

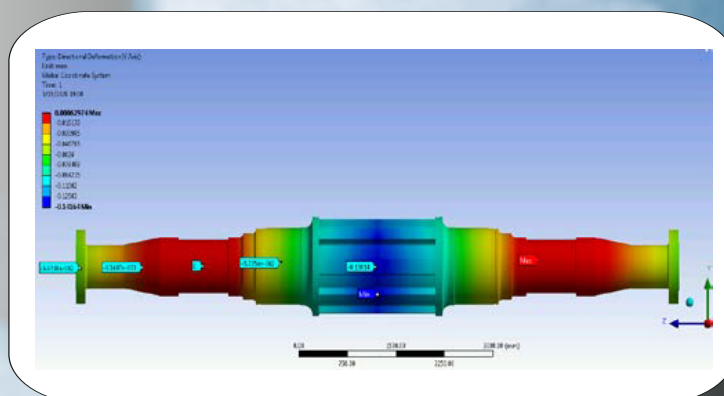
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EGR operated engines process water equipment operational safety procedure

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Abstract: In this publication the wash water subsystem features of an exhaust gas recirculation (EGR) system of marine diesel engine are considered. In regard with the safety of the operation, a procedure for handling the wash water system of the EGR is proposed. The chemical reactions between the flue gas and the process water are observed. The wash water system components and their specifics related to the chemical reactivity are presented. The problems with the water impurities, pH value and the operation of the EGR system are highlighted. The engineering crew special precautions on safety on using caustic soda on board is considered. Recommendations are proposed.

Keywords: EGR WASH WATER, CAUSTIC SODA, MARINE ENGINE EGR, EGR WASH WATER SAFETY PROCEDURE

1. Introduction

There are unusual circumstances for the engine operation with additional EGR. Chemical reactions force aggressive chemical impact on the metal surfaces in the EGR scrubber. Routine maintenances must be carried with special precautions from the operators view. The engineers used to the daily routines are not familiar with the new challenges of the aggressive chemicals as it is the caustic soda.

The aim in this publication is to be determined the weak points of the EGR process water system form operational point of view. The tasks related to the aim are concluded in a review of the specifics of the wash water system particulars and to suggest a safety procedure for the companies operating EGR systems concerning a safe and efficient operation of the EGR wash water system.

In this publication the intention is to underline the specifics of the physical and chemical properties of the caustic soda related to the personal safety of the personal on board. From other side it is important to be known the delicate behavior of the washing water chemical stability and ability to keep the system operational without to build up large deposits through the system.

Considering the specifics of the above stated a procedure with explanations of the importance of the described steps in it is proposed to be incorporated in the ship management companies SMS to obtain a reasonable and practical guide for the engineering department to safely handle the EGR wash water system.

2. The EGR wash water system components

The EGR wash water system has the following main components: scrubber unit with water spraying nozzles to the gas stack, process tank, circulation pump as main unit and water treatment system for the water quality conditioning shown on figure (1). The water treatment system contains a filtering unit and additional buffer tank not shown in the figure (1).

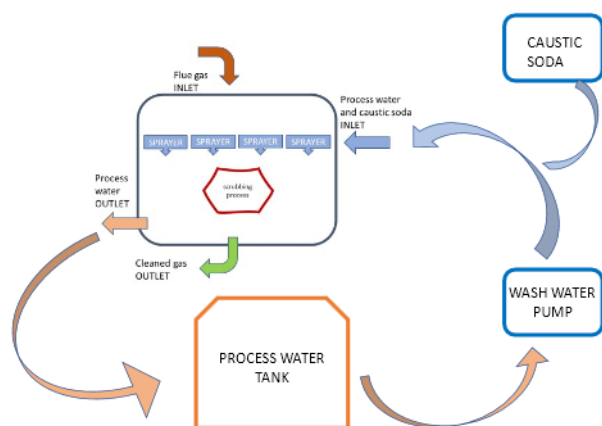


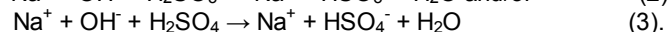
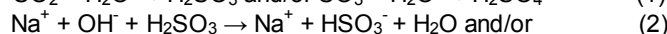
Fig. 1 EGR water washing system.

The EGR water washing system has basic function to neutralize the acidity of the flue gases returned to the engine scavenge system and to reduce the sulfur content, black carbon and particular matters. Proper operation of the cleaning system is a must for normal operation of the engine without contamination. Improper cleaning of the gases returned to the scavenge system will lead to contamination and probable failure of the engine.

EGR system operation failure means in most cases not compliant operation of the engine to the environmental requirements in force. There are several critical points which may lead the EGR system to shut down for short or long term, depending on the circumstances. Mode fluctuations and controller misalignment may lead to short stoppages of the system, but severe contamination and system components failure seems to lead to long term shut down. Further this condition may lead to extensive repair works, delays in the engine operation and profit losses. Material strength and durability is important for the reliability of the volume where the chemical neutralization is performed. The proper operation and maintenance of the EGR components are critical for increasing of the probability the system to fail. Related to the latter the operator's knowledge determines the safe operation.

3. The chemical reaction of the sulfur oxides and the salinity/alkalinity ingredients of the wash water

The wash water chemical composition changes with the process of the EGR operation due to the combustion products contamination. Not only the visible particles of ash and black carbon are inserted, but also the pH value is reduced as the interaction between the exhaust gas stack and the water continues. The sulfur oxides SO₂ and SO₃ reacts with the water and the injected caustic soda in the following manner [1]:



With the pH value varying and the reaction products build up in the system it can be reached level of the sulfites and sulfates to dissolve from the process water and to soft plug the pipelines and the process tanks [2]. The water cleaning system must be kept with special precautions in fit condition so to keep the ability of the water to be sprayed through the scrubber nozzles. If closed loop water system is used, the proper cleaning of the water is on vital importance for the system operation.

Depending on the approach, if sea water is used the process water must be refreshed to keep the salinity at reasonable range to keep the sulfates and sulfites solved. In case of fresh water, the chemical composition must be kept by proper dosing of caustic soda and freshwater addition, so to not to reach the saturation of the sulfates and sulfites and latter to precipitate and to plug the system lines. Meanwhile the reaction of the CO₂ with the water changes

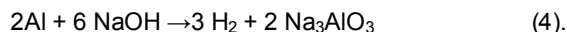
the pH value thus changing the tendency of the water to change its dilution properties to the sulfites and sulfates produced [3]. It is very important to keep continuously the pH at an optimum value to not to overlap the lower limit and to start soft contamination build up in the process water system.

The set-up of the pH control system must be fast reacting to changes in the process. The unreasonable addition of process water to restore the quality may become problematic in case of closed loop operation by filling up the process tank and the overflow tanks (if any). This process must be controlled carefully especially in case of long-term operation without to be possible the wash water to be discharged.

Depending on the fuel type and its sulfur content there may be divided two basic differences. The new fuels with low sulfur content up to 0,5% have lower impact on the required capacity of the EGR unit compared to the fuels with sulfur content up to 3,5%. This old fuels with high sulfur content have greater capacities of the scrubbers and higher demand on their performance due to the larger amount of sulfur oxides present. With the new low sulfur fuels and with the gaseous fuels with virtually no sulfur content, the scrubbing process is facilitated but still there is a need of special attention to be paid to the system performance.

4. *Caustic soda application on EGR gas cooling/cleaning system*

The application of the caustic soda in the marine engineering practice is not widely known. The recent requirements of the new EGR technology and the general sulfur oxides (SO_x) scrubbing applications have forced the need to use caustic soda in the everyday routines in the engine room. For safety reasons there must be underlined the hazard potential of the caustic soda to the human health and its aggressive nature to the surfaces which it gets in contact. Main milestones to be considered are the health hazards and its incompatibility with color metals as aluminum, magnesium, tin, and zinc with which the caustic soda forms flammable hydrogen [4, 5] The chemical reaction of the caustic soda with the metal is done as:



The physical properties of the caustic soda tend to be problematic with its appearance – clear colorless and odorless liquid just like the water. In case of spillage, it may be not recognized from first impression. Any spilled water looking liquid must be investigated with care. Mixing caustic soda and water in relatively comparable quantities is related with exothermal reaction. Diluting caustic soda with water may become problematic. Before any mixing of caustic soda and water all the precautions must be taken to face the potential hazards of the heat release.

Depending on the solution percentage, the commonly commercially used 50% solution with water has freezing temperature at 12 °C. This temperature is relatively high and in the range of the temperatures seen in the engine room, especially in winter conditions. For that reason, proper heating arrangements must be used to keep the tanks and pipelines for the caustic soda at warm condition and in no case, they may be left non-operational.

In case of caustic soda leakage, it can be very dangerous given its toxicity and corrosive nature. Once exposed to air the chemical will begin to crystalize forming into a white scale. When pumping caustic soda its primary leak paths are flange gaskets and mechanical seals. When caustic crystalizes on a mechanical seal its abrasive crystals and corrosive properties damage the seal face increasing the potential for increased leakage. This leads to frequent mechanical seal maintenance [7]. Gasket materials for general use are not suitable to handle caustic soda. Acceptable performance with sealing this liquid has the Teflon material. In no

circumstances the Teflon may be replaced by general purpose gasket material.

5. *Construction materials for pipelines and scrubber unit*

Conventional materials as carbon steel or color metals are not suitable when handling aggressive chemicals as the caustic soda. Known from the chemical industry the stainless steels are suitable to be used for construction material of the wash water system.

Usually, the pipeline material is stainless steel but for the scrubber body it must be used more specific material as it is the duplex stainless steel. Duplex stainless steel gets their name from the fact that they contain both a ferritic and austenitic microstructure. They have a relatively high chromium content of between 18 and 28%. Nickel content is moderate at 4.5 to 8%. At this level, the nickel content is too low to generate a fully austenitic structure. This results in a duplex microstructure containing both ferritic and austenitic phases. Duplex stainless steel also tends to contain 2.54% molybdenum [8]. The prime advantage of duplex stainless steel is the combination of properties derived from both austenitic and ferritic stainless steel.

Duplex stainless steel has: Excellent corrosion resistance; Increased resistance to chloride attack; Good resistance to stress corrosion cracking; Tensile and yield strength higher than austenitic or ferritic grades; Good weldability; Good formability [8, 9]. Fabrication and repair works of all stainless steel should be done only with tools dedicated to stainless steel materials. Tooling and work surfaces must be thoroughly cleaned before use. These precautions are necessary to avoid cross contamination of stainless steel by easily corroded metals that may discolor the surface of the fabricated product [10]. Further it may result in intensive corrosion process. Proper washing of the surfaces from residual caustic soda is critical to be done before maintenance to be carried out.

6. *Safety procedure proposal to the ship management companies*

Respecting the problems considered in this publication, related to the chemical reactivity it may be stated a basic instruction for proper actions when handling the EGR wash water system as follows:

- Strictly follow the chemical composition of the wash water content. If marginal condition of frequent sediment builds up in the system occurs, consider readjustment of the process controlling the wash water refreshment or caustic soda addition.
- Handle with care the system for caustic soda storage and transfer. Avoid use of colored metals in the system pipelines and gasket material different than Teflon, especially during repairs.
- Metal surfaces of the scrubber/cooler keep with great care to avoid metal contamination and rapid corrosion.
- Use proper PPE when handling the caustic soda. Especially when working within the units flush the surfaces thoroughly before any action to be carried out.
- Keep caustic soda heated up above freezing temperature (relatively high). If for prolonged period the system to be out of operation, flush the system pipelines with water.

Conclusions:

The task in this publication was accomplished in respect to be created general safety procedure while handling EGR wash water systems, related to the subjects investigated in the present study. The background of the simple tasks to be performed was detailed with the nature of the problems which may occur, while working with the EGR wash water system. The following features remain due to be considered by the ship operators:

- The wash water system of the EGR requires additional special attention related to the safety of the crew.
- There are specifics in the chemical reactivity of the caustic soda which are to be considered by the engineering crew while handling the EGR system.
- System repairs with exchange of different components must be done only with respect of the proper material intended to use.
- Metal contamination of the stainless-steel material may lead to fast corrosion process and component failure.

7. References

1. Jingjing Liu, Sheng Fang, Qiming Bing, Fu-Ming Tao, Jing-yao Liu, *Theoretical study of the auto-catalyzed hydrolysis reaction of sulfur dioxide*, Computational and Theoretical Chemistry, **Volume 1076**, (2016), Pages 11-16
2. Calvin R. Nicholson, "pH Measurement and Installation Guidelines for SO₂ Scrubbers", Electric Utility and Co-Generation Congress, Houston, TX (1992)
3. Graeme Puxty, Steven Chiao-Chien Wei, Paul Feron, Erik Meuleman, Yaser Beyad, Robert Burns, Marcel Maeder, *A Novel Process Concept for the Capture of CO₂ and SO₂ Using a Single Solvent and Column*, Energy Procedia, **Volume 63**, (2014), Pages 703-714
4. OxyChem, *Caustic Soda Handbook*, Occidental Chemical Corporation (OxyChem) Basic Chemicals Group Occidental Tower 5005 LBJ Freeway Dallas, TX, (2009)
5. *Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic) Storage Equipment and Piping Systems*, **Edition 4**, The Chlorine Institute, (2012)
6. *Sodium hydroxide solutions (more than 10% NaOH)* Material safety data sheet, (2001)
7. Iwaki Amerika, *Solving Caustic Soda Crystallization Issues on Mechanical Seals*, online publication, (2020)
8. Davies. Michael, *Alloy selection for service in caustic soda, A guide to the use of nickel-containing alloys*, **Second Edition** (2019)
9. Thyssenkrupp Materials (UK) Ltd, Stainless Steel 1.4301 – 304, Material Data Sheet
10. Aalco Metals Limited, Stainless Steel LDX 2101, Material data sheet, (2019)

Analytical and numerical analysis of shafts' stress and strain states of the hydro-power unit

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Abstract: The paper presents both the analytical and numerical procedure for the analysis of the stress and strain states of the hydropower unit of the hydropower plant. Numerical analysis allows a comprehensive view of the states of stress and strain of the observed shaft. The analytical procedure is very difficult to apply to structural elements with complex geometry such as the shaft of a hydropower unit. Analytical analysis of stress and strain states serves to test only some of the results obtained on the basis of numerical analysis. A comparative analysis of stress and deflection values was performed on some characteristic shaft cross sections. Analytical determination of deflection, due to the complexity of the shaft construction, was performed on the basis of Mohr's graph - analytical procedure. The numerical procedure is based on the application of the finite element method. The obtained results confirm the extremely good match of the results obtained by analytical and numerical procedures. Within the numerical analysis based on the given load and boundary conditions, ie. on the basis of the formed computational model of the shaft, the analysis of stress and strain, and displacement, was performed. The analysis of both normal and tangential stresses, as well as equivalent stresses according to the Von-Mises criterion, was performed. The places of maximum stresses are located. Therefore, it is concluded that the numerical analysis of the stress and strain state will give quality results if the computational model is well formed. This means that it is necessary to take into account all the discontinuities in the geometry of the shaft, which is characterized by a variable cross section. Certainly, there is no need to apply a very, very demanding analytical procedure for integrating the differential equation of an elastic line or a procedure based on Mohr's graph - analytical procedure when calculating the shaft.

Keywords: STRESS AND STRAIN STATE, STRESS STATE ANALYSIS, STRAIN STATE ANALYSIS, HYDROPOWER PLANT SHAFT ANALYSIS

1. Introduction

Structural parts of the hydropower plant in which the conversion of potential and kinetic energy of water into electricity is performed are hydraulic turbines, shafts and generators. Together they form a structural unit called a hydro-aggregate. Depending on the type, size and mode of operation of the hydropower plant, the selection of the mentioned structural elements is made. The degree of energy utilization that accumulates largely depends on their maintenance, both regular and periodic. Also the revitalization of hydro power units after a certain time in operation is of great importance.

Observed hydro power turbines used to transform the potential energy of water into kinetic energy are Pelton turbines. Two impellers and one generator are screwed to the hydro turbine shaft. Simplified, it is a beam with two overhangs, whose geometric representation with basic dimensions is given in Fig. 1. The shaft has a rectilinear geometric axis with a total weight of approximately 42.700 kg.

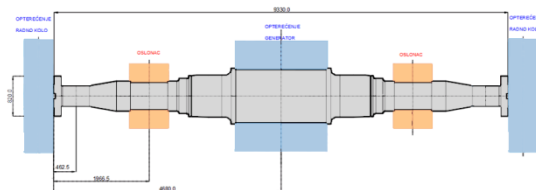


Fig. 1 Simplified drawing of the analyzed shaft.(blue - loadings, red - supports)

Basic characteristics of the hydropower plant's impeller are given in the Table 1.

Table 1: Basic characteristics of the hydropower plant's impeller

Turbine type	Pelton
Maximum drop [m]	537.20
Calculated drop [m]	508
Minimal drop [m]	506
Weight of the impeller [kg]	cca 7500
Turbine power in calc. drop [MW]	58.5
Diameter of the impeller [mm]	2710
Number of impeller blades	18
Rotational speed [rot/min]	428.5

Based on the analytical calculation, the shaft deflections and stress values were calculated in order to support the numerical procedure of shafts behavior diagnostics in order to check and compare the obtained results with the results obtained using the finite element method.

It is almost impossible to analyze a shaft of variable cross sections, such as a shaft of a hydro aggregate, based on the integration of the differential equation of the elastic line of the shaft. The differential equation of the elastic line is easier to solve using Mohr's graph-analytic method. Also, the stresses on individual shaft sections will be calculated.

2. Analytical calculation method

For more precise calculation, the shaft is divided into nine segments which are shown in the calculation drawing of the shaft given in Figure 2. Table 2 shows the values of forces acting on the shaft, and is shown in Figure 2. Due to symmetry with respect to the y axis only the first five forces are shown, as well as the forces acting due to the weights of the impellers and generators, and the reactive forces. Some of the basic technical characteristics together with the intensities of forces that replace the weight of the shaft by segments are given in Table 3.

Table 2. Forces that act upon the shaft

Loading forces of the shaft [kN]						
G _I	G _{II}	G _{III}	G _{IV}	G _V	G _T	G _G
8.55	34.42	21.62	76.35	136.87	73.57	1275.3

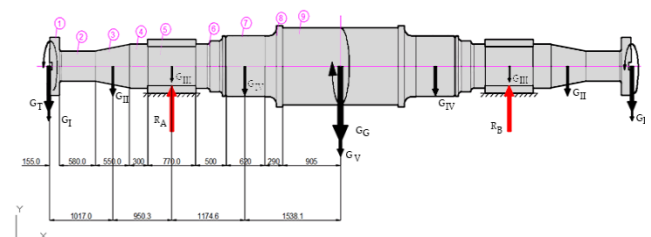


Fig. 2 Calculation drawing of the shaft

The weight of the impellers located at the ends of the shafts are 7.500 kg, while the weight of 130.000 kg was taken as the approximate weight of the generator rotor. Load values in the form

of twisting moments are: 1.30 kNm at the turbine impeller locations (shaft ends) and 2.60 kNm at the generator location (shaft center).

Table 3. Basic geometric characteristics of the shaft through shafts segments

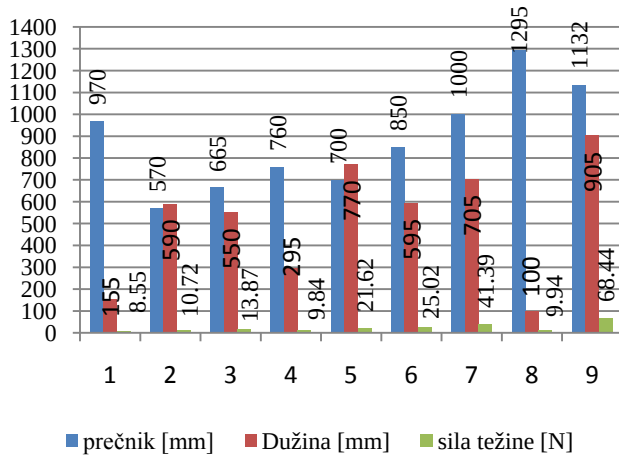


Table 4 [1] gives the necessary data for the calculation of the shaft of variable cross section by segments given in Figure 2.

Table 4. Values of axial moment of inertia, reduction coefficients and product EI_x

Segm.	Axial moment of inertia I_x [m ⁴]	Reduction coefficient	Product EI_x
1	0.04341	8.42	8681968
2	0.00515	1.00	1030840
3	0.00957	1.86	1913994
4	0.01634	3.17	3268696
5	0.01176	2.28	2351014
6	0.02559	4.96	5117219
7	0.04904	9.51	9807532
8	0.13796	26.77	27591834
9	0.08054	15.63	16107623

The sliding bearings A and B of the shaft allow rotation about the longitudinal z axis of the shaft, and all other movements and rotations of the shaft are prevented. Based on the above, the starting shaft can be separated into units: two consoles at the ends and a clamped beam in the middle of the shaft (Figure 3).

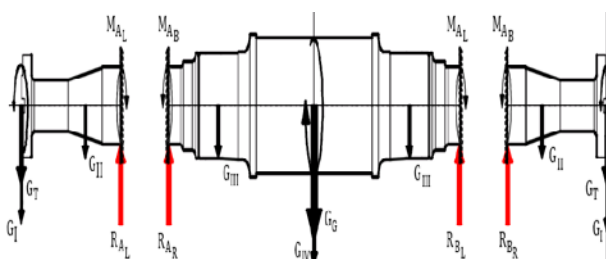


Fig. 3 Shaft divided on wholes

In order to verify the results based on the analytical procedure with the results obtained based on the numerical (FEM) procedure, the following will be calculated:

- deflection at the end of the shaft, ie. deflection at the end of the bracket in the variant of the split shaft (Fig. 4)
- normal bending stress at the clamping point of the bracket.

Deflection of the shaft at the end of the console calculus

The differential equation of the elastic line of the beam for the case that the beam is of variable cross-section, due to the bending of the beam, as is the case with the shaft of the hydraulic unit is:

$$E I_x(z) y'' = -M_{sx}(z), \quad (1)$$

or

$$E I_{x,min} i(z) y'' = -M_{sx}(z), \quad (2)$$

where

$$I_x(z) = I_{x,min} i(z),$$

where $I_{x,min}$ is the smallest axial moment of inertia of the beam (shaft) of variable cross section. The coefficient $i(z) \geq 1$ is called the bending moment reduction coefficient. Equation (2) by introducing the reduction coefficient takes the form:

$$E I_{x,min} y'' = \frac{M_{sx}(z)}{i(z)} = M_{s,red}(z),$$

where $M_{s,red}(z)$ is the reduced bending moment. The problem of determining the deflection and inclination of the beam (shaft) of variable cross section is now reduced to determining the deflection and inclination of the beam of constant cross section of the minimum moment of inertia, but instead of the actual bending moment $M_{sx}(z)$ should use a reduced bending moment $M_{s,red}(z)$, which is obtained when the actual bending moment is reduced, ie. reduce and (z) times. In the case of beams, of the so-called stepwise cross-sections such as the shaft of the hydro aggregate for determining the deflection and slope is most often used Mohr's graph-analytical method [2]. It is known from the theory of bending of beams that:

$$\frac{d^2 M_s(z)}{dz^2} = \frac{dF_T(z)}{dz} = -q(z), \quad (3)$$

where $q = q(z)$ is the continuous load of the beam. When $q = q(z)$ one time integrals we get $F_T(z)$, and when $F_T(z)$ integrals we get $M_s(z)$. It is much more efficient to do these integrations graphically, rather than analytically, by drawing diagrams of the transverse force and the bending moment.

The differential equation of the elastic line of the beam, as already mentioned, can be written in the form:

$$\frac{d^2}{dz^2} (EI_x y) = -M_{s,red}(z), \quad (4)$$

Observing equations (3) and (4) at the same time, it can be stated as follows. If $M_{s,red}(z)$ is understood as a continuous-fictitious load of the beam (shaft), then by drawing a diagram of the fictitious transverse force $F = F(z)$, we obtain the slope $y'(z) = \frac{F(z)}{EI_x}$. When a diagram of the fictitious bending moment $M = M(z)$ is drawn, then the deflection of the real support $y(z) = \frac{M(z)}{EI_x}$ can be determined. In this way, we essentially solved the differential equation graphically:

$$\frac{d^4}{dz^2} (EI_x y) = q(z),$$

ie. determined the deflection $y(z)$ based on the real load $q(z)$. From the expression for the deflection and inclination of the beam girder, it is clear that the dimension of the fictitious force is kNm^2 , and the fictitious moment is kNm^3 .

When applying the Mohr graph-analytical method, a fictitious beam must be observed instead of a real beam (shaft) (Figure 4). A fictitious beam must satisfy the boundary conditions.

At the point of clamping the console, ie. of the real beam girder, the deflection and inclination are equal to zero, and at the free end of the console the deflection and inclination are nonzero. From equations (3) and (4) it can be concluded that at the place where the deflection and the inclination are equal to zero, in the case of a fictitious beam the transverse force and the bending moment must be equal to zero. Similarly, in the place of a real beam where the deflection and the inclination are different from zero, the fictitious bending moment and the fictitious transverse force must be different from zero, i. in the case of a fictitious console, there must be a clamp (Fig. 4)

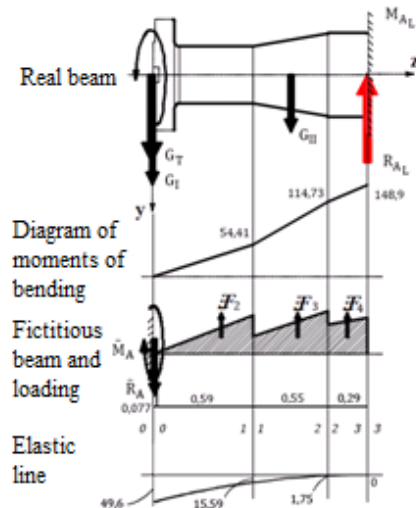


Fig. 4 Diagrams of the bending moments, fictitious loads and elastic line of the beam

The obtained values for both deflections (elastic line) and values of normal stresses will be used for comparison with the results obtained by numerical analysis.

