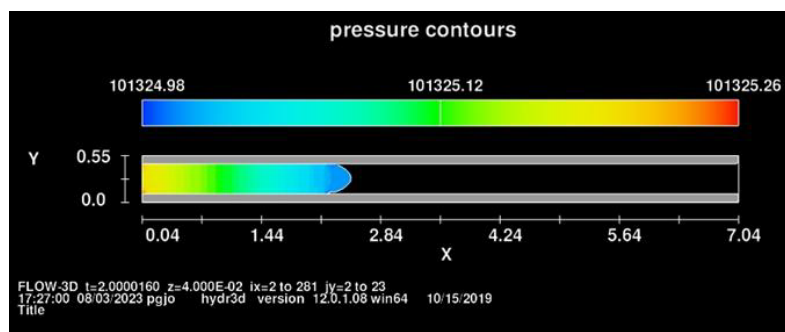


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Improvement of the design of the string extrusion machine based on the modernization of the worm

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Abstract: An option to modernize the worm of the strand extrusion machine is proposed. The technical solution of this worm of the string extrusion machine is the improvement of the mixing section of the extruder worm, which is located in the gap of the screw line in the homogenization zone of the extruder. This design of the mixing section of the worm of the strand extrusion machine allows to intensify the process of dispersion of agglomerates and mixing of the dispersed phase in the dispersed medium and as a result to obtain a homogeneous structure of the polymer, which in turn allows to improve the quality of the final product.

Keywords: WORM, MODERNIZATION, STRINGS, STRING EXTRUSION MACHINE, PRODUCT QUALITY, HOMOGENIZATION ZONE, MIXING SECTION, EXTRUSION

1. Introduction

Extrusion (extrusion – engl., german.) is a process of continuous injection molding into a bottomless mold - a spinneret, which makes it possible to obtain products of infinite length with various cross sections. For industrial purposes, extrusion technologies have been used since the middle of the 19th century. [1].

The strand extrusion machine is widely used in various industries such as plastic products, packaging, automotive, construction, medical equipment and other industries that use resin materials. The strand extrusion machine allows you to increase productivity and reduce the cost of pellet production, which makes them an important element in the production process.

2. Problem discussion

In the production of polymer materials for molding products from polymer composite materials, raw materials go through several stages of processing. Granulation is the final stage, the purpose of which is the removal of volatile substances, the introduction of additional components into the composition of the raw material (dye, filler), and the formation of granules. Most types of technological equipment work on granular raw materials.

Modern granulation equipment is suitable for processing many types of raw materials, including the most popular materials: any kind of polyethylene, polypropylene, polyethylene terephthalate, polyvinyl chloride, polystyrene.

The purpose of the article is to choose a way to improve the quality of the end product of a strand extrusion machine.

The object of the study is a machine for the manufacture of polystyrene strands (extruder), identifying its advantages and disadvantages in order to choose the modernization of the extruder screw to improve the quality of the finished product.

3. On the improvement of the design of the machine for the extrusion of strands based on the modernization of the worm

In the extrusion process, the injection of material into a forming tool (die) is carried out using a special machine called an extruder. The most commonly used in plastics processing are screw (screw) extruders, also referred to as worm presses. Piston (plunger) extruders are used to process hard-to-form low-plastic materials. There are also disc, drum and gear extruders, but they are not widely used in industry. Injection of material is the main function of the extruder, but far from the only one. Modern extruders make it possible to effectively mix various materials, carefully compound them, dry the working mixture, carry out chemical modification (chemical reactions), etc. As a rule, the equipment used in extrusion is built in the form of an automated production line, consisting of loading and dosing devices, an extruder with a die, calibration and cooling devices, pulling machines, etc. [1].

The main purpose of the single screw extruder is to produce and homogenize thermoplastic composite materials. The energy required for this is supplied both from an external electric heater 3 through the cylindrical wall of the housing 5, and due to dissipation in the volume of the processed material (Fig. 1). Due to the fact that in order to achieve the desired quality of the resulting composition, it is necessary to provide certain temperature conditions, the extruder is provided with temperature control. The extruder body is a cylinder with an internal channel to accommodate a worm 4 with a diameter of 90 mm. The worm has a single-western cut with a pitch of 60 mm, the depth of which varies from 10 mm in the feed zone to 3 mm in the homogenization zone. The rotation of the worm is provided by a DC electric motor 6 through a gearbox 1. To maintain the desired performance, a circuit for adjusting the worm speed is provided [2].

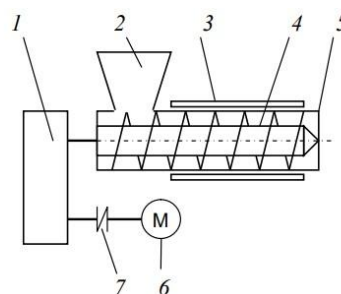


Fig. 1 Scheme of a single screw extruder:
1 - reducer; 2 - loading hole; 3 - electric heater; 4 - worm; 5 - body; 6 - electric motor; 7 - clutch.

The extruder can be conditionally divided into four technical zones: feed zone; dosing zone; degassing zone; pressure zone. The division into zones in the extruder is conditional.

In the feed zone, the material is fed through the hopper, it is melted to a fluid state and mixed by rotating the screw. In the dosing zone, the diameter of the screw expands, which makes it possible to dose a homogeneous mass when it is fed into the next section. Air and gas bubbles are removed from the homogeneous mixture into the degassing zone, which makes it possible to obtain granules without air cavities at the outlet. In the pressure zone, the melt is compressed and fed under pressure to the die of the extruder.

A spinneret is a forming head that molds the molten polymer into strands. The spinneret has calibration channels and works on the principle of a grate in a household meat grinder.

The design of the granulators includes electric heaters that provide heating of the body and melting of the polymer. Different types of heaters are used for each heating zone.

Clamp or semi-clamp type heaters are installed in the cylindrical body. Plate heaters are used for flat surfaces. For local heating of individual sections of the extruder, finger heat and power heaters are in demand. In the die zone, where the temperature of the polymer melt reaches its maximum value, brass heaters are used.

They are not damaged by contact with the molten polymer, are not subject to chemical attack.

The temperature of heating by heat elements in the supply zone reaches 160-2300 C. The exact value is determined in practice. Heating should be such that the polymer does not stick to the walls of the housing. In the next temperature zone, the heating level rises by approximately 600 C. The melting point is different for each type of polymer. In the degassing zone, the temperature decreases by 130 C from the melting point of the polymer material. To control the temperature in various parts of the extruder, thermal sensors are installed that ensure that the heaters are turned off when the specified temperature is reached in accordance with the technological process. This prevents overheating of polymers [3].

The purpose of the final stage of processing of polymer raw materials is granulation, which means obtaining material particles of the same size. For this purpose, a strand granulator is used, which cuts the granules. The difference between a strand cutter and underwater and water ring cutting is that threads are formed in it, which, at the exit from the die, are cut into granules of a given length.

If the strand granulator is equipped with a compactor, then by means of the latter the raw material is crushed, homogenized, that is, mixed, and dried from excess moisture. In parallel, it condenses and heats up, sintering. During rotation, the compactor knives constantly feed the agglomerate for the further formation of strands. The compactor in combination with a polymer strand granulator allows to save energy to a significant extent (electricity costs are reduced by an average of 40%), since the number of stages in the processing of raw materials is reduced [3].

4. Results and Discussion of the Improved Worm Design of the Strand Making Machine

The machine for making strands is designed for processing a wide variety of materials: polystyrene, polyethylene, etc.

As a result of the literature and patent search [1-4], the main advantages and disadvantages of the machine for extrusion of strands were identified.

Advantages: high productivity, flexible setting, high material processing efficiency. The disadvantages are high cost, complexity of maintenance, risk of contamination, high energy consumption.

In order to improve the quality of the final product and the general operating conditions of the machine for extrusion of strands, a literary and patent search was carried out for an option to modernize the extruder screw and the most appropriate design of the screw was selected.

The screws of modern extruders often have a complex geometric shape and uneven cutting, selected specifically for a specific material and mode of operation. Single-screw extruders can have not only cylindrical, but also conical design of the screw and sleeve. The tapered screw makes it possible to more effectively mix the compound, increase the pressure of the melt faster and make the machine more compact and productive [1]. Also, one of the ways to increase the efficiency of mixing agglomerates is to improve the mixing zone of the extruder screw. It is known that to improve the process of mixing the components of the polymer composition, one or more mixing sections are installed in the homogenization zone [4].

Based on the prototype [4], the design of the modernized extruder screw is proposed, which consists of a screw 1 and a torpedo 2 with an improved mixing section II (Fig. 2). The extruder screw performs the main function of mixing the material and is an important element of the strand extrusion machine.

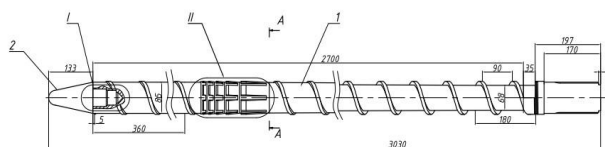


Fig. 2 The design of the upgraded worm of the strand making machine:

1 worm; 2 - torpedo

On fig. 3 in view I on an enlarged scale shows a worm 1 with a threaded connection with a torpedo 2.

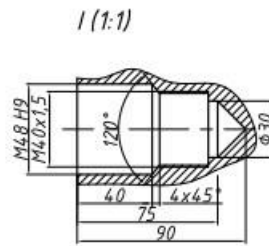


Fig. 3 Threaded connection of a worm with a torpedo

The upgraded design of the screw differs from the standard design of the screw in that there is a mixing section in the homogenization zone in the break of the helix. The proposed mixing section of the modernized screw has the form of cut cones with machined longitudinal grooves directed at an angle of 3 ° to the melt inlet channel, which are clearly shown in view II (Fig. 4).

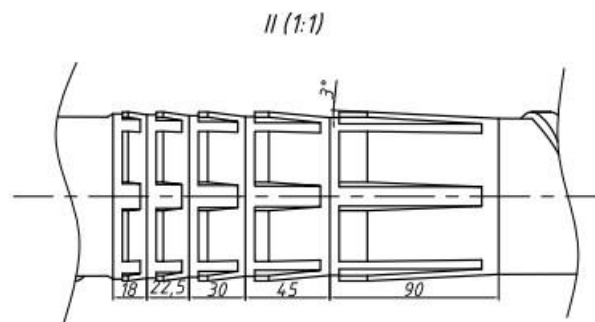


Fig. 4 Mixing section of the modernized worm in the form of cut cones with machined longitudinal grooves at an angle to the melt inlet channel

The total number of segment rows is 5, the number of longitudinal grooves corresponds to the number of segment protrusions and is the same in each segment row (Fig. 4). On fig. 5 shows a section of the mixing section of the modernized worm.

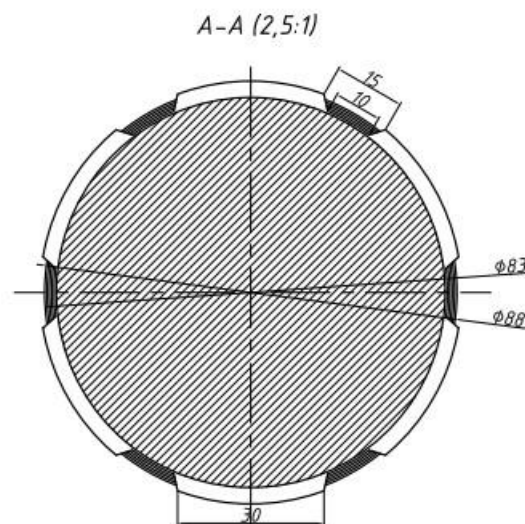


Fig. 5 Section of the mixing section of the upgraded worm

The depth of the longitudinal grooves along the worm of the mixing section decreases proportionally and discretely with each successive segment row in such a way that the step between the segment ledges along the worm is equal to the outer diameter of the helix of the worm, and the latter is 1/5 of the outer diameter of the helix of the worm (Fig. 5).

The mixing section works as follows. The polymer melt moves towards the mixing section due to the action of overpressure generated by the rotation of the screw. After the polymer melt enters the mixing section, the melt is compressed on the conical surface of the protrusions and the melt enters the longitudinal working grooves. Due to the fact that the screw 1 rotates, when the melt exits the longitudinal working groove, the high-viscosity flow breaks due to high shear rates. Next, the melt enters the next segment row, where there is a preliminary compression on the conical surface, the melt flow enters the next working groove and its subsequent rupture (Fig. 4). Since the depth of each subsequent working groove decreases, as a result of which the longitudinal shear rates increase in each successive degree, which intensifies the process of dispersive mixing of polymer compositions [4].

5. Conclusions

The use of this mixing section makes it possible to intensify the process of mechanical mixing of the mixture of the components of the composition as a result of the melt passing through the channels of the mixing section and breaking the flow due to the rotation of the screw, however, dispersion of the dispersed phase agglomerates is low due to low shear rates. Thus, the use of a modernized screw design in a machine for the production of polystyrene strands will improve the quality of the final product due to the intensification of the process of dispersion of agglomerates and mixing of the dispersed phase in a dispersed medium.

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Approbation of the process for obtaining highly porous ceramic filter materials using porous shells on removable spherical carriers

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Abstract: On the example of a powder based on mullite, the process of obtaining highly porous ceramic filter materials using porous shells on removable spherical carriers was tested, including the deposition of thin shell coatings from powder based on mullite on spherical granules of expanded polystyrene, pressing the mixture in the form of evenly distributed in the powder of the same composition (matrix) and sintering. It's shown that the resulting material is characterized by a good complex of filtering properties and a developed biporous structure.

KEYWORDS: HIGH POROUS CERAMICS, FILTERING MATERIALS, TECHNOLOGY, RESEARCH, STRUCTURE

1. Introduction

Highly porous ceramics are of great interest to science and technology because of their potential for a wide range of applications such as filtration of molten metal, hot gases and chemically aggressive substances, the manufacture of catalyst substrates, thermal and acoustic insulation, shock and sound absorption, biomedical implants, lightweight supporting structures, gas sensors, etc. [1-3]. In the last few decades, to create highly porous materials, considerable attention has been paid to the use of monodisperse hollow spheres, due to their unique properties and a wide range of potential applications of materials obtained with their help [4, 5]. This paper discusses the process of obtaining highly porous materials based on hollow spheres (HMPS) intended for filtering liquid and gaseous media, based on molding with the application of pressure, including the production of hollow ceramic shells on a spherical carrier removed during sintering, filling the charge into the mold chamber from ceramic shells distributed in a matrix of metal or ceramic powder on a spherical carrier, which plays the role of a blowing agent, pressing and sintering with holding at certain temperatures to remove the binder from the shell and the spherical blowing agent and control properties. In contrast to known similar works [6–8], the material of the sphere is removed during sintering (burnout), and not before sintering (dissolution); in addition, in known works there is no information about the filtering characteristics of the material.

The aim of this work is to study the possibility of using hollow spheres as a pore former in a ceramic matrix to obtain filter materials.

2. Experimental results and discussion

In the manufacture of HMPS with a ceramic matrix, a mullite-based powder obtained by grinding furnace mullite ceramics was used to obtain the matrix and shell. The granulometric composition of mullite powder and the appearance of powder particles at various magnifications are shown Figures 1 and 2, the chemical composition is in Table 1.

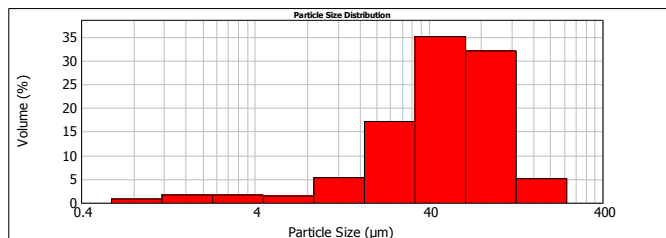
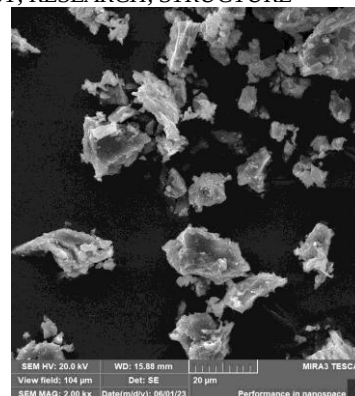
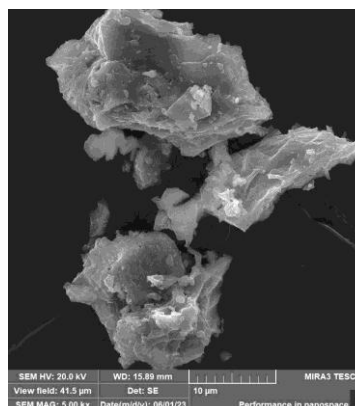


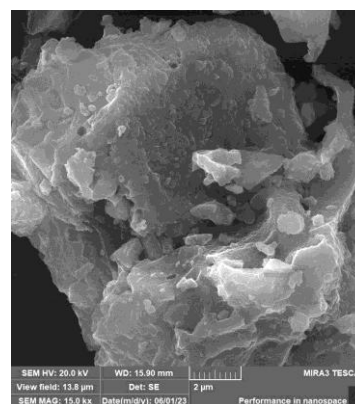
Fig. 1. The granulometric composition of mullite powder.



a)



b)



c)

Fig.2. Appearance of mullite powder at various magnifications: x20 (a); x40 (b); x150 (c).

Table 1. Chemical composition of powder based on mullite.

Ceramic matrix material and coverage	Powder chemical composition, %									
	Al ₂ O ₃ ·8SiO ₂	Na ₂ O	Quartz SiO ₂	Cristobalite SiO ₂	Fe ₂ O ₃	TiO ₂	K ₂ O	CaO	MgO	Other impurities
Mullite based powder	45,1	0,4	23,9	23,0	3,4	1,6	1,0	0,9	0,4	0,3

Expanded polystyrene (EPS) granules with a diameter of no more than 1 mm were used as a material for forming the internal space of hollow spheres. The manufacture of spheres with shells included applying polyurethane foam varnish, mullite-based powder to the surface of the granules, drying at a temperature of 85 °C for 15 minutes, applying an aqueous solution of liquid glass to the granules with the first layer of powder applied, applying the next layer of powder, drying at a temperature of 85 °C for 15 minutes with the repetition of the last three operations until the required number of layers of ceramic powder is applied (during the experiments, it was considered sufficient to apply three layers of powder to ensure a high-quality coating of granules with it: the application of one or two layers does not guarantee the application of a powder coating over the entire surface of the granule; applying more layers is impractical, since the sphere is introduced into the matrix as a pore-forming agent, in which the granule, and not the shell, makes the main contribution to porosity). Figure 3 shows PPS granules with three applied layers of ceramic powder (mullite).

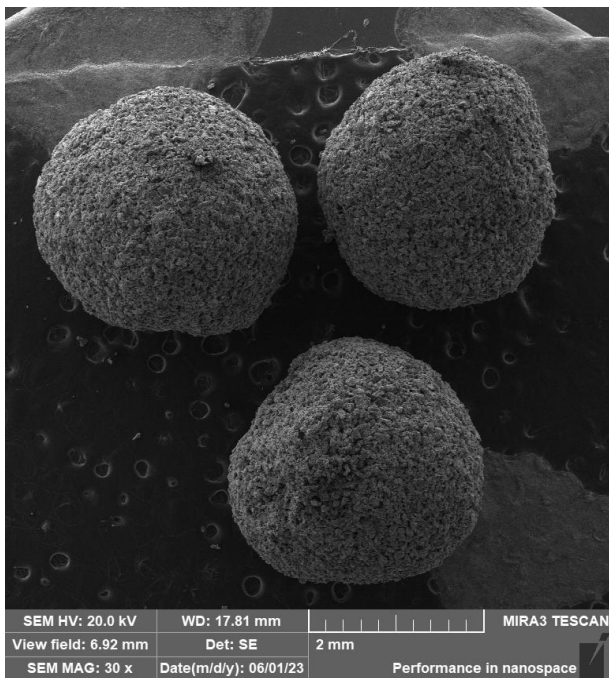


Fig. 3. PPS granules with three applied layers of powder based on mullite.

The main stages of the technology for manufacturing experimental samples of VMPS included the following main operations: preparation of charge components; layer-by-layer backfilling on the lower punch of spheres with filling the pore space between them with matrix ceramic powder until the required number of layers is formed; pressing molding; sintering. The pressing pressure range was 60–130 MPa and was chosen on the basis that the pressure ensured the preservation of the compact without shedding edges, defect-free transportation, and did not lead to a significant decrease in intergranular porosity.

Figure 4 shows the heating curve of compacts during sintering, which has two sections of constant temperature for removing binders and blowing agent.

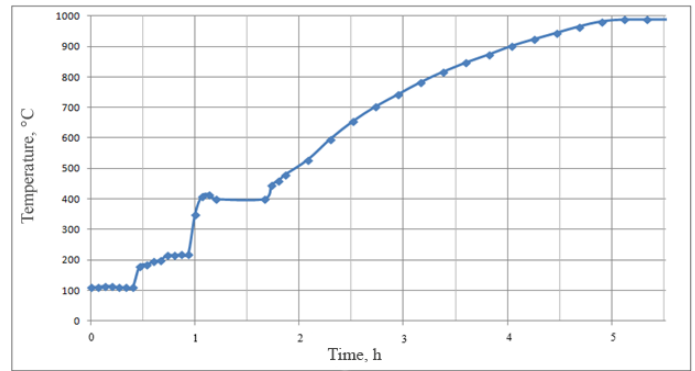


Fig. 4. Heating curve of compacts during sintering of WMPS with a matrix based on mullite powder.

For the manufactured samples, the dependences of porosity (Figure 5), pore size and permeability coefficient (Figure 6) on the pressing pressure were determined and the structure of the material was studied (Figure 7).

