applied. This made it possible to form a sufficiently continuous layer due to mutual diffusion on the surface of the substrate (Fig. 3). X-ray phase analysis showed that the Co-based solid solution ($a=0.3420 \pm 0.0009$ (nm)), niobium carbide ($a=0.4400 \pm 0.0009$ (nm)), and the $\text{Cr}_{0.7}\text{Fe}_{0.3}$ phase ($a=0.2872 \pm 0.0009$ (nm)) preserved in the coating structure during the formation of the protective coating.

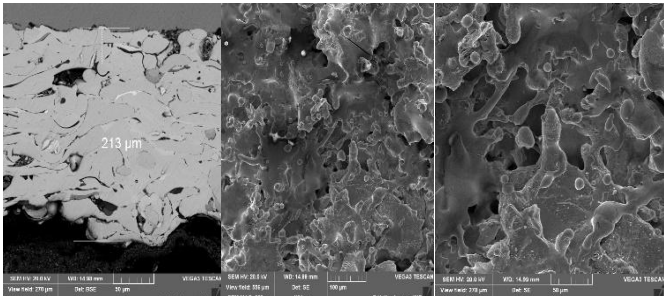
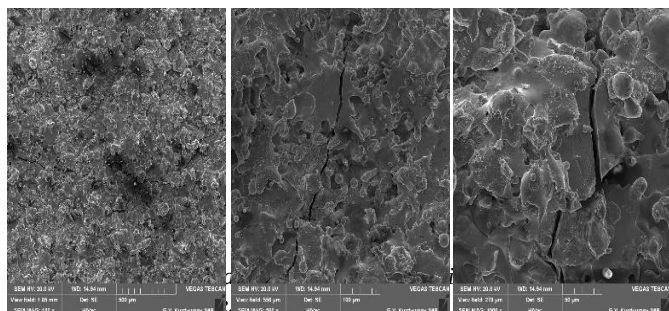


Fig. 3. Appearance of protective coating.

Depending on the size of the powder particles, partial or complete melting of the particles occurred (Fig. 3). During deposition, the melting of the particles (i.e. the formation of a liquid phase) caused their interaction with each other and with the substrate surface, which, in turn, led to a rather high adhesion of the particles with each other and with the substrate. The carbide phase was observed as fine white inclusions.

Despite the phase composition of the powder did not change during the deposition, and taking into account the difference in the coefficients of thermal expansion of the coating and the substrate, a somewhat different method of testing stability in a hydrogen environment was developed. At the first stage, the sample was kept at room temperature and a hydrogen pressure of 0.5 MPa for 68 hours. After that, the pressure was increased to 0.6 MPa at the same temperature, and the sample was additionally kept for 50 hours.

Then the sample was heated up to 400 ± 10 °C, annealed for 3.5 hours, and cooled to room temperature – during this heating, the hydrogen pressure in the chamber varied from 0.6 to 0.62 MPa. After this, the sample was additionally kept in the chamber for 20 hours at room temperature and at a hydrogen pressure of 0.6 MPa. After this treatment, there were no noticeable changes in the hydrogen pressure in the reactor, which indicated the absence of interaction between the coating and hydrogen atmosphere (Fig. 4).



Based on the above results, it can be stated that the formed coating had a rather high, but relatively short-term stability in a hydrogen atmosphere. However, under real conditions, the coating can be in contact with hydrogen at a much lower pressure, but for a longer time (thousands of hours). Besides, the above-mentioned heat treatment in a hydrogen atmosphere for a long time can activate diffusion processes and interaction with hydrogen. Therefore, the sample after the above-mentioned heat treatment was additionally kept at room temperature and a hydrogen pressure of 2.0 MPa for 140 hours (6 days). The pressure in the closed volume was monitored every 12 hours. This additional treatment allows us to confirm the almost zero catalytic ability of the coating (after the treatment described above).

4. Conclusions

1. It was experimentally proven that no interaction between the powder under study and hydrogen occurred during heating up to 630 ± 10 °C in a hydrogen atmosphere (pressure 2.0–3.0 MPa).
2. It is shown that partial or complete melting of the powders occurs when the protective coating is deposited. As a result, the powder particles actively interact with each other and the substrate, which provides the formation of a sufficiently continuous layer on the surface of titanium due to mutual diffusion.
3. The protective coating allows titanium to be heated up to 400 ± 10 °C in a gaseous hydrogen environment without interaction between the material and hydrogen.