3. Numerical calculation based on the FEM

- **Calculation of the displacement**

The subject of the analysis of displacement using the finite element method is a shaft loaded with a combined stress. The shaft is loaded to bend around the axis transverse under the action of the shaft weight. Also, it is loaded on twisting under the action of twisting moments that act along the axis of the shaft. This analysis should answer the question of which areas are critical from the aspect of shaft displacement that is exposed to complex and combined stresses. By looking at the obtained results, it will be known in which sections the maximum deflections occur under the influence of the previously mentioned loads.

Loads and boundary conditions are given in Figure 5. Two sliding bearings shown in Figure 3 and marked with the letter A (purple) appear as supports. Only rotations about the z-axis (longitudinal) are allowed in the supports. Loads are marked in red and marked with letters B to J.

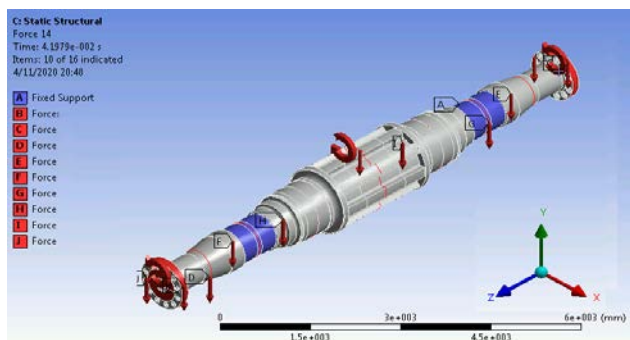


Fig 5. Calculation model of the shaft with the supports and loads

- Values of the displacements

The results of the numerical analysis are given as follows. The values of deflection in the y-axis direction can be seen in Figure 6. The characteristic values of deflection are given in the cross sections in which the forces act.

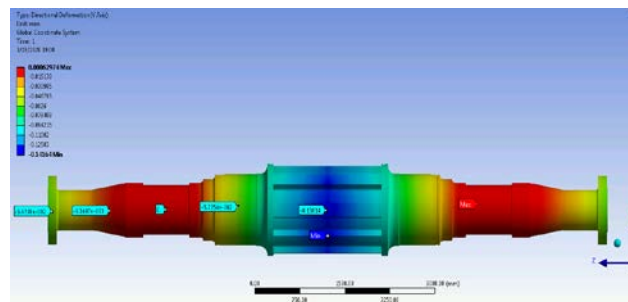


Fig. 6 Values of the deflection in the direction of y axis

The maximum value of the displacement in the y-axis direction under the action of forces that replace the masses of individual shaft segments, therefore, under the action of the shaft's own weight, is 0.142 mm. The curve of the deflection of the axis under the gravity of the shaft with the maximum and minimum values is given in Figure 7.

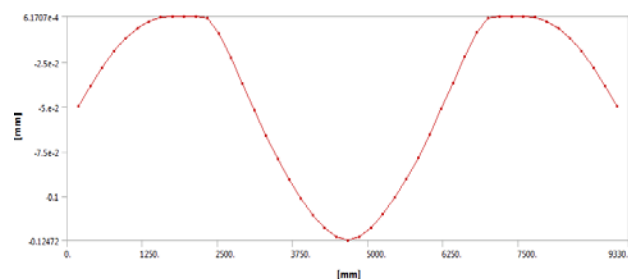


Fig 7. Values of the deflection in the direction of y axis for the axis of the shaft which passes through the xy plane of symmetry of the shaft

It can be seen in the diagram that the deflection values are equal to zero at the bearing locations, while the largest negative values, due to the orientation of the y axis, are at the points of action of external loads in the form of generators and impellers.

- **Calculation of the stresses**

On the basis of numerical methods of research of the shaft stress state, it is possible to consider the shaft stress state as a part of hydro aggregates with greater accuracy and comprehensiveness in relation to analytical methods. With power transmissions, and especially with shafts, stress concentrations occur at the geometry discontinuity points. Cracks can often occur in these places, leading to loss of shaft function[3],[4],[5].

The stress state of the shaft, which is loaded by forces in the direction of the axis perpendicular to the shaft axis, and moments in the direction of the longitudinal axis of the shaft, is predominantly manifested by normal stress in the z direction of the σ_z axis, and tangential stresses τ_{zy} and τ_{zx} .

Figure 8 shows the state of normal stresses in the direction of the longitudinal z axis. Stresses in sections in which the forces of gravity of the segments by which the shaft is divided are separated. As can be seen in Figure 8, the value of the maximum stresses is 95 MPa much lower than the value of the allowable stress for the material from which the shaft is made (Steel with maximum allowed stress of 470 MPa).

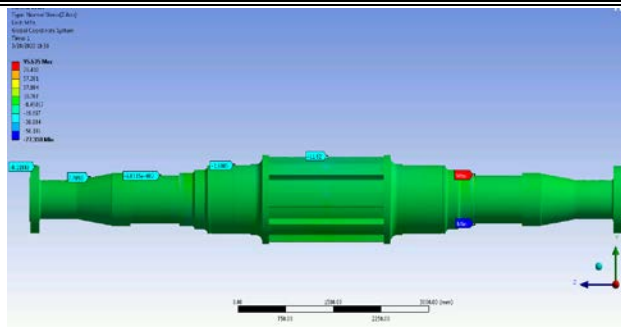


Fig 8. Normal stresses in the direction of the z axis of the shaft

Tangential stresses are predominantly caused by torsion moments acting on the shaft ends and in the middle of the shaft. Figure 9 and Figure 10 show the tangential stresses in the yz plane, i. τ_{zy} i τ_{zx} . It can also be seen, as in the case of normal stresses, that the values are much less than allowed, so it can be concluded that there is no risk of indications on the shaft due to static load.

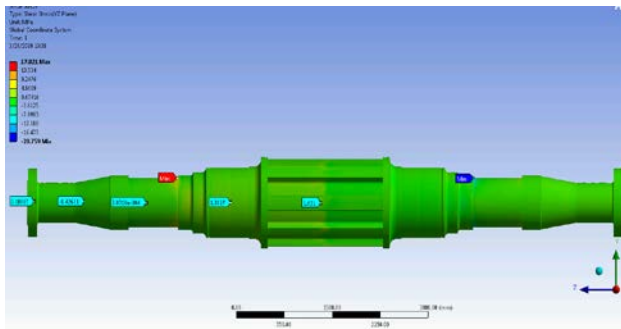


Fig 9. Tangential stresses τ_{zy} in the plane of the z axis of the shaft

Maximum (and minimum) stress values appear in the support zones, while in the cross sections where the forces (moments) act, stress values appear that are largely in the safe zone of elasticity.

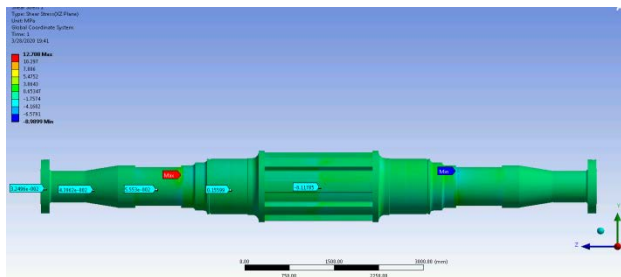


Fig 10. Tangential stresses τ_{zx} in the plane of the z axis of the shaft

Figure 11 shows the equivalent stresses calculated using Von-Mises - this criterion for calculating stresses at combined stresses. In this case, too, the numerical value of the maximum stresses is significantly below the limit value of the allowable stresses. Figure 12 shows the position of the maximum stresses, which corresponds to the position of the shaft bearing.

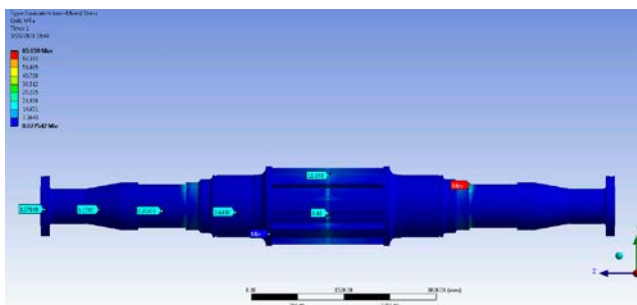


Fig 11. Illustration of the equivalent stresses (Von - Mises criterion)

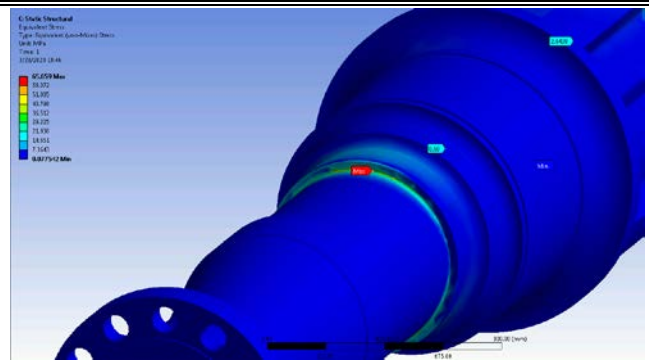


Fig 12. Position of the maximum equivalent stresses (shafts bearing position)

4. Conclusion

Based on the analytical and numerical (FEM) diagnostics of shaft behavior from the aspect of static load, the following can be stated:

- numeric values for deflection at the end of the shaft due to bending in the vertical plane were obtained,
- numeric values of normal stresses at the end of the shaft due to bending in the vertical plane were obtained (section 3-3, Figure 4),
- numeric values of normal stresses due to bending in the vertical plane were obtained (section 1-1, Figure 4).

The mentioned numeric values are compared and presented in Table 5.

Table 5. Comparative values of analytical and numerical shaft calculation

	Deflection [mm]	Normal stresses σ [MPa] (section 3-3)	Normal stresses σ [MPa] (section 1-1)
Analytical calculation	0.049	3.40	3.01
Numerical calculation	0.049	3.25	3.24

It can be concluded that the stresses, including the Von Mises stresses are evenly distributed along the entire shaft. The stress values, given in Table 5, refer to sections 1-1 and 3-3 from Figure 4. It is clear that they, as well as the stress values along the entire shaft, are well below the maximum stresses from the point of view of strength.

A similar conclusion can be drawn for the values of displacement in the direction of the y-axis (deflection). In the analytical calculation, the maximum value of deflection of 0.049 mm at the end of the shaft was obtained, which was confirmed by numerical analysis.

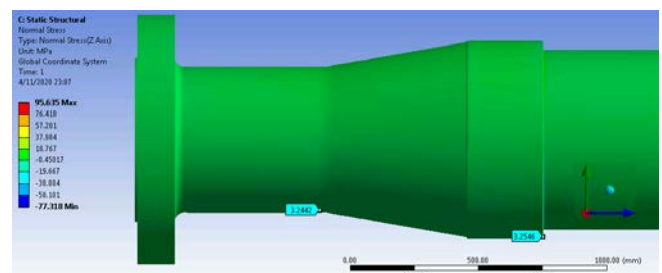


Fig 13. Values of the normal stresses in the sections 1-1 and 3-3

Dynamic analysis of the behaviour of the shaft is also very interesting problem which is not presented in this paper, but is a part of a wider research which is included in the reference [6].

5. References

- [1] Katedra za otpornost konstrukcija: "Tablice iz Otpornosti materijala", Mašinski fakultet, Univerzitet u Beogradu, 2015.,
- [2] Pejović R., Otpornost materijala, Građevinski fakultet, Univerzitet Crne gore, 2015.,
- [3] Bachschmid N, Cracked Rotors - A survey on static and dynamic behaviour including modeling and diagnosis, Springer, pp 1-13, 2010.,
- [4] Vullo, V., Vivio, F., Rotors Stress Analysis and Design, Mechanical Engineering Series, Springer, pp. 205, 2013.,
- [5] Ishida, Y., Cracked Rotors: Industrial machine case histories and nonlinear effects shown by simple Jeffcot rotor, Mechanical systems and signal processing 22(4), pp. 805-817, 2008.,
- [6] Čulafić, S., Numeričko-eksperimentalna analiza čvrstoće strukturnih elemenata hidroelektrane, doktorska disertacija, Mašinski fakultet, Univerzitet u Beogradu, 2021

Kinetic and equilibrium study of the CO₂ adsorption on activated carbon

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Abstract: The presented research are concerned with the modelling of isotherms and chemical kinetics of mass transport for the CO₂ adsorption on activated carbon, taking place in the fluidized and fixed bed. To determine the nature of CO₂ binding under low-pressure conditions, adsorption complex and thermodynamic effects occurring during the process, four isothermal models were used: Langmuir, Freundlich, Temkin and Halsey. The evaluation of the factors affecting the course and rate of CO₂ binding was based on four kinetic models, i.e. pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion (IPD) and the Elovich model. The validation of mathematical models showed that the linearized Freundlich and Halsey isotherms models are best suited to empirical data. In the case of process kinetics, the analysis showed that the non-linearized pseudo-first-order model (PFO) proved to be unrivalled in fitting to experimental data. The comparison of two types of tested beds suggested faster kinetics for a fluidized bed, while a larger amount of CO₂ at equilibrium was adsorbed by the fixed bed.

KEYWORDS: ISOTHERMS, THERMODYNAMICS, KINETICS, MATHEMATICAL MODELING, COMPARISON OF LINEAR AND NON-LINEAR EQUATIONS

1. Introduction

The energy sector based on non-renewable energy sources, together with the associated global climate threat (greenhouse effect), the main causative factor of which is high carbon dioxide emissions to the atmosphere, searches for technologies enabling its reduction the most urgent goal in many industries [1, 2]. The adsorption process, against the background of the above issues, is quickly gaining popularity and is now widely used as a separation technique due to the potentially low energy consumption, increased CO₂ carrying capacity, minimal pressure drop and playing a large role in the future flexibility of the energy system. As a result, in the field of developing CO₂ adsorption technology, new materials with an extensive porous structure are searched for and a method of modifying those already available [3]. According to the literature, the most promising materials for CO₂ separation are activated carbons, and the amount of adsorbed gas depends on the porous structure, the properties of the chemical structure of their surface [3, 4]. Their performance can be determined based on the isotherms, which define the equilibrium state as a function of adsorbate pressure, and adsorption kinetics, which describe the amount of adsorbed gas as a function of time, until the equilibrium state is reached [3]. Therefore, the mathematical description seems to be an effective method of predicting the behaviour of given materials under various conditions, which is important for the effective design of adsorption systems as well as the scaling and optimization of the process.

2. Preconditions and means for resolving the problem

2.1. Review of mathematical models of the adsorption isotherms

Langmuir model

The equation given in 1916 by Langmuir presents an extremely accurate model of monolayer adsorption on a homogeneous (energetically homogeneous) microporous surface. The nonlinear equation of the Langmuir isotherm model takes the following form [5]:

$$q_e = q_m \frac{K_L \cdot P}{(1 + K_L \cdot P)} \quad (1)$$

where, q_e - amount of adsorbed substance at equilibrium per 1 gram of adsorbent [mg/g], q_m - maximum adsorption value [mol/g], K_L - equilibrium constant of adsorption, P - relative pressure of the adsorbate [Pa].

Freundlich model

The Freundlich isotherm model is the first and the best known empirical equation that describes the non-ideal, reversible process of monolayer and multilayer adsorption on the surfaces of

heterogeneous microporous adsorbents [6]. The equation of the Freundlich model in the nonlinear form takes the following form [6]:

$$q_e = K_F \cdot P^{\frac{1}{n_F}} \quad (2)$$

where: K_F - the empirical constant of the Freundlich isotherm related to the adsorbent capacity, P - relative pressure of the adsorbate [Pa], n_F - constant related to the affinity of the adsorbate to the adsorbent.

Temkin model

The Temkin model from 1940 is an experimental isotherm equation describing adsorption on a heterogeneous surface of a solid, taking into account the interaction between the adsorption complex, in which it ignores the exceptionally high and low values of the relative pressure of the adsorbate [6]. The equation of Temkin model in a non-linearized form takes the following form [6]:

$$q_e = B \cdot \ln(K_T \cdot P) \quad (3)$$

where: B - Temkin constant [-], K_T - equilibrium constant of adsorption [1/Pa], P - relative pressure of the adsorbate [Pa].

Halsey model

The Halsey isotherm model, similarly to the Freundlich model applies to the description of adsorption on heterogeneous adsorbent surfaces on which the heat of adsorption is distributed unevenly. However, in contrast to it [6], the authors of this work only characterize multilayer adsorption at a relatively large distance from the surface of the solid. The Halsey model equation in non-linearized form is represented as [6]:

$$q_e = e^{\frac{\ln(K_H) - \ln(P)}{n_H}} \quad (4)$$

where: K_H - equilibrium constant of adsorption [1/Pa], P - relative pressure of the adsorbate [Pa], n_H - Halsey model constant [-].

2.2. Review of mathematical models of adsorption kinetics

Pseudo-first-order model (PFO)

In 1898 the kinetic equation of the pseudo-first order model (PFO) was introduced by Lagergren. Of all the kinetic models, the PFO model is the simplest to describe the adsorption kinetics and adsorbent interactions, i.e. it can characterize the reversible interaction between the adsorbent and the adsorbate, which is more suitable for predicting the physisorption behaviour [7]. In differential form, the PFO model equation is determined as follows [7]:

$$\frac{dq(t)}{dt} = k_1 \cdot [q_e - q(t)] \quad (5)$$

where: t - time [min], $q(t)$ - the amount of adsorbed adsorbate by the adsorbent mass as a function of time [mg/g], q_e - value of q in the state of adsorption equilibrium [mg/g], k_1 - pseudo-first-order constant [g/(mg·min)].

Pseudo-second order model (PSO)

The kinetic pseudo-second-order (PSO) was proposed in 1995 by Ho. According to the PSO model, the adsorbate-adsorbent complex is caused by strong bonds, ensuring its better fit with the experimental data, when the adsorption process involves chemical bond interactions (chemisorption) [8]. In differential form, the above model is presented as follows [8, 9]:

$$\frac{dq(t)}{dt} = k_2 \cdot [q_e - q(t)]^2 \quad (6)$$

where: t - time [min], $q(t)$ - the amount of adsorbed adsorbate by the adsorbent mass as a function of time [mg/g], q_e - value of q in the state of adsorption equilibrium [mg/g], k_2 - pseudo-second-order rate constant [g/(mg·min)].

Intraparticle diffusion model (IPD)

In 1962, the intramolecular diffusion (IPD) model was developed by Weber and Morris based on Fick's second law. The main application of this model is to identify the next steps in the process mechanism, i.e. mass transfer during the adsorption process [10]. The IPD model is defined as the following linear equation [10]:

$$q(t) = k_i \cdot t^{\frac{1}{2}} + c_i \quad (7)$$

where: t - time [min], k_i - intraparticle diffusion constant [mg/(g·min^{1/2})], c_i - direct constant proportional to the thickness of the boundary layer [mg/g].

Elovich model

The Elovich kinetic model assumes that the real surface of the solid adsorbent is energetically heterogeneous, otherwise, it describes chemical adsorption on inhomogeneous surfaces. Therefore, it is often used to interpret the kinetics of second-order reactions [11], confirming the assumptions of the PSO model. In differential form, the above model is presented as follows [11]:

$$\frac{dq(t)}{dt} = \alpha \cdot e^{-\beta at} \quad (8)$$

where: t - time [min], α - initial adsorption rate [mg/(g·min⁻¹)], β - adsorption constant, related to the degree of surface coverage and activation energy for adsorption [mg/g].

2.3. Error functions as optimization criteria for adsorption modelling

To determine the adsorption process, its speed and the factors affecting it, equilibrium and sorption kinetics studies are required. To verify the theoretical assumptions of the process. The curves of mathematical models of isotherms or kinetics are fitted to the experimental data. The final choice between them is based on the comparison of one or more statistical criteria describing the degree of model compliance and the correct interpretation of their values [12]. This is a particularly important stage that allows to avoiding modelling errors that affect the correct recognition of the adsorption character. Coefficient of determination (R^2), correlation coefficient (R), error sum of squared deviations ($ERRSQ$), average relative error (ARE), chi-square test (χ^2), complex fractional error function ($HYBRID$), Marquardt's percent standard deviation ($MPSD$), the sum of absolute errors ($EABS$) and relative standard deviation (Δq) are some of the error functions used to model the adsorption process [12, 13]. The selection of the optimal model consists in minimizing each of these functions, except for R^2 and R .

3. Results of discussion

3.1. Modeling of CO₂ adsorption isotherms

The experimental data used to model CO₂ isotherms includes the analysis of the adsorption capacity of activated carbon, where the amount of adsorbed CO₂ at equilibrium was measured depending on the change in its concentration in the volume of the gas mixture (1, 2, 3, 5, 10 and 15%), which corresponds to relative pressures: 0.01, 0.02, 0.03, 0.05, 0.1 and 0.15 atmospheres, at different adsorption temperatures. These are typical values for flue gas under low-pressure conditions, from which carbon dioxide is separated by the carbon adsorbents in the adsorption process. These data were derived from the work [15].

3.1.1. Thermodynamic effects of the adsorption equilibrium

In order to thoroughly understand the thermodynamic phenomena occurring during the adsorption of CO₂ on activated carbon at equilibrium and to confirm the obtained assumptions from the analyzed isotherm models, the change of the standard free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated from Van't Hoff linear equation. The interpretation of the obtained thermodynamic parameters clearly shows that the change of the standard free entropy and enthalpy are independent of the adsorption temperature. Moreover, the negative value of the change in the standard free entropy ($\Delta S^0 < 0$) and enthalpy ($\Delta H^0 < 0$) imply reduced randomness of the CO₂ - adsorbent system, CO₂ degree of freedom, adsorption capacity with temperature intensification, with the exothermic nature of the process. On the other hand, the change in the standard free energy ($\Delta G^0 < 0$) provides information about the more favourable and more spontaneous nature of the process at lower temperatures.

Tab. 1. Comparison of thermodynamic parameters of CO₂ adsorption

T [°C]	ΔG^0 [kJ/mol]	ΔS^0 [kJ/mol · K]	ΔH^0 [kJ/mol]
18	-7.938	-0.0359	-18.384
40	-7.149		
70	-6.073		
100	-4.997		
130	-3.920		

3.1.2. Analysis of the error functions of the adsorption isotherm models

To verify the correctness of linearized and non-linear isothermal models, as well as to determine the choice of the best-fit isotherm model to determine the nature of CO₂ binding, nine commonly used statistical error functions were used to examine the minimum distribution of discrepancies between the experimental and model data. In the case of the linearized form of the adsorption isotherm equations, where the linear regression by the least-squares method was used. The comparison of the obtained error functions reflects the fact that the Freundlich and Halsey isotherms are characterized by the highest values of the determination coefficients: $R^2 = 0.983 \div 0.993$ with the lowest values (Δq , $ERRSQ$, $EABS$, $HYBRID$, $MPSD$, ARE , χ^2) which means that they are best able to describe the empirical data of CO₂ adsorption equilibrium compared to the Langmuir and Temkin isotherm. A full analysis of the error function of the linearized models is presented below:

R^2 : Freundlich = Halsey > Langmuir > Temkin
 R : Freundlich = Halsey > Langmuir > Temkin
 Δq : Temkin > Langmuir > Freundlich = Halsey
 $ERRSQ$: Temkin > Langmuir > Freundlich = Halsey
 $EABS$: Temkin > Langmuir > Freundlich = Halsey
 $HYBRID$: Temkin > Langmuir > Freundlich = Halsey
 $MPSD$: Temkin > Langmuir > Freundlich = Halsey
 ARE : Temkin > Langmuir > Freundlich = Halsey
 χ^2 : Temkin > Langmuir > Freundlich = Halsey

Additionally, non-linearized forms of model equations were analyzed using non-linear regression. The obtained error analysis confirmed the best fit of the Freundlich and Halsey models in most of the

obtained error functions to the experimental data, where the Temkin model was characterized by the highest error values. A comparison was also made between the linear and non-linear forms of the best-fit isotherm models to select the most appropriate form of the equation to study the CO₂ adsorption equilibrium. The obtained results allowed us to conclude that the linear form of the Freundlich and Halsey adsorption isotherms better correlates with the empirical data. The course of curves of the linearized models is shown in Fig. 1., on the example of a temperature 18 °C (the choice was dictated by the highest adsorption capacity as a function of pressure).

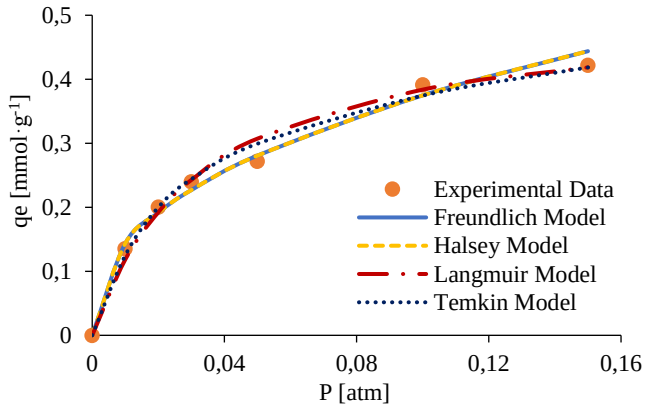


Fig. 1. Curves of linearized models vs. experimental points at 18 °C

3.2. Modeling of the kinetics of CO₂ adsorption's mass transport

The research on the kinetics of CO₂ adsorption on activated carbon in the form of a fluidized bed was carried out at the following temperatures: 18, 40, 70, 100 and 130°C, while for a fixed bed: 25, 50, 70 and 90°C - in both cases their initial concentration in the mixture gas (CO₂ + N₂) was 10% by volume. These data were derived from the works [15, 16]. To study the kinetics of CO₂ adsorption on activated carbon in the form of a fluidized bed and a solid bed, four kinetic models were used to describe the different nature of the process, including: pseudo-first-order model (PFO), pseudo-second-order model (PSO), intramolecular diffusion (IPD) model and Elovich model. The IPD model was not included in the analysis, because it played the role of identifying the exact diffusion mechanism during adsorption. Analyzing the obtained values of the statistical error functions for the linearized model equations, the pseudo-second-order model (PSO) was characterized by the most accurate correlation with the experimental data, which would indicate chemisorption on the adsorbent surface.