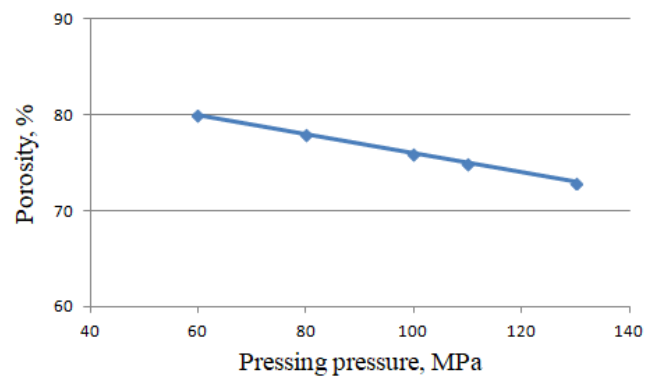


Fig. 5. Dependence of porosity on pressing pressure for VMPS with a ceramic matrix based on mullite powder.

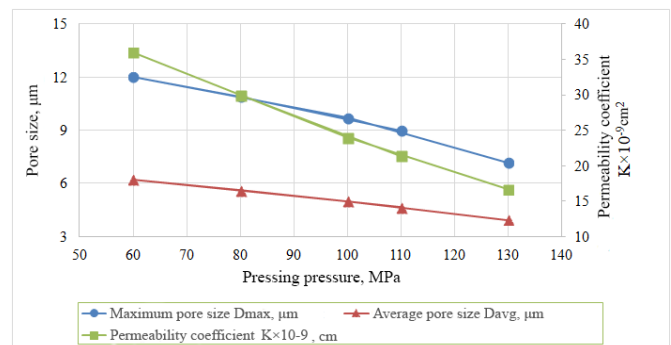
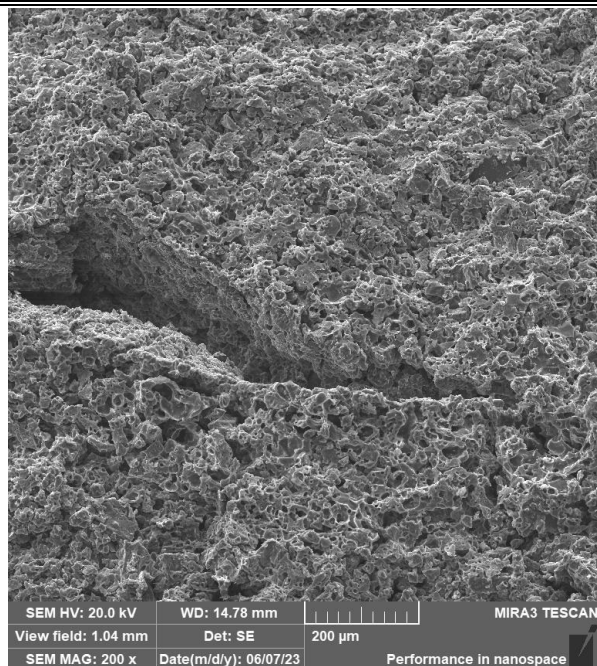
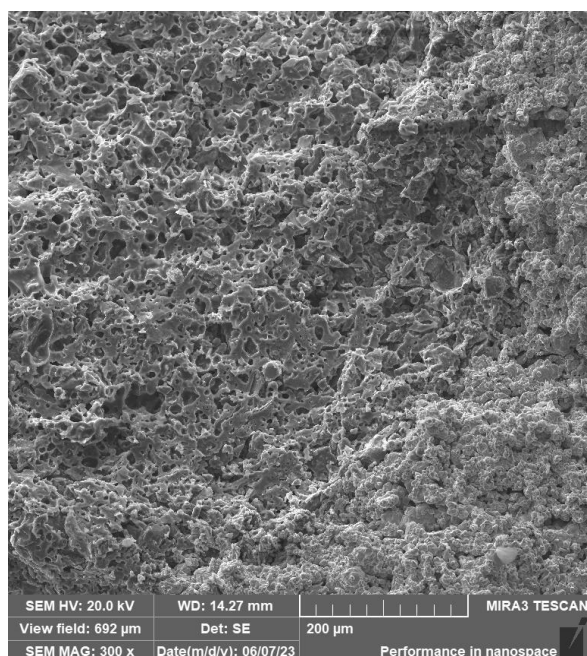


Fig. 6. Dependences of pore sizes and permeability coefficient on pressing pressure for VMPS with a ceramic matrix based on mullite powder.

An analysis of the research results allows us to conclude that it is expedient to continue research in the field of developing highly porous filter materials based on hollow spheres: the obtained samples have high porosity and a good combination of filter characteristics (permeability coefficient and maximum pore size, which determine the throughput and fineness of material purification). The samples have a developed biporous structure; there are no structural changes at the interface between the matrix and the shell.



a)



b)

Fig. 7. Structure of an IMPS with a matrix and a powder shell based on mullite powder: trace of a pore formed by a sphere (a), structure of a ceramic matrix (b).

3. Conclusion

The possibility of obtaining highly porous ceramic filter materials using porous shells on removable spherical carriers has been confirmed. The modes of application of thin shell coatings from powder based on mullite on spherical granules of expanded polystyrene with a diameter of up to 1 mm, pressing and sintering of VMPS have been worked out. It is shown that the resulting material is characterized by a good complex of filtering properties and a developed biporous structure.

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Innovative plasma-deposited nanothin films for oxygen evolution reaction and their prospective application for electro-ozonation

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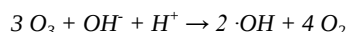
Abstract: Water recycling plays a prominent role, especially for water-consuming industries. Thus, wastewater purification becomes indispensable to achieve the ideal degree of quality. Electrochemical processes combined with ozonation are chosen as advanced treatments to be studied and developed in this work since they can operate at ambient conditions and are more efficient and compact when compared to other technologies. The plasma-deposited film used as an electrode seems to be a promising and interesting option. The main objective is to investigate the role of synergistic effects between ozone and plasma-deposited thin film electrodes in hybrid electrochemical and ozonation processes of water contaminants degradation. The essence of the process is to find both the active, sustained, and photostable plasma-deposited thin-film electrocatalysts, which enhance the degradation process with the combined action of ozone. Therefore, the chemical stability of developed thin films after contact with ozone is one of the significant requirements for further application.

KEYWORDS: THIN-FILM ELECTROCATALYSTS, COLD PLASMA, ADVANCED OXIDATION PROCESSES, MICROPOLLUTANTS, OZONATION, WATER REUSE

1. Introduction

The development of the global industry, beyond numerous advantages, also brought the growing problem of water contamination. Therefore, the need for efficient methods for wastewater treatment is one of the most significant branches of current chemical and environmental engineering. Closing the water loops is recommended as the most advantageous approach, which builds a sustainable circular economy [1-2]. Among, numerous pollutants, one can mention contaminants of emerging concern (CECs), e.g. Pharmaceuticals and Personal Care Products (PPCP), Persistent Organic Pollutants (POPs), endocrine disruptors (EDCs), etc.). These substances exhibit high toxicity even at a trace level of concentration [3]. Their efficient removal is possible via Advanced Oxidation Processes (AOPs) [4-7]. The wastewater treatment mechanism with AOPs is based on the formation of highly-reactive and non-selective $\cdot\text{OH}$ radicals. This unstable molecule may react with a wide range of organic compounds, including pollutants.

Another oxidizing agent- ozone can oxidize the contaminant via two mechanisms, depending on pH [5]. In acidic media, ozone attacks the molecules in molecular form. This electrophilic agent reacts with the nucleophilic parts of the molecules: unsaturated carbon-carbon bonds and numerous functional groups, including hydroxyl, methoxyl, or methyl groups. Ozone is also aggressive for the organic molecules' nitrogen, sulfur, and phosphorus-bearing parts. In a basic or neutral environment, the wastewater treatment becomes AOPs, because ozone transforms to the $\cdot\text{OH}$ radicals, following the reaction:



In this study, the series of cold-plasma deposited electrodes were synthesized and studied. The method, widely known as plasma-enhanced metal-organic chemical vapor deposition (PEMOCVD) is a perfect tool for depositing a wide range of catalytically active layers [8]. In brief, the vapors of volatile compounds are introduced to the low-pressure reactor, where the glow discharge is ignited. The gas's ionisation causes highly reactive radicals to form, which fragments the precursors. The as-formed fragments collide with themselves and with the support with subsequent growth of the desired material. Importantly, the growing material exhibits low crystallization and the ordering is rather random. A thickness below $1\mu\text{m}$ characterizes the synthesized materials. The versatility of the method allows obtaining the thin film onto a wide variety of supports, regardless of the shape and chemical composition. The initial step of argon plasma treatment of the support creates the radical states, which significantly enhances the adhesion of the desired layer to the support by forming chemical bonds.

Prospectively, the studied cold-plasma deposited materials will be applied for catalytic electro-ozonation, where wastewater treatment with ozone and electro-oxidation is performed in hybrid

mode. Herein, we present the results of seeking highly active, chemically and mechanically stable electrodes for the electro-ozonation of wastewater.

2. Materials and methods

Four materials were studied as electrodes: tungsten oxide-based, cobalt oxide-based, iron oxide-based, and nickel oxide-based. For the latter case, the additional deposition was performed with the addition of acrylonitrile ($\text{C}_3\text{H}_3\text{N}$). This additional precursor was applied to introduce the CN_x phase. The synthesis was performed via the PEMOCVD method, where W-, Co-, Fe-, and Ni-containing metal-organic precursors were applied. The plasma deposition and subsequent thermal treatment conditions were established via the optimization step (not shown here). All samples were deposited onto the steel support after initial argon plasma treatment. The radio-frequency (13.56 MHz) plasma generator was applied to ignite glow discharge in a parallel-plate glass reactor. The basic information on the preparation is shown in Table 1.

Table 1: Materials studied

Label	Precursor(s)	Deposition power and time	Thermal treatment: atmosphere, temperature and time
WOx	$\text{W}(\text{CO})_6$	60W, 30 min	air, 400°C, 30 min
CoOx	$(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$	60W, 30 min	air, 400°C, 30 min
FeOx	$\text{Fe}(\text{CO})_5$	80W, 30 min	air, 500°C, 30 min
NiOx	$\text{Ni}(\text{CO})_4$	40W, 2 min	air, 300°C, 30 min
NiOx-CN	$\text{Ni}(\text{CO})_4$, $\text{C}_3\text{H}_3\text{N}$	40W, 2 min	air, 300°C, 30 min or Ar, 300°C, 30 min
CN	$\text{C}_3\text{H}_3\text{N}$	40W, 2 min	

The materials were analyzed to determine their electrochemical properties in OER. The sample was a working electrode, a platinum plate was applied as a counter electrode, and a calomel ($\text{Hg}_2\text{Cl}_2/\text{Hg}$) electrode was applied as a reference electrode. The studies were performed in 1M KOH, which played a role of the electrolyte. The dependence between current density and the applied potential was determined using the linear sweep voltammetry method (LSV).

Further characterization involved the determination of chemical composition XPS with the application of Kratos Analytical Axis Ultra DLD, with the monochromatic X-ray Al K α lamp (1486.6 eV). The survey spectra were collected from three spots (300 x 700 μm) in the binding energy region between 1200 and -5 eV. The exact contents of the elements were determined with the usage of narrow scans for the specific regions: carbon (C1s, 300-270 eV), oxygen (O1s, 540-510 eV), and cobalt (Co2p, 820-770 eV). The content of each element was calculated from 3 spots and averaged. The morphology (SEM) imaging was performed with Thermo Fisher Scientific Apreo 2S LoVac scanning electron microscope. The materials were also tested for resistance to the treatment with the ozone stream in a glass reactor (volume 250 mL) for 3h and 5h.

3. Results and discussion

The materials were labelled as MeOx-gas, where Me is metal, and 'gas' presents the atmosphere of thermal treatment (air or Ar). Some samples were studied before the thermal treatment, so the label is free from this sign. For NiOx samples, 'CN' means the synthesis was performed with the additional precursor- acrylonitrile.

Oxygen evolution reaction

All synthesized samples were characterized in OER. As presented in Figure 1, the nickel oxide-based electrode (NiO_x) exhibited the best performance. The nickel oxide-based electrodes with additional CN_x phase as well as acrylonitrile-based electrodes were found to possess promising electroactivity. The determined overpotential for oxygen evolution at the current density of 4 mA·cm⁻² in ascending order was found to be as follows: 310 mV for NiO_x, 430 mV for NiO_x-CN and CN, 440 mV for NiO_x-CN-air, 540 mV for NiO_x-CN-Ar, and 610 mV for FeO_x-air.

However, all nickel-containing and acrylonitrile-based samples were unstable in 1M KOH. CoO_x-air showed the best resistance to the strong basic environment among all materials studied. The previous studies of the air-treated plasma deposited sample from the same precursor showed that this phase is stable in aqueous solutions [9].

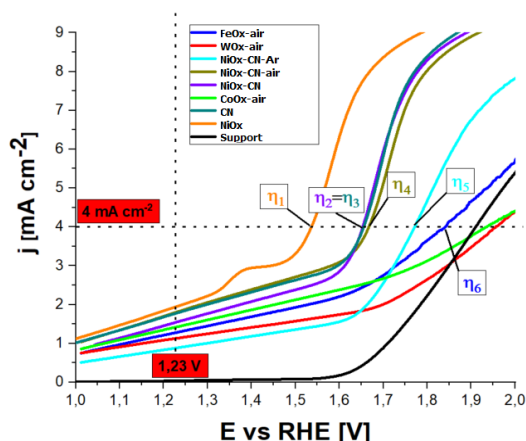


Fig. 1 Oxygen evolution reaction LSV curves.

The CoO_x-air and FeO_x-air electrodes were subjected to further characterization.

The next step involved studies on the effect of ozonation on the OER performance of the electrodes. Interestingly in case of CoO_x-air electrode, the ozone treatment has a positive effect on its activity in the oxygen evolution reaction. Importantly, the studied electrode did not delaminate from the support and did not dissolve.

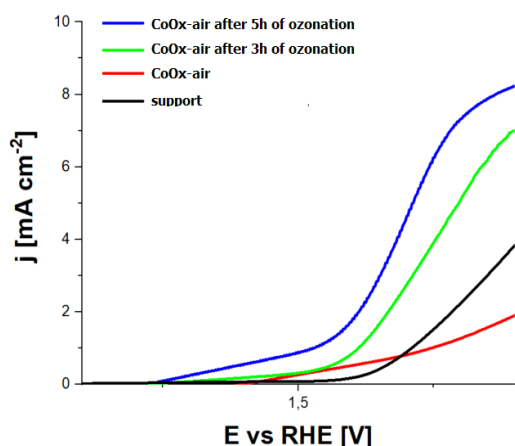


Fig. 2 Oxygen evolution reaction LSV curves.

While FeO_x-air electrode has not indicated similar behavior. This may be explained by the XPS results obtained for that electrode.

Chemical composition

The XPS analysis performed for the cobalt oxide-based sample and the samples after 3h and 5h of ozonation revealed that the ozonation caused slight chemical changes on the surface of the electrodes. The contents of the elements, presented in Table 2, at each stage, are quite similar with a small increase of oxygen content indicating the partial oxidation.

On the other hand, iron-based samples were significantly changed with ozone (Table 2). The oxygen content increased rapidly by a third, whilst carbon gasified noticeably. Therefore, the FeO_x-air electrode is considered as not suitable for electro-ozonation.

Table 2: Chemical composition of Co- and Fe-containing electrodes determined via XPS

Label	Carbon content (at. %)	Oxygen content (at. %)	Metal content (at. %)
CoO _x -air	22.4 ± 1.4	49.2 ± 0.5	28.5 ± 1.0
CoO _x -air after 3h of ozonation	20.7 ± 1.4	50.0 ± 1.0	26.3 ± 0.4
CoO _x -air after 5h of ozonation	20.8 ± 1.6	52.6 ± 1.4	26.6 ± 0.2
FeO _x -air	33.0 ± 0.9	43.8 ± 2.0	23.2 ± 1.3
FeO _x -air after 3h of ozonation	29.2 ± 1.4	53.6 ± 0.4	17.2 ± 1.6
FeO _x -air after 5h of ozonation	22.2 ± 1.0	59.3 ± 1.1	18.6 ± 1.1

The detailed analysis of the Co 2p_{3/2} spectrum (Figure 3) undoubtedly proves the chemical stability of the CoO_x-air electrode during ozonation. The materials comprise Co₂O₃ and CoO phases, represented by the bands at 779.5 ± 0.4 eV and 780.8 ± 0.2 eV, respectively [9]. The content of these phases changed slightly, despite the treatment with a strong oxidizing agent, i.e. CoO takes 51.4 at.%, 55.7 at.%, and 52.4 at.%, whilst Co₂O₃ takes 48.6 at.%, 44.3 at.%, and 47.6 at.%, for untreated CoO_x-air, and CoO_x-air treated with O₃ for 3h and 5h, respectively.

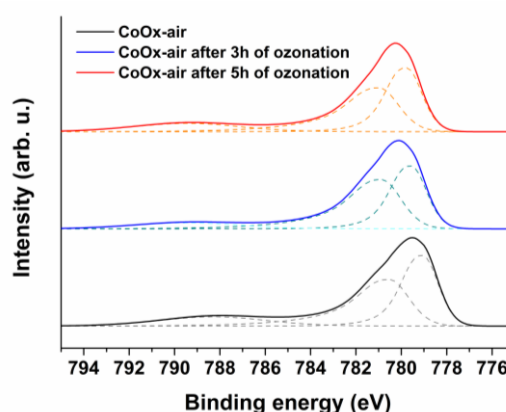


Fig. 3 Co 2p spectra for Co-containing electrode before and after ozonation.

The XPS for the nickel-containing samples (Table 4), which were the most promising, revealed nickel, carbon and oxygen content. Addition of acrylonitrile in the synthesis resulted in the presence of nitrogen and increase of the carbon content. As seen in Tab. 4, the thermal treatment of NiO_x-CN in the atmosphere of Ar did not significantly changed the chemical composition, because the composition is almost identical, whilst the air-treatment caused gasification of some carbon phase with parallel increase of O-, N- and Ni-content.

Unfortunately, similarly to the low resistance for the KOH aqueous solution, the nickel-containing electrodes are sensitive for ozonation. The XPS analysis revealed that the treated samples are virtually free from nitrogen and nickel.

Table 4: Chemical composition of Ni-containing electrodes determined via XPS

Label	Carbon content (at. %)	Oxygen content (at. %)	Nitrogen content (at. %)	Metal content (at. %)
NiOx	24.5 ± 1.4	44.7 ± 1.3	N.A.	30.8 ± 1.2
NiOx-CN	59.1 ± 0.3	22.6 ± 0.2	8.1 ± 0.2	10.3 ± 0.4
NiOx-CN-air	55.0 ± 0.4	24.0 ± 0.4	10.0 ± 0.5	11.0 ± 0.5
NiOx-CN-Ar	59.9 ± 0.2	22.0 ± 0.5	7.7 ± 0.5	10.5 ± 0.2

Morphology

SEM imaging of the samples (Figure 4) revealed that independently from the ozonation step, the samples are quite similar. The treatment with the ozone stream did not introduce any significant and detectable changes in the morphology. The layer is composed of quasi-spherical or elongated particles with a diameter below 1 µm. The particles are connected forming a homogeneous layer.

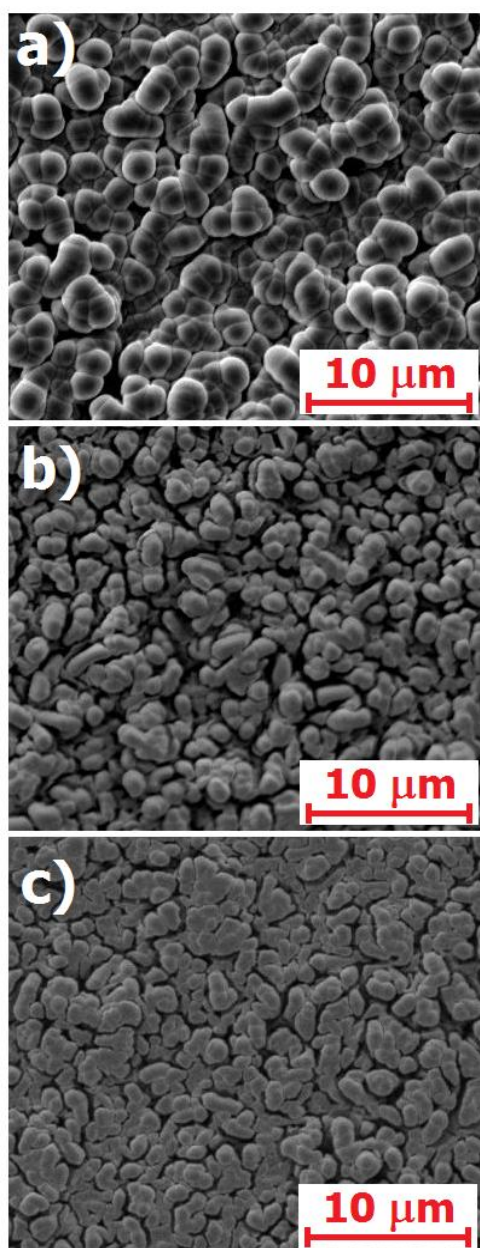


Fig. 4 Morphology of a) CoOx-air, b) CoOx-air after 3h of ozone treatment, c) CoOx-air after 5h of ozone treatment

4. Conclusions

Herein, the research focused on the search for active electrode material in advanced oxidation processes is presented. The nanothin materials were deposited onto steel support with the application of plasma-enhanced metal-organic chemical vapor deposition. As a result of the studies on the activity of the materials obtained in the oxygen evolution reaction, the electrode based on cobalt oxide was chosen for further investigation. This electrode was found to be chemically and mechanically stable during the ozonation. Moreover, the ozonation process enhanced its activity in the oxygen evolution reaction.

Taking into consideration all data and results, one can conclude that the combination of electrooxidation and ozonation has a high potential to be an efficient method for the removal of contaminants of emerging concern. Therefore, the results presented above are the onset of more advanced studies on the combined treatment of wastewater in electro-ozonation.