5. Acknowledgement

The work has been carried out within the framework of the project of scientific research works («Coating of modified quasi-binary Co-NbC eutectic for protecting titanium against hydrogen environments») of young scientists of the National Academy of Sciences of Ukraine in 2023-2024 (State Reg. No. 0123U102939).

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Characterization of self-cleaning coated composite materials for solar cells applications

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Abstract: The development of solar cell technologies is critical for advancing sustainable energy solutions. One of the significant challenges faced by solar cells is the accumulation of dust and debris on their surfaces, which can significantly reduce their efficiency. Our research work will be focused on new development composite material which are designed to repel dirt, dust, and other contaminants, ensuring that the solar cells maintain optimal performance. The optimum WO₃-B composition was utilized in this research work to prepare the SiO₂/WO₃-B₅/ZnO film sample. The composite film sample resulted the highest photocatalytic dye degradation efficiency (92%) with the SiO₂/WO₃-B₅/ZnO(70/30) film sample after 240 min of the UVA light irradiation.

Keywords: COMPOSITE MATERIALS, FILM SAMPLES, SOLAR CELLS, DEGRADATION EFFICIENCY.

1. Introduction

The development of solar cell technologies is critical for advancing sustainable energy solutions [1-7]. One of the significant challenges faced by solar cells is the accumulation of dust and debris on their surfaces, which can significantly reduce their efficiency. To address this issue, self-cleaning coatings have been used in many applications as a potential solution [8-12]. These coatings, often composed of composite materials, are designed to repel dirt, dust, and other contaminants, ensuring that the solar cells maintain optimal performance. In order to maintain the efficiency of the solar cell, the cover glass can be coated with a self-cleaning layer against the pollutant accumulation, reducing the solar cell efficiency [13-16]. For this purpose, hydrophilic self-cleaning coating based on the photocatalytic activity was coated on the top surface of the solar cell.

Our research work focuses on the characterization of new fabricated self-cleaning coated composite materials type SiO₂/WO₃-B₅/ZnO film sample, exploring their properties, effectiveness, and potential applications in solar cells. A new development composite material has been designed to repel dirt, dust, and other contaminants, ensuring that the solar cells maintain optimal performance. The optimum WO₃-B composition was utilized in this research work to prepare the SiO₂/WO₃-B₅/ZnO film sample. By understanding the behaviour and performance of these materials, we can enhance the longevity and efficiency of solar energy systems.

2. Materials and Methods

The photocatalytic activity of the as-prepared film, soiled with a model organic compound (methylene blue), was monitored under the UVA light irradiation (12 W). For this purpose, the coated film sample SiO₂/WO₃-B₅/ZnO composite with varying dip-coating cycles) were immersed into the methylene blue solution (10 mg/l) and then dried in the air atmosphere. The film coatings adsorbed with methylene blue were irradiated with the UVA light. At certain time intervals (30 min), the degradation of methylene blue on the film coatings was evaluated by measuring the reduction in the absorbance maximum peak of the model compound (664 nm) using a Genesys 10S model (Thermo Scientific) spectrophotometer by the following equation [17-23].