However, in the case of the modelling results of the non-linearized models, the error functions of the PFO model are defined as the best fit, characterized by the lowest values (Δq , $ERRSQ$, $EABS$, $HYBRID$, $MPSD$, ARE , χ^2), with the highest coefficients of determination $R^2 = 0.999$ compared to the PSO and Elovich models, at any temperature (for the fixed and fluidized bed conditions). Based on the results of fitting linearized and nonlinear models, it can be concluded that they are quite diverse. To determine which form of the PFO model best correlates with the experimental data, they were confronted with each other:

- R^2 : $PFO(non - linear) > PFO(linear)$
- R : $PFO(non - linear) > PFO(linear)$
- Δq : $PFO(linear) > PFO(non - linear)$
- $ERRSQ$: $PFO(linear) > PFO(non - linear)$
- $EABS$: $PFO(linear) > PFO(non - linear)$
- $HYBRID$: $PFO(linear) > PFO(non - linear)$
- $MPSD$: $PFO(linear) > PFO(non - linear)$
- ARE : $PFO(linear) > PFO(non - linear)$
- χ^2 : $PFO(linear) > PFO(non - linear)$

The above observations suggested that using the non-linear regression method there is no problem with transforming the non-linearized form of the equations into linear forms. In addition, converting a nonlinear equation to a linear form can change its error distribution. That phenomenon is best illustrated by fitting the PFO model curve to the experimental data e.g. for a fluidized bed at 18°C (Fig. 2.).

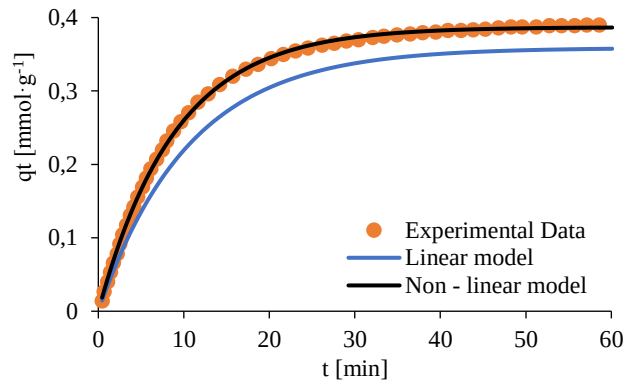


Fig. 2. Model curve vs. experimental points - PFO model at 18 °C for the fluidized bed

Additionally, Fig. 3. and Fig. 4. show the course of curves of non-linearized models for two types of beds at 70 °C (a common process temperature), as those that better correlate with the experimental data than their linear equations.

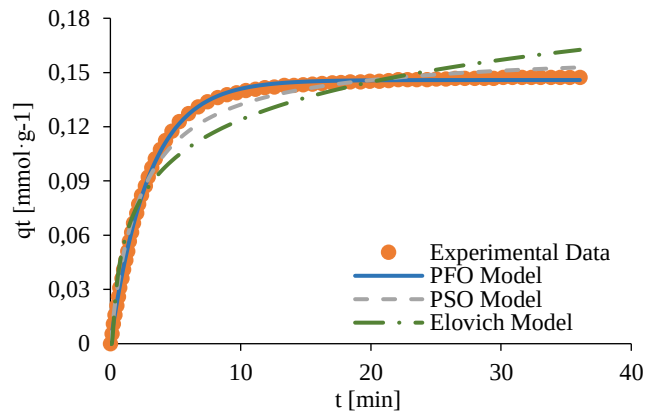


Fig. 3. Curves of non-linearized models vs. experimental points for the fluidized bed

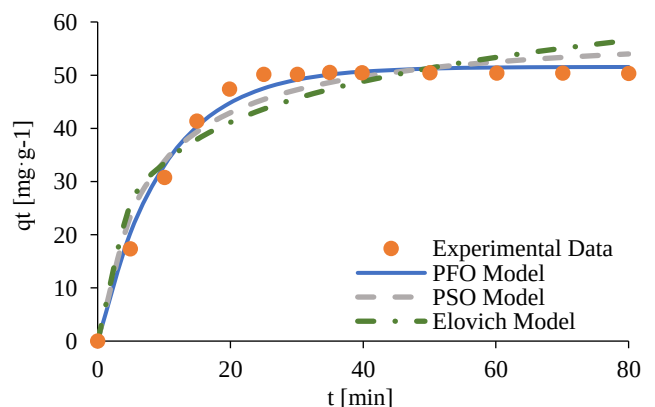


Fig. 4. Curves of non-linearized models vs. experimental points for the fixed bed

3.3. Comparison of a fluidized bed and a fixed bed

In order to finally compare the researched beds in the form of activated carbon, the kinetic model best suited to the experimental data was selected, i.e. the non-linearized pseudo-first-order (PFO)

(Tab. 2). As it results from the kinetic modelling, the parameters of the PFO model indicate that for the fluidized bed the adsorption process is much faster. The kinetic constant of the adsorption rate is characterized by higher values with increasing temperature than in the case of the fixed bed. On the other hand, the amount of adsorbed CO₂ at equilibrium for a fixed bed is greater than that adsorbed in the fluidized bed.

Tab. 2. Parameters of the non-linearized PFO model

T [°C]	Parameters of the non-linearized PFO model for a fluidized bed		T [°C]	Parameters of the non-linearized PFO model for a fixed bed	
	$q_{e,mod}$ [mmol · g ⁻¹]	k_1 [min ⁻¹]		$q_{e,mod}$ [mmol · g ⁻¹]	k_1 [min ⁻¹]
18	0.387	0.111	25	2.610	0.0568
40	0.253	0.188	50	1.742	0.0763
70	0.146	0.340	70	1.172	0.102
100	0.0960	0.554	90	0.820	0.132
130	0.0741	0.724	—	—	—

The obtained dependencies correspond closely with the theoretical knowledge. The use of a fluidized bed intensifies the mass exchange between the gas mixture passed and the solid particles of active carbon, through a large surface of interfacial contact and good mixing of the material with the gas phase, which accelerates the adsorption process. However, the effectiveness of the contact of the gas mixture with the fluidized bed is often seriously compromised, in particular by agglomeration of the bed solids at higher temperatures, which has been identified for the two types of beds studied [14]. This phenomenon causes heterogeneity of the material and is characterized by the formation of cracks and channels in its structure, through which the gas phase tends to bypass the adsorbent particles. In practice, the working capacity defined for a short adsorption time is preferable to the equilibrium capacity, which is confirmed by many studies in this field [14].

4. Conclusion

The modelling of adsorption isotherms in the first stage of the work concerned the analysis of the adsorption capacity of active carbon, where the amount of adsorbed CO₂ at equilibrium was measured depending on the change in its partial pressure. According to the statistical analysis, it was found that the Freundlich and Halsey isotherms best correlate with the experimental data in the entire temperature range, due to the highest coefficient of determination (R^2) - close to one, with the lowest values of the rest of the function errors, which proves the occurrence of the phenomenon of physical adsorption. Finally, the thermodynamic analysis showed that CO₂ adsorption is a spontaneous process at lower temperatures, where the disruption and randomness of the CO₂ - activated carbon system decreases with increasing temperature, and the process is exothermic by nature, which confirmed the preliminary interpretation of the measurement points and assumptions of the models Freundlich and Halsey.

In the second stage of the research work, the kinetics of the adsorption mass transport was modelled based on measurements of the amount of adsorbed CO₂ as a function of time, from the gas mixture N₂+CO₂ in a different temperature range, for a fluidized bed and a fixed bed. The obtained model parameters suggested that the initial adsorption rate was increasing, and the amount of adsorbed CO₂ at equilibrium decreased proportionally to increasing temperatures. A comparative statistical analysis of linearized and nonlinearized forms of kinetic models showed that the best fit to the experimental data for two types of deposits was obtained for the non-linearized pseudo-first order (PFO) model. Obtaining such relationships suggests that chemisorption did not play a significant role in shaping the mechanism of the kinetics of CO₂ adsorption on activated carbon.

Finally, two types of the studied beds were compared for the best-fitted model, i.e. non-linearized pseudo-first-order (PFO), where the values of kinetic parameters were interpreted by literature knowledge in the context of intensifying the adsorption method of carbon dioxide separation. The set of parameters suggested faster kinetics for the fluidized bed, while the greater amount of CO₂ in equilibrium was adsorbed by the fixed bed.

5. References

- [1] Sofoklis S. Makridis, Hydrogen storage and compression, Methane and Hydrogen for Energy Storage, 2016.
- [2] Katsumi K., Rodriguez R., Nanoporous Materials for Gas Storage, Springer, 2019.
- [3] Dubiński, J., Wachowicz J., Koteras A., Underground storage of carbon dioxide - the possibilities for using CCS technology in Polish conditions, Mining and Geology, Publishing house of the Silesian University of Technology, 5, 2010, 5-19.
- [4] Younas M., Sohail M., Leong L. K., Bashir M. Jk., Sumathi S., Feasibility of CO₂ adsorption by solid adsorbents: a review on low-temperature systems, International Journal of Environmental Science and Technology, 13, 2016, 1839–1860.
- [5] Langmuir I., The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum, J. Chem. Soc, 40, 9, 1918, 1361–1403.
- [6] Freundlich M. F., Over the adsorption in solution, J. Phys. Chem, 57, 1906, 385–471.
- [6] Mohammad A. Al-Ghouti, Dana A. Da'ana, Guidelines for the use and interpretation of adsorption isotherm models: A Review, Journal of Hazardous Materials, 393, 2020, 122-383.
- [7] Yuh-Shan H., Citation review of Lagergren kinetic rate equation on adsorption reactions, Scientometric, 59, 2004, 171–177.
- [8] Yuh-Shan H., Review of second-order models for adsorption systems, Journal of Hazardous Materials, 136, 2006, 681-689.
- [9] Singh V. K., Kumar E. A., Comparative studies on CO₂ adsorption kinetics by solid adsorbents, Energy Procedia, 90, 2016, 316-325.
- [10] Weber W., Morris J., Advances in water pollution research: removal of biologically resistant pollutant from wastewater by adsorption, International Conference on Water Pollution Symposium,, 1962, 231.
- [11] Cheung C. W., Porter J. F., McKay G., Sorption kinetics for the removal of copper and zinc effluents using bone char, Water Research, 35, 2001, 605-612.
- [12] Lin J., Wang L., Comparison between linear and non-linear forms of pseudo-first-order and pseudo-second-order adsorption kinetic models for the removal of methylene blue by activated carbon, Frontiers of Environmental Science & Engineering in China, 3, 2009, 320–324.
- [13] Kumar K.V., Comparative analysis of linear and non-linear method of estimating the sorption isotherm parameters for malachite green onto activated carbon, Journal of Hazardous Materials, 136, 2006, 197-202.
- [14] Valverde J. M., Pontiga F., Soria-Hoyo C., Quintanilla M. A. S., Espin M. J., Improving the gas solids contact efficiency in a fluidized bed of CO₂ adsorbent fine particles, Chem. Phys, 13, 2011, 14906–14909.
- [15] Ammendola P., Raganati F., Chirone R., CO₂ adsorption on a fine activated carbon in a sound assisted fluidized bed: Thermodynamics and kinetics, Chemical Engineering Journal, 322, 2017, 302-313.
- [16] Ibrahim H. G., Al-Meshragi M. A., Experimental Study of Adsorption on Activated Carbon for CO₂ Capture, CO₂ Sequestration, 2019.

Biosensor based on directly immobilized hemoglobin and myoglobin

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Abstract: Immobilization of proteins on a surface plasmon resonance (SPR) transducer is a delicate procedure since loss of protein bioactivity can occur upon contact with the untreated metal surface. Solution to the problem is the use of an immobilization matrix having a complex structure. In this paper we study the impact of direct immobilization of heme proteins (hemoglobin (Hb) and myoglobin (Mb)) on their bioactivity. We have used spin coating, for direct immobilization and matrix-assisted pulsed-laser evaporation (MAPLE) [1] for elaboration of the SPR biochip. The performance of both SPR chips – direct and MAPLE immobilized, was studied by SPR registration of the binding activity of Hb and Mb ligands with carbon monoxide (CO), carbon dioxide (CO₂) and nitride oxide (NO). The experimental facts showed that direct immobilization of an intact molecule was achieved.

KEYWORDS: BIO-SENSING, MAPLE, PROTEIN

1. Introduction

In addition to the great physiological importance of hemoglobin (Hb) and myoglobin (Mb), they play also an important role as effective recognition agents in chemical and biological sensors. Hb is a protein with four polypeptide subunits and each subunit has an iron containing heme group. The activity of the porphyrin core determines the hemoglobin applications. Hb is widely used as a recognition medium in different biosensors. Variety of immobilization technics were developed and applied for NO₂ [2], NO₂ and H₂O₂ [3], C₆H₈O₃ [4], NO [5] and CO [6] sensing. All known sensing applications of Hb are realized as electrochemical sensors. Myoglobin (Mb) is a single-chain protein of amino acids containing a porphyrin complex with Fe in the center. The biological activity of Mb is based on the unique redox property due to the iron ion in its core. Thereby, Mb can be used to detect hydrogen peroxide (H₂O₂) [7], nitric oxide [8], hydrogen sulfide [9]. It is interesting that Mb has never been used for CO sensing although the prosthetic heme group can reversibly bind CO.

In this aspect the key factor in developing a reliable biosensor is the immobilization on the transducer. Usually immobilization can be produced by chemical methods, but there is frequently a need for homogeneous films of well-controlled thickness or films which can be deposited in a dry environment. The film thickness is of main importance for the optical transducer detected by Surface Plasmon Resonance (SPR) what is used in our study.

Hundreds of immobilization protocols have been developed in an effort to ensure high performance sensing. All of them are focused on finding and deposition of appropriate matrices in which the recognition medium can be incorporated. However, the matrix always deteriorates the effectiveness of recognition. It seems that the best approach is to perform direct immobilization of the recognition medium. However, this is not always possible regarding the organic materials – the problem is whether the deposition retains the bioactivity of the recognition agent. On the other hand, the type of the transducer also imposes constraints. For example, the direct immobilization of the proteins is not possible for electrochemical sensors. Evaluating the pros and cons of organic (protein) film deposition we have considered the possibility for direct immobilization of Hb and Mb on SPR transducer. To best of our knowledge, SPR biochip with immobilized Hb and Mb has never been constructed before. We have used spin coating, for direct immobilization and MAPLE for elaboration of the SPR biochip.

The performance of both SPR chips – direct and MAPLE immobilized, was studied by SPR registration of the binding activity of Hb and Mb ligands with carbon monoxide (CO), carbon dioxide (CO₂) and nitride oxide (NO).

2. Deposition techniques

2.1 Spin coating

Spin coating has been used for direct immobilization of recognition agents. An appropriate solvent and right concentration of the recognition agent was established. The concentration is related

to establishing spin speed and duration for obtaining required layer thickness what is very important for providing SPR detection with maximum accuracy and sensitivity. As a transducer we have used a gold covered diffraction grating. Experimentally we have found that the optimal layer thickness is 100 – 150 nm for the applied concentrations of the recognition agents. The solvent for Mb and Hb is deionized water. The obtained layers have been very uniform and with good optical quality.

2.2 MAPLE technique

Mb and Hb are dissolved in a solution of a volatile matrix (polyethylene glycol, PEG). The deposition occurs in a vacuum chamber under the irradiation of UV light. Before the deposition starts the solution is frozen. The idea of the technique is that the matrix absorbs the laser light, so that decomposition of the recognition agent is avoided.

In our experiment, PEG was chosen as a matrix because of its well-expressed absorption at 355 nm. This coincides with the irradiation that we apply – the third harmonic at 355 nm of Nd:YAG laser. The pulse duration is 10 ns, the repetition rate 10 Hz and the controllable energy is between 1 mJ and 10 mJ. The laser irradiation is focused with a quartz lens with focus length 50 cm. The laser fluency of our experiments varied from 100 mJ/cm² to 500 mJ/cm². During the deposition process the laser light scans continuously the target by managing the tilt of a control mirror. The target is frozen at temperature between 15 C – 20 C. The substrate temperature is not controlled - during the deposition it is in the range 25 C – 32 C. The vacuum is about 2.10-5 mbar, achieved by using standard rotary and turbomolecular pumps.

2.3 Layer's properties

The deposition of layers was performed simultaneously on glass substrate and on a diffraction grating covered with a gold layer. The glass substrate is with optical quality 40 -10, that permits to measure the layer thickness with accuracy up to 10 nm. The layer thickness was measured by 3D Optical Profiler Zeta 20 and by Talystep Filmetrics F20. We are able to control the layer thickness in the range 100- 150 nm for both spin coating and MAPLE deposition.

3. Results and discussion

3.1 Layer's properties

Fig. 1a shows a SEM picture of a Hb layer with thickness 110 nm. It shows that on the relatively uniform background there are particles with regular and irregular form. The SEM shows that they have spatial or flat shape. We have found that their quantity and shape strongly depend on the pulse energy and on the distance to the target, while the background was influenced in its density and hardness. Obviously, bigger particles come from PEG during the deposition. Unfortunately, SEM cannot resolve the background structure, but based on our measurements, addressing the Hb functionality, one can conclude that this is a Hb layer. Similar observations and conclusions are made for the Mb layer.

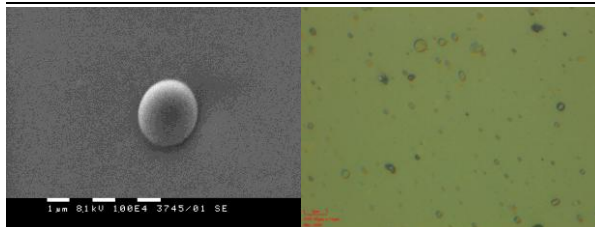


Fig 1(a). SEM pictures of a deposited Hb layer **Figure 1 (b).** An optical microscope picture of the same layer

The thickness uniformity of the layer is in the framework of the accuracy of the measurement – 10 nm, what is rather a good result for MAPLE deposition. This is confirmed by SPR excitation at different points on the gold diffraction grating having dimensions 16x11 mm. The resonance shift was no more than 2 nm. Regarding spin coated layers, the uniformity and optical quality is very good.

3.2 SPR excitation and registration

The transducer is a gold diffraction grating. The spectral readout is used for SPR excitation and registration. White light under angle of incidence in the range 35 – 42 degrees excites resonances between 708 nm and 610 nm for a bare grating. The angle of incidence is controlled with accuracy 0.01 deg. The spectrometer registers the spectrum in the zero order reflection. SPR is measured with accuracy of 3 nm.

3.3 Functionality of the Mb and Hb layers

The functionality of Mb and Hb consists of the functionality of their various functional groups. It can be examined by checking the affinity for the ligand of interest. Besides the oxygen, Mb and Hb ligands also include CO, CO₂ and NO that bind to different functional groups. The binding reaction has been registered by SPR, proving the existence of corresponding functional group and respectively demonstrating the functionality of the Mb and Hb deposited layer. The functionality of layers deposited by spin coating and MAPLE technique has been examined.

3.4 Functionality of spin coated layers

The affinity of iron in the porphyrin core towards CO is very high for Mb and Hb and it displaces the oxygen bound to the iron atom. This reaction has been clearly observed blowing the Mb/Hb layer, deposited on a gold diffraction grating, with CO having concentration 1000 ppm. The resonance shift as a results of the CO binding is about 6 nm, shown in Fig.2a

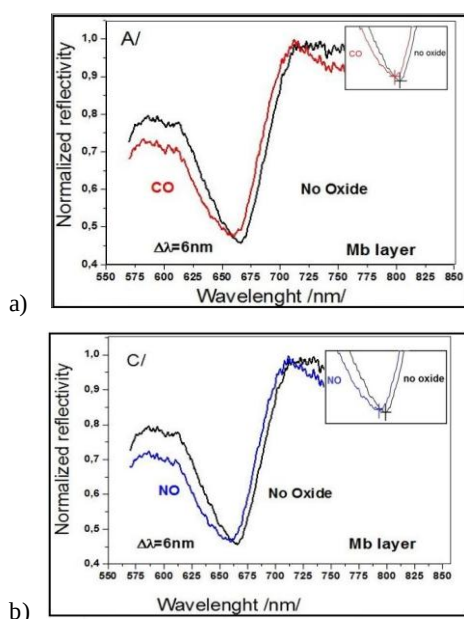


Figure 2. SPR detection of the binding activity of different functional groups of Mb layers

The registration of CO₂ binding proves the presence of small amount of corresponding functional groups, in this case – an amino group of the globin protein. Despite the binding activity is much lower than the one to CO, the effect is well pronounced. The resonance shift is about 6 nm showing that the functional group is “alive” and keeps its activity.

The same conclusion can be made for thiol groups in the globin protein which are responsible for NO binding (Fig.2b). Comparing the binding activity of CO and NO, the latter is higher – their resonance shifts are compatible, despite that the NO concentration is five times lower (200 ppm). It is worth mentioning that we have registered activity of all samples that we have prepared by spin coating, but the sensitivity (namely the activity) of the deposited layers was different despite the deposition parameters were exactly the same. Here we present the highest activity we have achieved.

3.5 Functionality of MAPLE deposited layers

The problem about repeatability regarding bioactivity is more serious for MAPLE deposited layers. Fig. 3 proves the activity of heme and thiol groups of the Hb layer after deposition and shows the most expressive SPR shift for CO binding and for NO binding.

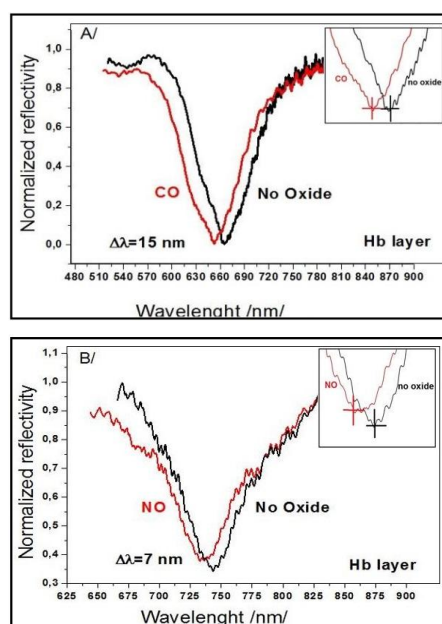


Figure 3. SPR detection of the binding activity of a Hb layer deposited by MAPLE technique

Despite the illustrated activity, more pronounced than in the case of a spin coated layer, we cannot argue that MAPLE deposition is more effective. The problem is that it was not possible to get the same results although we followed the same technology recipe

Probably, we face the problem related to the abundance of particulates of regular or irregular shape, deposited by MAPLE. This could alter seriously the biological activities of proteins as far as it is related to their three-dimensional structure. The structural alterations of proteins, probably depending on aggregation during the deposition, frequently result in the loss of the activities.

4. Conclusion

We have shown that myoglobin and hemoglobin can be deposited directly by spin coating and by MAPLE technique keeping their functionality. The functionality has been proved by SPR detected binding of CO, CO₂ and NO to the corresponding functional groups of the proteins. The deposition has been performed by one step and in one technological cycle, which is extremely useful.

It is difficult to access which deposition method is more effective but for both methods the tight control of the technology parameters is very important.

In fact, we have made gas sensors based on heme proteins with SPR transducer, that is reported for the first time, to the best of our knowledge.

Acknowledgments

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References

1. Functionalized Nanoscale Materials, Devices and Systems, Springer, Dordrecht, The Netherlands, 2008
2. H. Liu, C. Duan, C. Yang, W. Shen, F. Wang, Z. Zhu, A novel nitrite biosensor based on the direct electrochemistry of hemoglobin immobilized on MXene-Ti3C2, *Sensors and Actuators B: Chemical* (2015), <http://dx.doi.org/10.1016/j.snb.2015.04.090>
3. Qu. Wang, G. Lu, B. Yang, Direct electrochemistry and electrocatalysis of hemoglobin immobilized on carbon paste electrode by silica sol-gel film. *Biosensors and Bioelectronics* 19,1269–1275(2004)
4. A. Hajian, J. Ghodsi, A. Afraz, O. Yurchenko, G. Urbana, Nanomolar detection of methylparaben by a cost-effective hemoglobin-based biosensor, *Materials Science and Engineering C* 69 ,122–127(2016)
5. Michael E.Murphy, EikeNoack, Nitric oxide assay using hemoglobin method, *Methods in Enzymology*, 233, 240-250(1994)
6. Y.Takada, R. Otsuka, and K.Tsukada. A Carbon Monoxide Sensing Film Based on Hemoglobin Allosteric, *J. Biomedical Science and Engineering* 7, 173-180(2014)
7. J.Yoon. *Biosensors and Bioelectronics* (2016), <http://dx.doi.org/10.1016/j.bios.2016.11.064>.
8. J. Yoon et al., *Colloids and Surfaces B: Biointerfaces* <http://dx.doi.org/10.1016/j.colsurfb.2017.08.033>.
9. A. Boffi, M. Rizzi, F. Monacelli, P. Ascenzi, *Biochim.Biophys. Acta.* 1523,206(2000)

Dynamic mesh adaption in shockwaves simulations

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Abstract: The goal of the article is to compare the accuracy and computational time of the shock wave simulations, using the standard, structured mesh and the dynamic mesh adaption. The coarse and fine mesh will be compared with the dynamically adapted mesh in terms of computational time and accuracy. Based on the results, histograms depicting computational time will be created. The simulation, on which those meshes will be examined will be a simple, two-dimensional oblique shock wave forming over a wedge inclined at 15°, with the Mach number at the domain inlet being equal to 2. The adaption will be based upon the pressure gradient criterion.