5. Acknowledgements

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The influence of the composition of the working fluid on the characteristics of high-voltage electric discharge in the "hydrocarbon liquid–Al powder" disperse system

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Abstract: Physical modeling of processes in a layer of Al powder in kerosene and ethyl alcohol during high-voltage electrical discharges in the spark discharge mode was carried out. The regularities of the distribution of plasma formations in the volume of the discharge chamber were studied when using ethyl alcohol and kerosene as working substances with an increase in the number of discharges. It is shown that the use of kerosene as a working fluid leads to an increase in the intensity of the formation of discharges between particles. It has been established that ethyl alcohol as a working fluid makes it possible to relatively stabilize the discharge mode, as well as to increase the number of discharges before the appearance of visual signs of the presence of residual nanocarbon, as a result of which it is possible to achieve greater dispersion of the processed powders. The possibility of synthesis of submicron and ultradisperse particles during high-voltage electric discharge processing of aluminum powder in a hydrocarbon liquid (alcohol or kerosene) due to the electrothermal effect of the discharge plasma on the powder particles has been confirmed.

KEYWORDS: KEROSENE, ETHYL ALCOHOL, ELECTRIC DISCHARGE, SPARK DISCHARGE, NANOCARBON, ELECTRIC DISCHARGE DISPERSION, ALUMINUM, PLASMA, PLASMA TECHNOLOGIES.

1. Introduction

Currently, high-strength, light composite materials, in particular, multi-component heteromodal powder aluminomatrix composites that combine components with a high Young's modulus and elements with significantly lower values of the modulus of elasticity are increasingly being used in the creation of a number of parts and assemblies in machine building, shipbuilding, aviation and rocket and space technology. By controlling the volumetric content of the components, it is possible to obtain composite materials with the required levels of the main physical, mechanical and functional properties.

Aluminum is one of the most promising metals in modern metallurgy, which provides a unique complex of basic physical, mechanical and operational properties. Having such properties as low density, high plasticity and corrosion resistance, quite high strength indicators, significant thermal and electrical conductivity and wear resistance in a wide temperature- power range of operation, aluminum is widely used in various branches of modern technology. In many cases, it successfully replaces other non-ferrous metals and is even used as a substitute of steel. The wide usage of aluminum and its alloys can also be explained by the possibility to adjust the properties of the matrix material by heat treatment, to subject it to almost all types of pressure treatment, to obtain composite materials (CM) based on aluminum both by foundry methods and by powder metallurgy methods.

The creation of new metal-matrix materials with higher physical and mechanical properties than those obtained by conventional metallurgical methods is possible by physical methods of dispersion and synthesis of solid phases. One of these methods is the high-energy preparation of powders with the help of high-voltage electric discharges (HVED) [1, 2]. Further consolidation of HVED-treated powders allows obtaining materials with increased mechanical and operational properties.

The main idea behind the use of HVED for the preparation of initial powder mixtures is that during the treatment of powders in a hydrocarbon liquid, their particles are dispersed and the simultaneous synthesis of nanocarbon of various allotropic modifications occurs. This creates conditions for the carbidization reactions of the processed powder, which leads to the creation of dispersion-strengthening fillers of different stoichiometry during processing [1–4].

During HVED treatment, powder particles are thermally affected by plasma formations of interparticle discharges, which causes the transfer of metal (ablation) from the surface of the particles into the working liquid with subsequent recrystallization, as well as the impact of compression-decompression waves that arise as a result of the rapid expansion of plasma formations [1–5].

The prospects of using HVED for powders treatment are associated with the possibility of obtaining ultra-dispersed micro-

and nano-sized particles with an increased level of free energy and, as a result, with an enhanced ability to intensively interact with the environment, in particular, with nanocarbon particles that are formed as a result of the pyrolysis of hydrocarbon liquids by a plasma discharge channel [1].

However, the processes of HVED treatment of metal powders in liquid dielectrics remain insufficiently studied, despite a number of known assumptions and hypotheses [1–5]. In particular, there are currently virtually no results of studies of the influence of the composition of the working environment on the patterns of development of high-voltage electric discharge. There are known works in which similar studies were performed for volumetric electrospark dispersion (electric discharge machining) [6–12], which makes it possible to use a similar methodology to study the HVED treatment of metal powders.

Therefore, the **goal of the work** is to study the distribution of plasma formations during the HVED in "Al powder – hydrocarbon liquid" disperse system.

2. Methodology

In order to evaluate the influence of the composition of the working fluid on the processes of high-voltage electric discharge, physical modeling of electric discharge processes that occur in "Al powder–hydrocarbon liquid" disperse system was performed. For this purpose, aluminum powder of the PA1 aluminum grade (DSTU 2651-94) was used. Hydrocarbon liquids with different numbers of carbon atoms in the molecule were used as a working medium during the high-voltage processing of titanium powder, namely kerosene (DSTU 3664:2013) and rectified ethyl alcohol (DSTU 4221:2003).

For physical modeling of electrical discharge processes in a layer of Al powder in kerosene and ethyl alcohol, a flat transparent discharge chamber (see Fig. 1) was made for photographic recording of discharges in the powder layer.

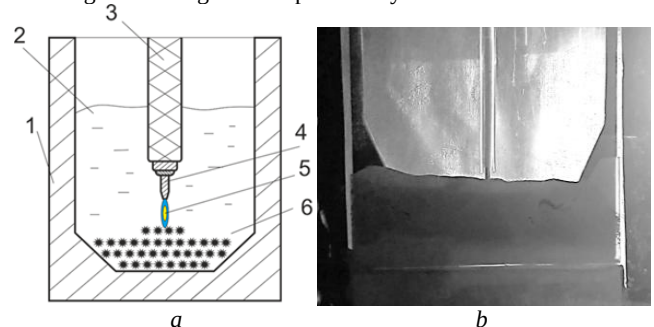


Fig. 1. General schematics of HVED process (a) and appearance of the processing chamber (b): 1 – processing chamber; 2 – hydrocarbon liquid; 3 – insulator; 4 – electrode; 5 – plasma channel; 6 – metal powder

The use of a hydrocarbon liquid as a working medium for a high-voltage discharge makes it possible not only to grind treated powders particles, but also to synthesize various allotropic modifications of nanocarbon, which can form metal carbides due to its high chemical activity [2].

The distance between the transparent walls of the chamber was $k = 5$ mm. During processing, the "point-plane" electrode system was used, which allows to realize a spark plasma discharge in the powder layer. For photo-registration of plasma formations in the powder layer, a mobile camera was used, which recorded video at 1080p, 60 fps. The discharge chamber was connected to a capacitor bank with a capacity of $C = 0.2 \mu\text{F}$ through an air spark gap switch that assured circuit commutation at the necessary operating voltage, and the charging voltage U was 20 kV.

3. Results and discussion

The analysis of the results of the study shows that at the beginning of the [HVED treatment in a hydrocarbon liquid (ethyl alcohol or kerosene) with a "point-plane" electrode system, plasma formations are concentrated mainly in the near-electrode zone (see Fig. 2, a, b) and are visually almost invisible.

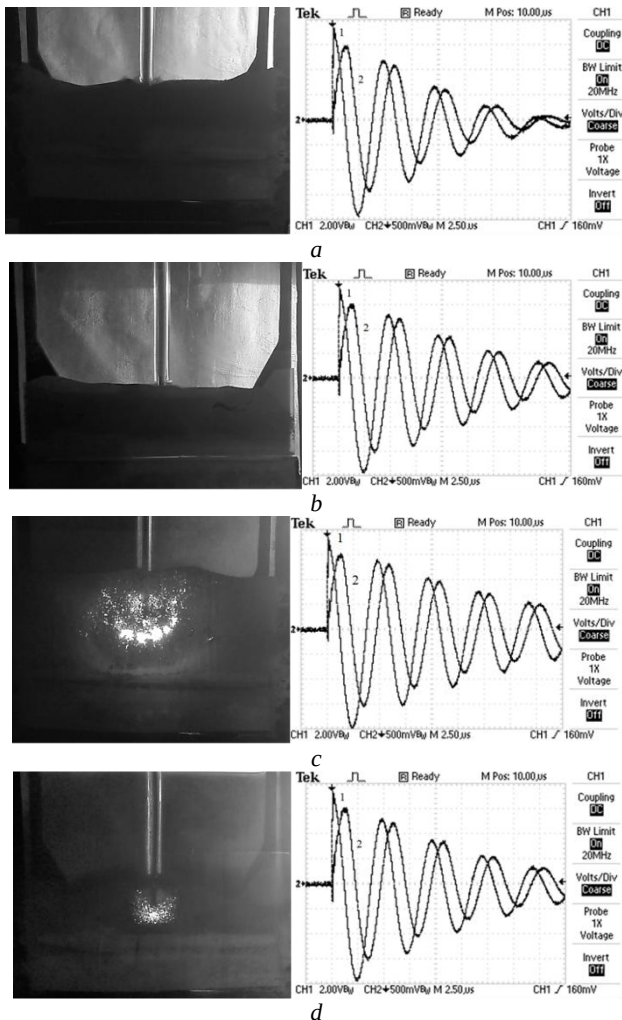


Fig. 2. Integral photos and oscillograms of the first (a, b) and 50th discharges (c, d) during HVED treatment of Al powder in kerosene (a, c) and ethyl alcohol (b, d) with the "point-plane" electrode system: 1 - discharge voltage; 2 – discharge current

It is worth noting the change in the location of the powder relative to the electrode system during treatment. After the first pulse the change in the configuration of the powder is almost not noticeable (see Fig. 3, 4), but then the cyclic appearance of plasma

formations (and, as a result, vapor-gas cavities) in the near-electrode zone leads to the displacement of the powder from the central part of the chamber to its walls, which contributes to the strengthening of the hydrodynamic influence and the weakening of the ablation effects (see Fig. 5, 6).

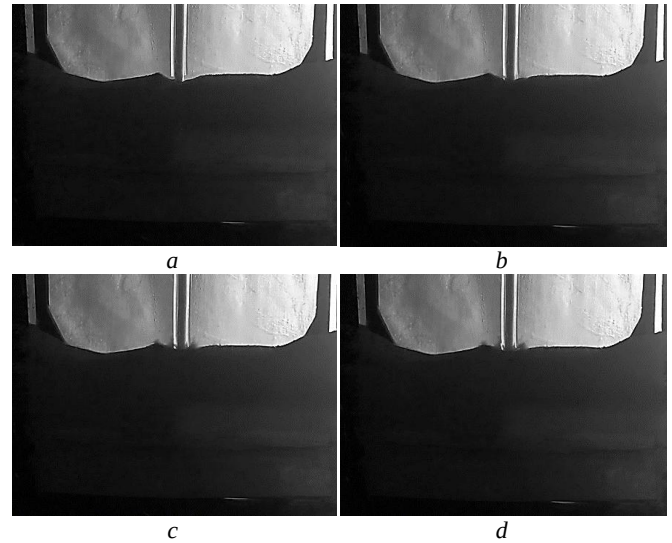


Fig. 3. The dynamics of the first discharge in kerosene after 0 (a), 17 ms (b), 34 ms (c), 51 ms (d)

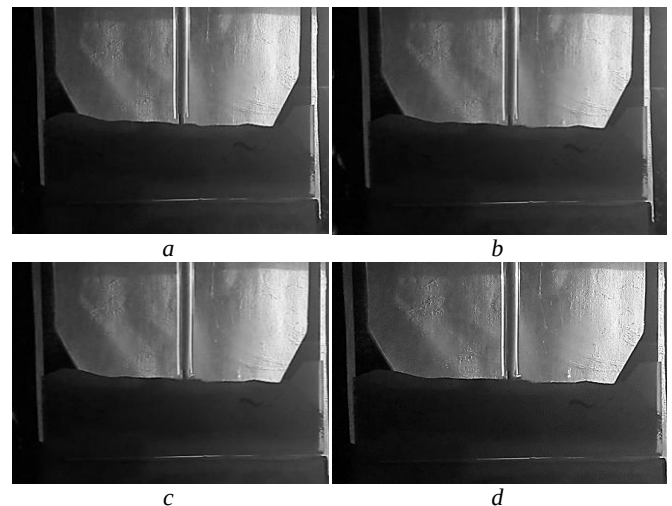


Fig. 4. The dynamics of the first discharge in ethyl alcohol after 0 (a), 17 ms (b), 34 ms (c), 51 ms (d)

According to the physical modelling of HVED treatment of Al powder in ethyl alcohol, the effect of nanocarbon synthesis is less noticeable, which correlates with the results, shown in [13], according to which, during HVED processing in the similar modes, the amount of synthesized nanocarbon using kerosene is ~ 5 times greater than the amount of nanocarbon synthesized in ethyl alcohol. This leads to less darkening of the working fluid after the same number of pulses (see Fig. 6).

During HVED treatment in ethanol, the pattern of distribution of plasma formations in the chamber volume remains practically unchanged as the number of discharges increases. In contrast to treatment using kerosene, where the intensity of formation of discharges between particles increases with an increase in the number of discharges, in ethyl alcohol plasma formations occupy approximately the same volume of the near-electrode zone regardless of the number of work cycles.

Thus, the use of ethyl alcohol as a working fluid for the HVED treatment of metal powders makes it possible to stabilize the discharge mode to a certain extent, as well as to increase the number of discharges before the appearance of residual nanocarbon,

as a result of which it is possible to achieve greater dispersion of the processed powders. Instead, for faster and more effective carburization of the processed material, it is desirable to use kerosene as the working fluid.

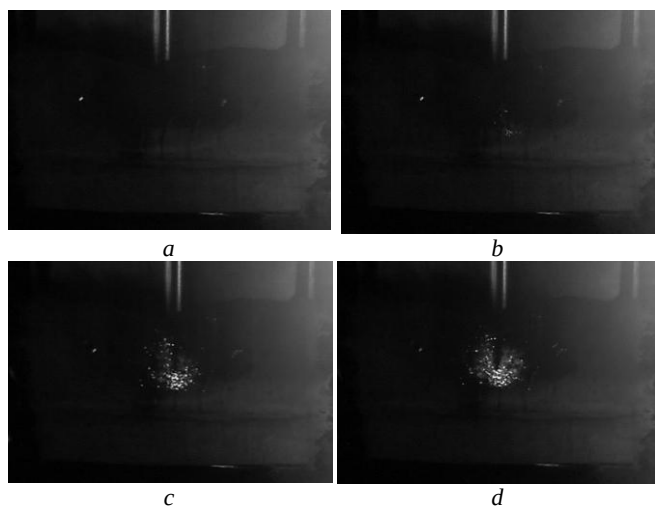


Fig. 5. The dynamics of the 50th discharge in kerosene after 0 ms (a), 17 ms (b), 34 ms (c), 51 ms (d)

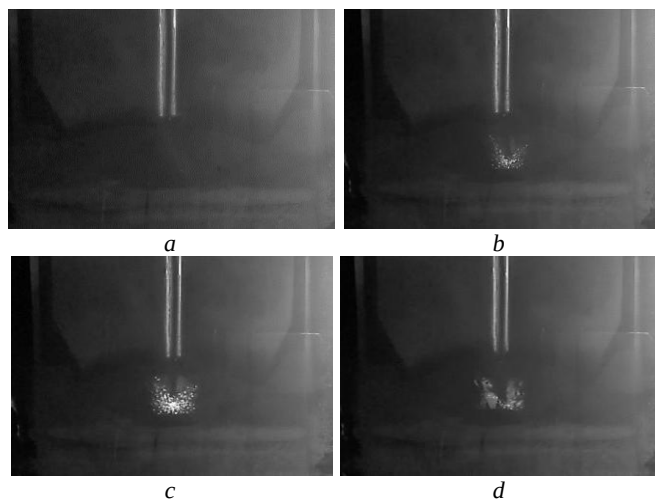


Fig. 6. The dynamics of the 50th discharge in ethyl alcohol after 0 ms (a), 17 ms (b), 34 ms (c), 51 ms (d)

4. Conclusions

1. It is shown that the use of kerosene as a working fluid leads to an increase in the intensity of the formation of discharges between particles with an increase in the number of discharges, and in ethyl alcohol plasma formations occupy approximately the same volume of the near-electrode zone regardless of the number of operating cycles.

2. Usage of the ethyl alcohol as a working fluid makes it possible to stabilize the discharge mode to a certain extent, as well as to increase the number of discharges before the appearance of residual nanocarbon, as a result of which it is possible to achieve greater dispersion of the processed powders.

3. Research has confirmed the possibility of synthesis of particles of the submicron and ultradisperse range by HVED treatment of aluminum powder in a hydrocarbon liquid (alcohol or kerosene) due to the electro-thermal effect of the discharge plasma on the particles of the powder.

Acknowledgements

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Analysis of strength, microstructure and hardness of the butt-welded K-joint

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Abstract: It is well known that there are several ways to make a butt weld depending on the thickness of the plates to be welded. This paper shows how important it is to prepare the surfaces to be joined by welding. In this paper, the 15 mm thick plates, made of mild steel S235JR, were welded face-to-face with a K-weld using the MIG welding method. The preparation of the plates before welding was not satisfactory, according to empirical instructions, and the resulting weld has defects. Four plates were welded face to face, resulting in two welds. The welds cooled in different ways after welding, one was cooled more slowly in air, and the other was cooled more quickly in water. After welding and cooling the welds, a metallographic analysis of the microstructures of the welds was carried out, and then their hardness was measured using the Vickers method. The conducted metallographic tests concluded that the heat-affected zone has a fine-grained structure, and the melting zone has a cast structure. After the hardness measurement, it can be seen that the hardness values in both the melting zone and the heat-affected zone increase from the root to the surface of the weld. Finally, a strength calculation was performed to determine how much static and dynamic alternating force the realized welded K-joint can withstand compared to the ideal value with good surface preparation.

Keywords: STRUCTURAL STEEL, BUTT-WELDED K-JOINT, VICKERS HARDNESS, METALLOGRAPHIC ANALYSIS, STRENGTH CALCULATION

1. Introduction

Welded joints belong to non-separable joints and are mainly used above all for joints supporting machine parts and structures. Welding can be done by pressure with or without additional material by melting. It is known that in butt welds there is no redirection of the force flow in the welding zone and there are several possibilities of butt welds depending on the thickness of the plates to be welded. Butt welds are a type of weld formed by joining two materials along their interface or edge. This welding process is often used to join metal plates or pipes that are opposite each other. Care should be taken in the design of welded structures to avoid notch effects (stress peaks). The poor joining of parent and filler materials will result in large notch effects in the root and face of the weld. Under dynamic loading, such poor bonding of base and filler material leads to a drop in dynamic strength and failure due to material fatigue. The quality of the weld depends on the skill of the welder [1-3].

The butt welding process includes the following steps: (I) Material preparation: The plates or pipes to be joined must be clean and prepared to ensure good weld quality. This may include cleaning the surface, removing oxides or grease, and smoothing the edges. (II) Placement of Materials: Materials are placed opposite each other so that their interfaces are aligned. Depending on the type of joint, clamps, guides or other tools may be used to ensure proper alignment. (III) Welding: After the materials are properly placed, the welding process is performed. The welder applies heat and filler material along the interface, creating a permanent joint. (IV) Re-welding: After welding, the joint may undergo a re-welding process to improve the properties of the weld. This may include heat treatment, weld testing, grinding, or other treatments [1]. Butt welds can be very strong and durable, but it is important to ensure proper alignment and weld quality to achieve the desired result. In addition, specific welding guidelines and procedures may vary depending on the material being joined and the application conditions [3].

In this paper, steel specimens were welded using the MIG welding method, with a melting electrode with the addition of material in an inert gas atmosphere, where the metal electrode and base material were melted by the heat of the arc.

This paper shows the importance of preparing the surfaces to be joined by welding. In this paper, the 15 mm thick plates of mild steel S235JR with a K-joint were welded face-to-face using the MIG welding method. The preparation of the plates before welding was not satisfactory, according to the empirical instructions, and the resulting welded joint has defects. Four plates were welded face to face resulting in two welds.

The welds were cooled in different ways after welding, one was cooled more slowly in air and the other more quickly in water. After welding and cooling of the welds, a metallographic analysis of the microstructure of the welds was performed, and then their hardness was measured by the Vickers method [4]. The metallographic examinations carried out showed that the heat-affected zone has a fine-grained structure, and the melting zone has a cast structure. After measuring the hardness, it can be seen that the hardness values increase from the root to the face of the weld in both the melting zone and the heat-affected zone. Finally, a strength calculation [5] was performed to determine how much static and dynamic alternating force the realized welded K-joint can withstand compared to the ideal value achieved by good surface preparation.

2. Prerequisites and means for the analysis of a weld seam

2.1. Properties of mild steel S235JR

The basic material of this butt-welded joint is mild steel S235JR, which is often used in construction. Steel S235JR can be welded without restrictions, without subsequent heat treatment, and without heating. When welding thicker steel products, the risk of cold cracking increases. Table 1 shows the chemical composition of S235JR steel.

Table 1. Chemical composition of steel S235JR

C	Mn	P	S	N	Cu
≤0.17	≤1.40	≤0.035	≤0.035	≤0.12	≤0.55

From the Smith diagram for mild steel S235JR, values of yield strength (R_e) of 235 MPa and dynamic strength (R_d^{-1}) for an asymmetry factor of -1 of 120 MPa can be read [3]. The read values of yield strength and dynamic strength are used for strength calculation.

2.2. Material preparation for welding

Preparation of steel specimens for butt welding begins with cutting on a band saw. The base material with dimensions 35x15 mm was placed in the stationary lower jaw of the saw to fix it for cutting. A total of four specimens with a length of 65 mm were cut. A belt sander was used to clean the specimens and prepare them for butt jointing. Since the sheet of the base material is thicker than 15 mm, it must be prepared from above and below. When preparing the K-seam, only one side of the plate may have a slope, while the other side is without a slope.

A properly prepared weld, shown in Fig. 1a, is used for plates thicker than 15 mm (dimension s), and the dimensions are as follows: $s_1 = 2-4$ mm, $h = 0-3$ mm, and $\alpha = 50-55^\circ$. Four plates are welded face to face so that two welds are obtained (Fig. 1b).

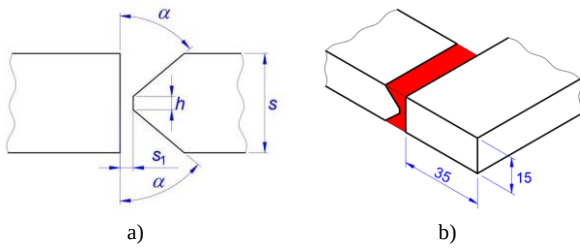


Fig. 1. a) Preparation of material for K-joint welding, b) Welded K-joint

The geometry of the specimen preparation was not fully considered in this paper. The slope and the distance between the plates were not within the limits. Material preparation was followed by MIG welding. The specimens were first spot-welded at the ends of the ground grooves to bring the pieces closer together to fully weld them to the electrode. The two L-shaped specimens were welded as shown in Fig. 2. One piece of the welded mild steel was left on the table to cool gradually to room temperature in the air while the other piece was cooled in water.