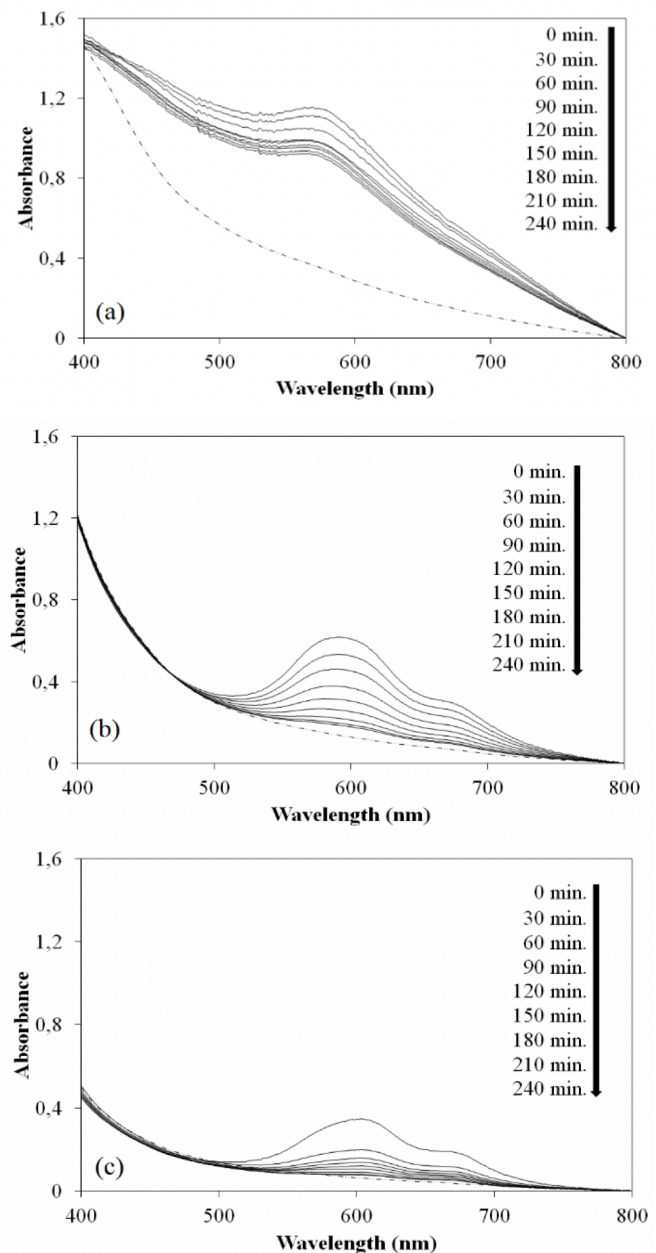
$$\text{Degradation efficiency (\%)} = (A_0 - A) / A_0 \quad (1)$$

where A_0 is the initial absorbance of methylene blue and A is the absorbance of methylene blue after the UV light irradiation. The dye solution with varying concentrations (10, 25 and 50 mg/l) was also prepared, and the photocatalytic dye degradation experiment on the SiO₂/WO₃-B₅/ZnO(70/30) film sample was performed. Thus, the possible effects of the contamination density of the glass cover on the solar cell efficiency was tried to be examined.

In addition, the photocatalytic activity of the as-prepared film coating SiO₂/WO₃-B₅/ZnO(70/30)) were analysed using the water contact angle measurement.

3. Measurement Results

The photocatalytic activity of the SiO₂/WO₃-B₅/ZnO in comparison to WO₃-B₅ film and SiO₂/WO₃-B₅ film are shown in Fig. 1.



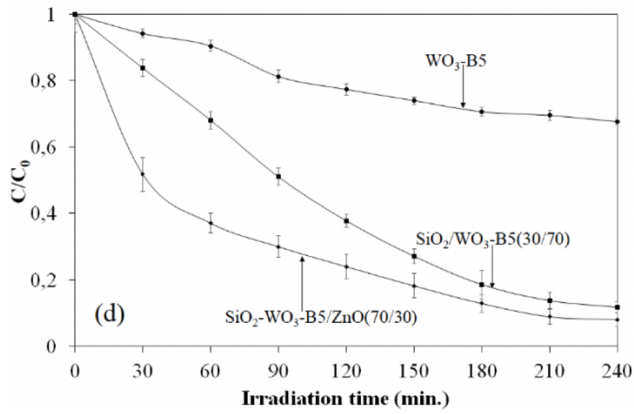


Fig. 1 The variation in the UV-Vis absorption spectrum of methylene blue with time on (a) the WO_3-B5 film, (b) the SiO_2/WO_3-B5 film, (c) $SiO_2/WO_3-B5/ZnO(70/30)$ film samples, and (d) the photocatalytic dye degradation efficiency of all the film samples under the UVA light irradiation.