KEYWORDS SHOCKWAVE, MESH ADAPTION, DYNAMIC MESH ADAPTION

1 Introduction

The dynamic mesh adaption methods are a subject worthy of examination, as supersonic air travel is being considered to be reintroduced to commercial air travel [1-4], which rises a necessity to be able to simulate supersonic flow and all of the phenomena related to it efficiently. Dynamic mesh adaption allows for obtaining results which accuracy comparable to results obtained from very fine mesh, while using only a fraction of the mesh element used by the fine meshes and allows for significant reduction of computational expense and time.

2 Methods

The geometry for the computational domain was designed in SpaceClaim software, and all of the simulations were conducted in Ansys Fluent 2021 R1, on the Academic license. The geometry generated for the computational domain can be observed in the figure below. Two versions of the mesh, fine and coarse are presented in the figures below.

The coarse mesh serves as a base for dynamic adaption. The procedure of adapting mesh is described in detail in [5].

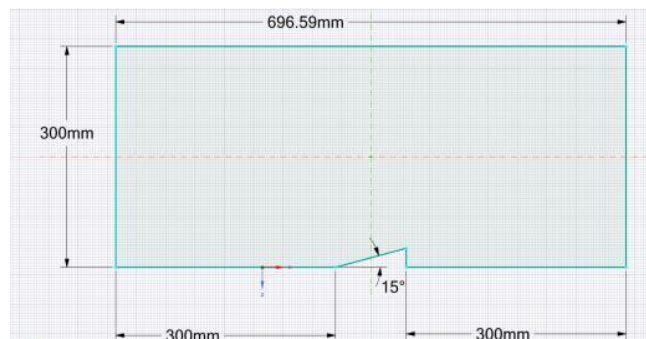


Figure 1: Domain geometry

Mesh details are presented in the table below.

Table 1: Mesh details

	Coarse	Fine
Mesh elements	2251	209096
Mesh nodes	2353	210085

The following assumptions were made regarding the study:

All meshes used in the simulations are quad-dominant meshes;

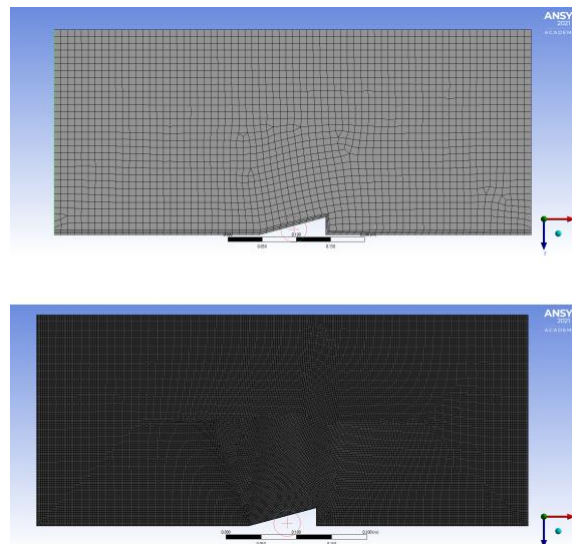


Figure 2: Meshes used for computations

Inflation, consisting of 4 layers, with a growth ratio of 1.1 was applied to all walls;

3rd MUSCL scheme was used for all calculations, to reduce numerical diffusion;

A density-based solver was used for all simulations;

1000 iterations were conducted for each case;

A gradient of pressure was used as a refinement and coarsening criterion, cells with gradient values above 10000 Pa/m are refined, while cells with a value below 10000 Pa/m are coarsened;

Refinement and coarsening levels are equal to 3;

Fluid in the domain is air, and it is assumed to be an ideal gas;

Compressible Aerodynamics Calculator [6] is used as an analytical means of validation of the results, the value compared with the numerical result is the wave angle;

Wave angles are measured based on the Mach number contour.

3 Results

After conducting computations results had been obtained, the computational time needed for 1000 iterations is presented in the bar graph below.

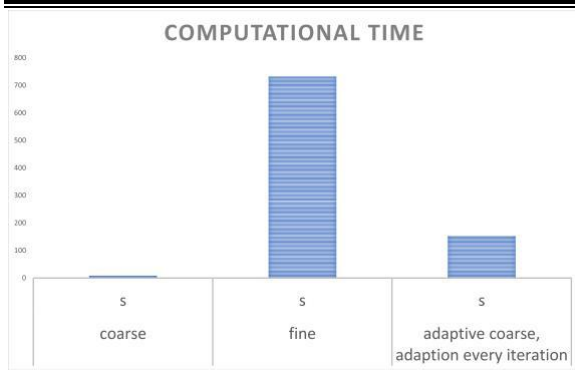


Figure 3: Computational time comparison

The mesh elements and nodes in coarse mesh after adaption had been increased to 6898 elements and 7922 nodes. The graphical representation of the results, in a form of Mach number contours and pressure contours, are presented in the figures below.

To validate the results of the numerical computations, the wave angle was calculated by using the $\Theta - \beta - M$ equation, which is presented below.

$$\tan\theta = 2 \cot\beta \frac{M_1^2 \sin^2\beta - 1}{M_1^2(\gamma + \cos 2\beta) + 2}$$

The equation is solved numerically by bisection, by the Compressible Aerodynamics Calculator [6], to obtain β , which is, in this case, the wave angle. The Mach number contours, needed for the wave angle measurement, are presented in figures 4 and 5.

The comparison of the numerical and analytical results is also presented in the following table.

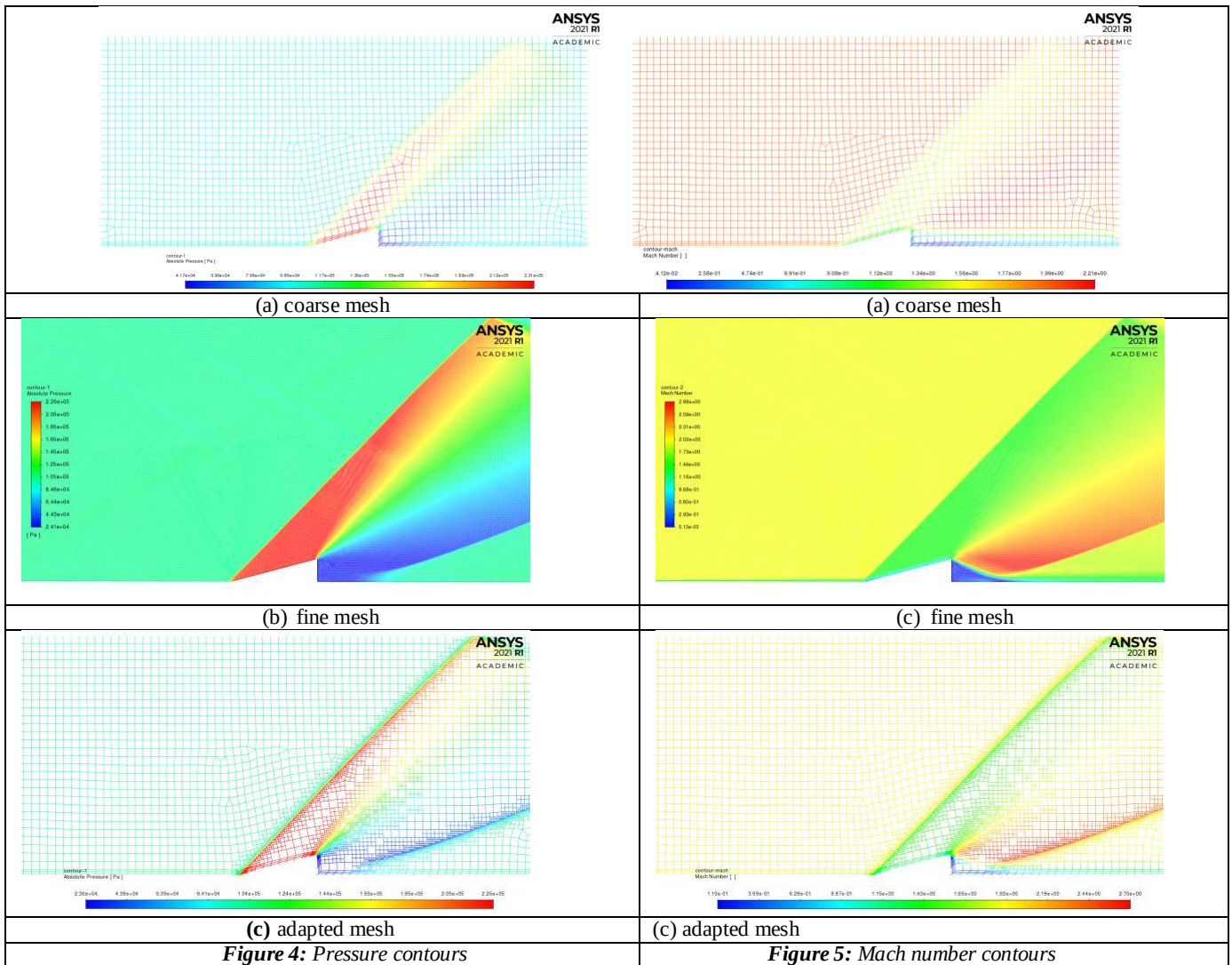


Figure 4: Pressure contours

Figure 5: Mach number contours

Table 2: Accuracy of the simulations

	coarse	fine	adapted
analytical	45.34	45.34	45.34
numerical	46.74	45.93	45.77
relative error	2.98%	1.27%	0.93%

4 Conclusions

In the article, the oblique shock angle was examined. Three meshes in total were subjected to the examination, coarse, fine and dynamically adapted coarse mesh. The results obtained had proven the coarse mesh to be inapplicable for the examination of shock angle, due to the significant underestimation of the Mach number, as well as the inability to depict properly the Prandtl-Meyer expansion fan [7], which should have formed behind the wedge, and it is depicted in the fine and adapted cases. It is worth noticing that, the dynamically adapted mesh had led to better accuracy than the fine mesh, which is most likely caused by the

higher local density of the mesh in the area, in which the oblique shock is forming. The expansion fan is depicted more accurately in the fine mesh case, as it does not have as high a gradient of pressure as the oblique shockwave. The measurement method used for measuring the wave angle is depicted in figure 6, it is important to take the accuracy of the wave angle measurement into account, as it generates a possibility for the measurement error to occur. The approach, which would allow reducing the measurement error, is to measure the angle multiple times to be able to obtain the standard deviation value.

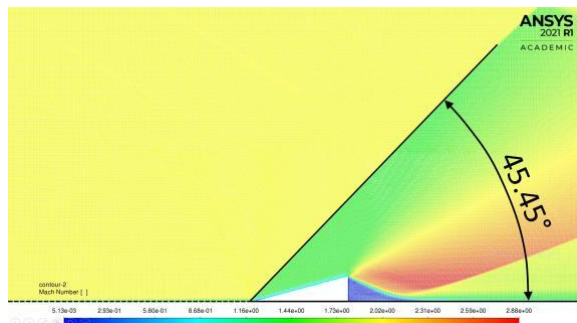


Figure 6: Measurement of the wave angle in the refined mesh case

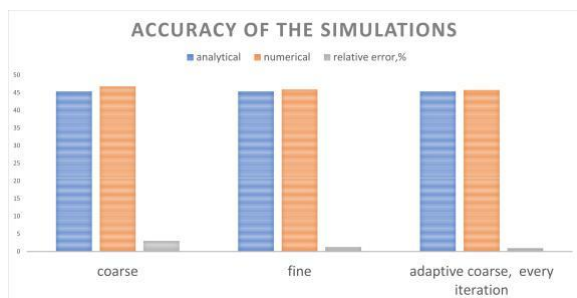


Figure 7: Accuracy of the simulations

The adaptive mesh refinement shows a potential to reduce the computation time of the numerical simulations, without compromising on the accuracy and precision of the computations. It is worth noticing, that the method does not apply exclusively to the shockwaves, it might be used to simulate mixing in multiphase flow, with the volume fraction being a refinement criterion.

References

- Y. Sun, H. Smith - Progress in Aerospace Sciences, Volume 90, Review and prospect of supersonic business jet design, [2017]
- H. Smith - Innovation in supersonic passenger air travel, [2012], Chapter 8
- Startup dealing with the commercial supersonic air travel: <https://boomsupersonic.com>
- Startup dealing with the commercial supersonic air travel: <https://www.spikeaerospace.com>
- K. Ewertowski - Conceptual Ramjet Engine Design and Performance Analysis (Analiza sprawno'sci koncepcyjnego silnika strumieniowego), pages 37-46, [2021]
- W.J. Devenport, 2021, Compressible – Aerodynamics Calculator 3.0, accessed 10 July 2021 <http://www.dept.aoe.vt.edu/devenport/aoe3114/calc.html>
- R. Von Mises [1958]. Mathematical theory of compressible fluid flow.

Ultrafine-grained structure and thermal stability of the two-phase titanium alloy vt8m-1

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Abstract: In this work, the method of backscattered electron diffraction (EBSD) and transmission electron microscopy (TEM) was used for microstructural analysis of the improved VT8M-1 alloy (Ti-5.7 Al-3.8 Mo-1.2 Zr-1.3 Sn) subjected to equal-channel angular pressing (ECAP) and rotary forging (RF). It was found that the process of globularization induced during deformation processing is regulated by the conventional boundary-splitting mechanism. It was shown that an orientation relation is established between the spheroidized α - and β -phases. This result is achieved due to the high activity of dislocation sliding at the boundary of the α - and β -phases. The thermal stability of the VT8M-1 alloy with an ultrafine-grained (UFG) structure is studied. It is shown that at $T=450^\circ\text{C}$ and long-term (up to 500 hours) annealing the UFG structure is thermally stable. The mechanical properties and the effect of annealing on the microstructure are discussed. It is shown that particles of the Ti-Zr-Si system are isolated at the interphase boundaries.

KEY WORDS: TWO-PHASE TITANIUM ALLOYS, ULTRAFINE-GRAINED STRUCTURE, ROTARY SWAGING, THERMAL STABILITY, STRENGTH

1. Introduction

Two-phase Ti alloys combine low specific weight and high mechanical properties, which make them extremely attractive to aviation industry particularly for the fabrication of such critical components as stiffeners, engine pylon spar elements, fan blades, compressor discs, aircraft engine compressor blades, etc. [1].

This paper focuses on the heat-resistant two-phase VT8M-1 with a service temperature of 450-500°C. VT8M-1 alloy is considered as a replacement to the widely applied VT6 alloy with a service temperature of no more than 350°C. Severe plastic deformation techniques or combined strain treatment leading to the formation of an ultrafine grained (UFG) microstructure with high boundary density are increasingly frequently used to achieve enhanced strength properties in alloys [2, 3].

There are several aspects making UFG Ti alloys so attractive for aircraft industry: first, UFG microstructure has an enhanced ultimate tensile strength and fatigue life [3,4]. Second, superplasticity is manifested in UFG microstructures at rather low strain temperature, which optimises the manufacturing of semi-finished articles and products [5, 6]. The shaping of Ti alloys usually includes both thermal treatment and hot deformation, which leads to the modification of structural parameters and thus of mechanical properties in the context of UFG structures. Secondary intermetallic particles like $(\text{Ti,Zr})_5\text{Si}_3$, $(\text{Ti,Zr})_6\text{Si}_3$ and others are possible to precipitate in the highly doped alloy of this class at heat and thermomechanical treatments (TT) [7, 8]. With this in view, the paper briefly reviews the thermal stability of the VT8M-1 alloy with an ultrafine-grained (UFG) structure is studied. The mechanical properties and the effect of annealing on the microstructure are discussed.

2. Material and Experimental Procedure

A two-phase VT8M-1 rod (produced by VSMPO-AVISMA, Russia) with the chemical composition of Ti-5.7Al-3.8Mo-1.2Zr-1.3Sn (wt %) was used as a research material. In as-delivered state the alloy had a globular lamellar microstructure with the temperature of β -transus of $980^\circ\text{C} \pm 5^\circ\text{C}$. A rod was processed by a rotary swaging at $T=750^\circ\text{C}$ with an incremental compression along a diameter from 70 to 32 mm ($\epsilon \sim 1.56$ with a strain rate above 300 mm/s-1). The alloy also was subjected to 4 ECAP passes at 750°C via BC route using a die with a 120° round channel. The accumulated true strain was evaluated to be 2.8.

Isothermal die forging of the UFG VT8M-1 was performed at $T=780 \pm 10^\circ\text{C}$. The alloy was subjected to annealing in Noberterm

furnaces. The alloy mechanical properties were examined in the course of tensile testing using Instron universal testing machine with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ in correspondence with ISO 6892-1-2009, and microhardness was measured based on ASTM E384-16. TEM and SEM techniques were applied to study the alloy microstructure (JEOL JSM 6390 and JEOL JEM 2100), and EDS on JEOL JEM 2100 microscope was used to analyse the alloy elementary composition.

3. Results and discussion

In this work, the evolution of the microstructure and mechanical properties of the UFG VT8M-1 alloy after prolonged annealing at a temperature of 450°C were studied. It was found that after 50 hour annealing, an increase in the strength of the UFG alloy VT8M-1 by an average of 50 MPa is observed (Fig. 1). Prolonged annealing (over 400 hours) of the short-circuit state leads to a decrease in strength and an increase in plasticity (Fig. 1). It was found that after 50 hour annealing, an increase in the strength of the UFG alloy VT8M-1 by an average of 50 MPa was observed (Fig. 1).

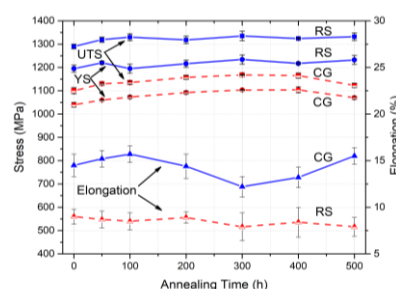


Figure 1 – Dependence of the mechanical properties of VT8M-1 alloy specimens under tensile tests on the exposure time in the range from 0 to 500 hours at a temperature of 450°C

By transmission electron microscopy (TEM) it was found that small ellipsoidal particles with an average size of 50–100 nm are formed at the interfaces between α and β plates (Fig. 2). Results of EDS analysis indicate the Si and Zr content of the particles. Deciphering the diffraction patterns showed that the particles are silicides of the $(\text{TiZr})_6\text{Si}_3$ type with a hexagonal close-packed lattice [9].

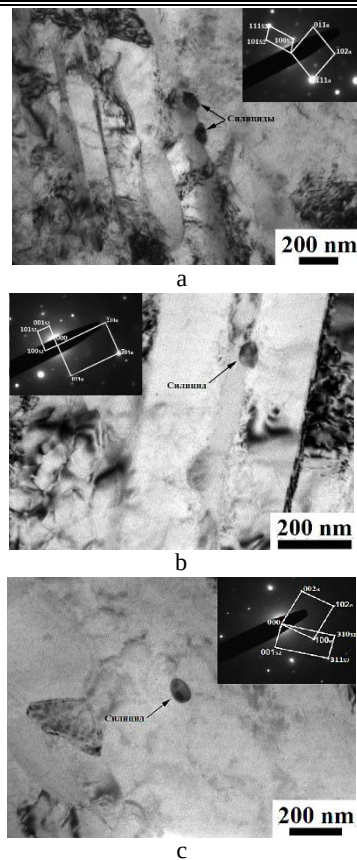


Figure 2 – Microstructure of VT8M-1 alloy after: a) RS; and subsequent annealing at a temperature of 450C for: b) 50 hours; c) 500 hours.

Thus, the results of the study indicate the thermal stability of the UFG structure of the VT8M-1 alloy. The research results indicate that silicides of the $(\text{TiZr})_6\text{Si}_3$ type can help maintain the thermal stability of the nonequilibrium UFG structure at temperatures up to 450 C.

Conclusions

1. An ultrafine-grained microstructure processed by rotary swaging maintains thermal stability within the area of the alloy service temperature ($\leq 450^\circ\text{C}$) and contributes to UTS enhancement from 1050 MPa in an initial coarse-grained state up to 1290 ± 10 MPa in an UFG state.
2. Hot isothermal forging of the UFG alloy at $T \sim 780^\circ\text{C}$ led to the recrystallization development and growth of secondary α - and β -

phases up to $0.7 \mu\text{m}$. The resulting strength of the alloy constituted 1100 ± 30 MPa.

3. It has been shown that a thermal treatment of a forged VT8M-1 blade at $T \sim 500 \div 550^\circ\text{C}$ can promote additional strengthening of the material by 10-15% due to the formation of extra interphase α/β boundaries with the precipitation of a tertiary α -phase as well as a silicide disperse strengthening.

Acknowledgements

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References

- [1] G. Lütjering, J. C. Williams, Titanium, Springer, Berlin, Heidelberg, 2007, p. 335.
- [2] R. Z. Valiev, Y. Estrin, Z. Horita, T. G. Langdon, M. J. Zehetbauer, & Y. Zhu, Producing bulk ultrafine-grained materials by severe plastic deformation: ten years later. *Jom*, 68(4), (2016) 1216-1226.
- [3] R.S. Mishra, V.V. Stolyarov, C. Echer, R.Z. Valiev, A.K. Mukherjee, Mechanical behavior and superplasticity of a severe plastic deformation processed nanocrystalline Ti-6Al-4V alloy, *Mater. Sci. Eng. A* 298 (2001) 44-50.
- [4] I.P. Semenova, E.B. Yakushina, V.V. Nurgaleeva, R.Z. Valiev, Nanostructuring of Ti-alloys by SPD processing to achieve superior fatigue properties, *Int. J. Mater. Res.* 100 (2009) 1691-1696.
- [5] S.L. Semiatin, P.N. Fagin, J.F. Betten, A.P. Zane, A.K. Ghosh, G.A. Sargent, Plastic flow and microstructure evolution during low-temperature superplasticity of ultrafine Ti-6Al-4V sheet material, *Metall. Mater. Trans. A* 41 (2010) 499-512.
- [6] S.V. Zhrebtsov, E.A. Kudryavtsev, G.A. Salishchev, B.B. Straumal, S.L. Semiatin, Microstructure evolution and mechanical behavior of ultrafine Ti-6Al-4V during low temperature superplastic deformation, *Acta Mater.* 121 (2016) 152-163.
- [7] A.A. Popov, M.O. Leder, M.A. Popova, N.G. Rossina, I.V. Narygina, Effect of alloying on precipitation of intermetallic phases in heat-resistant titanium alloys, *The physics of metals and metallography*. 116 (2015) 261-266.
- [8] A. Popov, M.A. Zhilyakova, O. Elkina, K.I. Lugovaya, The Precipitation of Silicide Particles in Heat-Resistant Titanium Alloys, in: S. Syngellakis, J. J. Connor (Eds.), *Advanced Methods and Technologies in Metallurgy in Russia*, Springer International Publishing AG, Switzerland, 2018, pp. 19-25.
- [9] Singh A. K., Characterization of silicides in high-temperature titanium alloys / A. K. Singh, C. Ramachandra // *Journal of materials science*.1997. V.32. P.229-234.

The methodology of functional modifiers choice for nanocomposites based on industrial thermoplastics

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Abstract: The methodological principles for the implementation of the concept of multilevel modification of polymer matrices by components with given energy parameters to obtain nanocomposites with a synergistic combination of performance characteristics have been developed. These principles based on:

- established crystal-chemical prerequisites for the natural and synthetic carbon-, metal- and silicon-containing semi-finished products choice for the directed formation of active nanosized particles with given structural, morphological and energy parameters under optimal technological impact (mechanical and chemical, thermal, laser);
- implementation of the conditions for the energetic compliance of nanomodifiers to the prevailing mechanism for the formation of the optimal structure of polymer, oligomer and blend matrices at various levels of organization – molecular, supramolecular and interphase;
- creating the conditions for the reveal of the prevailing mechanisms of interphase physical and chemical interactions of components with the formation of boundary layers of the optimal structure, which determine the mechanisms of destruction of products from nanocomposites under various operational factors impact;
- achieving the conditions for the synergistic effect of structuring by using a complex of modifiers with a certain combination of parameters of dimensional, geometric and energy characteristics.

KEYWORDS: NANOCOMPOSITES, INDUSTRIAL THERMOPLASTICS, NANOSTATE, MULTILEVEL MODIFICATION, ENERGY AND TECHNOLOGICAL COMPLIANCE

1. Introduction

In the brand range of modern engineering materials, a special place belongs to nanocomposites based on polymer, oligomeric and blend matrices, which for a variety of performance characteristics parameters are no alternative materials in the production of road transport, special, agricultural machinery and technological equipment for heat power engineering, petrochemical and processing road transport. At the same time, the potential of such matrices produced by the domestic industry in the creation of functional nanocomposites is not fully realized, although the base of its large-tonnage production is highly developed and enterprises have a lot of modern technological equipment.

The mechanism and kinetics of the processes of formation of the structure of composite materials at various levels of organization is determined by the activation energy, which depends on the parameters of the energy characteristics of the components at a given technological impact. Studies of domestic and foreign experts have shown the existence of the effect of the transition of a material particle when a certain size range is reached into a state with special parameters of energy characteristics, which according to the established terminology is called a nanostate. Obviously, the achievement of the nanostate by the component will have a significant impact on the structural processes in the composite material at different levels of organization, which determine the parameters of stress-strain, tribological, adhesive and other characteristics of products in metal-polymer systems [1–4].

At the same time, despite the experimentally established influence of energy parameters on structuring processes, there are no systemic studies of methodological approaches to the implementation of the nanostate phenomenon in materials science and the technology of nanocomposite materials based on industrial polymers. Therefore, the development of methodological approaches to the implementation of the phenomenon of nanostates at various levels of organization of the structure of nanocomposites is the actual problem of domestic materials science and polymer technology, which have a great scientific and applied importance.