Fig. 2. Specimens: a) cooled in air and b) cooled in water

2.3. Preparation of specimens for metallographic analysis

Because of the metallographic analysis and hardness testing, the butt-welded parts must be cut so that the K-weld can be seen in the section. The cut specimens are shown in Fig. 3.



Fig. 3. Cut specimens: a) air-cooled joint, b) water-cooled joint

The cutting of the specimens is followed by grinding and subsequent polishing, which was performed on the BUEHLER Phoenix Beta unit.

The grinding is done with water-based sandpaper in different gradations. It starts with the coarsest grit and ends with the smallest grit to obtain a finely polished surface of the specimens. The procedure starts with the use of 400-grit sandpaper, and then 600 and 800 grits are used. During grinding, the specimens should be constantly cooled with water so that the microstructure of the specimens does not change.

After grinding, all specimens were polished again to a mirror-like surface (without scratches) on a microfiber cloth (so-called felt) at a speed of 150 rpm with the occasional addition of an aqueous Al_2O_3 suspension. The grinding and polishing parameters are listed

in Table 2. After grinding and polishing, the specimens are etched with Nital (a 5% solution of nitric acid in alcohol).

Table 2. Parameters of grinding and polishing of steel specimens by hand

Grinding				
Base	Grain granulation	Media	Plate rotation speed, rpm	Time, min
SiC-paper	400	water	150	6
	600			5
	800			5
Polishing				
Base	Grain granulation	Media	Plate rotation speed, rpm	Time, min
fabric	microfiber	water + Al ₂ O ₃ (0.3μm)	150	5

2.4. Light microscopy

A light microscope was used to obtain information about the appearance of the surface and phenomena in the sample, such as inclusions, porosity, cracks, and others. Metallographically prepared samples were used for this purpose.

In this paper, the specimens were observed at 50x magnification using an Olympus GX 51 light microscope. The surfaces of the welded steel test specimens were photographed under the conditions of metallographic preparation using an Olympus DP 70 digital camera connected to the light microscope.

2.5. Hardness measurement

Hardness is a mechanical property that indicates the resistance of a material to penetration by another, harder material into its surface or structure. Hardness is influenced by the chemical composition of the material as well as by mechanical and heat treatment. In addition, hardness is closely related to yield strength, modulus of elasticity, ultimate strength, tensile strength, and toughness [4,6,7].

In this paper, the hardness of experimental welded steel specimens was measured by the Vickers method on a Mitutoyo hardness testing machine with an indentation force of 10 kg and with an indentation time of 10 seconds. HV10 hardness measurements were performed 1 to 3 times at random points on the polished surface: in the melting zone and in the heat-affected zone at the surfaces, center and root of the weld (Fig. 4.).

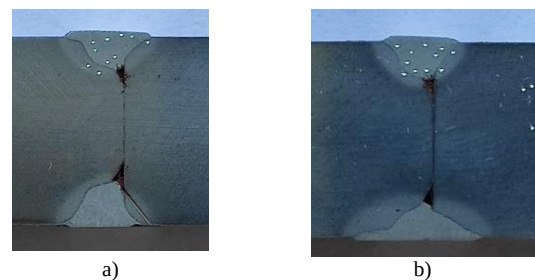


Fig. 4. Imprints of the indenter by the specimens: a) cooled in air, b) cooled in water

2.5. Strength calculation

In order for the welded joint to withstand the tensile load, the strength condition must be satisfied. The strength condition is represented by the following equation

$$\sigma_{\text{weld}} \leq \sigma_{\text{allow,weld}}, \quad (1)$$

where are σ_{weld} stress of welded joined and $\sigma_{\text{allow,weld}}$ allowed the stress of welded joined. The stress in the weld is equal to the ratio between the axial force F and the bearing surface of the weld A_{weld}

($\sigma_{\text{weld}} = F/A_{\text{weld}}$). A force, F , can be static (F^{stat}) or dynamic (F^{dyn}). The strength calculation can be performed both for a static force and for a variable dynamic force. Then the allowable stresses are calculated according to different expressions

$$\sigma_{\text{allow, weld}}^{\text{stat}} = \frac{b \cdot b_1 \cdot R_e}{S}, \quad (2)$$

$$\sigma_{\text{allow, weld}}^{\text{dyn}} = \frac{b_1 \cdot b_2 \cdot b_3 \cdot b_4 \cdot R_d^{-1}}{S_{\text{dyn}}}, \quad (3)$$

where b the value of the strength reduction factor in the welded machine part in relation to the non-welded part (static), b_1 the value of the weld quality factor, b_2 the value of the shape factor, and the method of loading the weld, b_3 the value of the size factor of the machine part, b_4 the value of the material quality factor, S a safety factor for static load and S_{dyn} safety factor for dynamic loading.

When preparing the specimens for metallographic analysis, it was found that the welding was not done correctly. The bearing surface of the weld was significantly reduced. This strength calculation was used to calculate the maximum force (static and dynamic) with which the butt-welded joint can be subjected to tensile loading. Figure 5 shows the load-bearing surfaces of a well-designed weld and a poorly-designed weld. The load-bearing surface of the weld is marked with a red shaded field.

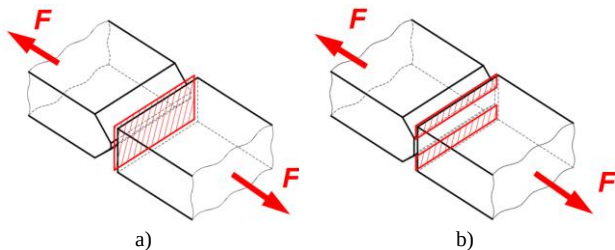


Fig. 5. Bearing surface (A_{weld}) of a butt-welded joint: a) well and b) poorly executed joint.

The values of the required parameters are taken from [3] and shown in Table 3. The required safety factor is 1.5 for the static load (S) and 2.5 for the dynamic alternating load (S_{dyn}). The bearing surface of a poorly designed connection is only 40% of a well-designed connection.

Table 3. Required parameters

Welded joint	Parameter				
	b	b_1	b_2	b_3	b_4
WELL	0.75	1	0.45	1	1.1
POORLY		0.8			

3. Results and discussion

3.1. Light microscopy results

Images of the surface of the specimens after grinding, polishing, and etching are shown in Fig. 6.

The metallographic images show the gaps at the weld root, which should not have happened. The poor penetration of the weld root is very noticeable in both specimens. It is the initiation for the crack propagation when the weld is loaded and at the same time the reason for the corrosion formation.

From the metallographic images provided, it can be seen that the material in the melting zone has the structure of cast iron. The specimen cooled in water after welding has finer grains in the center of the surface of the weld than the specimen cooled in the air after welding. The grains are elongated towards the heat-affected zone.

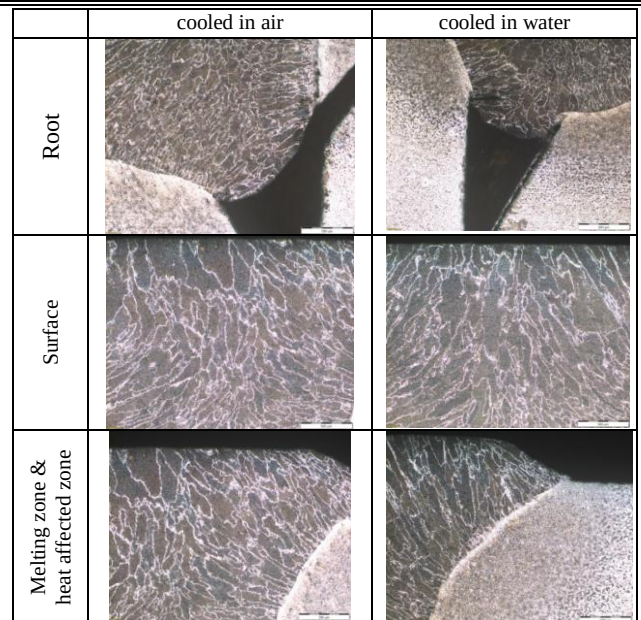


Fig. 6. Microstructure of the welded joint at 50x magnification

3.2. Hardness measurement results

The results of the hardness measurement are shown for the samples cooled in the air in Table 4, and for the samples cooled in water in Table 5.

Table 4. Results of hardness measurement for the air-cooled samples after welding (HV 10)

BASIC MATERIAL	First plate		Second plate	
	179.6		181.9	
	178.6		180.5	
HEAT AFFECTED ZONE	Root	Centre	Surface	
	177.2	184.4	213.2	
MELTING ZONE	Root	Centre	Surface	
	249.6	261.9	263.2	
	249.7	259.1	265.1	
			263.8	

Table 5. Results of hardness measurement for a samples cooled in water after welding (HV 10)

BASIC MATERIAL	First plate		Second plate	
	177.6		181.1	
	179.3		183.8	
HEAT AFFECTED ZONE	Root	Centre	Surface	
	206.3	210.2	225.5	
MELTING ZONE	Root	Centre	Surface	
	253.3	258.0	270.1	
	252.1	262.0	262.9	
		263.7	272.3	

The tables show that several measurements were made in a given area. The measured values per area are averaged and represented by the hardness dependence diagram per area for the melting zone (Fig. 7) and for the heat-affected zone (Fig. 8). The dependencies of the hardness change on position are shown in the same diagram for both specimens for better comparison.

From both diagrams, it can be seen that the hardness values increase from the root to the surface of the weld, both in the melting zone (Fig. 7) and in the heat-affected zone (Fig. 8). The hardness increase in the melting zone is similar for both the air-cooled and water-cooled specimens after welding.

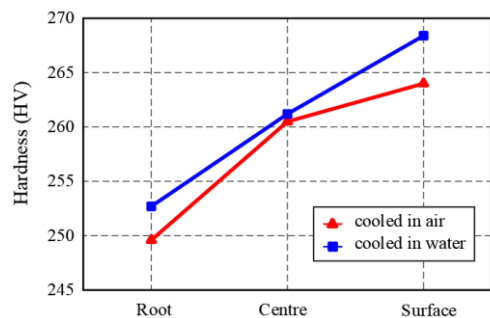


Fig. 7. Average measured hardness values by position in the melting zone

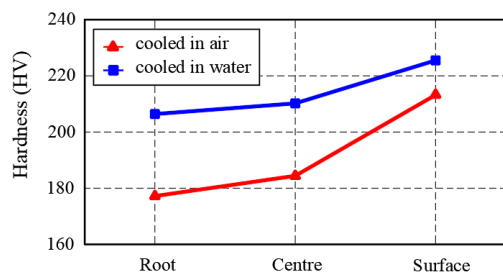


Fig. 8. Average measured hardness values by position in the heat-affected zone

From the comparison of metallographic analysis and hardness measurement, it can be concluded that the finer the grain size structure, the higher the hardness in both the melting zone and the heat-affected zone.

3.3. Strength calculation results

Using the strength conditions and all the given parameters, it is possible to calculate the maximum force that a butt-welded joint can withstand under tensile load. The amounts of calculated maximum forces are shown in Table 6.

Table 6. Results of the maximum forces of a butt-welded joint under tensile load

Welded joint	Force [kN]	
	Static (F^{stat})	Dynamic (F^{dyn})
WELL	61.69	12.47
POORLY	19.74	3.99

From the results shown in Table 6, it can be concluded that the capacity of a poorly butt-welded joint is reduced by 68% compared to a well-designed welded joint under both static and dynamic tensile loading.

4. Conclusion

The aim of this paper was to analyze butt-welded specimens that were welded using the MIG method and cooled differently after welding. One specimen was cooled in air after welding, while the other was suddenly cooled in water. The analysis of the two specimens revealed their differences. The analysis included a metallographic examination, a hardness measurement, and a strength calculation.

The investigations carried out revealed the following:

- the butt-welded joints were not well prepared before welding according to the standard for K weld, therefore there was a poor penetration of the roots on both sides of the weld and thus an accumulation of air in the middle of the welded plates, which can be the starting point for the beginning of corrosion

and the starting point for the beginning of crack propagation due to high stress concentrations caused by the loading;

- the strength analysis showed that the maximum force of a tensile-loaded welded joint with this type of poor weld preparation was reduced by 68% compared to a good preparation;
- the metallographic analysis showed that the grain in the melting zone was finer for the specimen cooled in water than for the specimen cooled in air;
- the metallographic analysis showed that the grain in the melting zone is elongated in the direction of the heat-affected zone in both specimens;
- the metallographic analysis showed that the specimen cooled rapidly in water has a finer-grain structure in the heat-affected zone than the specimen cooled in the air;
- the metallographic analysis showed that the structure in the heat-affected zone is finer-grained than that of the base material in both specimens;
- by measuring the hardness, it was found that the hardness increases from the root to the face of the weld, both in the melting zone itself and in the heat-affected zone;
- by measuring the hardness, it was found that the increase in hardness in the melting zone and in the heat-affected zone is approximately the same for both specimens;
- the results of the metallographic analysis and the hardness measurement show that the hardness is higher with a finer-grained structure.

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Development of diamond-hard alloy plate (D-HAP) manufacturing technology on the GY850 multi-punch press and study of the characteristics of experimental batches of samples

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Abstract: A two-layer, diamond-hard alloy plate (D-HAP) is the cutting element of a drill bit and consists of a layer of polycrystalline diamond compact (PDC) sintered on a superhard alloy (WC-Co) substrate. The entire D-HAP is manufactured using high pressure and high temperature technology. In the FSBI TISNUM the GY850 multi-punch press with a working reaction volume of $\approx 135 \text{ cm}^3$ is used to create high pressure. In one working cycle, sintering takes place from 2 to 12 (depending on the dimension-type) of the D-HAP, consisting of a PDC with grains of 20-10 microns, impregnated with a binder metal and bonded to a hard alloy substrate, forming the working element of the drill bit.

The report describes the manufacturing process of various amounts of D-HAP in one working cycle and the results of the study of the profiled contact layer (interface) of the diamond layer with the substrate and the presence of defects in this layer.

KEYWORDS: SUPERHARD MATERIALS, POLYCRYSTALLINE DIAMOND COMPACT (PDC), DIAMOND-HARD ALLOY PLATE (D-HAP), ACOUSTIC MICROSCOPY, ULTRASONIC FLAW DETECTION, INTERFACE PROPERTIES

1. Introduction

The main element of drilling equipment is a rotary drilling milling bit (Fig. 1, a), the cutting elements (cutters, Fig. 1, b) of which move along the bottom of the well and cut the rock.

The use of polycrystalline diamond compact synthetic polycrystalline diamonds (PDC) in drill bits is one of the most important achievements in the field of materials for oil drilling tools in recent years.

A polycrystalline diamond compact (PDC) cutting tool is a chisel that uses synthetic diamond discs called "cutters" to cut through rock in a continuous scraping motion. The PDC bit is particularly suitable for drilling in shale formations, which present some specific problems related to the instability of the wellbore, such as the narrowing of the wellbore.

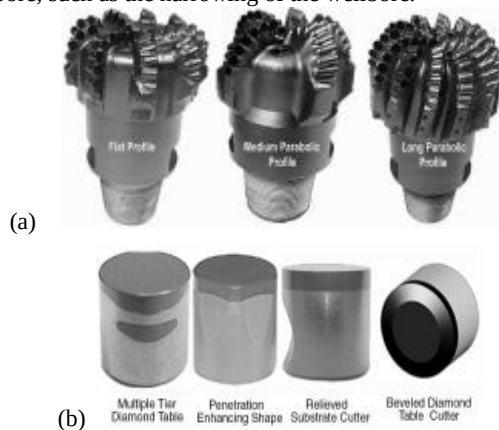


Figure 1. The PDC bit profile types (a) and D-HAP cutters (b).

Diamond cutters are made of synthetic diamond material, but not from a single synthetic diamond. Rather, clusters of diamond chips (about 0.00004 inches = 10 microns in size) combine into larger masses of crystals with random orientation. These aggregated crystals are shaped into cutting surfaces called diamond tables. Since they easily and well connect with tungsten carbide materials (which themselves can be soldered to the bit housings), they solve the problem of fastening by soldering to the bit, which synthetic diamonds cannot do without assistance. I.e., a two-layer, diamond-hard alloy plate (D-HAP) is obtained.

The classification of PDC, D-HAP and the corresponding drill bits, as well as their production technologies are presented in [1-3].

2. Design and Manufacture of D-HAP

D-HAP are made up of a working component, the diamond table, and a supporting component called the substrate (Fig. 2).

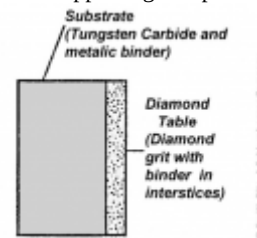


Figure 2. Design of D-HAP.

D-HAP are a multi-component system, which includes: a) the diamond grains themselves, b) the binding phases used in the sintering process of the cutting PDC-elements and c) the method of connecting the diamond elements with the tool body. All elements require high-quality performance.

To make a diamond table, diamond powder is sintered with tungsten carbide and a metal binder to form a diamond-rich layer. They are shaped like plates, and they should be made as thick as possible from the point of view of construction, since the volume of the diamond increases the service life. Diamond tables of the highest quality have a thickness from 2 to 4 mm, and technological advances will increase the thickness of diamond tables. Tungsten carbide substrates are usually about 12-15 mm high and have the same cross-sectional shape and dimensions as the diamond table. Two parts, the diamond table and the substrate, make up the milling cutter D-HAP.

The shape of the diamond table is determined by two design goals. It should include the maximum possible volume of the diamond and the general availability of the diamond for its processing. It should also provide the lowest possible stress level inside the diamond table and when connected to the substrate.

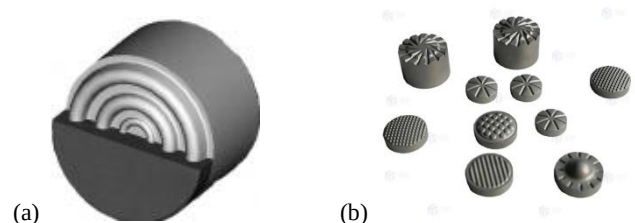


Figure 3. Interface of D-HAP (a), Various interface profiles of substrates (b).

Geometric features of an interface between a diamond table and substrate can significantly improve the ability of the diamond table to withstand impact (Fig. 3a).

The substrates are a composite material consisting of tungsten carbide (WC) grains bonded with a metal binder. This material effectively adheres to diamond tables, but is very hard and is able to prevent erosion damage to the working mill.

The geometry of the milling cutter at the interface between the diamond table and the substrate is aimed at strengthening the adhesion between them. As a rule, geometry that increases the interface surface area improves adhesion (Fig. 3b). Geometry also aims to reduce the stresses in the joint to the lowest possible level. Various interface profiles between the PDC and the substrate are used in the manufacture of the D-HAP.

In D-HAP cutters developed in FSBI TISNCM the plate of PDC, 2-4 mm thick and up to 18 mm in diameter, is bonded with a substrate of hard alloy, forming the working element of the drill bit. PDC consists of a diamond frame with grains of 20-10 microns impregnated with a binder metal. The ratio of the diamond fraction and the binder metal, as well as the size of the diamond grains vary, depending on the specifications.

D-HAP cutters are manufactured by the method of high pressure and high temperature using an installation based on the GY850 multi-punch press [4]. Up to 12 PDC cutters are synthesized/sintered in one working cycle in a high-pressure chamber. After sintering, the surfaces of the PDC plates are ground and polished to the required values.

Full-scale tests of PDC cutters in PDC bits have shown that their strength, wearability, and especially heat resistance, are determined by the quality of the contact layer (interface) between the PDC and the substrate [5].

In this paper, we investigated the possibility of studying these characteristics by acoustic microscopy and ultrasonic flaw detection.

3. Studies of the interface characteristics of D-HAP cutters

In the previous works [3,4], we studied of the profiled interface on D-HAP incisors by non-destructive acoustic microscopy (AM) and on plates 4 mm thick cut from the central part of the D-HAP incisors. A SIAM Scanning impulse acoustic microscope (50 ÷ 200 MHz), designed and fabricated in the AM-laboratory of Emmanuel's Institute of Biochemical Physics, Russian Academy of Science, was used to make the measurements. The study of the interface of a two-layer PDC/WC-Co plate revealed the presence of defects in the PDC layer and D-HAP interface.

3.1. The study of the profiled boundary layer (interface) by means of acoustic microscopy

Using SIAM Scanning impulse acoustic microscope, we investigated two types of interfaces shown in Fig.4.

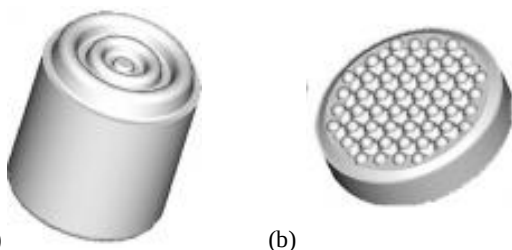


Figure 4. Two types of substrate profile. Type 1 (a) and type 2 (b)

Fig. 5 shows the SAM-images of three samples of the D-HAP interface type 1. Image 5b shows a defect in the form of a discontinuity on the annular groove of the interface profile.