Fig. 2 depicted the results of the water contact angle measurements for $SiO_2/WO_3-B5/ZnO(70/30)$ film sample.

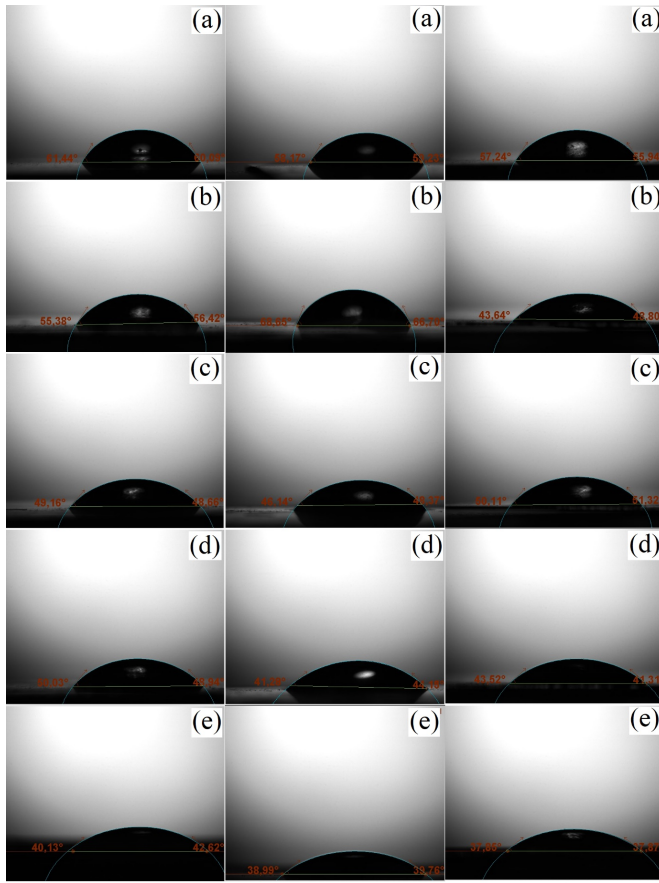


Fig. 2 Images of the water droplet on the $SiO_2/WO_3-B5/ZnO(70/30)$ film with the irradiation time of (a) 0 min, (b) 60 min, (c) 120 min, (d) 180 min and (e) 240 min

The water contact angle measurement revealed that the composite film samples were able to degrade the model dye adsorbed on itself with time and the film samples exhibited photocatalytic activity. When the water contact angle values are compared, the highest change in the water contact angle value was obtained by the $SiO_2/WO_3-B5/ZnO(70/30)$ film, which also exhibited the highest dye degradation efficiency.

Both the photocatalytic dye degradation and the water contact angle measurements verified the high photocatalytic activity of the $SiO_2/WO_3-B5/ZnO(70/30)$ film.

The measurement results of variation in the water contact angle on the $SiO_2/WO_3-B5/ZnO(70/30)$ film under the UVA light irradiation are shown in Fig. 3.

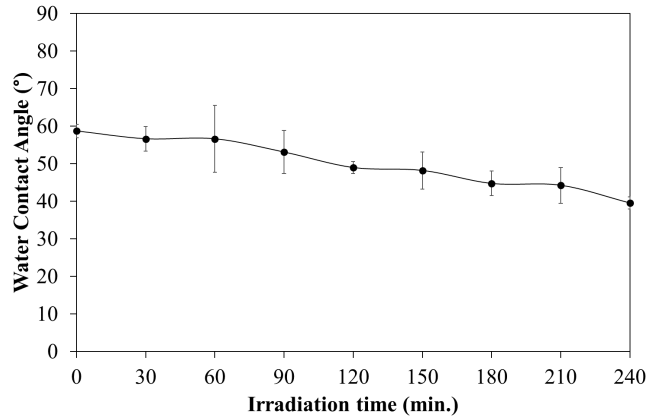


Fig. 3 Images of the water droplet on the $SiO_2/WO_3-B5/ZnO(70/30)$ film with the irradiation time of (a) 0 min, (b) 60 min, (c) 120 min, (d) 180 min and (e) 240 min

Fig. 4 illustrates the Field Emission Scanning Electron Microscopes (FE-SEM) images of the $SiO_2/WO_3-B5/ZnO(70/30)$ films.