2. Methods of research

The main objects of study were nanodispersed particles of carbon-containing (graphite, DND, CNT, shungite, carbon fibers), metal-containing (oxides, salts of organic acids) and silicon-containing (mica, tripoli, opal, clay) compounds obtained by technological impacts on natural and synthetic semi-finished products produced at industrial enterprises in Belarus and the Russian Federation. Nanosized components were obtained by mechanical crushing and

heat treatment of dispersed semi-finished products at temperatures of 673–1473 K.

Two main types of thermoplastic materials were used as polymer matrices: the first, with a hereditarily high viscosity (HHV) of the melt due to the chemical structure of the chain and molecular weight: polytetrafluoroethylene (PTFE) and super high-molecular polyethylene (SHMPE); the second are materials with acquired high viscosity (AHV): industrial thermoplastic polymers such as polyamide PA 6, high density polyethylene (HDPE), ethylene-vinyl acetate copolymers (EVAC), polypropylene (PP), thermoplastic polyurethane (TPU), etc. with characteristic parameters of rheological properties that changed with the introduction of nanosized modifiers.

Polymer materials were used in the state of industrial delivery in the form of granules or powder obtained by cryogenic dispersion of granules at a temperature of 87 K.

The structure and properties of nanocomposite materials and products produced from its were investigated using modern methods of physical and chemical analysis: IR spectroscopy (Specord), electron paramagnetic resonance (EPR) spectroscopy (RE 1306, Bruker), X-ray diffraction (Dron 2.0, Dron 3.0), differential thermal analyzes (Q-1500), optical (MIM-10, MF-2), scanning electron (ISM-50A, Nanolab-7) and atomic force (Nanotope III) microscopy. The energy state of nanoscale modifiers and composite materials was assessed from the EPR spectra and the spectra of thermally stimulated currents (TSC) on the original equipment of the V.A. Belyi Metal-Polymer Research Institute of National Academy of Sciences of Belarus (MPRI NASB). The dielectric characteristics of materials after energy exposure (laser, ion, temperature) were determined according to the appropriate standardized methods. The regulation of the nanorelief of the surface layer of polymer samples and fillers was carried out using a short-pulse laser and accelerated ion irradiation with a given power density.

The parameters of the stress-strain characteristics of the developed materials were evaluated on standard samples in accordance with the relevant standards (GOST). Tribological characteristics were determined on universal or original friction machines (UMT, MI-2, SMC-2M, etc.) according to the "indenter – disk", "shaft – partial insert" schemes. Evaluation of the performance of products from the developed nanomaterials in the designs of automotive units for various purposes and technological equipment was carried out at the stands and in the process of virtual tests using the SKIF supercomputer and field tests. The test data processing was carried out by the methods of mathematical statistics using the standard software Microsoft Office 2020.

3. Results and discussion

Multicomponent materials based on high molecular weight matrices are systems the parameters of characteristics (stress-strain, tribological, adhesive, thermophysical, etc.) of which are determined by the structure at various levels of organization, formed by physical and physicochemical processes, the mechanisms and kinetics of which depend on the composition components and parameters of technological characteristics. In the interphase region of the system, a complex of physical and physicochemical reactions occurs simultaneously with the dominance of one or several, for which the most favorable conditions are realized, determined by the value of the activation energy. This dominant reaction, the kinetics of which is in accordance with the conditions of formation and operation of the system, determines the resistance of an element made of a composite or a metal-polymer system to the action of operating factors.

The methodological approach to the formation of composites based on the establishment of the dominant physicochemical reaction made it possible to establish a correlation between the parameters of the structure and the energy characteristics of the components (energy state) [5, 6, 8, 11].

To characterize the energy state a complex parameter was used, which is the cumulative result of the transformation of the initial individual parameters of the components (structure, composition, morphology, shape, size) under the influence of technological and operational factors. A feature of the proposed methodological approach is the ability to purposefully intensify the dominant interfacial reactions by forming the energy state of components with certain parameters of electrophysical characteristics.

Using the concepts of condensed matter physics, the conditions for the acquisition of a nanostate by a material object are determined, which can manifest itself when the size parameter L_0 is reached both by a single particle and by the components of the surface layer of a particle or substrate in the micro- and macro-range. For the analysis of various types of interphase interactions in systems based on the energy factor, the definition of "nanostate" has been proposed, which makes it possible to single out the main forms of its manifestation [9, 10].

The concept of energy and technological compliance of components for the formation of systems with optimized parameters of structural characteristics at various levels of organization has been developed [12, 13].

The energetic compliance of the components implies the possibility of achieving a total energy state by its that corresponds to the activation energy of the dominant physicochemical process, which ensures the formation of an optimal structure at the intermolecular, supramolecular, interfacial levels of organization in composites or metal-polymer systems.

To implement the principle of energy compliance of components, it is necessary not only a certain combination of initial parameters (thermophysical, dimensional, electrophysical, structural, elemental, etc.), but also the possibility of changing them in the specified ranges of values under technological influences on the components (deformation, temperature, ionizing, laser and etc.). When choosing an adequate technology for obtaining, preparing, mixing components or processing composites into products, conditions are created for changing the initial energy state and achieving a nanostate directly in the interphase interaction zone, which ensures the dominant physicochemical process of forming the optimal structure of the boundary layer [13].

The formation of an interphase (boundary) layer of the optimal structure indicates the technological correspondence of the components of functional materials and metal-polymer systems, which is understood as the possibility of achieving the specified energy parameters at a certain stage of the formation of a composite, product or structure, ensuring the dominant mechanism of interfacial interaction. The absence of such a compliance does not allow realizing the potential of individual components in the selected technological process of manufacturing the system, since it can manifest itself in various ranges of temperature, mechanical, physicochemical and other influences, not ensuring the achievement

of the required value of the activation energy at a specific technological stage, leading to a negative phenomenon called the structural paradox. The implementation of the principle of energy and technological compliance has made it possible to develop a methodology and practical technologies for the use of the phenomenon of nanostate in materials science of metal-polymer systems of various composition, design and functional purpose.

To develop methodological principles for creating optimized systems and algorithms for their implementation that are adequate to common technologies of polymer composites and systems, the factors that determine the nanostate of components (dimensional parameters and shape of individual particles, structure at various levels of organization, composition of components, morphology of the surface layer) are substantiated. Taking into account the selected factors, the analysis of the mechanisms of realization of the nanostates of dispersed particles and substrates of various compositions, structures and geometrical parameters for their practical applications in materials science and technology of nanocomposite materials based on industrial polymers was carried out.

Physical and physicochemical processes are caused by the transfer of electrons during the formation of intermolecular, supramolecular, interfacial structures, which led to the choice of the maximum value of the thermally stimulated current (TSC) in the temperature range adequate for the technological modes of obtaining, processing of composites and operation of metal-polymer units.

Analysis of the parameters of the energy state of dispersed particles of various composition, structure and production technology, which have found wide application in materials science of polymer nanocomposites (silicon-containing (clays, mica, talc, tripoli), carbon-containing (detonation nanodiamond (DND), carbon nanotube (CNT), carbon fibers (CF), shungite, colloidal graphite (CG)), metal-containing (particles of metals and oxides)), indicates the nonlinearity of the dependence of the TSC value on temperature, the presence of extrema in temperature ranges characteristic of each type of modifier, and instability $I = f(T)$ with a change in dimensional parameters, dispersion modes, the intensity of exposure to temperature, mechanical and other energy and technological factors. A typical form of the TSC spectra of particles of thermogasdynamic synthesis products (ultrafine polytetrafluoroethylene (UPTFE)), flint, shungite with a size of 50–100 μm is shown in Fig. 1 and 2. The nonlinearity of the $I = f(T)$ dependence is also typical for other organic and inorganic objects with different composition, structure and molecular weight.

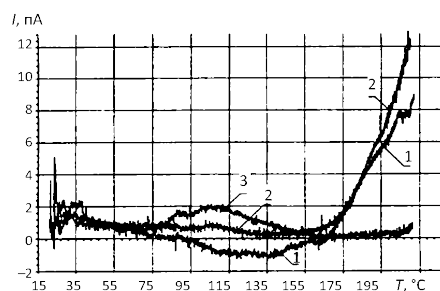


Fig. 1. Typical form of the TSC spectrum of initial (1) and heat-treated at 373 K (2), 473 K (3) products of thermogasdynamic synthesis (UPTFE)

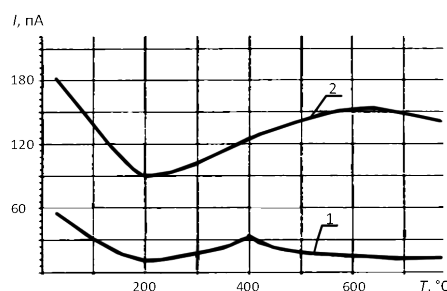


Fig. 2. Dependence of the value of the maximum thermally stimulated current (TSC) on temperature for UPTFE

stimulated current (TSC) on temperature for particles of silicon (1), shungite (2).

Dispersion of particles is 50–100 μm

As follows from the research of prof. G. I. Distler, V. A. Goldade, L. S. Pinchuk, the parameters of the electrophysical characteristics of material objects are determined not only by their composition and structure, but also by the type of technological impact.

The feature of dispersed particles of most common modifiers of high molecular weight matrices is the presence of an uncompensated charge with a long relaxation time, which is confirmed by EPR spectroscopy data (Fig. 3). Along with the special parameters of the electrophysical characteristics, due to the peculiarities of the composition and structure, material particles can be in a nanostate, ideas about which were proposed by prof. P. von Weimarn, P. M. Ajan, I. P. Suzdalev, A. I. Gusev and others, with certain types of technological impact that change the size, geometric characteristics and morphology of the surface layer. The size range of the transition of material objects to the nanostate is individual for particles of different composition and structure and is determined by the analytical expression proposed by V. A. Liopo, according to which the limiting size is $L_0 = 230 \cdot \theta_D^{-1/2}$, where θ_D is the Debye temperature. The validity of the use of this expression for the analysis of the structure of polymer nanocomposites is confirmed by systemic studies, the results of which are summarized in monographs [5, 6, 8, 11].

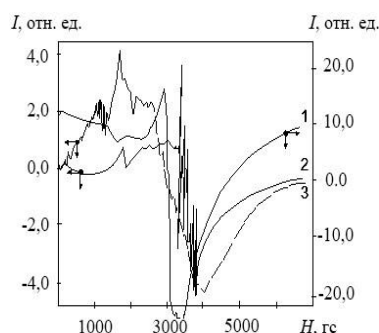


Fig. 3. EPR spectra of opal (1) and clay minerals of various compositions (2, 3). Dispersion of particles is 50–100 μm

An analysis of the morphological features of dispersed particles, widely used in the material science of polymer composites, by SEM and AFM methods, indicates the presence of nanosized components in objects of the micron range, which form the morphology of the surface layer (Fig. 4).

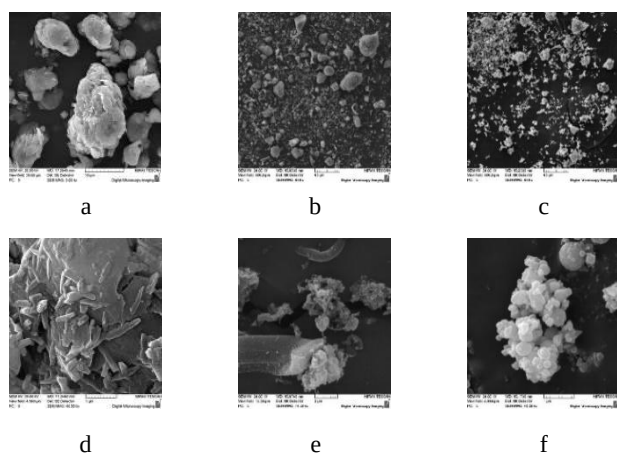


Fig. 4. Typical morphology of dispersed particles of clays (a, d), carbon nanotubes CNTs (b, e), metal oxides (c, f)

The presence of such components is the most important factor determining the activity of modifiers in the formation of polymer composites at various structural levels (intermolecular,

supramolecular, interphase) due to the manifestation of the surface layer of particles of energy parameters characteristic of the nanostate. Therefore, the technologies for activating modifiers of polymer matrices should ensure the formation of nanosized components in quantities sufficient for the implementation of the determining process of the required intensity, by establishing the mechanisms of their formation under various types of technological impact on the semi-finished product.

Using the concepts of condensed matter physics on the basis of a barrier model of the formation of a juvenile surface, mechanisms of dispersion of layered minerals such as mica, talc, and kaolin with the formation of nanosized lamellar components are proposed. It has been established that the determining processes of degradation of particles of the micrometer range are dehydration and dehydroxylation, which cause the destruction of the initial layered structure and the formation of nano-sized lamellar elements in the active state with a long relaxation time sufficient for implementation in the technology of polymer nanocomposites [5, 6]. It has been experimentally established that the activity of such elements in the processes of interaction with the environment (system components) depends on its composition, temperature and time characteristics. To intensify the process of dispersion of layered minerals, it is advisable to use thermal impact at temperatures of 800–1000 K or diffusion saturation of interlayer regions with low molecular weight and oligomeric media based on carbon-containing products with low resistance to thermal degradation [6].

Model studies of the dispersion of layered minerals of the mica type (muscovite) have shown the possibility of the formation of nanoparticles with a size of 30–50 nm under a shock thermal effect on the initial semi-finished product at 1073 K for 5–20 min. The lamellar particles formed under thermal shock have an increased adsorption activity in the process of interaction with the environment, including polymer matrices in a viscous-flow state, and intensify the intermolecular structuring of the composite.

Dispersion of particles from layered silicates can be realized directly in the process of obtaining or processing composite materials under thermomechanical action on the components of the screws of mixers, extruders or injection molding machines. The formation of an intercalated or exfoliated structure of the nanocomposite provides a technically significant effect of increasing the parameters of stress-strain and tribological characteristics even with a doping content (0.1 ÷ 1.0 wt.%) of the modifier.

Thermal action on dispersed particles changes the energy parameters of not only layered silicates (clays, talc), but also framework and chain (silicon, zeolites) and multiphase natural (tripoli, shungite) products (Fig. 1, 2).

An effective technology for activating dispersed particles is its dispersion under mechanical or mechanochemical action. It was experimentally established not only an increase in the specific surface area, but also the formation of nanosized components in the surface layer of particles. Modifiers activated in this way retain their activity for a technologically significant time (up to a year) [14].

Nanoscale components of the structure of the surface layer can also be formed as a result of exposure of a semi-finished product to energy flows – ionizing, laser radiation. In this case, not only does the specific surface area of the particle increase, which provides the mechanical component of the interfacial interaction, but also the parameters of the characteristics that determine its nanostate, which affect the supramolecular structure and adsorption capacity of the surface layers of modified substrates (PET, PTFE, PP, HDPE, CF) (Fig. 5).

An energetic assessment of the nanostate of polycrystalline particles is carried out to establish the temperature equivalent of the geometric parameters. It is shown that for a nanoparticle, due to the increased role of surface energy in comparison with a bulk sample, there is a correlation between the particle size and its energy state, which can be estimated from the temperature factor.

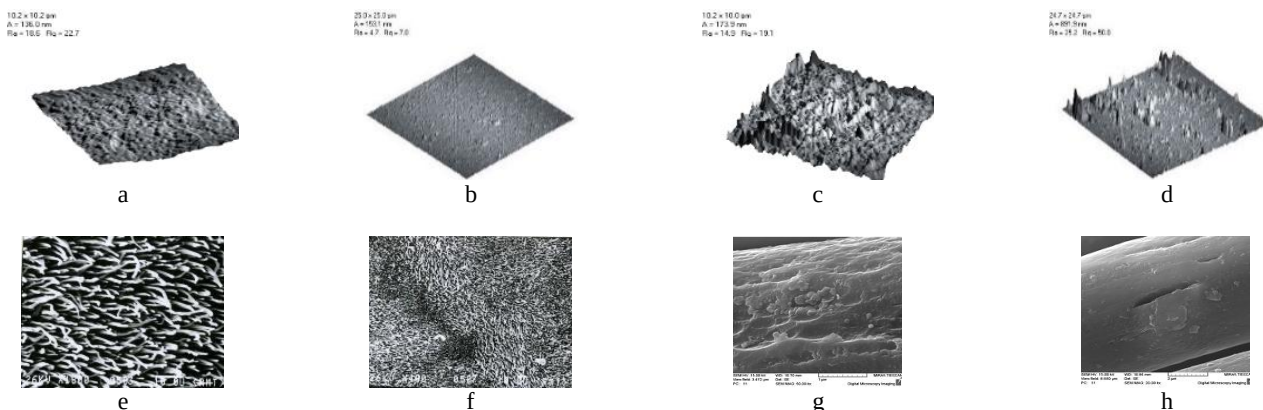


Fig. 5. Typical morphology of the surface layer of the substrate PTFE (e, f), PET (b, d), HDPE (a, c), carbon fiber (g, h), initial (a, b) and exposed to nitrogen ions at a dose of 1016 ion/cm^2 (g, h), pulsed laser radiation with a power density of 2.0 W/cm^2 (c, d). AFM data (a – d) and SEM (e – h)

When the particle size δ decreases by 1 %, the energy parameters increase by $\delta t = k (\delta T) \approx 3.5 \cdot 10^{-28} \text{ J}$. Therefore, the formation of nanosized particles or nanosized components in the structure of the surface layer of a macroparticle (substrate) is accompanied by an increase in the parameters of energy characteristics, estimated by the maximum value of the thermally stimulated current and the intensity of interfacial processes in the systems.

The carried out complex of studies on modeling the processes of formation of the structure of material objects with a pronounced manifestation of nano-state made it possible to determine the effective directions of its achievement in the technological processes of obtaining and processing nanocomposite materials based on industrial matrix polymers.

The choice of the conceptual direction of the technological embodiment of the phenomenon of nanostate is determined by a

combination of materials science, technological, economic, and operational factors. An algorithm for the implementation of the methodological approach has been developed, which allows, on the basis of the factors that determine the nanostate of the components of a system of a specific purpose and design, to select the technology for their implementation at a specific stage of the process, taking into account the material, economic, ergonomic, environmental and other aspects.

The methodological principles of the implementation of the phenomenon of nanostate in materials science and technology of functional nanocomposites based on industrial polymer matrices and metal-polymer systems with its use, focused on the state of the domestic technological base of industrial enterprises, related mainly to IV and V techno-economic paradigms, are proposed (Fig. 6).

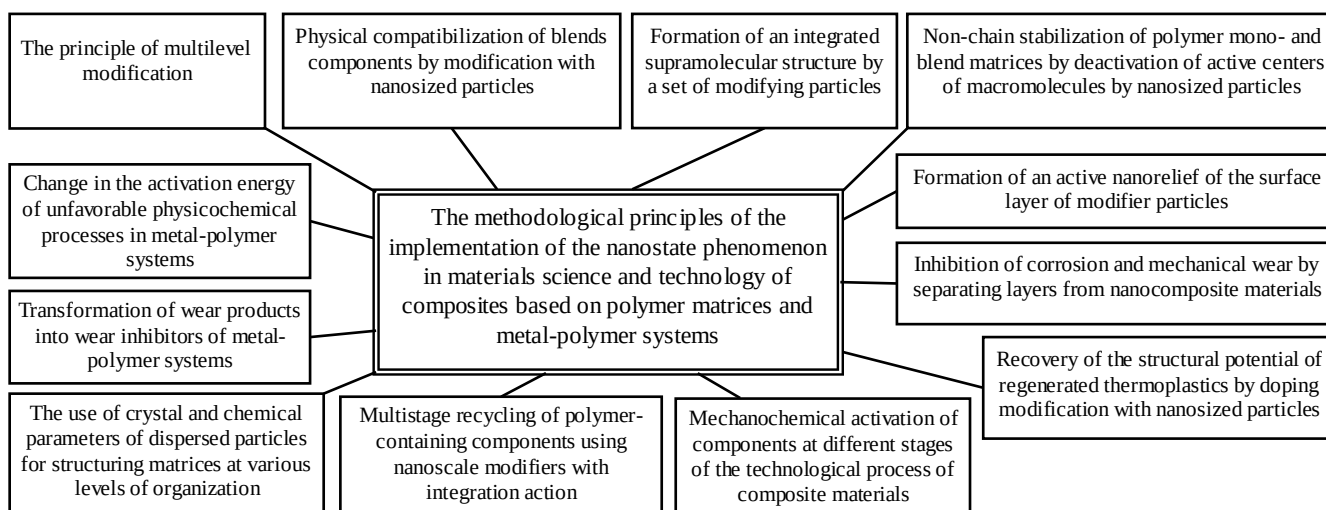


Fig 6. The methodological principles of the implementation of the nanostate phenomenon in materials science and technology of composites based on polymer matrices and metal-polymer systems

4. Conclusion

Based on a systematic analysis of the features of the morphological and energy parameters of dispersed components of condensed media of various compositions, its structure and production technologies, methodological approaches to the implementation of the phenomenon of nanostate in the formation of the optimal structure of composite materials and metal-polymer systems at different levels of organization have been developed. Scientifically-based foundation for the creating nanocomposite materials with increased parameters of stress-strain, adhesion and tribological characteristics based on industrial thermoplastics for functional

metal-polymer systems and efficient technologies for its manufacture and processing into products are proposed.

The concept of energy and technological compliance of the components of functional composite materials and systems has been developed. This concept consists in the implementation of the parameters of energy characteristics of the components of functional composite materials and systems adequate to the value of the activation energy of the dominant structural process, which determines the optimal parameters of the stress-strain, adhesive and tribological characteristics under technological impact on the components in the process of obtaining composite and its processing. Theoretically and experimentally substantiated the

reliability of estimating the parameters of the nanostate of material objects using an analytical expression to determine the limiting size of the transition to the nanostate of a particle or a component of the morphology of the surface layer according to the Debye temperature θ_D criterion. A definition of the nanostate of material objects is proposed. This definition characterizes the relationship between structural, morphological and energy parameters.

5. Acknowledgements

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5. References

1. Hussain C.M. Handbook of Nanomaterials for Industrial Application. Imprint: Elsevier, 2018. – 1130 p.
2. Eklund P.C., Roa A.M. Fullerene polymers and fullerene polymer composites. Berlin: Springer Science & Business Media, 2013. – 395 p.
3. Silva M., Alves N.M. Graphene-polymer nanocomposites for biomedical applications. Polymers for Advanced Technologies. 2018. Iss. 29. Vol. 2. – P. 687–700.
4. Grady B.P. Recent developments concerning the dispersion of carbon nanotubes in polymer. Macromolecular Rapid Communications. 2010. Iss. 31. Vol. 3. – P. 247–257.
5. Avdeychik S.V., Kostyukovich G.A., Kravchenko V.I., Lovshenko F.G., Lovshenko G.F., Panteleenko F.I., Rogachev A.V., Struk V.A., Tochitskiy E.I. Nanokompozitsionnye mashinostroitel'nye materialy: opyt razrabotki i primeneniia [Nanocomposite construction materials: development and application experience]. Grodno, GrSU, 2006. – 403 p. (in Russian).
6. Struk V.A., Prushak V.Ya., Avdeychik S.V., Liopo V.A., Dmitrochenko V.V., Protaseny A.V. Polimer-silikatnye mashinostroitel'nye materialy: fiziko-khimiia, tekhnologiia, primeneniie [Polymer-silicate construction materials: physical chemistry, technology, application]. Minsk, Tekhnologiia, 2007. – 431 p. (in Russian).
7. Avdeychik S.V., Voropayev V.V., Skaskevich A.A., Struk V.A. Mashinostroitel'nye ftorkompozity: struktura, tekhnologiia, primeneniie [Engineering fluorine composites: structure, technology, application]. Grodno, GrSU, 2012. – 319 p. (in Russian).
8. Avdeychik S.V., Liopo V.A., Ryskulov A.A., Struk V.A. Vvedenie v fiziku nanokompozitsionnykh mashinostroitel'nykh materialov [Introduction to the physics of nanocomposite construction materials]. Grodno, GGAU, 2009. – 439 p. (in Russian).
9. Avdeychik S., Goldade V., Struk V., Antonov A. Methodological approach to the dimension estimation of modifying particles for nanocomposites. Theoretical & Applied Science. 2020. Iss. 04. Vol. 84. – P. 638–644.

10. Avdeychik S., Goldade V., Struk V., Antonov A., Ikromov A. The phenomenon of nanostate in material science of functional composites based on industrial polymers. Theoretical & Applied Science. 2020. Iss. 07. Vol. 87. – P. 101–107.
11. Avdeychik S.V., Struk V.A., Antonov A.S. Faktor nanosostoianiia v materialovedenii polimernykh nanokompozitov [The nanostate factor in the material science of polymer nanocomposites]. Saarbrücken, LAP LAMBERT Acad. Publ., 2017. – 468 p. (in Russian).
12. Avdeychik S., Goldade V., Struk V., Antonov A., Ikromov A. Realizatsiia fenomena nanosostoianiia v materialovedenii funktsional'nykh nanokompozitov na osnove promyshlennykh polimerov [Realization of the phenomenon of nanostate in materials science of functional nanocomposites based on industrial polymers]. Electronic Processing of Materials. 2021. Vol. 57(1). – P. 7–18. (in Russian).
13. Avdeychik S., Struk V., Antonov A., Goldade V. Rol' energeticheskogo faktora v tekhnologii polimernykh kompozitov [The role of the energy factor in polymer composite technology]. Polymer Materials and Technologies. 2021. Iss. 7. Vol. 1. – P. 60–70. (in Russian).
14. Avdeychik S.V., Kravchenko V.I., Lovshenko F.G., Ovchinnikov E.V., Struk V.A., Lovshenko G.F. Tribokhimicheskie tekhnologii funktsional'nykh kompozitsionnykh materialov [Tribocchemical technologies of functional composite materials]. Part 2. Grodno. GGAU, 2008. – 399 p. (in Russian).
15. Abdurazakov A.A., Avdeychik S.V., Antonov A.S. Kompozitsionnye materialy v konstruktivnykh lentochnykh konveierov povyshennogo resursa [Composite materials in the design of belt conveyors with high resource]. Tashkent. Vneshinvestprom, 2019. – 351 p. (in Russian).
16. Antonov A.S. Avdeychik S.V., Ikromov A.G. Energeticheskii faktor materialovedeniia i tekhnologii polimernykh kompozitov [Energy factor of materials science and technology of polymer composites]. Tashkent. Vneshinvestprom, 2019. – 214 p. (in Russian).