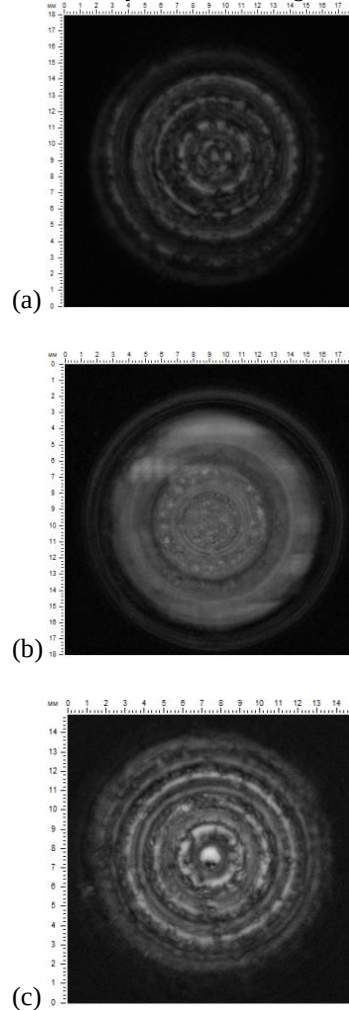
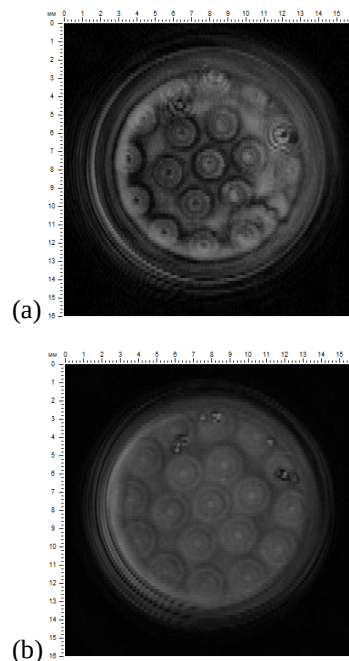


Figure 5. SAM-images of three samples of the D-HAP interface type 1.

Fig. 6 shows the SAM-images of three samples of the D-HAP interface type 2. Image 6b shows defects in the form of inclusions in the recesses of the interface.



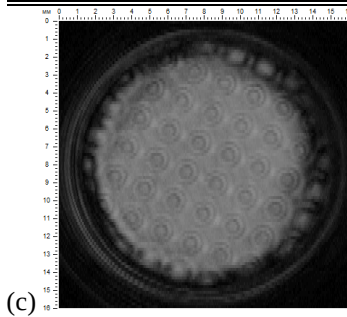


Figure 6. SAM-images of three samples of the D-HAP interface type 2.

3.2. Measuring the thickness of the diamond layer using a laser-ultrasonic flaw detector.

The laser ultrasonic flaw detector can operate in the mode of measuring the thickness of the sample. With its help, we determined and controlled the thickness of the diamond layer in the D-HAP. The ultrasonic pulse was excited at the boundary of the substrate. The reflected ultrasonic pulses from the interface and the free boundary of the diamond layer were used to determine its thickness (Fig.7).



Figure 7. Screenshot of the UDL-2M screen. Measuring the thickness of the diamond layer. The time difference between pulse 1 and pulse 2 allows you to calculate the thickness of the diamond layer. In this case, it is 4 mm.

4. Conclusion

In this paper, we investigated D-HAP with an interface of various profiles. It is shown that acoustic microscopy makes it possible to accurately determine the type of interface profile, as well as to detect the presence of defects on the interface.

5. Acknowledgments

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6. Literature

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Effective shrinkage compensating admixture for joint-less fiber-reinforced concrete industrial floorings

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Abstract: The shrinkage is an inherent characteristic of Portland cement concretes, leading to their volume changes, which potentially create preconditions for the development of different types of cracking - prerequisites for integral decreasing of their durability. The elimination of the negative processes from the development of shrinkage in all its varieties (autogenous, plastic, thermal and carbonization) is based on optimization of complex mix design and technological factors, including the use of innovative chemical products - mainly minimizing and/or compensating the volume changes during setting and hardening of the concrete.

In recent years, new innovative products have entered the world and Bulgarian practice aimed to compensate the shrinkage by initiating of specific additional hydration interactions. These processes give some attractive possibilities for manageable early age increasing of the concrete volume, leading to partial or complete compensation of the negative effect of later shrinkage.

The report presents full-range complex results for the effective action of a special shrinkage compensating modifier ShCA KEPTONITE on the strength-deformation characteristics of fiber-reinforced concrete for advanced joint-less industrial flooring systems with different purposes, especially for heavy loaded logistic bases.

It is concluded that ShCA KEPTONITE demonstrates very good performance in direction to strongly minimize the final shrinkage of the concrete tested. The different dosage rate of the product is an optimal for Bulgarian cement used for testing.

Keywords: JOINT-LESS CONCRETE FLOORINGS, CONCRETE DRYING SHRINKAGE, SHRINKAGE COMPENSATING ADMIXTURE, CONCRETE COMPRESSIVE STRENGTH

1. Introduction

The industrial concrete internal floorings and external pavements are specific building constructions with constantly increasing importance for industrial practice in all over the world.

The fact that they are not defined separately as in the current Eurocode 2 [1] contributes to the existing relative ambiguity in the definition and in the methods of construction and static calculation of industrial concrete floorings/pavements. In this sense, and in the aspect of the present exposition, is the definition proposed by the author below for INDUSTRIAL CONCRETE FLOOR is: cast-in-place reinforced or non-reinforced concrete structure with geometric dimensions in plan many times exceeding the size in height, designed as a ground supported slab and surface executed by step-by-steps power floating processes, for long-term bearing of specific types of operating loads with ensured full-range resistance to environmental and production factors [2].

Regarding the design and implementation of fiber-reinforced internal industrial concrete floorings, there is essentially a lack of an unambiguously formulated normative base, both in Bulgaria, Europe and the world as a whole.

In America, the specialized documents of the American Concrete Institute (ACI), American Highway Association (AHTA), US Army Corps of Engineers, Association of Concrete Industrial Flooring Contractors (ACIFC), Contract Flooring Association (CFA), etc. are used with authority.

In Europe, apart from the partially applicable Eurocode 2, with recognized significance and practical usability are the principles laid down in the relevant Technical Report No34, 3-rd (2003) and 4-th (2013) Edition, "Concrete Industrial Ground Floor, A Guide to Design and Construction", The Concrete Society [3,4], etc. In essence, these documents are the most widely used in Bulgarian production practice related to the design and implementation of industrial concrete floors.

The Bulgarian regulatory framework, based on relevant BDS EN standards, covers fragmentarily separate parts of the "puzzle", called industrial concrete floorings/pavements.

For example, there are relevant standards for determining the strength-deformation characteristics of the slab-base, for concrete as the main construction material, for the different types of fibers (in the context of their material characteristics - geometric dimensions, material qualities, etc., as well as their relationships under bending loads), for serviceability as the main characteristic of the finish surface, for the qualities of powdered surface hardeners and some impregnating systems.

However, regulations related to construction and calculation for different loads and operating conditions, evaluation of the effective action of different types of joints, typical details, design of the concrete composition (to the extent that a number of additional requirements are imposed on it), the specific action of protective coatings, deep crystallizing and shrinkage compensating concrete systems, limits of flatness and levelness, planned service life, specified technological methods of implementation and control, repair works are completely missing, maintenance during operation, warranty conditions, etc.

The above brings a lot of confusions to the system and the relationship between the contracting authority - designer, controlling body and the contractor. Moreover, the lack of a comprehensive regulation essentially does not provide an opportunity for an unambiguous formulation of a correspondingly adequate technical assignment, which directly has a negative impact on the communication between the participants in the investment process.

2. Concrete floorings types

In modern practice, two major structural types of concrete floorings are currently specified - from the so-called "jointed" to "joint-less" types.

In classical "jointed" floorings, in addition to the necessary expansion, working and insulation joints, within the day-casting field (limited by working and/or expansion joints), are constructed and executed over a certain distance, the so-called "saw-cut" joints in depth of 1/3 of the cross-section thickness. The dimensions of the fields limited by the all type of joints are subject to calculation procedures. In general, they depend on the type and quality of the compacted slab-base, the type of loads, the concrete cross-section thickness, the characteristics of the concrete and the reinforcement systems used. In this type of flooring, a critical factor is the presence of a large total length of cut joints - for example, within a

single field of dimensions 30x30 m, limited by dilation profiles, with a grid of apparent joints 6x6 m, the total length of these joints is of the order of more than 300 linear meters.

This construction flooring type in itself has the potential for operational efficiency, but in certain conditions they prove to be problematic - above all, in intensive traffic from mobile cargo with rigid tires and in conditions of aggressive impacts. Moreover, the prerequisites for breaking and compromising the performed saw-cut joints can create insurmountable technological problems in the operation of the electronics of the used manipulators-high lifters in the presence of high racks systems. In addition, the saw-cut joints, although technologically processed, interrupt the surface uniformity and create prerequisites for breaking the impermeability of the concrete section.

In this sense, the jointed type of flooring is generally defined as a lower technological level of performance and operation, usually when looking for a "budget" type of execution.

All that logically leads to the idea of eliminating saw-cut joints, seeking to maximize the continuity of the structural fields within the floorings. This idea has recently been implemented very successfully in world practice through the implementation of "joint-less" floorings [5,6].

In terms of construction, this type of steel fibre-reinforced concrete floorings can limit relatively large single one-day casting fields with a configuration close to the square (at a side ratio of up to 1:1.5), with areas of the order of 1000-2000 m² and more. The individual fields are limited by special dilatation industrially ready-made profiles (with a corresponding doweling system), pre-installed in plan and level, which also play the role of working joints. With the highest degree of innovation and optimal operational performance are the so-called sinusoidal and cosinusoidal joints, providing a maximum high coefficient of transfer of moving loads, durability, gentle mode of wear of moving traffic, combined with comfort of operation. This type of joints, in addition to the necessary transfer of the load when moving from one field to another, ensures smooth horizontal movement in parallel with the development of the free deformations of the concrete during hydration, hardening and temperature changes – **Fig. 1 and 2**.



Fig. 1 HCJ Cosinus Slide Joint



Fig. 2 HCJ Cosinus Slide Joint with T-crossing detail

No saw-cut joints are subsequently performed within the individual field. In this way, monolithic and continuity of the surface is ensured, which is a guarantee for future trouble-free operation

On the other hand, it should be taken into account that with joint-less systems, the requirement to minimize size and volume of free deformations (mainly concrete shrinkage in all 4 basic forms) is of key importance - especially considering the formation of significant areas with not always correct geometry, limited only by expansion profiles.

3. Innovative joint-less fiber-reinforced industrial concrete floorings

The existing possibilities for obtaining high-tech fiber-reinforced concretes joint-less floorings mainly is based on the

possibilities for overcoming of all negative problems, caused by the concrete shrinkage as its internal irrevocable characteristic.

The concretes shrinkage is their inherent characteristic, leading to volumetric changes that potentially create prerequisites for the development of cracking and an integral reduction in the durability of built structures and facilities. The elimination of the negative consequences of the development of this problem in all its varieties (autogenous, plastic, temperature-humidity and carbonization) is based on the optimization of complexes of recipe-technological factors, including the use of innovative chemical products - mainly minimizing and/or compensating the shrinkage volume changes.

In recent years, new innovative products have entered global and Bulgarian practice aimed at shrinkage compensating by specific chemical processes of an initial manageable volume increase, leading to partial or complete compensation of the negative effect of shrinkage. Unlike known types of shrinkage-compensating special cements, these innovative chemical agents have not yet been standardized, despite their presence in the product range of various manufacturers.

As a result of our research, original scientific results have been obtained, confirming the effectiveness of the use of special shrinkage-compensating modifier ShCA KEPTONITE for ordinary concretes, specified as an expanding agent by the so-called type G, in accordance with the definitions of ACI Technical Report 223-10 "Standard Practice for Use of Shrinkage-Compensated Concrete" [7], for the use of which BULGARIAN TECHNICAL APPROVAL (BTO) № 0192/01.03.2021 was issued [8].

ShCA KEPTONITE is obtained after firing at a special temperature regime of a specific type of CaO (originating in South America), as a result of which, in the process of concrete hydration, portlandite Ca(OH)_2 is formed with an active expanding effect in the first 24-48 hours from the start of the process – **Fig. 3 and 4**.

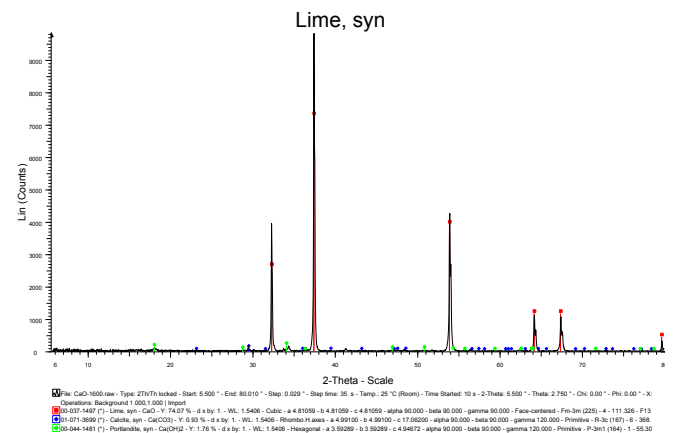


Fig. 3 ShCA KEPTONITE X-ray analysis

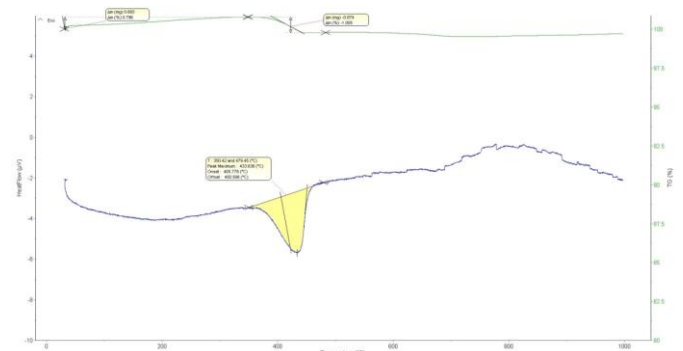


Fig. 4 ShCA KEPTONITE DTA analysis

ShCA KEPTONITE is an innovative product capable of counteracting the natural shrinkage processes of cement composites, reducing their micro-porosity and causing a compacting effect. Its specific action compensates for volume changes, and, in special cases, it can completely overcome it to a degree of controlled self-stressing. In this way, when designing the composition of the concrete, a certain controlled level of expansion can be achieved, by which the physico-mechanical properties of the concrete, as well as its corrosion resistance, can be increased. Depending on the dosage, the product has a direct positive effect on the characteristics, both at the level of the fresh concrete and also of the hardened composite. After homogenization in the composition of the concrete, the product directly affects the ongoing hydration processes by causing volume expansion, which counteracts the drying processes in its various phases. In this way, the intermolecular structural parameters are increased, which in turn increases the physical-mechanical and structural characteristics of hardened concrete, increasing its corrosion resistance under aggressive impact.

ShCA KEPTONITE is a hydration activator for professional use in cement concrete and mortar compositions, increasing their physical-mechanical and structural characteristics and compensating for their inherent volumetric drying. In this way, cement composites with its participation have fully compensated shrinkage, eliminated cracking and minimized porosity

ShCA KEPTONITE is dosed within 5-20 kg/m³ depending on the set design expansion levels. When using cement-replacement materials (eg. fly ash), their participation should be considered based on their hydraulic activity. The expansion and compaction action is intensified at a lower water-cement ratio and increased cement content.

There are original studies of ours [9-11] directed to the specific application of this product related to different efficiency of shrinkage compensation, in function of the type of cement used and the quantitative participation of the expanding agent.

Table 1: Concrete compressive strength

ShCA KEPTONITE, kg/m ³	CEMENT CEM I 52,5R HOLSIM BG plant	
	Compressive strength (MPa) at	
	7 days	28 days
0,00	24,80	36,20
12,00	26,30	39,40
15,00	27,80	40,30
18,00	28,60	42,40

The concrete mixture for the various compositions tested was manufactured under laboratory conditions by mechanical homogenization. The samples (cubes 10x10x10 cm) and prisms (beams) (10x10x40 cm) are cured in lab-condition until the day of testing. The compressive strength was determined at 7- and 28 days of age (**Table 1**), and the change in linear dimensions (free deformations) of the beams - every day up to 30 days by using special strain gauge device with accuracy of 0,001 mm (**Fig. 5 and 6**).



Fig. 5 Concrete test specimens prepared



Fig. 6 Shrinkage strain gauge device

Below is presented the kinetics of expansion/shrinkage processes as a function of quantitative participation of ShCA KEPTONITE (Reference concrete mix design based on CEM I 52,5 R, HOLSIM cement plant, Bulgaria) - **Fig. 7**.

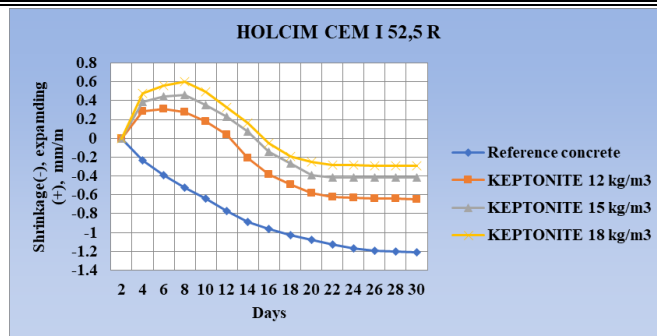


Fig. 7 Kinetics of expansion/shrinkage processes as a function of quantitative participation of ShCA KEPTONITE

The results visualizations give enough possibilities to perform reasonable analysis in direction to make respective conclusions about ShCA KEPTONITE efficiency to minimize concrete free deformations.

In **Table 2** concrete free deformations (expanding "+" and shrinkage "-") are presented as their maximal value in parallel of the age of appearances. This approach is practically usable to gaining an idea of ShCA KEPTONITE (in different dosage rates) efficiency compared to different type of cement involved in testing program.

Table 2: Shrinkage/expanding kinetics of the concrete with HOLSIM CEM I 52,5R

ShCA KEPTONITE, kg/m ³	CEM I 52,5R HOLSIM	
	Concrete free deformations (expanding "+" and shrinkage "-") up to 30 days of age	
	max "+" (at days)	max "-" (at 30-th day)
0,00	-	-1,210
12,00	0,31 (6)	-0,645
15,00	0,46 (8)	-0,418
18,00	0,60 (8)	-0,289

4. Discussion

The results obtained provide an opportunity for a comprehensive analysis of the behavior of the tested concrete in function of the dosage of ShCA KEPTONITE.

The results obtained for the compressive strength of 7- and 28-days of reference concretes (excluding ShCA KEPTONITE) are within the expected range. They are strongly influenced by the type of cement, and as a whole - the investigated concrete with cement CEM 52,5 Type I shows higher strengths. In addition, it can be confidently predicted that ShCA KEPTONITE (regardless of dosage) has virtually no significant effect on the compressive strength of the test ages, regardless of the type of cement in the concrete.

In this sense, the design of the concrete composition with the participation of ShCA KEPTONITE should be approached in a conventional manner without expecting the effect of this admixture on the mechanical characteristics of the concrete.

Discussion is possible in several different aspects regarding the linear expansion (expanding/ shrinkage) of the tested concrete with different dosage rates of ShCA KEPTONITE.

As an initial conclusion, with respect to reference concretes, it can be noted that HOLSIM cement- based concrete have the highest absolute shrinkage rate - of the order of 1,210 mm/m. For the other types of concrete, this size could be reduced by in range of about 40%.

It is also apparent significant influence of this admixture dosage rate, regardless of the type of the cement in the composition of the test concretes. For different types of cements, different dosages practically greatly reduce the final shrinkage time of 30 days. The

effect of ShCA KEPTONITE on HOLSIM-based concrete is particularly emphasized - the maximum dosage reduces about 3,5 times the nominal final drying shrinkage.

Of interest is the analysis of the absolute value of the initial expanding as a function of the dosage of the admixture used. It is evident that the HOLCIM cement-based concrete shows the highest expanding values at different dosages of the ShCA KEPTONITE. This occurs at 6-8 days of age after process monitoring.

Of interest is the analysis of the absolute value of the initial expanding as a function of the dosage of the admixture relative to the different types of cements used in the test compositions. It is evident that the HOLCIM cement-based concrete shows the highest expanding values at different dosages of the ShCA KEPTONITE. This occurs at 6-8 days of age after process monitoring.

Most categorical is the effect of this admixture in HOLSIM cement-based concrete - the dosage of 18 kg/m³ reduces about 2,2 times the final shrinkage, compared to that of concrete with 12 kg/m³ ShCA KEPTONITE.

At the moment, this original product is widely used in the innovative practice for the design and implementation of joint-less industrial concrete floorings with large one-day fields (of the order of more than 2000 m²), limited by expansion joints - **Photos 8 -13**.

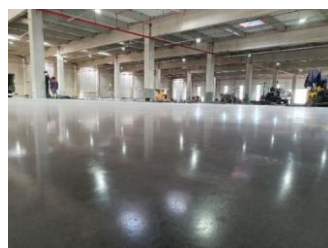


Fig. 8



Fig. 9



Fig.10



Fig. 11

Fig. 8-11 Joint-less fiber-reinforced concrete floorings

5. Conclusions

The original scientific results obtained from the study make it possible to evaluate the application of ShCA KEPTONITE as particularly effective in reducing drying shrinkage of fiber-reinforced concrete produced on the basis of one of various typical for Bulgaria cement - HOLCIM CEM I 52,5 R. It could be expected that the different type cements would be predetermined the different kinetics of free deformation, which, obviously, was provoked primarily by the different chemical and mineral composition of the base clinker.

The tested dosage range of the ShCA KEPTONITE is within the optimum ratio between technical characteristics and reasonable price.

In conclusion, the use of ShCA KEPTONITE with optimized dosage-rate in fiber-reinforced concrete joint-less flooring system for high-racking logistic centers gives good perspectives for great durability and high-level of performance of these type of special building constructions

7. Acknowledgments

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3D Design and Prototyping of a Microfluidic Device for Blood Cells' Investigations

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Abstract: The present study offers an important technological approach for the development of a disposable microfluidic channel using 3D nanoprinter - Photonic Professional GT2 (Nanoscribe, Germany). This publication aims to present 3D modelling, simulation, and prototype of a 3D nanoprinted microfluidic device for the investigation of blood cells. The design of 3D model of a microchannel is realized by the 3D CAD analysis software – SOLIDWORKS. A suitable laminar flow is generated by using computational fluid dynamics (CFD) software. As a result, the critical points of the pressure, velocity and wall shear stress into the microfluidic channel are obtained. An actual physical prototype of the proposed microfluidic device is developed, using a highly innovative technology of 3D nanoprinting by two-photon polymerization. Experimental studies with dilute erythrocyte suspensions are conducted to test the functionality of the developed real-world prototype of nano 3D printed microchannel.