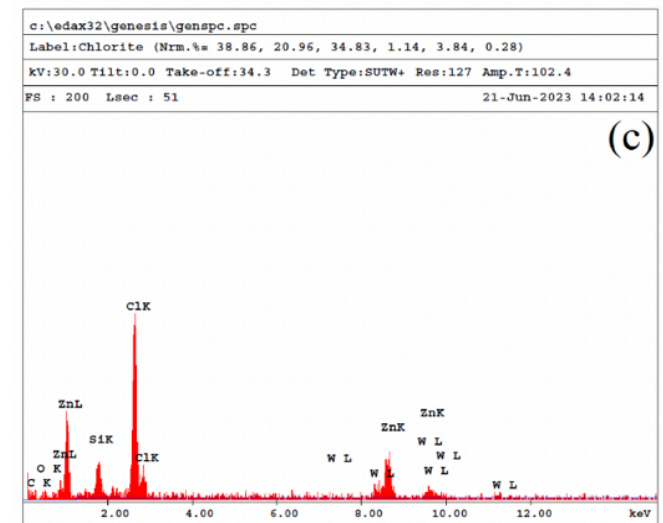
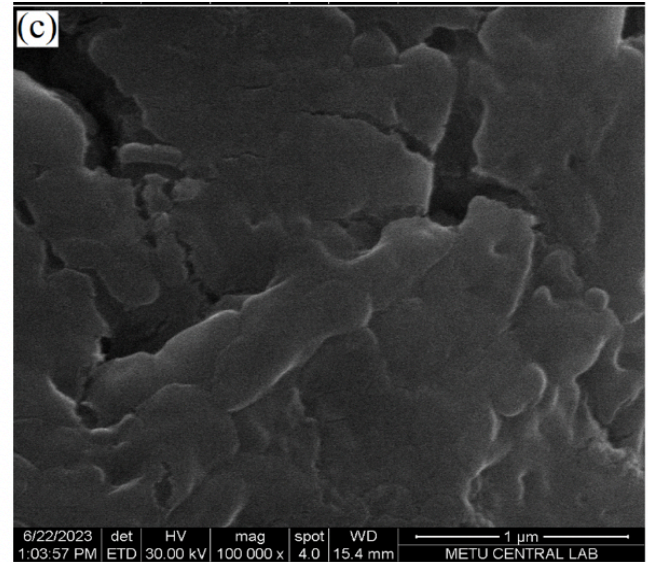


Fig. 4 FE-SEM image and EDX spectrum of the $SiO_2/WO_3-B5/ZnO(70/30)$ films

On the FE-SEM image of the $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}(70/30)$, there is an almost smooth surface structure with cracks over a wide area. The two phases of the composite, which might be the $\text{WO}_3\text{-B5}$ and ZnO phases or the $\text{WO}_3\text{-B5}$ and SiO_2 phases, were embedded in the remaining phase of the composite. The boron atom doping made the surface structure smoother [8].

The Energy-Dispersive X-Ray (EDX) spectroscopy is a micro-analytical technique and proved the successful synthesis of the composite films [24-26]. Due to the atomic size of the boron atom and the measuring capacity of the instrument, boron atoms could not be observed in the EDX spectra.

4. Conclusion

In this research work we have briefly described the characterization of the new developed self-coated composite materials type $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}$ film sample. It has been analyzed the photocatalytic activity, water contact angle and morphology analysis of the $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}$.

The photocatalytic dye degradation and the water contact angle measurements verified the high photocatalytic activity of the $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}(70/30)$ film. The composite film sample resulted the highest photocatalytic dye degradation efficiency (92%) with the $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}(70/30)$ film sample after 240 min of the UVA light irradiation.

The future research work would reveal on the analysis of the life cycle of $\text{SiO}_2/\text{WO}_3\text{-B5/ZnO}(70/30)$ film sample due to different environmental conditions.

5. Acknowledgement

This research has been supported by The Scientific and Technological Research Council of Turkey (TÜBİTAK) with the Project Number 122N383 and National Agency of Scientific Research and Innovation (NASRI) Project Number 91106AB.