Investigation of the coalescence of twin coplanar semi-elliptical fatigue cracks in structural steel elements under cyclic loading

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Abstract. The solution to the scientific task of identifying the fundamental laws of surface cracks development during their coalescence in the elements of steel structures under cyclic loading is presented in this article. A simulation model of coalescence of identical coplanar surface cracks has been developed. The model considers the solution to two problems: substantiation of the crack geometry during coalescence, and obtaining calculation formulas for estimating the stress intensity factors along a series of saddle-shaped contours. Based on the definition of stress intensity factors for contours modeling the gradual propagation of cracks in the coalescence zone using the finite elements method, the proposed model was tested to compare the calculated durability with experimental data.

KEYWORDS: SEMI-ELLIPTICAL SURFACE CRACK; COPLANAR CRACKS; COALESCENCE; STRESS INTENSITY FACTORS.

1. Introduction

The development of new advanced machines and structures is associated with ensuring their high load-bearing capacity and reliability taking into account minimal material consumption [1, 2]. A significant part of machines and structures is subjected to cyclic loading during operation. In such structures, the center of the destruction occurs in the local areas of structural and technological stress concentrators: welds, holes, notches, connections of structural elements.

Scientifically reasonable solutions obtained on the basis of modern research methods are used to ensure the necessary technical and economic characteristics of the created and operated machines and structures. Methods for estimating the dynamic properties of mobile machines using modern measuring equipment and modeling of multiple modes of operational loadings are presented in [3, 4]. The use of simulation methods is promising when it comes to assessing the durability of such structures at the design stage and determining the residual durability of structural elements with possible defects, especially when schematizing the geometry of defects and their coalescence during the propagation process.

Criteria assessment of the durability (residual life) of structures with existing cracks is based on the principles of fracture mechanics and is associated with the determination of the stress intensity factor (SIF), which characterizes the stress-strain state (SSS) at the crack tip [5]. Calculation of SIF in real structures is a challenging task taking into account the geometry and boundary conditions, especially for three-dimensional bodies.

The task of determining the SIF becomes significantly more complicated taking into consideration several surface cracks that are close and interact with each other. Such cracks grow and merge with each other under cyclic loading. Analysis of the existing standards indicates a conservative approach, when the stage of coalescence of surface cracks is neglected [6]. This is largely due to the lack of methods that would adequately assess SIF in the area of coalescence of the cracks.

To estimate the SIFs describing the stress field along the contour of a semi-elliptical surface crack propagating in a homogeneous stress field, the Newman-Raju equations [7] obtained based on finite element method (FEM) are usually used. They are applied to calculate the SIF along the contour of a single semi-elliptical surface crack. These results are generally accepted and most suitable for this class of cracks.

The study of the coalescence process of surface cracks is considered in [8, 9]. It is established that when two coplanar surface cracks are combined, a major crack with a saddle-shaped front is formed. With the development of the crack the saddle gradually decreases and the contour acquires a semi-elliptical shape. In [8], a model of crack coalescence is considered, in which the idea of relative crack overlap is implemented. The major crack changes its sizes both in a coalescence zone and on a surface. The disadvantage of this model is the conjugation zone, which is modeled by the intersection of the semi-ellipses. This conjugation does not correspond to the experimental data [10], especially in the final

stage of cracks coalescence. This will significantly affect the distribution of SIFs in the conjugation zone.

In the second model [9], the process of crack coalescence is modeled by a series of contours that gradually fill the saddle-shaped front. The conjugation zone of the semi-ellipses is modeled by the radii of concentric circles, the center of which is on the rear surface of a sample cross-section. It should be noted that the geometry of such model is insufficiently substantiated.

The process of coalescence of surface cracks is analyzed by the values of SIF in the saddle-shaped front zone, which, in turn, significantly depends on the geometry of the conjugation.

2. Method of SIF determination along the contour of a saddle-shaped surface crack using finite element method

The finite element method was used to determine the SIF in the coalescence zone. The calculation of SIF K_I by the finite element method is based on the calculation scheme, which includes a description of the object geometry, its mechanical characteristics and the description of boundary and initial conditions as a set of possible constraints and loadings applied to the object (Fig. 1).

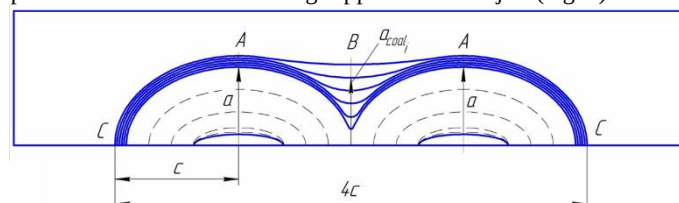


Figure 1. The model of coalescence of two identical surface cracks under cyclic loading

Coplanar cracks of various shapes modeled in a low-alloy steel 09Г2С samples were investigated with $\sigma_T = 380$ MPa and $\sigma_U = 540$ MPa. Chemical composition of steel is next: C – 0.08; Mn – 1.53; Si – 0.78; P – 0.021; S – 0.012; Cr – 0.04; Cu – 0.65; Ni – 0.12. The Poisson's ratio during elastic deformation was $\nu = 0.3$. The cross section of the samples is 80 mm × 20 mm. The tensile stress was $\sigma = 187.5$ MPa.

Modeling of surface cracks in objects was carried out using the software complex of finite-element analysis ANSYS Workbench, which is widely used to solve problems of mechanics of deformable solids and mechanics of structures. SIF K_I along the front of the surface crack was determined by the method of integration along the contours surrounding the tip of the crack. To achieve accurate calculation of the correct value, a maximum radius of integration within which contours will be located, their quantity, the quantity of divisions of the contours in the circular direction and the quantity of divisions along the front of the surface crack were predetermined.

In [11] the model of coalescence of two identical cracks is substantiated using the method of filling the saddle-shaped contour. In the process of coalescence of two cracks in the proposed model, the dimensions of their semi-axes remain unchanged, and only the

configurations of the crack coalescence area change. Thus, when modeling the coalescence of cracks, first of all, the crack grows in the saddle-shaped region a_{coal} ($a_i \dots a_j$), and the growth is minimal in the directions of the axes of each of the cracks (Fig. 2). This postulation of the process of coalescence of two identical surface cracks into one is confirmed by experimental data [10].

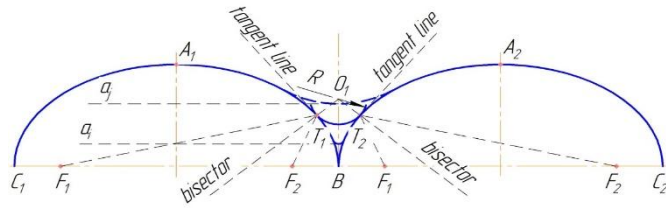


Figure 2. Illustration of the method for modeling the conjugation region of a contour when the surface cracks are merging

The growth of a surface crack with a various shape of a saddle-shaped contour, which changes under cyclic loading, is modeled in the software package ANSYS Workbench 19.2. To do this, the saddle-shaped front of the crack is divided into a number of fixed contours that simulate the gradual growth of two merging surface cracks. Conjugation of semi-ellipses is carried out by arcs of circles of different radii for each fixed contour.

The generally accepted procedure for solving the problems of fracture mechanics using FEM for objects with surface cracks is to generate three types of meshes: the initial (global) for the whole object, a local mesh with a surface crack that is integrated into the object, and finite element mesh in the transition zone. A fragment of a finite-element model of a saddle-shaped contour is presented in Fig. 3.

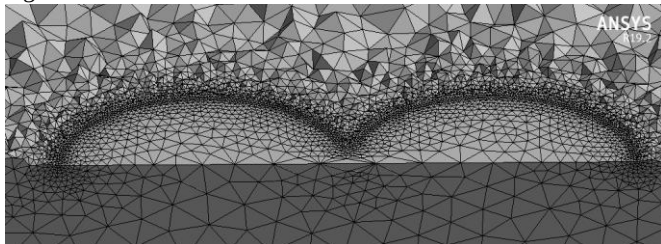


Figure 3. Fragments of a finite-element model of a plate with a semi-elliptical surface crack with noncanonical shape

The model of a surface crack of arbitrary configuration is formed using a surface body of zero thickness [12].

3. Research results

When determining the SIF K_I along the saddle-shaped contour of the crack, the initial shape of two identical merging cracks a/c (a and c are the semi-axes of the surface cracks (Fig. 1)) will have the most significant impact. After all, the shape of the coalescence zone depends on the geometry of surface cracks. The influence of one crack on another, as well as the geometry of the conjugation zone will have an influence on the change of the SIF along the contour in the coalescence area. In Fig. 4, a and Fig. 5, a the models of surface cracks with a saddle-shaped contour with the same ratio $a_{coal}/a = 0.2$ and different cracks depth $a = 3$ mm (Fig. 4, a) and $a = 5$ mm (Fig. 5, a) are presented.

The radius of curvature in the conjugation zone for the first model was 0.41 mm, and for the second model it was 0.31 mm. The tensile stress for both cases was $\sigma = 187.5$ MPa.

In Fig. 4, b and Fig. 5, b the stress distribution along the saddle front is shown. The maximum values of the stress intensity factors K_I are observed at the deepest points of the saddle-shaped surface crack front $K_I = 24.1 \text{ MPa} \sqrt{m}$ and $K_I = 44.85 \text{ MPa} \sqrt{m}$, respectively.

Another factor that affects the value of SIF K_I is the ratio a_{coal}/a , where a_{coal} is the distance from the surface of the sample to the deepest point of the saddle-shaped front of each of the simulated contours.

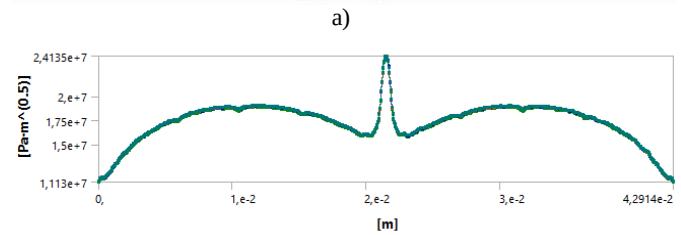
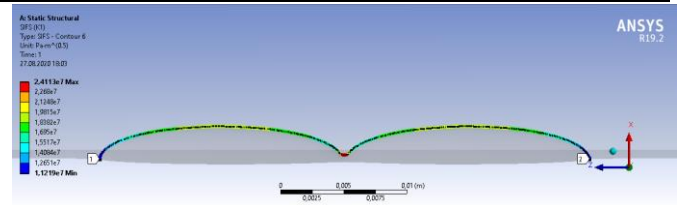


Figure 4. The model of a surface crack with a saddle-shaped contour with $a_{coal}/a = 0.2$; $a = 3$ mm (a) and the results of SIF K_I at $\sigma = 187.5$ MPa (b)

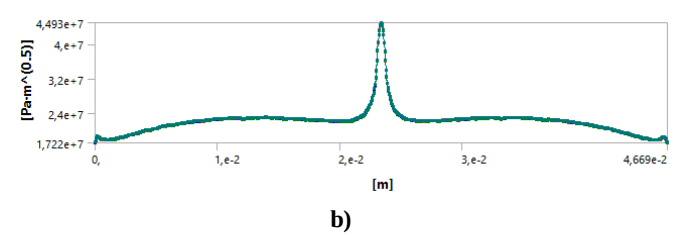
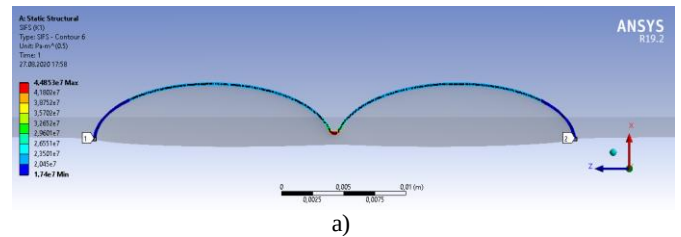


Figure 5. The model of a surface crack with a saddle-shaped contour with $a_{coal}/a = 0.2$; $a = 5$ mm (a) and the results of SIF K_I at $\sigma = 187.5$ MPa (b)

The results of the calculation of SIF K_I along the contours of identical surface cracks in the simulation of their coalescence are shown in Fig. 6. The results are presented for eight different contours modeling the gradual propagation of the crack in the coalescence zone. The filling of the saddle-shaped is characterized by the ratio a_{coal}/a , where a is the depth of each of the two merging symmetrical cracks; a_{coal} is the distance from the surface axis of the major crack to the deepest point of the saddle-shaped contour of each of the simulated contours.

The geometrical parameters of the model in determining the SIF K_I were as follows: $a = 7.0$ mm; $c = 10.0$ mm; a_{coal} varied from 1.043 to 6.65 mm with a_{coal}/a changing from 0.149 to 0.95. The radius of curvature in the conjugation zone under such conditions varied from $R = 0.14$ mm at $a_{coal}/a = 0.149$; $R = 7.0$ mm at $a_{coal}/a = 0.626$ and up to $R = 129.0$ mm at $a_{coal}/a = 0.95$.

Analysis of the distribution of SIF K_I shows that their maximum values are observed in the area of the coalescence of cracks (in the middle of the contour), and the highest value of SIF is observed at the lowest value of $a_{coal}/a = 0.149$.

Moreover, when the cracks merged from 14.9% to 62.6%, the SIF significantly decreased from $K_I = 79.51 \text{ MPa} \sqrt{m}$ to $K_I = 37.02 \text{ MPa} \sqrt{m}$ (2.15 times). Upon further coalescence of surface cracks up to 95%, the SIF decreased only by 1.07 times (to $34.68 \text{ MPa} \sqrt{m}$). It should be noted that in accordance with the change of SIF at the initial stage of surface cracks coalescence, the crack growth rate at the deepest point of the saddle-shaped front is ten times higher than the growth rate of the outer (surface) points of the saddle-shaped crack.

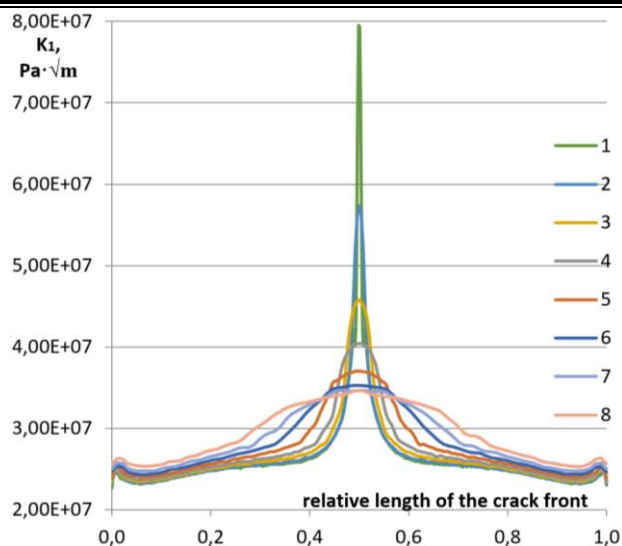


Figure 6. Distribution of SIF K_I values along the contour of the surface saddle-shaped crack in the simulation of gradual coalescence with a_{coal}/a :

1) 0.149; 2) 0.256; 3) 0.378; 4) 0.491; 5) 0.626; 6) 0.754; 7) 0.85; 8) 0.95 at $\sigma = 187.5$ MPa.

Comparative analysis of the interaction coefficients γ_{coal} characterized by the ratio of SIF at the deepest point of the saddle-shaped front of the crack with semi-axes a/c to the value of SIF for the surface point shows that the results obtained by the proposed method (at $a/4c = 0.175$; $a/t < 0.5$) agree with the data [9].

The obtained values of γ_{coal} (as well as SIF) by the method of crack overlapping are significantly higher (up to 60%), which indicates the conservatism of the method.

To test the proposed model of surface cracks coalescence, the durability of the saddle-shaped crack growth was calculated. For this purpose, according to the proposed model, 8 saddle-shaped contours of different shapes were modeled, showing the development of the major surface crack from the coalescence of two smaller cracks. The distribution of SIFs along each of the contours was obtained by the finite element method.

The calculation of the durability of N_{model} (Fig. 7) was carried out on the basis of the integration of the modified Paris equation [5], which describes the average amplitude section of the kinetic fatigue fracture diagrams of steel 50D BS 4360:

$$N_{model} = \int_{a_{coal\ min}}^{a_{coal\ max}} \frac{1}{C(\Delta K_{a_{coal}})^n} da_{coal},$$

where $\Delta K_{a_{coal}}$ is the SIF difference for the deepest point a_{coal} for each of the studied saddle-shaped contours of the surface crack (obtained by the proposed method);

a_{coal} is the distance from the deepest point of each of the contours to the surface of the sample.

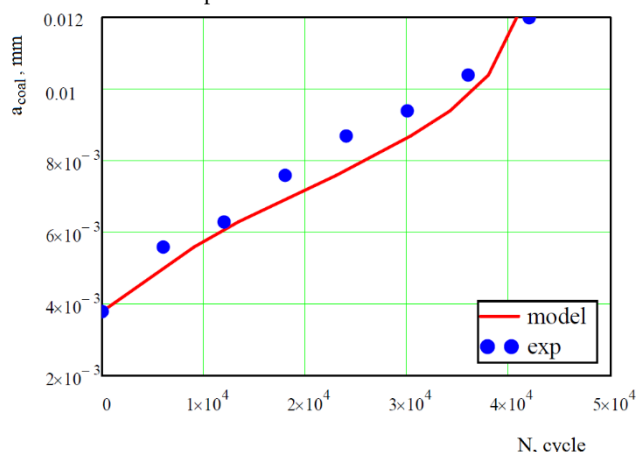


Figure 7. Comparison of the results of simulation modeling of the coalescence process for surface cracks with experimental data [10]

It should be noted that the obtained value of the number of cycles required for crack coalescence N_{model} agrees well with the experimental value of the number of cycles N_{exp} (error does not exceed 5%). It is also worth noting the durability curves obtained during modeling and on the basis of experimental data match in terms of qualities.

4. Conclusion

A simulation model is proposed to determine the durability of the crack at the coalescence stage. The least studied stage is the period of coalescence of surface cracks. The coalescence of the cracks is represented by a series of curved lines that mimic the development of a saddle-shaped contour of a surface crack. The results of the calculation of the durability of the saddle-shaped crack according to the proposed model agree well with the known experimental data.

5. References

1. Махненко В. И. Ресурс безопасной эксплуатации сварных соединений и узлов современных конструкций. – К.: Наукова думка, 2006. – 619 с.
2. Альгин В.Б. Расчет мобильной техники: кинематика, динамика, ресурс. – Минск: Беларуская навука, 2014. – 271с.
3. Пидгурский Н. Прогнозирование и обеспечение усталостной надежности несущих конструкций мобильных машин // Пидгурский Н., Рыбак Т., Сташків Н., Попович П. / Международен конгрес «Машиностроителни технологии» International congress "Mechanical engineering technologies'04" 2004, Varna, Bulgaria, Volume 6. – С.139 – 142.
4. Mykola Pidgurskyi, Yevgen Ripetskyi, and Ivan Pidgurskyi (2020). Research and simulation of load modes in the evaluation of mobile machines resource. AIP Conference Proceedings, 2020, 020064 (2018): 7p.
5. Ted L. Anderson, Fracture Mechanics Fundamentals and Applications, Fourth ed., Boca Raton, CRC Press, 2017.
6. Kai Lu, Yinsheng Li. Fatigue crack growth calculations for two adjacent surface cracks using combination rules in fitness-for-service codes / AIMS Materials Science, 2017, 4(2): 439-451.
7. J.C. Newman, I.S. Raju An empirical stress-intensity factor equation for the surface crack. Engineering Fracture Mechanics. –Volume 15, Issues 1–2, 1981, 185 – 192.
8. S. K. Patel, B. Dattaguru, K. Ramachandra, Multiple Interacting and Coalescing Semi-Elliptical Surface Cracks in Fatigue P. 1: FEA, SL, V. 3, N.1, (2010), 37 – 57.
9. C.J. Bayley, R. Bell Parametric investigation into the coalescence of coplanar fatigue cracks, Int. J. of Fat., V. 21, I. 4, (1999), 355 – 360.
10. B. Bezensek, J.W. Hancock, The re-characterisation of complex defects: Part I: Fatigue and ductile tearing, Eng. Fract. Mech. V. 71, I. 7 – 8, (2004), 981 – 1000.
11. Pidgurskyi, M., Stashkiv, M., Pidgurskyi, I., Makar, A. (2020) Numerical investigation of stress intensity factors for surface cracks under coalescence. *Procesy zmęczenia i mechanika pękania. Opole, 2020.* – Vol. 536, 231 – 246.
12. H.H. Lee. Finite Element Simulations with ANSYS Workbench 19, SDC Pub., 2019.

Decreasing pressure losses by applying drilling mud with nanoparticles

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Abstract: During mud circulation pressure losses occur in all sections of the wellbore: surface pipeline, inside drill string, drill bit and around drill string. The sum of the pressure losses calculated for each section is equal to the total pressure loss in the system, i.e. the pressure that is read on the manometer of the mud pump. The mud flow through annulus (between drill pipes/collars and open hole/casing) causes an increased pressure loss for the certain flow rate which increases the pressure exerted on the wellbore wall, so it is important to manage it. In this paper, the influence of SiO₂ nanoparticles on the rheological properties of bentonite mud was examined. After that, for a typical wellbore construction and selected mud flow was calculated their influence on pressure losses in the area around drilling pipes and collars. The pressure losses were determined using the Bingham model which provides an easy way to obtain data of acceptable accuracy for the case of application in conventional vertical wells. The results indicate that the addition of SiO₂ nanoparticles can reduce the pressure loss during mud circulation, in some cases by more than 50%.

Keywords: SiO₂ NANOPARTICLES, DRILLING MUD, RHEOLOGY, PRESSURE LOSS

1. Introduction

The conventional drilling tools consists of drill pipes and drill collars that bring mechanical energy which include rotation and weight on bit, as well as hydraulic energy. Whole drilling tools are pulled out of the wellbore each time a drilling bit or bottomhole assembly (BHA) needs to be replaced or the depth of the casing shoe has been reached. After that, the casing pipes is lowered into the wellbore and cemented. In Figure 1 is presented typical wellbore construction.

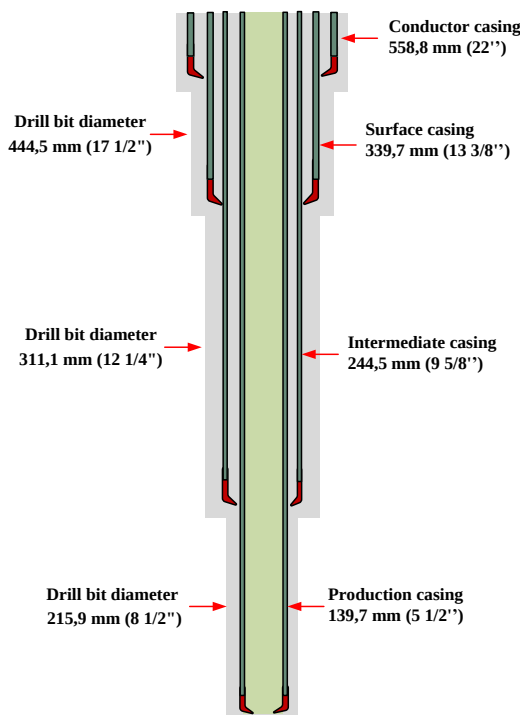


Fig 1. Typical wellbore construction [1].

The mud circulation cycle consists of several components or intervals, with pressure losses occurring on each of them. The sum of the pressure losses during each interval is equal to the total pressure loss in the system, i.e. the pressure measured on the mud pump. Figure 2 shows a simplified mud flow in the wellbore during drilling.

Knowing the flow of fluids that have different rheological properties in the annular space (between drill pipes/collars and wellbore walls/casing) is important because the precise determination of the flow properties of different fluids is the basis for planning and designing hydraulic analysis of well during planning of wellbore construction [2]. A significant increase in pressure loss due to flow resistance occurs in a confined space (annular) which requires its precise assessment. Determining the

pressure loss due to friction (flow resistance) is useful for calculating the required power of the mud pump, the pressure at the bottom of the wellbore, and the maximum pressure at the wellhead. Accurate determination of pressure loss is also important from an economic point of view. Calculating the pressure reduction in the annular space due to flow resistance allows an appropriate assessment of the flow conditions, which is crucial to reduce problems and avoid high costs during drilling.

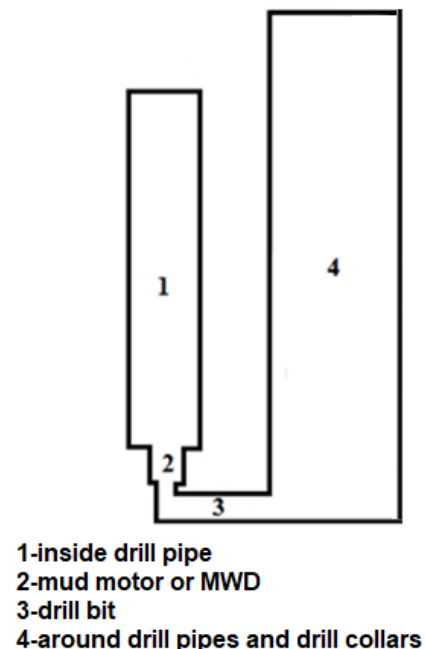


Fig 2. Simplified schematic of the mud circulation.