Keywords: MICROFLUIDICS, MICROCHANNELS, 3D MODELING, 3D NANOPRINTING, TWO PHOTON POLYMERIZATION, RED BLOOD CELLS

1. Introduction

Microfluidics is the science and technology of systems that process or manipulate small (10^{-9} to 10^{-18} l) quantities of fluids using channels from tens to hundreds of micrometers in size [1, 2]. The first applications of microfluidic technologies are for the analysis, separation and detection with high resolution and sensitivity of various substances in blood rheology –hemorheology, and chemical analysis [2, 3]. In recent years, microfluidics has had wide application from fluid physics to the food industry, cell biology, biomedicine, pharmacy, etc. [4, 5, 6].

The microfluidic device (also referred to as lab-on-a-chip or micro total analysis systems – μ TAS) is one or some microfluidic channels with inlet/outlet openings to perform respective micro-functions and biomedical analysis [5]. It allows for single unit operation (e.g., mixing, separation, droplet generation, particle manipulation, heating, and detection) or incorporates multiple unit operations [3, 7].

One of the long-term, goals in the field of microfluidics is to create integrated and portable clinical diagnostic devices for home usage, eliminating time-consuming laboratory analysis procedures [8]. Through the application of microfluidic technologies, it is expected to improve the efficiency in the detection of biomolecules and the monitoring of individualized diagnostic and therapeutic studies *in vitro* and *in vivo* [8].

Hemorheological alterations in the majority of different diseases are connected with blood rheology disturbances, such as the increase of blood and plasma viscosity, cell aggregation enhancement, and reduction of the red blood cells (RBCs) deformability. Thus, the visualizations and measurements of blood cells' deformability, flowing in microfluidic devices, can provide vital information to diagnose early symptoms of blood diseases and consequently to be used as a fast clinical tool for the early detection of biomarkers. For instance, RBCs rigidity is correlated with myocardial infarction, diabetes mellitus, and hypertension, among other blood diseases [8, 9, 10].

Various microfluidic devices are used, in order to understand better the cells' behavior in blood vessels. The analysis of rheological properties of blood cells is of a great interest among the scientist of the biomedical field, since it is strongly dependent on the interactions and mechanical cells' proprieties [8, 9, 10].

The study of the rheological properties of blood and mimicking the RBC's flow at *in vitro* conditions is essential for the design, performance, and optimization of the microfluidic devices. Valuable progress in personalized medicine for new treatments and diagnosis approaches can be achieved by combining the unique features of hemorheology and microfluidic technology for single-cell analysis [8, 9, 10].

Microfluidic devices can be categorized into active and passive types, according to the fluid flow control principle [6]. The passive microfluidic devices (microchannels, microvalves, and microfilters), use physical properties, such as surface tension, capillary action, and gravity, to manipulate the fluid flow. These devices can automate simple operations such as fluid transport, separation, and mixing.

Active microfluidic devices use an external power source to manage the fluid flow and manipulate samples. These devices can be controlled precisely in dynamic mode by using electric, magnetic, thermal, or acoustic fields. They can automate complex operations such as sample manipulation, cell sorting, and drug screening with high throughput, but this process would require more complex manufacturing and control techniques. Usually, these devices are more expensive from the passive one [6].

Hybrid microfluidic devices combine both methods to achieve better functionalities. The hybrid microfluidic devices offer a versatile platform for different applications, including biomedical research, clinical diagnostics, and new drug discovery.

Microfluidic technologies have many useful characteristics such as: small size of microfluidic devices and usage of few very small amounts of samples and reagents (at microliters size), low price, short analysis time, small footprints for analytics devices, etc. These features offer fundamentally new possibilities for controlling the concentrations of molecules and cells in space and time [1, 3].

In general, two types of techniques can be used to manufacture microfluidic devices: subtractive and additive [11, 12, 13]. In subtractive techniques, the material is removed from a substrate to create microchannels and other features, whereas in additive techniques, the material is added layer by layer to build a three-dimensional structure [14]. Common subtractive techniques include hot embossing and laser ablation, while general additive techniques include 3D printing, soft lithography, and inkjet printing [15]. These techniques offer various advantages, including low-cost, rapid prototyping, and the ability to manufacture microfluidic devices with complex geometries [16, 17].

3D printers are a synonym for unique rapid prototyping devices. The affordability and speed of these printers allow their implementation in the field of mass production [17]. 3D printing, also known as additive manufacturing, has become one of the world's best tools for small-scale manufacturing [18].

Among the various 3D printing approaches, two-photon polymerization (2PP) enables the highest spatial resolution, with characteristics smaller than the Abbe diffraction [17, 18] limit that are produced due to nonlinear light-induced effects in the photosensitive material.

Micro 3D printing from 2PP finds many applications, in micro-robotics, biosensing, biomedical research, optical data storage, micro-optics, antireflective surfaces, photonic metamaterials, photonic crystals or mechanical metamaterials [18].

Nano-3D printing, is a hybrid process that combines digital light projection 3D printing with nanoscale-relief patterning. Nano-3DP enables a variety of novel applications with higher-resolution surface details than currently available [19].

All of the above said, the authors of these study dedicate their scientific efforts in the field of the microfluidics combined with 3D printing of special technical devices. Hence, the present study aims to create a design, simulation, and prototype of a 3D nanoprinted microfluidic device mimicking a postcapillary vessel for blood cells' investigations.

2. Materials and Methods

The design of 3D model of a microchannel is done by 3D CAD analysis software – SOLIDWORKS. A file of type STL (mesh format file) is generated on the basis of SOLIDWORKS software environment. For studying fluid flow dynamics, this file is very important during the transfer of complex 3D geometries into the computational fluid dynamics (CFD) software - Flow 3D.

A highly innovative two-photon polymerization (2PP) technology is used for 3D printing of the designed microfluidic device. The 3D nanoprinter - Photonic Professional GT2 (Nanoscribe, Germany) is applied for two-photon polymerization to produce a filigree structure from a 3D shape via high-precision 3D printing. 2PP 3D printing is a direct laser writing (DLW) technique in which a solid structure is written into a liquid resin voxel by voxel by scanning a femtosecond-pulsed tightly focused laser beam.

The 3D model of the microchannel, designed in SOLIDWORKS (.stl file) is imported into the specialized design Photonic Professional GT2 (PPGT2, Nanoscribe) software (Describe), which is used to select the recipe (printed material, substrate and resin type), mode of operation, dimensions of the printing layers.

In Describe a special job file is generated that is used as an input to the nanoprinting process. A glass substrate is fixed on a special holder. A drop of a photoresist suitable for working with glass substrates is put on the substrate. The holder is placed in the 3D printing machine (PPGT2 Nanoscribe). PPGT2 3D printer is controlled by an easy-to-use graphical user interface of the specialized software (NanoWrite) from Nanoscribe. NanoWrite is launched, which calibrates the overall system, loads the work file from Describe, and performs the nanoprinting operation.

After turning on the 3D printing process, the holder with the polymer microstructure is removed from the 3D printer. The glass substrate with the microchannel is washed exclusively with isopropanol solution and the geometry of the printed microchannel is analyzed under a microscope.

The manufactured microchannel is tested for patency by filling it with a diluted erythrocyte suspension. The flow of erythrocytes is created with a syringe pump and observed using a light microscope Primostar 3 Zeiss with integrated digital camera.

3. Results

Postcapillary blood vessel sizes are less than 1 mm in diameter. Multiple microfluidic channels with different heights and widths and different printing modes are designed and prototyped in order to mimic these post-capture venules.

In this study, a microfluidic device is presented that is most suitable for monitoring blood cells throughout the channel volume, and in close proximity to the channel walls. This is a necessary condition when covering the channel with endothelial cells or

adhesion molecules when creating *in vitro* experimental models of blood vessels.

The designed microfluidic device is elaborated with the following dimensions: height/width /length - 0.075 x 0.35 x 7 mm. A 3D model of the microchannel is created (Fig. 1) by using SOLIDWORKS software environment. The thickness of the wall of the microchannel is 0.05 mm. The height of the bottom of the channel is 0.02 mm.

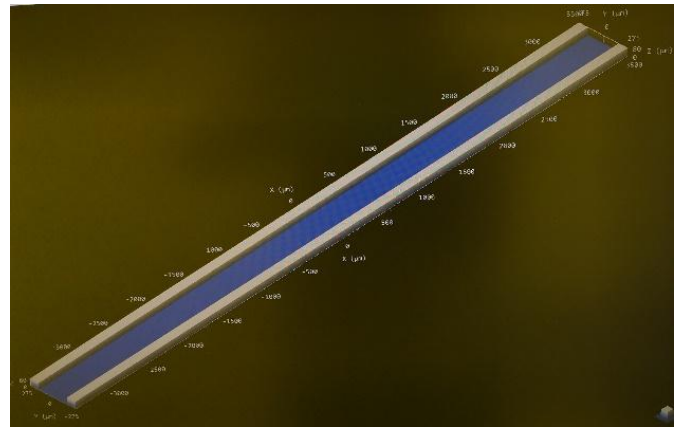


Fig. 1 3D model of the microchannel, generated in SOLIDWORKS.

The selected 3D design of microchannel should be tested for the suitable input fluid flow parameters, which will create the laminar flow that is required when studying dilute blood cell suspensions.

For this purpose, the .stl file created in the SOLIDWORKS is imported in Flow 3D (CFD software). A suitable mesh for simulation of the fluid flow in the microchannel is generated (mesh cell size of 0.025 x 0.025 mm). The flow through the microchannel is tested with a fluid - water, at a temperature of 20°C. The boundary conditions of the model are defined by setting a fluid flow rate of 0.026 mm³/s, which is obtained at a Reynolds number <1 (a necessary condition for laminar flow). The pressure contours (Fig. 2), x-velocity contours (Fig. 3) and wall shear stress contours (Fig. 4) are obtained as a result.

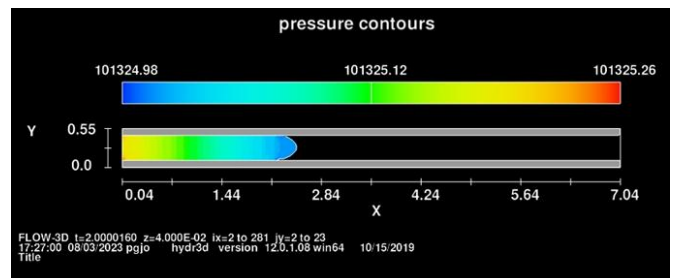


Fig. 2 Simulation results of the pressure (g/mm²) in the microfluidic channel.

From the simulation results, the pressure along the microchannel is approximately 101325 g/mm² (Fig. 2). In the central region of the flow, the fluid velocity increases to 1.41 mm/s, while at the channel walls it decreases to 0.02mm/s (Fig. 3).

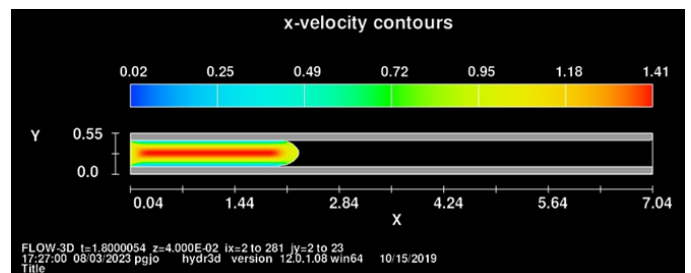


Fig. 3 Simulation results of the velocity (mm/s) in the microfluidic channel.

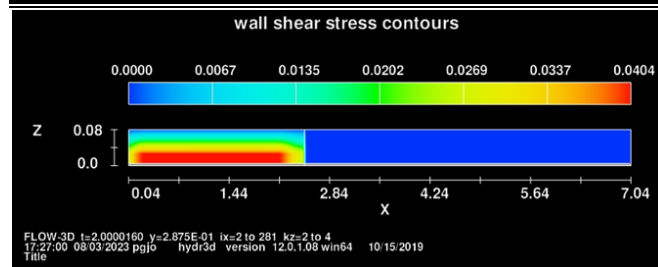


Fig. 4 Simulation results of the wall shear stress ($\text{g}/\text{mm}/\text{s}^2$) in the microfluidic channel.

The wall shear stress on the bottom of the microchannel has maximum value of $0.04 \text{ g}/\text{mm}/\text{s}^2$ (Fig. 4).

After simulating the fluid flow in the channel with the chosen geometry, the microfluidic device is constructed by nanoprinting with PPGT2 3D printer. The 3D model of the microchannel is imported in Describe using the .stl file. A special job file is generated in Describe, containing the whole information, regarding the recipe (printed material, substrate and resin type), mode of operation, dimensions of the printing layers. In this case, the recipe - IP-S 25x ITO Shell (3D MF) is used, which is suitable for printing on a glass substrate with an optical magnification of x25.

The Shell and Scaffold mode of operation is selected in order to reduce the printing time. The size of each layer is $1 \mu\text{m}$. A glass substrate is fixed on a special holder. A drop of a photoresist IP-S is put on the substrate. The holder is placed in the 3D printing machine and NanoWrite is launched for calibration of the whole system. The nanoprinting procedure is launched and the entire process can be monitored in real time using a special digital camera (part of PPGT2 3D printer) (Fig. 5). The Shell and Scaffold mode polymerizes the photoresist only along the skeleton of the selected network. In this way, the printing time is reduced, but the microstructure becomes more fragile.

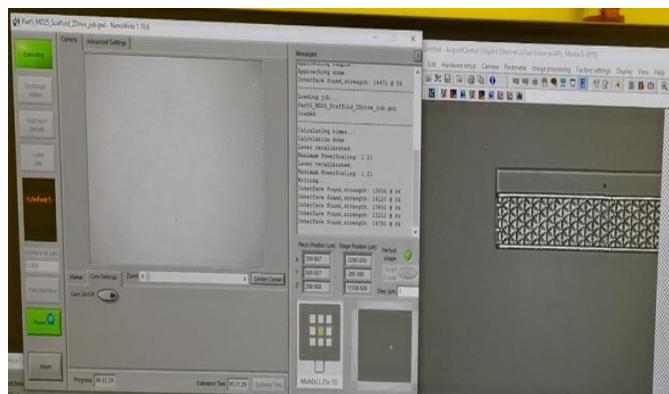


Fig. 5 Screenshot of the graphical user interface of the specialized software (NanoWrite) from Nanoscribe for control of PPGT2 3D nanoprinter (on the left) and visualization (part of the microchannel) of the nanoprinting procedure in real time (on the right) by a digital camera from Nanoscribe.

The holder with the polymer microstructure is removed from the 3D nanoprinter, after the end of the 3D printing process, when the 3D process is finished.

The glass substrate with the microchannel is carefully washed with a solution of isopropanol. The geometry and the size of the developed microchannel is studied under a microscope (Fig. 6).

Some defects of the geometry (blue circles – Fig.6) during the 3D nanoprinting procedure are clearly visible. The width of the microchannel is almost 0.37 mm measured by microscope Primostar 3 Zeiss. Future scientific work is related to the

optimization of the recipe and decreasing the number of defects in the microstructure.

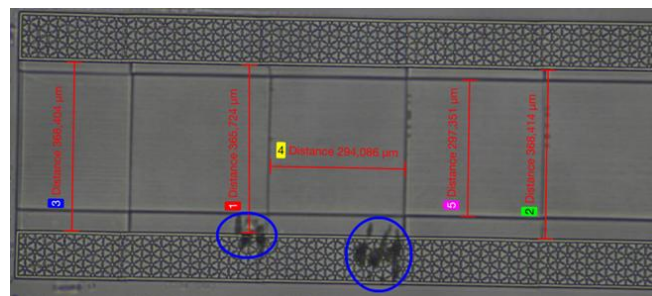


Fig. 6 Image from microscope Primostar 3 Zeiss, of the 3D nanoprinted microchannel.

The constructed microchannel is tested by filling it with a diluted erythrocyte suspension. The flow of erythrocytes is created with a syringe pump and observed using an optical microscope Primostar 3 Zeiss with integrated digital camera (Fig. 7). Experimental results with diluted erythrocyte suspensions show that the channel is passable and the flow through it is laminar.



Fig. 7 Image of the developed microchannel filled with a diluted erythrocyte suspension.

4. Discussion

3D printing has changed the field of microfluidics significantly and also created innovative microfluidic devices that are usually impossible to be designed employing other approaches. Three-dimensional printing allows science and technology to be transformed by producing custom-made low-cost equipment requiring specialized equipment [20].

So far, the 3D-printed microfluidic-based miniaturized devices have various biomedical applications. The group of scientists Yeong et al. fabricated porous scaffolds for cardiac tissue engineering by selective laser 3D printing technique [21]. Wu et al. fabricated 3D biomimetic microvascular networks embedded in the hydrogel matrix by multidirectional printing [22]. Towards the development of a rapid, sensitive and specific influenza virus detection system, Krejcova et al. have produced a 3D-printed bead-based microfluidic chip [23]. Among the innovators, Gowers et al are the first who developed a 3D-printed wearable microfluidic device integrated with clinical microdialysis probes and needle biosensors for continuous monitoring of human tissue metabolite levels [24]. Kadimisetty and others. have developed a novel, low-cost gravity flow microfluidic immunosensor for the detection of three cancer biomarker proteins [25]. Oh and others developed and elaborated a 3D-printed blood viscosity assay [26]. Chen et al. designed a 3D printed microfluidic device in order to isolate circulating tumor cells from human blood samples [27].

Visualization and measurements of blood cells flowing in microfluidic devices are of a great importance in providing not only essential information about the rheological properties of blood cells, but it is also vital information for diagnosing early symptoms of

diseases during clinical research. Microfluidic devices combined with flow imaging techniques can be used to assess the cardiac risk profile of a particular patient and help medical staff to decide on the appropriate treatment and therefore to increase the chances of patient's survival. Analysis of single cells, particularly red blood cells, provides unique and specific information on patient stratification, for example overall outcome of clinical care and treatment of diabetes, hypertension, among other blood diseases [8, 9, 10].

The present study offers an important technological approach for the rapid production of low-cost microfluidic channel with the help of which the rheological properties of blood cells can be studied in various diseases. By innovative two-photon polymerization (2PP) technology 3D nanoprinting microfluidic device was suggested and constructed. Our proposed 3D microchannel design and prototype can be embedded in a holder with micro-insert, connected to a micropump and microscope, forming an active microfluidic system. The nano 3D printed channel can be used to evaluate hemorheological properties - erythrocyte aggregation and deformability. The channel walls can be coated with suitable cells or adhesion molecules to create *in vitro* experimental models imitating *in vivo* conditions in blood vessels—for the purposes of laboratory and clinical practice.

5. Conclusion

The microfluidic device is developed for the study of the rheological properties of the blood. Every stage of 3D modeling and simulation of the prototype is described. The simulation results of the pressure, velocity, and wall shear stress measured in the microchannel are of a great importance for laminar flow generation. Innovative technology such as two-photon polymerization is used in the 3D nanoprinting process with extremely precise PPGT2 Nanoscribe equipment. Experimental studies with dilute erythrocyte suspensions are conducted to test the functionality of the developed real-world prototype of nano 3D printed microchannel.

Acknowledgment

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On the role of non-metallic inclusions in ensuring crack resistance of steel

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Abstract. The influence of non-metallic inclusions on the formation of defects in deformed steels and their role in providing crack resistance are considered. It is shown that non-metallic inclusions as stress and strain concentrators are one of the most dangerous sources of defect initiation in steels during pressure treatment. It has been established that the nature of cracks and the features of their growth near non-metallic inclusions are determined by the type of inclusions, as well as by the scheme of the local stress state, which depends on the loading conditions. An analysis was made of the features of the initiation and development of the cracks near non-metallic inclusions of various types during tensile strain, compressive and bending deformation. It is shown that the most severe way of deformation for the inclusion-matrix system is tensile strain, the softest is compression.

KEY WORDS: NON-METALLIC INCLUSIONS, STEEL, DEFORMATION, DEFECTS, CRACKS, CAVITIES, METAL WORKING BY PRESSURE, TENSILE STRAIN, COMPRESSION, BENDING.

1. Introduction.

It is known that the mechanical, technological and operational properties of steels largely depend on non-metallic inclusions, namely on their quantity, type and distribution in ingots, billets, finished metal products [1 - 5]. Many defects in cast and deformed steels are associated with non-metallic inclusions, which reduce their quality and also contribute to red brittleness [3, 4, 6]. The negative effect of non-metallic inclusions is primarily due to the concentration of deformation, thermal, interfacial stresses, the nature of which is determined by the type of inclusions, their level of plasticity, temperature-speed mode of deformation, stress state scheme and other factors [3, 4, 7 - 11]. Moreover, non-metallic inclusions contribute to stress concentration under different modes and methods of loading, as well as during various types of heat treatment [2, 3, 7, 9, 12]. Inclusions contribute to the embrittlement of steels, since the formation of a crack near an inclusion reduces the work of its initiation [3, 7, 9]. The goal of the work was to study the formation of defects near non-metallic inclusions in steels under different loading conditions.

2. Materials and Procedures.

Defects near nonmetallic inclusions of various types were studied during deformation by hot and cold rolling, tension, compression, and bending of specimens made of steels 08Yu, 08T, 08kp, 45KhGN, and 60G. The samples were subjected to tension, compression, and bending in vacuum at temperatures of 20...1200 °C on Instron-1195 and IMASH-5C units with special grippers, the movement speed of which was 20 mm/min. The sizes of defects and critical degrees of deformation were determined by the methods described in [3, 7, 9, 10].

3. Results and discussion.

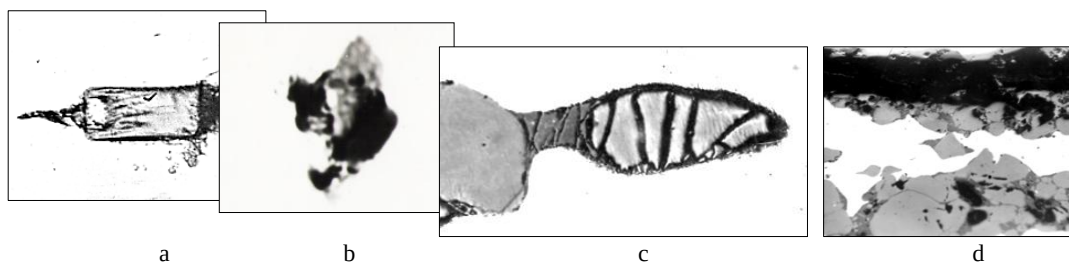
The inclusion during pressure treatment (during rolling) is affected more normally by compressive stresses from the pressure of a deforming tool transmitted through a metal matrix, longitudinal shear stresses arising in the matrix during its deformation, as well as friction stresses at the inclusion-matrix boundary. The value of normal stresses depends on the pressure of the deforming tool, shear stresses - on the plasticity of the metal matrix, determined by the temperature and its structure.