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Influence of ultrasound in the production of Frass extracts

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Abstract: The current direction of development is the Green Deal, the main objective of which is to create a sustainable and modern economy without harming the environment. In order to avoid the negative effects of intensive farming, various options for sustainable agriculture are often proposed such as partially replacing synthetic fertilizers and replacing chemical plant protection measures with biological ones [1]. Residues from other agricultural branches can be used as an alternative raw material to produce fertilizers. The current trends in insect breeding, which are gaining wider applicability and legalization for use in the food industry, also create opportunities for the development of waste treatment methods. In Lithuania, the cultivation of insects is developing rapidly, which means that the amount of frass will also grow rapidly, so finding effective ways to use it are essential.

Keywords: FRASS, ULTRASOUND, EXTRACTS, FERTILIZERS

1. Introduction

In order to engage in insect breeding, it is necessary to think about ways of solving the problem of using the generated waste (frass). During the creation and cultivation of insect farms for industrial use, large amounts of waste is generated. Ways to use insect waste (frass) are being explored. One of the uses of frass (Fig. 1) is the production of fertilizers. The use of insects for food, feed and fertilizer is expected to continue to grow, because it has the potential to help reduce the amount of waste and increase food reserves as well as increase yields [2].



Fig. 1 Frass

The main goal of the research is to find the most suitable way to use frass in fertilizer production. It is important to determine the most appropriate conditions, quantities, and extraction methods so that the produced fertilizers can be used for plant fertilization. It is also very important to determine the efficiency of the obtained product, and under what conditions the obtained fertilizer works most effectively.

2. Materials and Methods

Chemical analysis was performed using chemically pure or pure analytical reagents, along with the standardized methodology and appropriate laboratory devices. Each sample was analyzed two or more times (depending on the requirements for methodology or repeatability of measurements). All TOC analyses were performed by using TOC analyzer (TOC-L, Shimadzu, Japan) following the LST EN 1484:2002 (EN 1484:1997) standard. The 3L Ulsonix PROCLEAN 3.0 ECO ultrasonic bath was used in extract production.

3. Results

Ultrasound, using a simple ultrasonic bath for cleaning purposes, was first used to increase the extraction yield in scientific research laboratories in the 1950s [3]. Ultrasound waves that are above 20kHz facilitate the release of substances by increasing permeability and causing cracks or otherwise disrupting biological cell walls.[4].

Because frass contains a large amount of organic matter, carbon concentration studies were conducted using several methods. The highest concentration of carbon was obtained in the alkaline

extracts, when ultrasound was used. The samples were analyzed immediately after extraction, ensuring high reliability of the results. Table 1 shows total organic carbon in the alkaline extracts.

Table 1. Total organic carbon in the alkaline extracts

Sample	Conditions	Organic carbon, g/l
DF1	Using ultrasound (1h)	19.03
	Using ultrasound (2h)	20.20
	Using ultrasound (3h)	18.18
	Using mechanical mixing (1h)	15.09
	Using mechanical mixing (2h)	16.74
	Using mechanical mixing (3h)	16.11
DF2	Using ultrasound (1h)	16.18
	Using ultrasound (2h)	22.64
	Using ultrasound (3h)	21.23
	Using mechanical mixing (1h)	14.21
	Using mechanical mixing (2h)	16.96
	Using mechanical mixing (3h)	16.68
DF3	Using ultrasound (1h)	21.15
	Using ultrasound (2h)	22.24
	Using ultrasound (3h)	21.77
	Using mechanical mixing (1h)	16.96
	Using mechanical mixing (2h)	17.99
	Using mechanical mixing (3h)	16.68
DF4	Using ultrasound (1h)	17.21
	Using ultrasound (2h)	18.44
	Using ultrasound (3h)	18.10
	Using mechanical mixing (1h)	16.65
	Using mechanical mixing (2h)	16.99
	Using mechanical mixing (3h)	16.72

4. Conclusions

The conducted research provides the prerequisites for the complex use of waste of insect farming for fertilizers. Frass can be used to create fertilizing products that contain not only the nutrients needed by plants, but also bioactive components.

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