Consideration of drilling fluid flow conditions according to API procedures involves the application of either an exponential or Bingham plastic rheological model [2]. These models and the corresponding hydraulic calculations provide a simple way to obtain data of acceptable accuracy for the case of applications in conventional vertical wells and for the application of simple mud composition, such as bentonite muds.

Previous studies of the influence of nanoparticles on the rheological properties of drilling muds indicate that the influence of nanoparticles on the rheological properties of drilling mud cannot be determined with certainty because there have been cases of increasing and decreasing rheological parameters of tested mud for certain types of added nanoparticles [3-6]. So far, the positive influence of SiO₂ nanoparticles on most other properties has been determined, and in this paper their influence on rheological properties has been examined. Also, the pressure reduction according to the Bingham model has been calculated and the

influence of nanoparticles addition on the pressure loss is investigated.

2. Required data for calculation

The flow regime is a type of fluid flow in pipelines. Fluid flow in pipes can be plug-shaped, transitional from plug-shaped to laminar, laminar, transitional from laminar to turbulent and turbulent [7]. In hydraulic calculation, laminar or turbulent fluid flow is most often considered.

Since this paper only deals with the pressure loss calculation in the annular space (labeled with number 4 at Figure 2), the procedure for determining the pressure loss (Table 1) and relevant formulas (Table 2) are presented below.

Table 1: The procedure for determining the pressure loss [According to 8].

1	After the mud pump flow rate has been selected, it is necessary to determine the flow rate of the drilling mud in the annular space for a given construction of the wellbore.
2	For the Bingham plastic model, it is necessary to calculate the plastic viscosity and yield point. Input parameters for the calculation of rheological models are obtained by laboratory analysis of mud on a rotary viscometer.
3	Based on the obtained rheological parameters, it is necessary to determine the type of flow, depending on the selected rheological model. The type of flow is determined by calculating the Reynolds number and comparing the obtained value with the critical value. For Bingham plastic fluids the critical value of the Reynolds number is 2100. If the calculated values of the Reynolds number are higher than the critical ones, turbulent flow formulas are used, otherwise laminar flow formulas are used.
4	Fluids whose viscosity depends on the shear rate, such as muds, behave like non-Newtonian fluids. To distinguish Newtonian fluids from non-Newtonian fluids, the concept of effective viscosity was introduced and it should be calculated.
5	Calculate the pressure loss, depending on the type of flow (laminar or turbulent).

Table 2: The equations used for calculation of the pressure loss in annular [According to 8].

Flow rate of the drilling mud in the annular space	$v = \frac{4 \cdot Q}{\pi \cdot (D_2^2 - D_1^2)}$
Plastic viscosity (μ_p)	$\mu_p = \frac{\tau_{1022} - \tau_{511}}{1022 - 511}$
Yield point (τ_0)	$\tau_0 = \tau_{1022} - 2(\tau_{1022} - \tau_{511})$
Reynolds number	$Re = \frac{9,8 \cdot (D_2 - D_1) \cdot v^2 \cdot \rho_i}{\tau_0 \cdot (D_2 - D_1) + 12 \cdot v \cdot \mu_p}$
Effective viscosity	Laminar flow $\mu_e = \mu_p + \frac{\tau_0}{12 \cdot v} \cdot \frac{D_2 - D_1}{D_2 - D_1}$
	Turbulent flow $\mu_e = \mu_p$
Pressure loss	Laminar flow $p = \frac{48 \cdot l \cdot \mu_e \cdot v}{(D_2 - D_1)^2}$
	Turbulent flow $p = \frac{0,1275 \cdot l \cdot \rho_i^{0,8} \cdot v^{1,8} \cdot \mu_e^{0,2}}{(D_2 - D_1)^{1,2}}$

Where:

v – flow rate of the drilling mud in the annular space (m/s)

τ_{1022} – shear stress at shear rate of 1022 s⁻¹ (Pa)

τ_{511} – shear stress at shear rate of 511 s⁻¹ (Pa)

ρ_i – mud density (kg/m³)

τ_0 – yield point (Pa)

μ_p – plastic viscosity (Pa·s)

D_2 – drill bit diameter or inside diameter of casing (m)

D_1 – outside diameter of drill pipe/collar (m)

l – pipe length (m)

3. Laboratory testing

Laboratory testing was performed at the Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb, Croatia. In order to examine impact of the addition of SiO₂ nanoparticles on the pressure loss around drill pipes and drill collars during mud circulation, five types of drilling muds were prepared and subjected to laboratory testing: bentonite-based drilling mud as base mud (BM) and four drilling muds contain SiO₂ (Table 3). Drilling muds were prepared according to American Petroleum Institute Standards, API Specifications 13A and API 13B-1 [9]. SiO₂ nanoparticles were in the form of an aqueous suspension and were added to bentonite-based mud until nanoparticles concentration reach 1 wt% and 3 wt%. Average particle size used in this laboratory testing was 20 nm and 60 nm (Figure 3).

Table 3: Drilling mud formulations [According to 10-11].

Mud additives	BM	BM + 1% 60nm	BM + 3% 60nm	BM + 1% 20nm	BM + 3% 20nm
Water (l)	1	1	1	1	1
Bentonite (g)	70	70	70	70	70
NaOH (g)	2	2	2	2	2
PAC LV (g)	2	2	2	2	2
Aqueous suspension of nanoparticles (g)	-	25	75	33.3	100

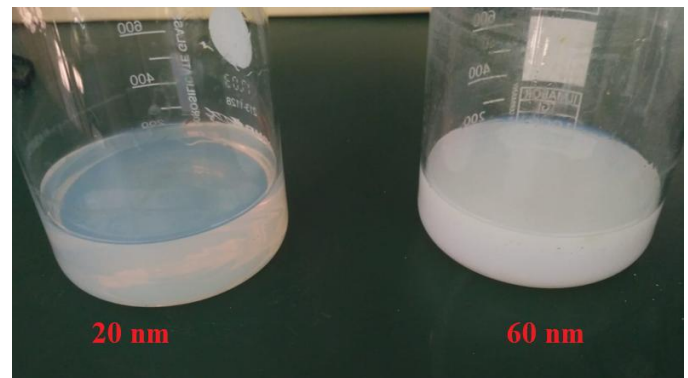


Fig 3. Nanoparticles used in laboratory testing.

After preparation of drilling muds, density and rheological properties were measured. The used equipment and conditions are shown in table 4.

Table 4: Laboratory test equipment and conditions.

Test	Equipment	Conditions
Density	Mud balance 	Atmospheric pressure and temperature
Rheology	OFITE Viscometer 900 	Atmospheric pressure, temperature 25, 50 and 75 °C

4. Results and discussion

Rheological properties were tested at 25, 50 and 75 °C using OFITE Viscometer 900. The following table 5 show the relation of shear stress measured at shear rate of 5.1, 10.2, 170, 340, 510 and 1020 s⁻¹ according to American Petroleum Institute Standards, API Specification API 13B-1 [9].

Table 5: Shear stress measured at a certain shear rate for all tested muds [According to 10].

T (°C)	Shear rate (s ⁻¹)	BM	BM + 1% 60nm	BM + 3% 60nm	BM + 1% 20nm	BM + 3% 20nm
		Shear stress (lb/100 ft ²)				
25	1020	36,5	34,3	35,9	45,9	42,2
	510	23,9	22,2	22,0	31,4	25,5
	340	19,0	17,5	17,1	25,5	19,4
	170	13,3	11,8	10,8	18,6	12,4
	10,2	6,1	4,3	2,7	9,0	2,2
	5,1	6,1	4,7	3,3	10,0	2,2
50	1020	37,3	33,7	33,1	45,1	41,2
	510	25,5	22,2	20,8	29,8	24,7
	340	21,2	17,6	17,1	25,9	18,6
	170	15,5	12,9	12,2	20,0	12,5
	10,2	8,6	6,5	4,9	10,4	2,5
	5,1	9,6	7,1	5,9	12,2	2,5
75	1020	41,6	30,2	27,1	39,8	37,1
	510	32,5	22,2	18,6	29,2	22,9
	340	30,6	19,8	15,3	27,1	18,2
	170	28,6	17,6	12,4	24,1	12,5
	10,2	24,9	12,4	6,3	16,1	3,3
	5,1	28,6	13,3	6,7	17,3	3,3

According to equations in Table 2 were determined plastic viscosity and yield point values for all tested muds and shown in Table 6.

Table 6: Plastic viscosity and yield point data for all tested muds.

T (°C)	Mud type	Plastic viscosity μ_p (mPas)	Yield point τ_o (Pa)
25	BM	12,6	5,8
	BM + 1% 60nm	12,1	5,1
	BM + 3% 60nm	13,9	4,1
	BM + 1% 20nm	14,5	8,6
	BM + 3% 20nm	16,6	4,5
50	BM	11,6	7,1
	BM + 1% 60nm	11,7	5,3
	BM + 3% 60nm	12,3	4,3
	BM + 1% 20nm	15,2	7,4
	BM + 3% 20nm	16,5	4,1
75	BM	9,1	12
	BM + 1% 60nm	8	7,3
	BM + 3% 60nm	8,5	5,2
	BM + 1% 20nm	10,5	9,5
	BM + 3% 20nm	14	4,6

According to equations in Table 2, the pressure loss values per 1 m of pipe length was determined for all tested muds (Table 7). The pressure loss was calculated around the drill collars which has outside diameter of 0.1288 m (6 1/4") and drill pipes which has outside diameter of 0.127 m (5). Drill bit diameter was 0.2159 m (8 1/2") with the mud pump flow rate of 1,600 l/min. The density of the base mud (BM) was 1030 kg/m³. By adding SiO₂ nanoparticles at a concentration of 1 wt% mud density increased to 1040 kg/m³, while adding 3 wt% of nanoparticles density increased to 1060 kg/m³.

Table 7: Pressure loss per 1 m of pipe length.

T (°C)	Mud flow	BM	BM + 1% 60nm	BM + 3% 60nm	BM + 1% 20nm	BM + 3% 20nm
		Pressure loss (Pa/m)				
25	Around drill pipe	344	313	279	485	314
	Around drill collar	975	975	1018	942	1056
50	Around drill pipe	395	321	277	437	301
	Around drill collar	962	967	994	876	1053
75	Around drill pipe	601	378	291	499	298
	Around drill collar	1051	899	921	913	1021

Table 8 shows the reduction of pressure losses values in the annulus compared to the value obtained with the base mud. The best results are marked in green and it can be seen that the addition of SiO₂ nanoparticles in most cases reduced the pressure loss. Also, it can be seen that the effect of nanoparticles is more pronounced at higher temperatures, and the best result was obtained by adding SiO₂ nanoparticles at a concentration of 3 wt% at 75 °C (reduction of 51.6% with 60 nm nanoparticles and 50.4% with 20 nm nanoparticles).

Table 8: The reduction of pressure losses values in the annulus compared to the value obtained with the base mud.

T (°C)	Mud flow	BM + 1% 60nm	BM + 3% 60nm	BM + 1% 20nm	BM + 3% 20nm
		Pressure loss (Pa/m)			
25	Around drill pipe	-9,0%	-18,9%	41,0%	-8,7%
	Around drill collar	0,0%	4,4%	-3,4%	8,3%
50	Around drill pipe	-18,7%	-29,9%	10,6%	-23,8%
	Around drill collar	0,5%	3,3%	-8,9%	9,5%
75	Around drill pipe	-37,1%	-51,6%	-17,0%	-50,4%
	Around drill collar	-14,4%	-12,4%	-13,1%	-2,9%

5. Conclusion

In this study was determined the impact of SiO₂ nanoparticles on rheology parameters of bentonite-based drilling mud. Used SiO₂ nanoparticles had different particle sizes (60 and 20 nm) and was added in two different concentrations (1 wt% and 3wt%). After the parameters of the Bingham model were determined, the pressure loss in the annular for one typical wellbore construction was determined in order to more clearly observe the positive influence of SiO₂ nanoparticles. Based on laboratory testing, the following conclusions can be drawn:

- In most tested muds the nanoparticles had a positive effect on reducing the pressure loss in the annular.
- The effect of nanoparticles is more pronounced at higher temperatures.
- The best result was obtained by adding SiO₂ nanoparticles at a concentration of 3 wt% at 75 °C.

However, these data provide a good basis for further testing with new nanoparticles added in different concentrations.

6. References

[1] N. Gaurina-Medimurec, B. Pašić, P. Mijić, I. Medved, K. Novak-Mavar, M. Hrgarek, I. Rak Zarić, M. Rak, A. Maderić, V. Dubovečak. Elaborat o zaštiti okoliša za ocjenu o potrebi procjene utjecaja na okoliš za zahvat „Istražna bušotina Ždala (Žd-1) s radnim prostorom za smještaj bušačeg postrojenja“, Rudarsko-geološko-naftni fakultet (2020)

[2] K. Simon. The Role of Different Rheological Models in Accuracy of Pressure Loss Prediction, Rudarsko-geološko-naftni zbornik, 16, 85-89 (2004)

[3] Z. Vryzas, O. Mahmoud, H.A. Nasr-El-Din, V. Kelessidis, Development and Testing of Novel Drilling Fluids Using Fe₂O₃ and SiO₂ Nanoparticles for Enhanced Drilling Operations, IPTC-18381-MS, International Petroleum Technology Conference, Doha, Qatar, 1-16 (2015)

[4] N. Wahid, M.A.M. Yusof, N.H. Hanafi. Optimum Nanosilica Concentration in Synthetic Based Mud (SBM) for High Temperature High Pressure Well, SPE-176036-MS, SPE/IATMI Asia Pacific Oil & Gas Conference and Exhibition, Nusa Dua, Bali, Indonesia, 1-14 (2015)

[5] A.H. Salih, H. Bilgesu. Investigation of Rheological and Filtration Properties of Water-Based Drilling Fluids Using Various Anionic Nanoparticles, SPE-185638, SPE Western Regional Meeting, Bakersfield, California, USA, 1-21 (2017)

[6] A.O. Gbadamosi, R. Junin, J.O. Oseh, A. Agi, N. Yekeen, Y. Abdalla, S.O. Ogiriki, A.S. Yusuff. Improving hole cleaning efficiency using nanosilica in water-based drilling mud, SPE-193401, SPE Nigeria Annual International Conference and Exhibition, Lagos, Nigeria, 1-16 (2018)

[7] M. Perić. Englesko-hrvatski enciklopedijski rječnik istraživanja i proizvodnje nafte i plina, Zagreb: INA Industrija nafte d.d. (2007)

[8] P. Mijić. Određivanje hidrauličkih otpora tijekom bušenja uz primjenu zaštitnih cijevi, Master thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering (2013)

[9] API, R. 13B-1, Recommended Practice for Field Testing Water-Based Drilling Fluids, and ISO 10414-1, American Petroleum Institute (2003)

[10] S. Mijić. Utjecaj nanočestica SiO₂ na smanjenje filtracije isplaka na bazi vode, Master thesis, University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering (2018)

[11] P. Mijić, S. Mijić, I. Medved, K. Perić. Influence of adding SiO₂ nanoparticles on rheological and filtration properties of water-based muds, Innovations, 7(1), 43-46 (2019)

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Impact of chemical composition on tribological properties of $\text{Al}_x\text{CoCrFeNi}$ high-entropy alloys

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Abstract: High-entropy alloys were first extensively described in 2004 [1]. Despite the increasing scientific interest in these materials, there is still much to discover. The AlCoCrFeNi alloy is one of the most popular HEAs. Scientists often study the mechanical properties of this alloy and the effect of varying the different component contents on its properties [2,3]. There are also studies on the effects of alloying additives on structure and properties [4,5]. In this study, high-entropy alloys were obtained by induction melting. The influence of aluminium content and titanium addition on tribological properties of $\text{Al}_x\text{CoCrFeNi}$ alloy was tested. Furthermore, the alloys were characterised by X-ray diffraction (XRD), hardness, and microstructure examination. The occurring wear mechanisms and tribological properties of the tested high-entropy alloys were analysed and compared with the results obtained for C45 steel. The received results confirm the influence of Al content in $\text{Al}_x\text{CoCrFeNi}$ alloy and Ti addition on tribological properties.

Keywords: HIGH-ENTROPY ALLOY, INDUCTION MELTING, TRIBOLOGICAL PROPERTIES, MICROSTRUCTURE

1. Introduction

High-entropy alloys (HEAs) are a relatively new group of materials that have good functional and structural properties according to the literature. HEAs differ from conventional alloys, because they are composed of 5 to 13 elements in amounts varying from 5 to 35% [6]. In this study, the tribological properties of $\text{Al}_x\text{CoCrFeNi}$, $\text{AlCoCrFeNiTi}_{0.5}$ alloys and, for comparison, the common steel C45 were investigated. Additionally, the presence of phases, hardness, and microstructure were examined.

2. Materials and methods

High-entropy alloys $\text{Al}_x\text{CoCrFeNi}$ ($x = 0.5, 0.7, 1$) and $\text{AlCoCrFeNiTi}_{0.5}$ were obtained by induction melting in a protective argon atmosphere. The C45 steel that was used to compare results was hardened in water and low tempered. Hardness was measured by the Vickers method under a load of 10 kG. A high-resolution SEM/FIB SCIOS 2 electron microscope was used to analyse the microstructure and chemical composition. Friction paths were analysed using a HITACHI S-3000N scanning electron microscope. Tribological tests were carried out on a T-11 disk-ball type tribometer. Each series was tested a minimum of two times, where the test parameters were:

- pressure $F=10\text{ N}$
- time $T=2\text{ h}=7200\text{ s}$
- linear speed $v=0.1\text{ m/s}$

Alloys obtained by induction melting may exhibit a slightly changed content of particular elements. This occurs because of the material deposition on the crucible (metal adhesion effect). The chemical composition of the produced specimens is presented in Table 1.

Table 1: Chemical composition of obtained alloys.

Materials	Element (at. %)					
	Al	Cr	Fe	Co	Ni	Ti
$\text{Al}_{0.5}\text{FeCrCoNi}$	11,22	14,24	24,95	25,07	24,53	-
$\text{Al}_{0.7}\text{FeCrCoNi}$	14,66	15,37	23,90	23,36	22,71	-
AlFeCrCoNi	18,72	21,26	21,22	20,07	18,72	-
$\text{AlFeCrCoNiTi}_{0.5}$	17,94	17,04	19,87	18,28	17,00	9,86

3. Results

The influence of the chemical composition on the crystal structure of high-entropy alloys was investigated (Fig. 1) In the $\text{Al}_{0.5}\text{FeCrCoNi}$ alloy, mainly the fcc phase appears, one small peak corresponding to the bcc phase is visible. For the $\text{Al}_{0.7}\text{FeCrCoNi}$ alloy the amount of the bcc phase increases, and for the AlFeCrCoNi alloy only bcc is present. In the $\text{AlFeCrCoNiTi}_{0.5}$ sample, titanium caused the appearance of additional intermetallic

phases with a complex chemical composition and a complicated crystal structure.

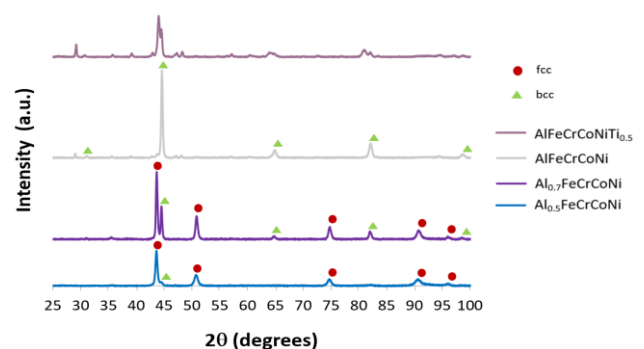


Fig. 1 XRD patterns of high-entropy alloy samples.

In the microstructure of $\text{Al}_{0.5}\text{FeCrCoNi}$ sample (Fig. 2a), two phases are visible where the bright phase is homogeneous. Large grains of alloy elements with fcc structure are observed. A dark phase is present in the spaces between the grains. The microstructure of the $\text{Al}_{0.7}\text{FeCrCoNi}$ sample (Fig. 2b) differs significantly from the previous one. The fcc and bcc phases are also present, with a higher contribution of the first one. Eutectic mixture (resembling Widmanstätten pattern) of fcc and bcc phases is observed. The AlFeCrCoNi sample (Fig. 2c) shows a diversified structure. The boundaries of large grains and the complex porous structure around them are visible. The structure of the $\text{AlFeCrCoNiTi}_{0.5}$ alloy (Fig. 2d) is much more complicated, which corresponds well with the obtained XRD results. There are equiaxial grains with eutectic mixtures at their periphery. Meanwhile, separations of an additional phase are observed at the grain boundaries.

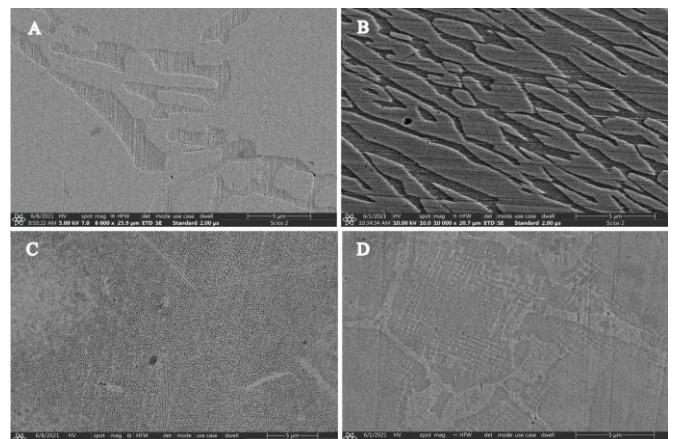


Fig. 2 SEM micrographs of: a) $\text{Al}_{0.5}\text{FeCrCoNi}$, b) $\text{Al}_{0.7}\text{FeCrCoNi}$, c) AlCoCrFeNi , d) $\text{AlCoCrFeNiTi}_{0.5}$ alloys.

The results of the Vickers hardness measurement are shown in Figure 3. Based on the results, it can be concluded that the hardness of $\text{Al}_x\text{CoCrFeNi}$ alloys increases with increasing aluminium content. Also the addition of titanium significantly improved the hardness - it raised by about 100 HV compared to the AlFeCrCoNi alloy.

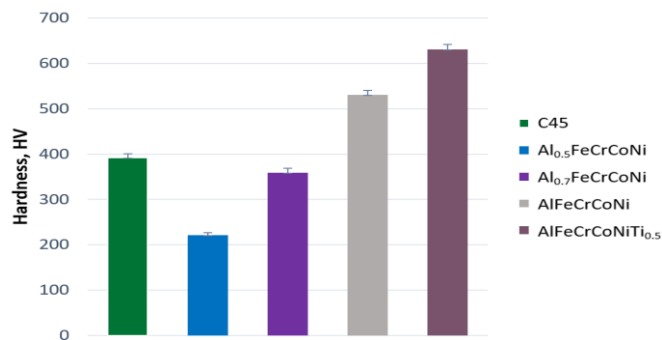


Fig. 3 The average hardness of the tested alloys.

After the friction test, the mass wear of the cooperating materials were measured. The wear of the ceramic balls was negligible in all cases (the highest mass loss was 0.001g). Significant differences were observed in the mass wear of the disks (Fig. 4). There is no analogy between the hardness of the samples and the obtained mass wear results. For $\text{Al}_{0.5}\text{FeCrCoNi}$, the average consumption was less than 0.008g. The $\text{Al}_{0.7}\text{FeCrCoNi}$ sample obtained the worst results - it lost almost 16g in weight. For AlFeCrCoNi , on the other hand, the wear decreased dramatically and reached just over 0.05. The most wear-resistant high-entropy sample turned out to be the one with titanium, which had a significant effect on the reduction of wear. In conclusion, the comparison sample made of C45 steel showed by far the least wear under similar conditions, although its hardness was comparable to that of $\text{Al}_{0.7}\text{FeCrCoNi}$, whose wear was the highest.

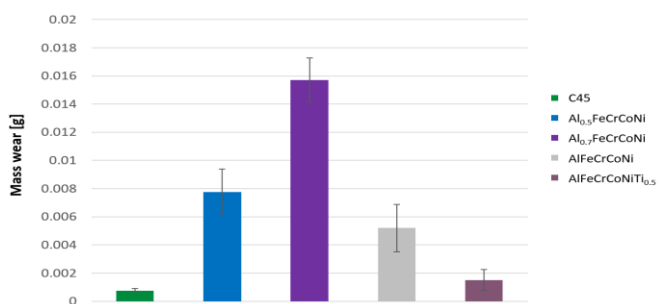


Fig. 4 Mass wearing of the samples after the friction test.

Pictures of the friction paths are shown in Fig. 5. In the case of the $\text{Al}_{0.5}\text{FeCrCoNi}$ sample, the wear mechanism is mixed. Traces of abrasive friction caused by abrasive contact with a ceramic ball can be identified. On the edges of the friction trace, plastically deformed microscopic fragments of material lifted outside the contact area can be seen. Oxide films covering a large part of the friction trace are also visible. The presence of oxide films may be responsible for reduction of material wear. There is much less protective oxide film in the $\text{Al}_{0.7}\text{FeCrCoNi}$ sample. The surface of the friction trace of the AlFeCrCoNi sample differs from the previous ones. It is more homogeneous, individual wear products are visible, which may be crushed oxide films. The grained microstructure of the material is also visible. The friction trace of the $\text{AlFeCrCoNiTi}_{0.5}$ sample is much narrower, which indicates less wear. The wear character itself is similar to the other high-entropy alloys. In sample C45, it is possible to observe the occurrence of an abrasive-adhesive mechanism. This created wear products which then contributed to adhesive wear.