Depending on the method of deformation, the scheme of the stress state near the inclusion changes. First of all, this is due to the general schemes of principal deformations and principal stresses [3, 4, 13]. For non-metallic inclusions in a plastic matrix, there are three types of schemes of principal deformations and nine types of schemes of principal stresses [13], and the ratios between the stress values in different schemes are different. The plasticity and resistance to deformation of inclusions depend on the scheme of principal deformations, which determine the nature of the redistribution of non-deformable inclusions in the plastic matrix and changes in the shape of plastic inclusions during deformation. Mainly, the inclusions are redistributed with the formation of lines in the direction of positive deformations.

The difference between the physical, mechanical, and chemical properties of the inclusion and the steel matrix leads to the localization of deformation near the inclusions and the appearance of stresses during rolling deformation. As a result, various kinds of defects arise, associated with the presence of non-metallic inclusions: bundles, cavities, cracks (Fig. 1).

Under different schemes of the stress state near the particles of non-metallic inclusions, stresses arise, which can be normal (tensile or compressive) and shear and have a local character. The strain energy accumulated near the inclusions, depending on the temperature and speed conditions of the deformation tests, can be spent on local plastic flow or fracture. Destruction can occur through the formation of cracks in the inclusion (Fig. 2, a, b, c), including along the interfacial boundaries in the inclusion itself; in a steel matrix (Fig. 2, d); or by lamination along the inclusion-matrix boundaries (Fig. 2, e). The mechanism of formation of microfractures depends on the type of inclusion, the degree of its plasticity, the composition and structure of the steel matrix, temperature, and the structure of the inclusion-matrix boundaries [3, 7, 9].

Brittle inclusions are destroyed by normal stresses, no matter how external load is applied. Both brittle and ductile cracks can develop within inclusions. The mechanism of destruction of the inclusions is not the same, which is due to the difference in the types of inclusions and mechanisms of plastic deformation at different temperatures [3, 7 - 9]. In the brittle region, the strength properties of refractory inclusions are determined mainly by the Griffith relation. In the brittle-ductile region, the role of plastic deformation of inclusions in the initiation of cracks increases [3, 7 - 9].



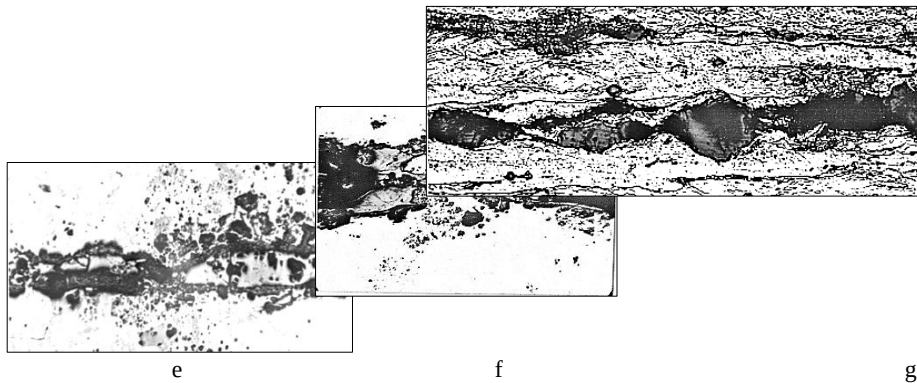


Fig. 1. Defects near non-metallic inclusions in hot-rolled (a-e) and cold-rolled (f, g) steels, x 500

Cracks form in the inclusions whose size is larger than the critical one. For example, for inclusions Ti_2O_3 , TiO , $TiO-TiC$, TiN , $TiCN$ at a temperature of 20 °C it is ~ 15 μm , for TiO_2 , $FeO-TiO_2$ - 21 μm and for silicates $MnO.SiO_2$ and $FeO.SiO_2$ - 23 μm [7]. With an increase in temperature, the critical inclusion size of all three groups increases due to an increase in the plasticity of the steel matrix [3, 4]. Since the phases in heterophase nonmetallic inclusions have different level of plasticity and strength at any deformation temperatures, stresses inevitably arise at the interfaces during loading, which can lead to the destruction of these boundaries. Cracks in inclusions appear when a certain (critical) value of the degree of deformation is reached, the value of which depends on the type of inclusion [3, 7].

Models for the initiation of brittle or ductile cracks in a steel matrix near inclusions are based on the concept of inhibition of sliding, rotation, or twinning by an inclusion and the interaction of the hindered strain stress field with the stress field near inclusions

[3, 7, 9, 14]. Non-metallic inclusions of metallurgical origin are "hard" barriers to the movement of dislocations, which contribute to the localization of stresses in the steel matrix. These stresses can exceed the ultimate strength of the matrix and lead to local failure. In the structural aspect, the initiation of cracks in the matrix near the inclusions obeys strict laws. Microcracks are formed after a structural state develops in the deformed metal, the specific form of which depends on the deformation conditions [3, 4, 14].

There is a large group of inclusions in the steels (corundum, spinels) prone to the formation of cavities by decohesion of inclusion-matrix interphase boundaries [5 – 7]. In steel 08Yu, cavities are formed near non-deformable inclusions of corundum Al_2O_3 , spinels $MnO \cdot Al_2O_3$, $FeO \cdot Al_2O_3$, the size of which is larger than a certain critical value depending on temperature [3, 7, 9]. For example, for these inclusions in steel 08Yu at a temperature of 20 °C it is 2...3 μm , at 1100 °C - 7...8 μm .

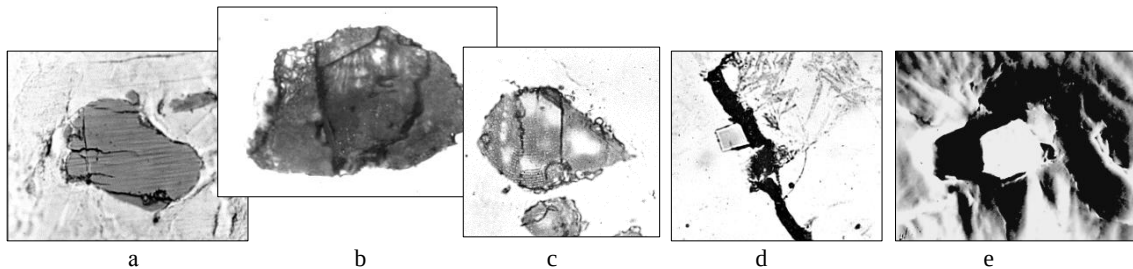


Fig. 2. Cracks near $TiCN$ inclusions in 08T steel (a, d), $MnO.SiO_2$ in 08Yu steel (b), $TiCN+(Fe,Mn)S$ in 08T steel (c), $MnO.Al_2O_3$ in 08Yu steel (e) after deformation stretching: a, c – $\varepsilon = 6\%$, $t = 25\text{ }^{\circ}C$; b – $\varepsilon = 6\%$, $t = 600\text{ }^{\circ}C$; d – $\varepsilon = 18\%$, $t = 900\text{ }^{\circ}C$; e – $\varepsilon = 15\%$, $t = 600\text{ }^{\circ}C$; a - d - x 900, e - x 600

The formation of the cavities near inclusions is the occurrence of cracks directly at the interphase boundaries as a result of their separation. This process is associated with the approach to the inclusion of lattice dislocations, the emergence of dislocations at the inclusion-matrix boundaries and their merging, which leads to the formation of a cavity. Only sufficiently high shear stresses can bring dislocations to the surface. The surface of the cavity attracts dislocations and this contributes to its growth during deformation.

For all types of defects described, at the initial stages of deformation, nonmetallic inclusions are practically the main source of their formation, and for each deformation temperature there is a state (interval of deformation degrees) when the process of fracture development is controlled by the inclusions [3, 7, 9]. With an increase in temperature, the interval of deformations, in which the harmful effect of inclusions is manifested, decreases.

The influence of the loading method (tension, compression, bending) on the features of defect formation was studied using the example of cavities near non-metallic inclusions. Such studies are necessary to determine the conditions for the deformation of steel and the operation of steel products.

Under all loading methods, the inclusions undergo localization of deformation, leading to a significant concentration of stresses, the relaxation of which proceeds through local plastic flow or the appearance of defects, the nature of which depends on the type of inclusion, temperature, and method of deformation. It is necessary to take into account the difference in the nature of the distribution of stresses and plastic deformation of the steel matrix in contact with the inclusion under different methods of deformation. Under conditions of tension and compression, the flow of the steel matrix near the inclusion is similar to [3, 7, 9]. It is carried out according to shear, rotational or twin mechanisms and differs in the

distribution of the stress level near the poles of the inclusion relative to the direction of external loading [3, 7, 9]. During bending, the steel matrix bends and rotates around the inclusion, creating tensile and compressive stresses, respectively, above and below the inclusion [3, 7, 9], which causes moment stresses that contribute to the rotation of the inclusion relative to the steel matrix and an increase in the share of rotational deformation in the steel matrix itself.

In 08Yu steel, inclusions of Al_2O_3 corundum, $\text{MnO} \cdot \text{Al}_2\text{O}_3$ spinels, and some $(\text{Fe}, \text{Mn})\text{S}$ sulfides, have cavities in tension and

bending in the form of viscous cracks (see Fig. 2, e, 3, a, c). No fracture of the inclusions themselves was observed during compression along with the formation of cavities, the destruction of corundum and spinel inclusions occurs, in which brittle cracks appear (Fig. 3, b). The nature of the cavities during compression is determined by the deformation temperature; in the temperature range of 25...600 °C, the cavities look like brittle cracks (Fig. 3, b, d); at higher temperatures, the cavities look like ductile cracks.

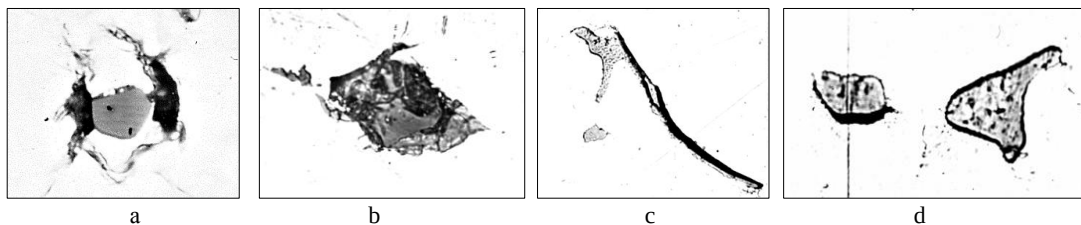


Fig. 3. Defects near Al_2O_3 , $\text{MnO} \cdot \text{Al}_2\text{O}_3$ (a, b) and $(\text{Fe}, \text{Mn})\text{S}$ (c, d) inclusions formed during (a, c) bending and (b, d) compression, $\times 1000$.

Obviously, during brittle delamination at the inclusion-matrix boundary, normal microstresses arise, which have a wedging effect either along this boundary or normally in each of its sections. During viscous separation associated with the plastic behavior of the steel matrix, shear stresses arise at the inclusion-matrix boundary, which play an important role both in the nucleation of the cavity and during its growth, acting in the steel matrix near the edge of the cavity [15 – 19]. In addition, during high-temperature deformation, slipping develops at the boundaries of the inclusion-matrix [4, 20 – 24], which also contributes to the viscous separation of these boundaries during the formation of cavities.

The critical size of inclusions D_{cr} depends on the method of deformation and increases with increasing temperature (Fig. 4, a). The minimum critical size corresponds to tension, the maximum to compression. The critical value of relative deformation ε_{cr} , upon reaching which cavities are formed, is also determined by the method of deformation [3, 7, 9]. The nature of curves 1, 2, 3 in Fig. 4, b testifies to the uniform nature of the influence of temperature on the critical deformation ε_{cr} under all loading methods, which can be explained by a change in the plasticity of the steel matrix. The maximum critical degree of deformation at all temperatures is observed in compression, the minimum - in tension.

Comparison of the values of ε_{cr} for different methods of deformation indicates that the most severe method of deformation for the inclusion-matrix system is tension, and the softest is compression. As shown in [25], the ratio of the normal maximum stresses near inclusions in tension (near poles 0° and 180°) and compression (near poles 90° and 270°) is 9.2, and in our calculations for steel this ratio about 15 [3, 7, 9]. The concentration of shear stresses in tension and compression near the inclusions is the same. The difference between local normal stresses near inclusions in tension and compression causes more stringent conditions for tensile deformation. When analyzing the distribution of micro inhomogeneous deformation, as well as intersurface (contact) stresses according to Goodyear near rigid inclusions, it was found that the maximum tensile stresses in uniaxial tension occur at the 0 and 180° poles, and in compression - at the 90 and 270° poles with respect to the external stress σ , which affects the nature of defects [3, 7, 9]. Both types of loading contribute to local stress concentration and the emergence of a triaxial stress state, which leads to the development of fracture near the inclusions.

For comparison, in Fig. 4 shows the results of studying the formation of defects - brittle cracks inside inclusions of $\text{MnO} \cdot \text{SiO}_2$ rhodonite in steel 08Yu under different loading methods.

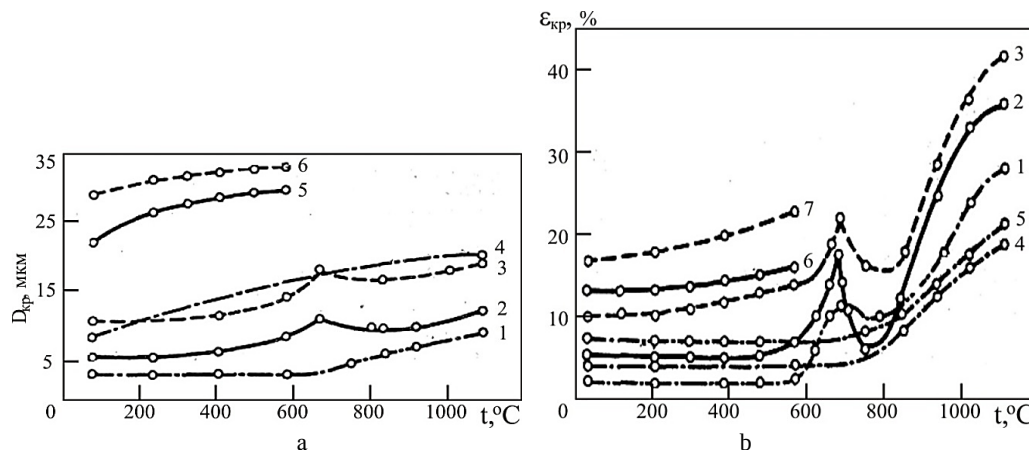


Fig. 4. Effect of temperature on the critical size D_{cr} of inclusions of corundum Al_2O_3 (1 - 3) and rhodonite $\text{MnO} \cdot \text{SiO}_2$ (4 - 6) under tension (1, 4), bending (2, 5) and compression (3, 6) (a) and the critical degree of deformation ε_{cr} , in which cavities (1 - 3) and cracks appear in corundum (4) and rhodonite (5 - 7) during tension (1, 5), bending (2, 6) and compression (3, 4, 7) (b).

In connection with the different nature of the destruction of steel 08Yu with different methods of deformation, the contribution of inclusions to the development of destruction also changes. The contribution of inclusions to the initiation of microcracks in steel 08Yu was evaluated based on the results of counting the number (N) and total length (L) of cavities and cracks

associated with inclusions and located far from them. The coefficients K_N and K_L were determined, indicating what proportion of the microcracks present arose due to the inclusion (K_N) and what is their role in the development of fracture of steel (K_L) [3, 7, 9].

In the case of tension, the values of the coefficients K_N and K_L at the first stages of deformation at all temperatures are

equal to unity. With the appearance of microcracks of dislocation origin, the coefficients K_N and K_L decrease, however, at each temperature, there is a certain range of deformation degrees in which inclusions are responsible for the development of fracture. The higher the deformation temperature, the narrower this interval and the further it shifts towards higher degrees of deformation; therefore, as the temperature increases, the role of inclusions in the development of tensile failure decreases. In bending and compression, the coefficients K_N and K_L are equal to unity at all stages of deformation. This means that inclusions play a major role in the development of microcracks and, despite the absence of fracture of ductile steel 08Yu, are dangerous, since they are ready fracture centers with a possible change in the loading method.

4. Conclusions.

Non-metallic inclusions as stress and strain concentrators are one of the most dangerous sources of defects in steels during pressure treatment. The nature of cracks and the features of their growth near non-metallic inclusions are determined by the type of inclusions, as well as by the scheme of the local stress state, which depends on the loading conditions. When analyzing the features of the initiation and development of cracks near non-metallic inclusions of various types during tensile, compression, and bending deformation, it was found that the most severe way of deformation for the inclusion-matrix system is tension, and the softest is compression

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Comparison of the mechanical characteristics of polycomponent high-entropy alloys based on the TI-CR-FE-NI system, produced by powder hot forging

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Abstract. Mechanical tests of 5- and 6-component high-entropy alloys, which were obtained for the first time by the method of hot forging, were carried out. The test results showed a fairly high hardness and strength of the obtained alloys. The TiCrFeNiC alloy (without annealing) has the highest mechanical properties. Its high strength is due to solid-solution hardening, as well as the formation of carbides in situ. Fractographic studies showed mostly quasi-brittle destruction of alloy samples.

KEYWORDS: HIGH-ENTROPY ALLOY, MECHANICAL TESTS, HOT FORGING, STRENGTH, HARDNESS, FRACTURE FRACTOGRAPHY, PLASTICITY.

1. Introduction

Recently, for the design of alloys with high physical and mechanical properties, the idea of a thermodynamic approach is used, the essence of which is to reduce the Gibbs free energy by creating the maximum entropy of mixing elements in the alloy. High-entropy alloys (HEAs) obtained in this way are characterized by high strength, hardness and wear resistance. But the term "high-entropy alloys" refers mainly to metal alloys, so there are few works in the literature relating to the synthesis of these alloys with the addition of non-metallic elements.

A feature of such alloys is the content in their composition of at least 5 basic elements in an approximately equiatomic ratio. The presence of a large number of heterogeneous elements, characterized by different individual properties, leads to the formation of solid replacement solutions with significant distortion of the crystal lattices of alloys. The high entropy of mixing determines the minimization of the Gibbs free energy, which favors the conditions for the formation of solid solutions with BCC, FCC or FCC+BCC structure. Alloys with such structures are characterized by high values of hardness and strength, increased thermal stability, high wear resistance and resistance to oxidation, in connection with which they attract the attention of an increasing number of researchers working in the field of modern materials science [1-5].

At the same time, in the literature there is practically no data on the possibility of obtaining multicomponent (high-entropy) alloys by hot forging methods. In this regard, the purpose of this work was to compare the mechanical characteristics of hot-forged multicomponent alloys based on the Ti-Cr-Fe-Ni system, as well as to study the effect of annealing temperature on the main physical and mechanical properties of equiatomic TiCrFeNiC multicomponent alloys.

2. Materials, technology and test methods

For the synthesis of alloys, Cr, Fe, Ni, Cu, Ti and C (graphite) powders were used as starting materials in an equiatomic ratio. In the table 1 shows the atomic and weight content of the elements of the mixture.

For all obtained alloys, the entropy of mixing, calculated by the Boltzmann equation, is $\geq 13.38 \text{ J / mol} \cdot \text{K}$, which is significantly higher than that of conventional alloyed alloys. Prior to forging in the manufacture of TiCrFeNiCu and TiCrFeNiC alloys, preliminary mechanical activation (PMA) of the powder charge was carried out. This operation was carried out in a planetary mill with a ratio of the mass of the charge to the mass of grinding bodies of 1 : 8. The rotation speed of the mill drums was about 1000 rpm, and the grinding time was 60 minutes. In order to prevent oxidation and segregation of powder particles, mechanical activation was carried out in the environment of ethyl alcohol. The

oxygen content in the mixtures after grinding did not exceed 0,5 %. During the production of the TiCrFeNiCu alloy, PMA was not carried out.

Table 1: Weight and atomic content of elements in alloys

Alloy	Content of elements	Cr	Fe	Ti	Ni	C	Cu
1	at. %	20	20	20	20	20	-
	mac. %	22,96	24,67	21,15	25,92	5,30	-
2	at. %	20	20	20	20	-	20
	mac. %	18,70	20,09	17,23	21,12	-	22,86
3	at. %	16,67	16,67	16,67	16,67	16,67	16,67
	mac. %	17,93	19,26	16,52	20,24	4,14	21,91

(1 – TiCrFeNiC; 2 – TiCrFeNiCu; 3 – TiCrFeNiCuC).

Cylindrical blanks with a diameter of 40 mm and a height of 20 mm were pressed from the obtained mixtures on a hydraulic press under a pressure of 700 MPa, the further consolidation of which was carried out by the method of hot forging (HF) on an arc stator press FB 1732. Heating for hot forging was carried out in an environment of flowing argon at a temperature of 1100 °C. The initial samples for forging had a porosity of about 30-36%, after hot forging and annealing their porosity did not exceed 2 ÷ 3%. The samples obtained as a result of forging were annealed for two hours in an induction furnace at temperatures of 1200, 1250 and 1300 °C.

Mechanical properties were determined using a uniaxial compression test, as well as by the method of automatic indentation according to the method of Yu.V. Milman [6-9]. Compression was carried out on a certified universal machine "CERAMTEST". For this, the samples were cut into rectangular parallelepipeds measuring 5x5x8 mm on an EDM machine and polished using diamond pastes. Special programs for calculating compression load curves made it possible to calculate the main mechanical characteristics of materials for this type of testing.

Automatic indentation was carried out on the Micron-gamma device in accordance with the ISO 14577-1:2002 standard with a three-sided Berkovich diamond pyramid with a sharpening angle at the top of 65° with a load on the indenter of $P = 1,50 \text{ H}$ and exposure under the load for 15 s. In parallel, the load-unload diagram was recorded in the coordinates "load P - depth h" and the values of mechanical characteristics were recorded. The plasticity

characteristic δA of the alloys was determined by the ratio of the areas under the loading and unloading curves of the samples according to the formula (1) [6, 7]:

$$\delta_A = \frac{A_p}{A_t} = \frac{A_p}{A_p + A_e} = 1 - \frac{A_e}{A_t} \quad (1)$$

where A_e and A_p are the elastic and plastic components of deformation during indentation.

3. Test results and their discussion

Compression tests made it possible to determine the limit of proportionality $\sigma_{0.01}$, yield limit $\sigma_{0.2}$, strength limit σ_b and deformation to failure ε_{pl} . According to the results of the tests, the compression diagrams of the samples were constructed (Fig. 1).

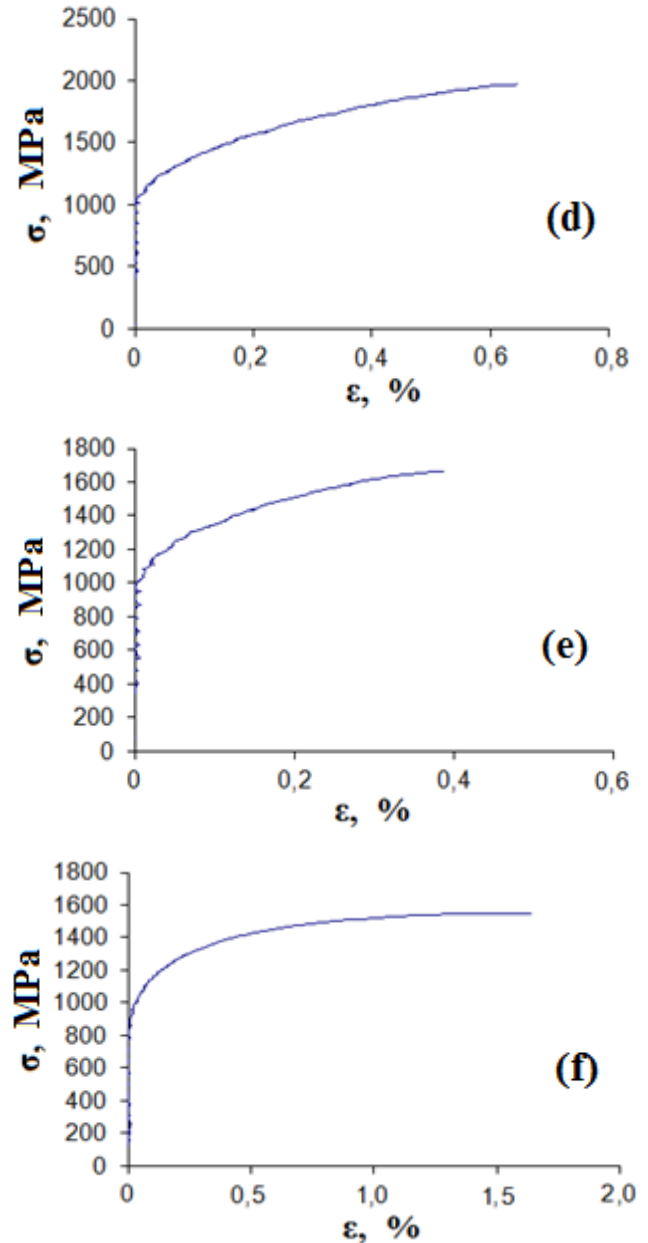
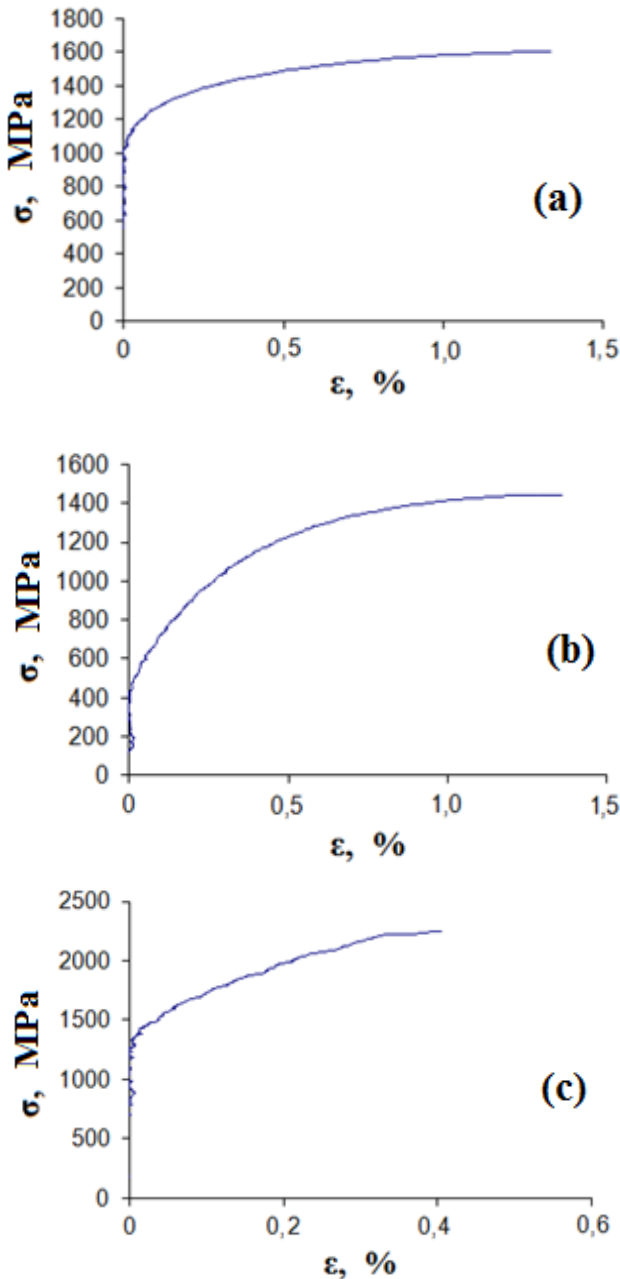
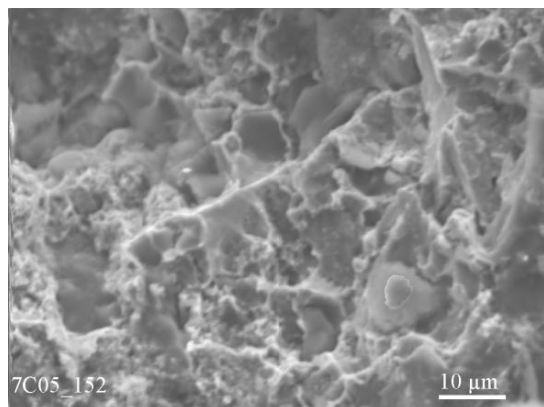


Fig. 1. "Stress-strain" diagrams of hot-forged alloy samples: TiCrFeNiCu (a), TiCrFeNiCuC (b) and TiCrFeNiC without annealing (c) and after annealing 1200 °C (d), 1250 °C (e), 1300 °C (f)

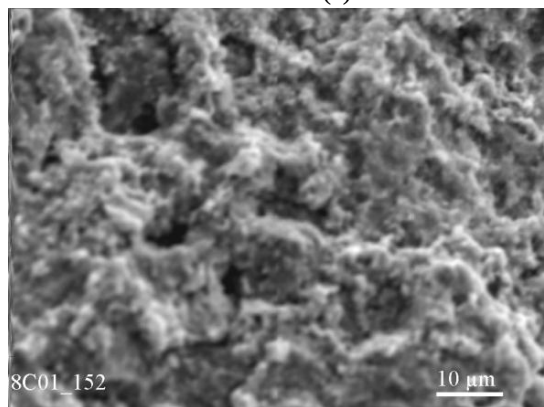
The nature of the curves indicates the microplasticity of all alloy samples, which is also confirmed by fractographic studies of fractures (Fig. 2). At the same annealing temperature (1200 °C), the plasticity of alloys containing Cu is ~ 2 times higher than that of alloys without Cu. In TiCrFeNiC alloys (Fig. 1 c, d, e), a microplastic deformation of up to 0,7% is observed, and only after annealing at 1300 °C, a deformation of 1,64% is observed in the sample (Fig. 1 f). This is explained by the fact that upon reaching the solidus temperature (1290 °C) a phase transition occurs in the alloy and the plasticity actually increases by 2-3 times compared to previous samples of the same composition, but is at a rather low level.

The hot-forged TiCrFeNiC alloy without annealing has the highest strength (Fig. 1 c) - more than 2 GPa. The high strength is due to solid-solution strengthening, as well as the formation of carbides in the synthesis process. The greater the curvature of the lattice due to the difference in the atomic radii of the elements, the better

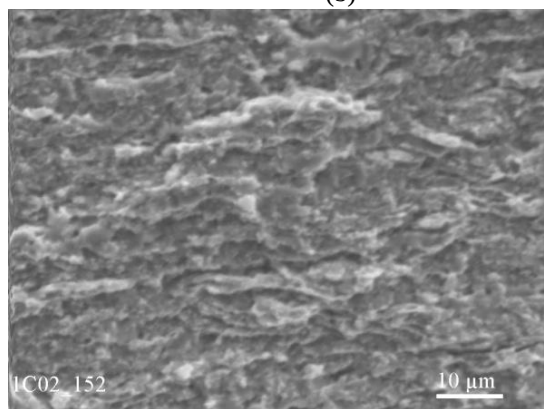
the mobility of dislocations is blocked and, thus, the deformation energy increases - the alloy has high strength.



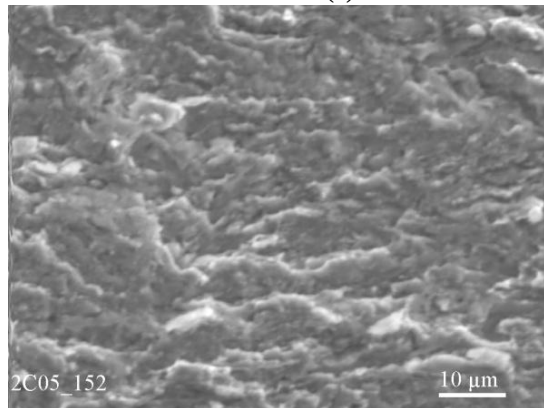
(a)



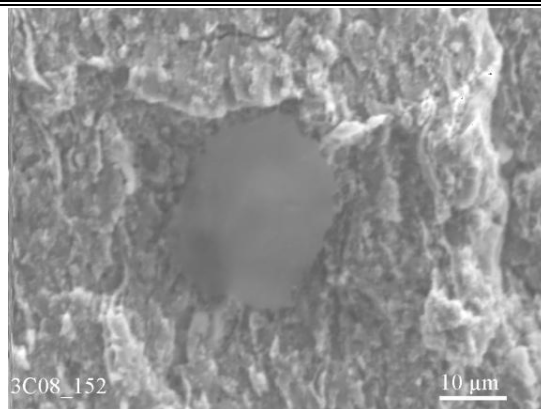
(b)



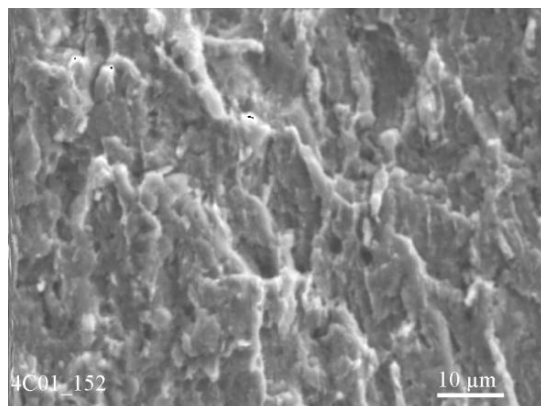
(c)



(d)



(e)



(f)

Fig. 2. Fractography of fracture surfaces of hot-forged alloys: *TiCrFeNiCu* (annealing 1200 °C, a); *TiCrFeNiCuC* (annealing 1200 °C, b); *TiCrFeNiC* (without annealing, c); *TiCrFeNiC* (annealing 1200 °C, d); *TiCrFeNiC* (annealing 1250 °C, e); *TiCrFeNiC* (annealing 1300 °C, f).

The destruction of samples of the *TiCrFeNiC* alloy is mostly quasi-brittle, as the beginnings of plastic deformation are visible on their fractures (Fig. 2 c-f). At the same time, the samples break transcrystalline, although a small number of open grain boundaries can be observed in the images, which indicates a certain percentage of intercrystalline fracture (Fig. 2 e). In general, as the annealing temperature increases, the plasticity of the *TiCrFeNiC* alloy increases, which can be explained by the relaxation of microstresses and the formation of new, more plastic phases in the alloy. In general, as the annealing temperature increases, the plasticity of the *TiCrFeNiC* alloy increases, which can be explained by the relaxation of microstresses and the formation of new, more plastic phases in the alloy. In the *TiCrFeNiCu* alloy, a mixed type of fracture is observed – both ductile and brittle (Fig. 2 a), the percentage of intercrystalline fracture is increasing. This can be explained by the localization of copper at the grain boundaries, as a result of which they weaken and open during destruction. Coarse-grained fracture characteristic of the *TiCrFeNiCuC* alloy is explained by the absence of a mechanical activation operation during its synthesis. It is also characterized by a mixed type of destruction, as shown in Fig. 2 (b). In the table 2 summarizes all the characteristics of the alloys obtained during the compression test.

Table 2: Mechanical properties of hot-forged alloys under uniaxial compression

Alloy	σ_{pr} , МПа	$\sigma_{0,2}$, МПа	σ_B , МПа	ε_{pl} , %
TiCrFeNiCu annealing 1200	1081	1357	1606	1,34
TiCrFeNiCuC annealing 1200	477	910	1443	1,36
TiCrFeNiC without annealing	1381	1978	2243	0,41
TiCrFeNiC annealing 1200	1081	1567	1971	0,65
TiCrFeNiC annealing 1250	1055	1507	1663	0,39
TiCrFeNiC annealing 1300	890	1266	1551	1,64

By the method of automatic indentation, the main mechanical characteristics of the obtained alloys were also determined and "load-unload" diagrams of the alloy samples were constructed in the coordinates P (load on the indenter) - h (depth of the indenter) (Fig. 3). The results obtained by this method differ from the previous results obtained by the compression method. This can be explained by the fact that these are different methods, but the trend is the same.

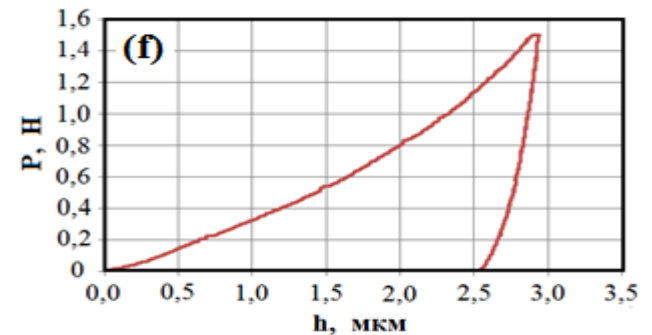
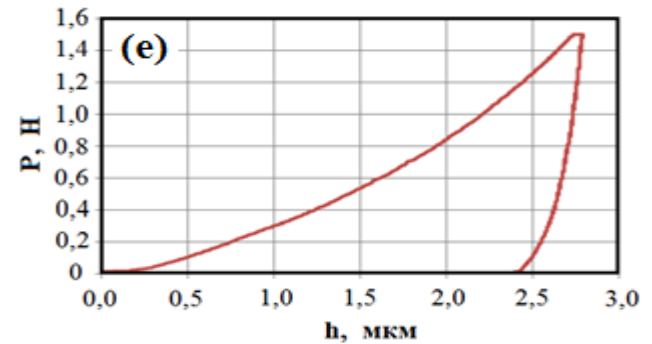
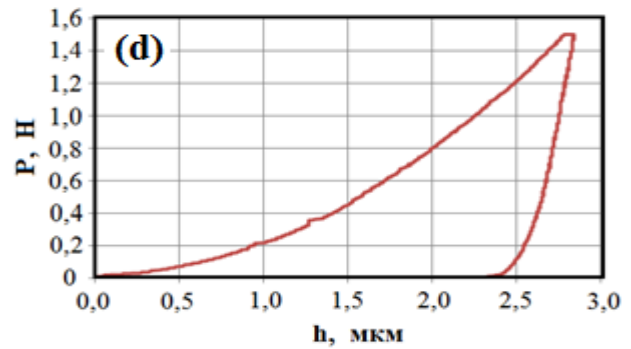
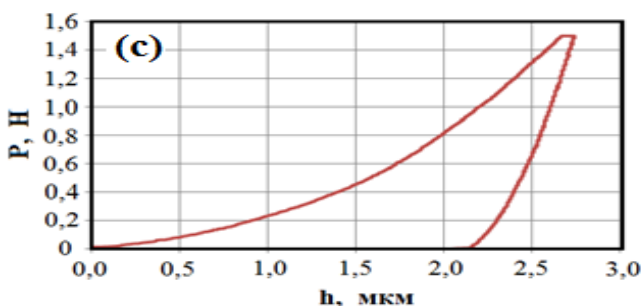
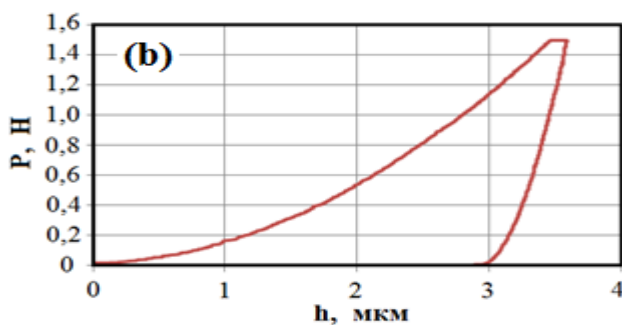
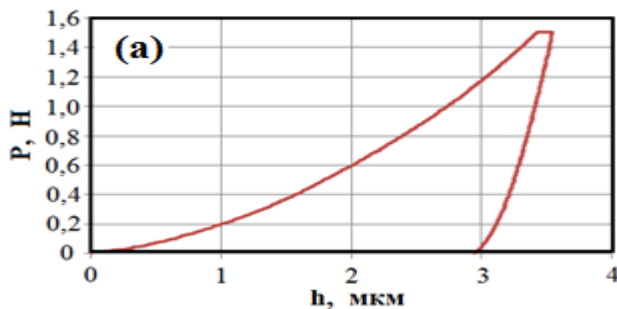


Fig. 3. Load-unload diagrams of hot-forged samples of TiCrFeNiCu (a), TiCrFeNiCuC (b) and TiCrFeNiC alloys without annealing (c) and after annealing at 1200 °C (d), 1250 °C (e), 1300 °C (f)

The diagrams of the TiCrFeNiCu alloy synthesized with PMA lasting 60 min and TiCrFeNiCuC (without PMA) are very similar to each other (Fig. 3 a, b), which indicates the similarity of their mechanical characteristics. Thus, the addition of carbon to the initial charge of the Ti-Cr-Fe-Ni-Cu system is equivalent to mechanical activation of this system (without carbon) lasting 60 minutes. The mechanical characteristics of the TiCrFeNiCu alloy (with PMA) are similar to the characteristics of the TiCrFeNiCuC alloy (without PMA) (Table 3). Therefore, in the TiCrFeNiCu alloy, high strength and hardness is achieved due to significant distortion of the crystal lattice in the PMA process, and in the TiCrFeNiCuC alloy - by in situ synthesis of carbides. In this case, the influence of these two factors on the mechanical properties is approximately the same.

Among all others, the TiCrFeNiC alloy has the best mechanical characteristics. It should be noted that its yield strength σ_s , calculated by this method, is more than 6 GPa, which is a very high indicator of the strength of the material. Its high hardness and strength compared to other synthesized alloys is primarily due to two factors - the effect of significant distortion of the crystal lattice and the synthesis of chromium and titanium carbides in situ. As the annealing temperature increases, the hardness, modulus of elasticity E , and conditional yield strength σ_s decrease

monotonically, which is also associated with the growth of grains in alloys. Instead, the plasticity characteristic δ_A increases, as evidenced by the increase in the angle of the sample unloading curve to the abscissa axis (Fig. 3, c, d, e, f).

Table 3: Mechanical characteristics of hot-forged HEAs, determined by the method of automatic indentation

Alloy	Thermo-mechanical treatment	HM, GPa	HV, GPa	σ_s , GPa	E, GPa	δ_A
1	HF 1050 Annealing 1200	5,90	5,46	2,47	187,8	0,88
2	HF 1100 Annealing 1200	5,78	5,35	2,83	177,2	0,82
3	HF 1100 Without annealing	13,6 7	12,6 5	6,80	317,2	0,81
	HF 1100 Annealing 1200	9,90	9,17	4,45	271,8	0,85
	HF 1100 Annealing 1250	9,84	9,11	4,43	254,3	0,85
	HF 1100 Annealing 1300	7,89	7,31	3,44	220,1	0,87

(1 – TiCrFeNiCu; 2 – TiCrFeNiCuC; 3 – TiCrFeNiC).

4. Conclusions

3 polycomponent equiatomic alloys – TiCrFeNiCu, TiCrFeNiCuC and TiCrFeNiC – were obtained in the process of hot forging. According to two methods, their main mechanical properties were determined and compared.

It was established that the mechanical properties of the TiCrFeNiCu alloy, which was produced with preliminary mechanical activation of the charge, similar to the mechanical properties of the TiCrFeNiCuC alloy (without PMA). This is due to the fact that in the TiCrFeNiCu alloy, high strength and hardness is achieved due to significant distortion of the crystal lattice in the PMA process, and in the TiCrFeNiCuC alloy - by in situ synthesis of carbides. In this case, the influence of these two factors on the mechanical properties is approximately the same.

The TiCrFeNiC alloy (without annealing) has the highest mechanical properties. Its high strength is due to solid-solution strengthening, as well as the formation of carbides in the synthesis process, plasticity is at a low level and is 0,41%. The presence of annealing and an increase in its temperature leads to a significant increase in plasticity from 0,41% to 1,64%. Fractographic studies show mostly quasi-brittle destruction of alloy samples.

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