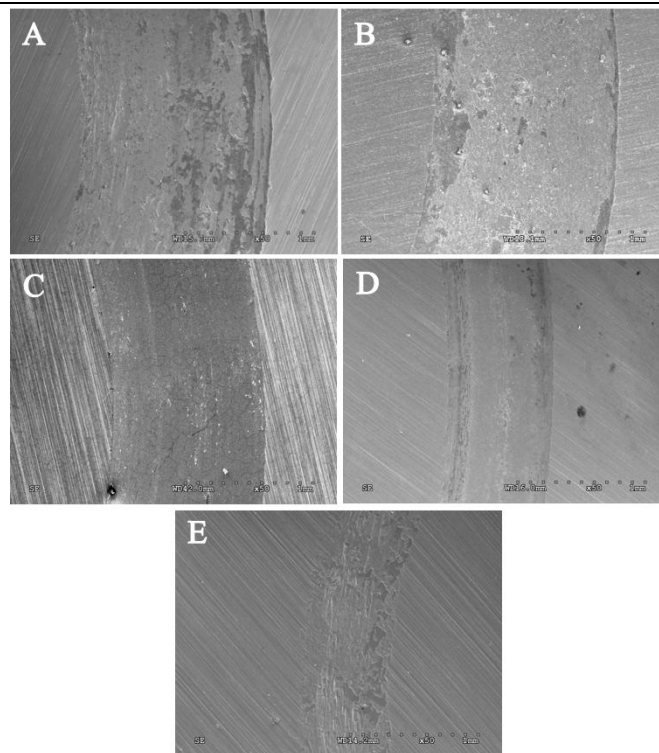


Fig. 5 Friction trace images of: a) $\text{Al}_{0.5}\text{FeCrCoNi}$, b) $\text{Al}_{0.7}\text{FeCrCoNi}$, c) AlCoCrFeNi , d) $\text{AlCoCrFeNiTi}_{0.5}$, e) C45 under magnification $\times 50$ (SEM).

4. Conclusions

- With higher amounts of aluminium the hardness of $\text{Al}_x\text{CoCrFeNi}$ alloys increases. The crystal structure also changes from fcc to bcc. The addition of titanium also had a positive effect on the hardness of the alloy (100 HV increase compared to $\text{Al}_{1.2}\text{CoCrFeNi}$ alloy).
- Steel has a completely different friction mechanism, accompanied by the formation of a large number of secondary layers to protect against wear. In the case of high-entropy alloys, the amount of secondary layers was dependent on the chemical compositions, but in each sample it was smaller than in C45 steel. The beneficial effect of the presence of titanium on tribological properties can be associated with a significant increase in sample hardness.

5. References

1. J.-W. Yeh, S.-K. Chen, S.-J. Lin, J.-Y. Gan, T.-S. Chin, T.-T. Shun, S.-H. Tsau, S.-Y. Chang, *Adv. Eng. Mater.* **6**, 299-303 (2004)
2. M. Ogura, T. Fukushima, R. Zeller, P.H. Dederichs, *J. Alloys Compd.* **715**, 454-459 (2017).
3. T. Borkar, B. Gwalani, D. Choudhuri, C.V. Mikler, C.J. Yannetta, X. Chen, R.V. Ramanujan, M.J. Styles, M.A. Gibson, R. Banerjee, *Acta Mater.* **116**, 63-76 (2016)
4. M.H. Chuang, M.H. Tsai, W.R. Wang, S.-J. Lin, J.-W. Yeh, *Acta Mater.* **59**, 6308-6317 (2011)
5. C.P. Lee, Y.Y. Chen, C.Y. Hsu, J.-W. Yeh, H.C. Shih, *J. Electrochem. Soc.* **154**, C424 (2007)
6. M. Tokarewicz, M. Grądzka-Dahlke, *Met.* **11**, 1302 (2021).

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Operational characteristics of nanocomposite lubricants

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Abstract: The study of the structure and physicochemical characteristics of carbon nanostructures, lubricants and cooling liquids was carried out by methods of scanning electron microscopy, atomic force microscopy, IR spectroscopy, physicochemical and physicochemical analysis. Tribotechnical tests were carried out on a friction machine operating according to the "sphere - plane" scheme. The possibility of modifying various liquid media with nanosized carbon particles of various composition, structure, production technology, including those obtained by the method of self-propagating high-temperature synthesis, has been studied. The studies carried out made it possible to establish general trends in the implementation of the synergistic effect in liquid matrices differing in structure, polarity of macromolecules, and molecular weight.

KEYWORDS: LUBRICANT, STRUCTURE, PROPERTIES, CARBON NANOPARTICLES, RHEOLOGY

1. Introduction.

According to the results of work [1-3], the introduction of nanomaterials into base lubricants used to reduce the friction coefficient and reduce wear in magnetic disks leads to a significant increase in the operating characteristics of magnetic disks.

A liquid medium such as oil or water is used as a heat transfer medium. To change their characteristics, it is necessary to determine and select the effective amount of carbon nanomaterials, which makes it possible to increase the thermal conductivity of the liquid [4-7]. One of the preferred carbon nanomaterials is graphite with a high thermal conductivity exceeding the thermal conductivity of a pure liquid dispersed therein, ground or naturally obtained with an average particle size of less than 500 nm, and more preferably less than 200 nm, and most preferably less than 100 nm. Graphite is dispersed in a liquid by one or more methods, including sonication, milling, and chemical dispersion.

Carbon nanotubes with a graphite structure are one of the most promising modifiers of the carbon class of nanomaterials, although the applicability of other carbon nanomaterials is quite substantiated. To ensure the long-term stability of the resulting solutions, one or more chemical dispersants must be used. It was found that the increase in the thermal conductivity of the modified liquid in comparison with the liquid without carbon nanomaterial is proportional to the amount of added carbon nanomaterials (carbon nanotubes or graphite) [5-9].

Thus, based on this review, it can be seen that the direction associated with the study of the structural features of nanofluids modified with nanosized carbon particles obtained by the technology of self-propagating high-temperature synthesis have sufficient patent purity.

This work is devoted to the study of various types of multifunctional additives on the structural features of modified liquids of various natures, viscosity, tribotechnical characteristics of petroleum oils and their stability at different temperatures.

2. Materials and Procedures

In the development of new nanodispersed modifiers, as well as for their comparison with the previously known antifriction fillers, the following materials were used in the research process. To modify the base lubricating bases, nanomodifiers obtained by various synthesis technologies were used: carbon particles obtained by the technology of self-propagating high-temperature synthesis, multilayer graphenes, nanodispersed carbon particles obtained by detonation synthesis. Nanodispersed clusters of synthetic carbon substances were obtained by explosive technology, SHS synthesis (DND, nanotubes). The dispersion of the clusters is 20 - 30 nm, the specific surface area is 350 m² / g. The content of mixtures of nanodispersed clusters of synthetic carbon in liquids was 0.001% wt. - 10% wt.

Tribotechnical studies were carried out on a friction machine of the FT-2 type, which operates according to the reciprocating motion scheme, the stroke length of the indenter is from 5 to 50 mm, made of steel and ground on a flat surface with emery cloth or grinding paste to the arithmetic mean deviation of the surface profile Ra = 0.1 - 0.3 microns. The samples were

fixed in the clamp of the friction machine, the working sphere and the working surface of the steel disk (counterbody) were wiped with a cloth "coarse calico", bleached, moistened with ethyl alcohol, and then dried for two minutes at room temperature. The tests were carried out at normal load on the sample up to 20 N, linear sliding speed 0.036 m / s, steel surface temperature (20 ± 5) °C. Investigations of structural changes in additives and nanoscale lubricants were carried out using infrared spectroscopy by transmission and ATR methods. IR spectra of starting components, additives, lubricants, model compositions, as well as samples taken after frictional action on a Tensor-27 spectrophotometer ..

The assessment of the state of the friction surface, the topography of the separating layer, the morphology of particles, the structure of additives and fillers were studied using a Mira / Tescan scanning electron microscope (Czech Republic) and an atomic force microscope (AFM) using an NT-206 setup. Images were visualized using original packages in the Windows operating system.

The rheological characteristics of the samples were determined by the Engler method. By this method, the viscosity is determined by the time the test liquid flows out of a viscometer type VZ-4 liquid with a volume of 200 ml at a certain temperature when compared with the time the amount of distilled water flows out of a viscometer of the same type at 20 °C (constant of the viscometer).

3. Results and discussion.

The additives and lubricants used in mechanical engineering are conventionally classified into five main groups: metal-cladding, polymer, chemically and surface-active, solid lubricating components, complex additives and fillers. This classification does not take into account the peculiarities of some types of additives and modifiers, for example, the size factor, however, it is generally accepted and used in tribotechnics.

In recent decades, a new direction in tribotechnics has been intensively developing, based on the use of modifiers of nanometer dispersion to create tribosystem components.

The introduction of various additives into the oil base in strictly metered and balanced concentrations can significantly change the properties of the original oil. The additives used for oil doping can be classified as follows: antioxidant, anti-corrosion, detergent, antifoam, viscous, depressant, anti-emulsifier, adhesion, multifunctional additives. Of the greatest interest among these additives are multifunctional additives, since any oil should contain as few additives as possible. This is due to the fact that the complexity of the formulation makes it difficult to obtain balanced properties of the oil, increases the requirements for its operating conditions and can cause undesirable side effects in the form of corrosion and precipitation. As a result of the introduction of multifunctional additives, the tribotechnical characteristics, stability, corrosive and viscous properties are increased [5-8].

In the course of the studies, the morphology of carbon nanoparticles obtained by the method of self-propagating high-temperature synthesis was studied. Based on the data obtained, it can be seen that carbon particles obtained by different technologies have different morphologies.

According to SEM data at low resolutions, for nanodispersed diamond-containing graphite particles obtained by the technology of the Elektrokhimpribor Combine, the formation of compact agglomerates with fractal dimensions is characteristic. An increase in scanning resolution shows the presence of cluster structures consisting on average of three to five globules with a lateral size of 20 to 50 nm.

The morphology of graphene grade "GPS" is characterized by the type of "crumpled paper", in some cases the presence of separate fairly even carbon sheets from 1 to 10 layers is observed.

The morphology of carbon particles obtained by the method of self-propagating high-temperature synthesis from a charge of the following composition: starch 50% wt. / Nitrate 50% wt. characterized by a globular porous structure. With an increase in the scanning resolution, the presence of nanotubes is observed in the structure of the globule.

The morphology of carbon particles obtained by the method of self-propagating high-temperature synthesis from a charge of the following composition: cellulose 50% wt. / Ammonium nitrate 50% wt. is a cluster structure with a developed surface.

When the resolution is increased by decreasing the scanning area in the structure of this material, the formation of globular agglomerates with a lateral size of 500×500 nm is observed.

Multilayer carbon nanotubes are large globular structures, based on the morphology of which the formed structures of multilayer nanotubes are not visible. When the resolution of the SEM survey is increased, these tubular structures are visualized. The morphology of highly dispersed graphite particles is in the form of "corrugated sheets".

The study of structural changes in nanofluids was carried out using the methods of IR spectroscopy. Studies of the structural features of colloidal solutions based on water, ethylene glycol, industrial oil containing nanosized carbon particles, including those obtained by explosive technology and their mixtures, showed that noticeable changes in the spectra of the studied colloidal solutions begin to be observed at a modifier concentration of more than 5 wt%. - 10% wt. depending on the type of the modified liquid and the introduced modifier.

Based on the data obtained, it was found that when the initial liquids are modified with the studied nanodispersed carbon particles, there is no chemical interaction between the modifier and the liquid matrix.

At given concentrations of modifiers, carbon particles most likely interact with each other to form an extended labile network structure, which should lead to a significant change in the viscosity characteristics of the modified liquids. Studies of the viscosity characteristics of various types of fluids showed a decrease in the viscosity of the modified fluids in the range from 0.01% wt. up to 1% wt. An increase in the concentration of the modifier above 1% wt. leads to an increase in the values of the viscosity of the investigated liquids measured in Engler degrees.

The main type of defects leading to the release of parts and products in mechanical engineering are mechanical failures during operation associated with friction and wear. The use of lubricants is a highly effective way to improve energy efficiency and reduce wear rates. In engineering applications, lubricants have a significant effect on the mechanical durability of a tribosystem, while allowing one to regulate the pressure in the contact of rubbing bodies, perform the functions of cooling systems, increase the stability of the tribosystem, and minimize the value of the friction force and wear between the contacting bodies.

The use of solid carbon nanoparticles as additives to lubricants can significantly increase the wear resistance of rubbing bodies and significantly reduce the coefficient of friction. This effect can be explained on the basis of the formation of a stable separating layer capable of withstanding large contact loads without destruction and allowing filling microroughnesses of rubbing bodies, which leads to stabilization of the friction process.

In recent years, a lot of research has been devoted to the study of the antifriction properties of various solid modifiers such as MoS_2 , WS_2 , graphene and fullerene, nanodispersed diamonds of detonation synthesis, various types of functionalized nanodispersed particles (clays, diamonds, metals, metal oxides and ceramics). In particular, a large number of works are devoted to particles of molybdenum disulfide used as an additive to various types of lubricants (plastic, liquid, etc.). In particular, we studied MoS_2 particles with a diameter in the region of 1 μm , and these particles had a developed surface. The introduction of these particles into the lubricating oil with a concentration of $\sim 2\%$ wt. leads to a decrease in volumetric wear by 10% - 30%. However, although solid modifiers lead to a significant improvement in tribotechnical characteristics, the complexity of the manufacturing technology, environmental insecurity, and high cost limit the scope of these modifiers.

Moreover, the limited mechanical and chemical stability in the lubricating medium of these modifiers can lead to a deterioration in the properties of the lubricating composition during long-term operation. For example, inorganic modifiers such as MoS_2 or WS_2 are destroyed by friction in the boundary lubrication mode. In addition, some additives containing sulfur can create acidic compounds in the lubricating medium during friction, accelerating the corrosion of the contacting bodies.

Thus, the development of optimal compositions of additives for lubricants to improve tribotechnical characteristics is extremely necessary, especially under extreme friction conditions. Carbon particles obtained by SHS synthesis from natural raw materials are of interest as additives to lubricants of various natures due to their unique properties, such as technological ease of production, high dispersion, and chemical stability. These characteristics of carbon particles obtained by SHS synthesis make them a very promising modifier for the production of environmentally friendly lubricants and can replace additives containing sulfur and phosphorus.

Conducted preliminary studies to study the tribotechnical characteristics of the PA6-52100 friction pair, tested in a lubricating medium of the composition "Oil I-20A, containing up to 10% wt. carbon particles obtained by SHS-synthesis" showed a decrease in the coefficient of friction for a given pair of friction. The tests were carried out on an FT-2 friction machine at a load of 30 N and a friction speed of 0.1 m/s.

Based on the data obtained, it can be seen that the introduction of a lubricating medium into the friction zone leads to a decrease in the values of the friction coefficient by 30% - 40%. However, the introduction of carbon-containing particles of various production nature into the lubricant composition leads to a slight increase in the friction coefficient, which is possibly due to the presence of a solid diamond core for ultradispersed diamond-containing graphite, as well as the presence of solid allotropic modifications of carbon for nanodispersed carbon particles obtained by SHS synthesis.

Another aspect that affects a slight increase in the coefficient of friction for petroleum lubricants is a sufficiently high concentration of the modifier in the composition (10% wt.), Which leads to thickening of the lubricant, i.e. increasing the viscosity of the modified liquid material. Experiments carried out to study the tribotechnical characteristics of lubricants at a modifier concentration in the range of 0.1% wt. - 5% wt. showed a decrease in the values of the coefficient of friction of the pair "metal - polymer". It should be noted that for all compositions based on I-20A oil modified with nanodispersed carbon particles, including those obtained by the method of self-propagating high-temperature synthesis, a decrease in the wear rate by 14% - 32% is observed.

The studies carried out to study the morphology of the surface layers of polyamide 6 after tribotechnical tests showed the possibility of forming a specific relief.

With friction without lubricant, a surface with a developed morphology and rather high roughness values is formed. The introduction of a lubricant into the friction zone leads to the smoothing of the surface layers.

The presence of globular carbon structures is possible on the surface. The use of lubricants with a low concentration of carbon nanoparticles makes it possible to obtain a more significant effect of smoothing out the surface layers of the polymer during friction, which can lead to a decrease in the values of the friction coefficient for the investigated friction pair 52100-polyamide 6. The studies on the study of lubricants after tribotechnical tests were not carried out. showed a significant presence of wear products of a pair 52100-polyamide 6 in nanoscale lubricants.

4. Conclusions

Studies of the structural features of colloidal solutions based on water, ethylene glycol, and industrial oil containing mixtures of nanosized particles have shown that noticeable changes in the spectra of the studied colloidal solutions begin to be observed at a modifier concentration of more than 3 wt%. - 5% wt. At given concentrations of modifiers, carbon particles most likely interact with each other to form an extended labile network structure, which should lead to a significant change in the viscosity characteristics of the modified liquids. It is shown that the introduction of nanodispersed carbon particles leads to a change in the viscosity characteristics of the liquids under study. Depending on the type of modifier, concentration, it can lead to both a thixotropic effect in the test fluid and an increase in viscosity values. Based on the data obtained, it can be seen that the introduction of a lubricating medium into the friction zone leads to a decrease in the values of the friction coefficient by 30% - 40%. However, the introduction of carbon-containing particles of various production nature into the lubricant composition leads to a certain increase in the friction coefficient, which is possibly due to the presence of a solid diamond core for ultradispersed diamond-containing graphite, as well as the presence of solid allotropic modifications of carbon for nanodispersed carbon particles obtained by SHS synthesis. The study was carried out with the financial support of the Russian Foundation for Basic Research and the BRFFR within the framework of research projects № 20-51-00001 and № T20P-352.

References.

1. Fuchs I.G. Additives to greases. - M: Chemistry, 1982. -- 248 p.
2. Klamann D. Lubricants and related products / Per. from English Ed. Prof. Yu.S. Zaslavsky. - M.: Chemistry, 1988. -- 488 p.
3. Vityaz P.A. Promising nanophase materials based on ultradispersed diamonds // Theoretical and technological bases of strengthening and restoration of mechanical engineering products: Collection of articles. Art. - Novopolotsk, 2001. -- S. 4 - 8.
4. Vityaz P.A. Nanocrystalline diamonds and prospects for their use // Nanostructural materials: obtaining and properties. - Minsk: NASB, 2000. -- S. 8 - 20.
5. Stekrac D., Neslusan M., Stancekova D. Influence of friction on plastic deformation in a cutting zone and surface quality when grinding. / Intertribo'99: Tribological Problems in Exposed Friction Systems: proceedings, Bratislava, 27-30 April 1999. - DOM TECHNIKY ZSVTS Bratislava, 1999. - P. 101-104.
6. Korobko E.V. Electrostructured (electrorheological) fluids: features of hydromechanics and possibilities of use. - Minsk: ANK "ITMO im. A.V. Lykov "National Academy of Sciences of Belarus, 1996. - 189 p.
7. Volneanko E.N. [and others] Features of the influence of a ceramic filler on the performance characteristics of lubricant compositions // Materials, technologies, tools. - 1996. - No. 2. - S. 66 - 67.
8. Ovchinnikov E.V. [et al.] The use of nanosized modifiers in the technology of obtaining composite lubricants // Innovative technologies in mechanical engineering: materials of international scientific and technical Conf., Novopolotsk, October 29-30. 2013 / Polots. state un-t; / under total. ed. V. K. Sheleg, A. I. Gordienko. - Novopolotsk: 2013. -- P. 196 - 199

Morphological study of rubber granules used in artificial turf systems with SEM and DSC methods

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Abstract: Rubber is different from other polymeric materials because it needs to be crosslinked or vulcanised and mixed with several additives like fillers to achieve its state. The recycled rubber materials presented as granules are rapidly used as infill material for different fields. One of the most important issues, especially in Albania is proving that these materials are recycled. One of the most important issues, especially in Albania is proving that these materials are recycled. Through the images provided by SEM we could study the microstructure of our samples. Also, after conducting an EDX spectrum analysis, we observed additives in the recyclable materials. The DSC methods analyses that will provide info regarding the composition in rubber granules. Thermal analysis is an essential technique to measure the temperature or time dependent response of physical and chemical changes that occur in materials.

Keywords: Recycled rubber, Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy and energy dispersive analysis (SEM), Synthetic a artificial grass, heating and cooling.

1. Introduction

Therefore the purpose of this paper is to investigate the components of granulated rubbers used in artificial turf. The samples are randomly chosen from different fields and for investigations are used two different test methods Scanning Electronic Microscope (SEM) and Differential Scanning Calorimetry (DSC).

Rubber can be recycled using one of three basic methods: by reusing (retreading old tires produces functional refurbished tires). By burning; tires produces energy used for different purposes [1]. By chopping down and forming an entirely new product, such as playground surfacing or using them directly as infill material especially in artificial turf. This group of recycled rubbers will be the focus of our study [2]. The high elasticity of rubber depends on the ability of these connections to organize and pull. Due to the extreme prevalence of rubber products the tires are discarded and rubber recycling has become more common [3]. The granulated rubbers used as infill material for artificial turf are recycled mostly from the tires of cars and trucks [4]. These tires are supposed to be abrasion resistance, aging resistance, temperature resistance, resistance to oxygen and chemicals therefore are added fillers like carbon black during vulcanization with sulfur [5]. It is very important to know what kind of additives they have. Rubber can be produced both naturally, through the latex found in certain plants; and synthetically, through a process that uses unsaturated

hydrocarbons. In addition, rubber is a polymeric material widely used in the automotive industry [6].

Chemical construction and physical state of rubber depends on carbon bond which can be coiled or complex. Therefore, the purpose of this paper is to investigate the components of granulated rubbers used in artificial turf. Samples are randomly chosen from different fields and for investigations are used test method Differential Scanning Calorimetry (DSC).

For rubbery materials this temperature is below the ambient temperature. Like semi-crystalline thermoplastics a few rubbery materials often show cold crystallization (exotherm) and a subsequent melting (endotherm) during a heating scan. So it is very important to know what kind of additives and to know are the recycled. Therefore, the purpose of this paper is to investigate the components of granulated to use a different investigation methods.

2. EXPERIMENT Materials and Methods

Investigation involved eight granulated rubbers from different football fields being used as fillers in artificial grass football fields, received by Albanian and foreign market. Information about color, shape and size of the samples are reposted in Table 1.

Sample	G-1	G-2	G-3	G-4	G-5	G-6	G-7	G-8
Color	White	Green	Black	Black	Black	Black	Black	Black
Shape	Granule 2.5mm	Granule 0.8mm	Granule 0.8mm	Granule 0.8mm	Granule 0.8mm	Granule 2.0mm	Granule 1.1mm	Granule Fine

Table 1: Studying rubber sample

For morphological study of the surface of the rubber materials a SEM JEOL6380LV scanning electron microscope was used (National Technical University of Athens, Greece). High resolution images were acquired, either in the secondary electron mode (SEM) for topography, or the backscattered electron mode (BSE) to reveal possible compositional variation. SEM is equipped with a X-ray microanalysis system (EDS of Oxford Instruments). EDS stands for "Energy Dispersive Spectroscopy" and it is based on X-rays emitted from a sample during electron irradiation. With this instrument chemical analysis, either qualitative or quantitative,

can be performed [2, 7]. In this case, only qualitative analyses are given because additives are impregnated in the rubber material and mixed analyses cannot be avoided.

In order to determine the thermal properties, we use Differential Scanning Calorimetry (DSC). The chosen temperature range for testing the rubber is from -80 0C to +200 0C with cool/heat step of 10 0C/min. The equipment used is DSC 200 F3Maia (costumer laboratory) rate of 10 C/min in a nitrogen environment.

The sample mass is between 3.5 and 4.5 mg, which is low enough to avoid problems caused by heat and material transfer. Samples are

heated from 40 to 200 °C at a heating rate of 10 K/min–1 using nitrogen as purging gas at a flow rate of 40 ml/min. The experiments are carried out in air atmosphere. Two pans are heated in the measurement chamber. The sample pan contains the material being investigated. A second pan, which is typically empty, is used as a reference. The computer is used to monitor the temperature and regulate the rate at which the temperature of the pans changes. The same temperature interval was covered during cooling at the same rate. The melted crystallization enthalpy values were calculated using the software.

DSC measures the heat flow into or from a sample as it is heated, cooled and/or held isothermally. The technique provides valuable information on softening temperatures (or T_g), melting temperatures, heats of melting, percent crystallinities, and re-crystallization (temperatures and heats) [8, 10-11].

3. Results and Discussions

After performing the SEM analyses for all samples a spectrum was taken as show a figures. Consequently, the provided chemical analyses are shown in the form of spectra. In Figure 1, stains with a lighter color are easily noticed in the BSE image on the surface of the crumb. These stains witness the presence of foreign elements in the matrix of rubber. Chemical analysis over a number of such stains reveals minor quantities of other elements, such as zinc, silicon, potassium, magnesium, iron, and sulfur. Zinc oxide, together with stearic acid, plays an important role in vulcanization chemistry, called activators. These compounds react together and with accelerators to form a zinc sulfurating compound, which in turn is the key intermediary in adding sulfur to a diene elastomer and creating sulfur interlinks.

Table 2: Chemical analysis compositions of Rubber

Element	Weight%	Atomic%
Cao	2.75	4.37
Sio2	6.32	9.05
Al2O3	3.65	5.03
Fe2O3	48.75	58.76
MgO	2.75	4.37
SO3	6.32	9.05
K2O	3.65	5.03
Zn K	38.53	22.78

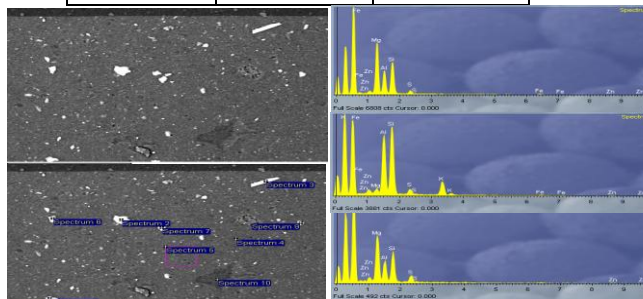


Fig 1. (left) Micrographs of first rubber crumb with the interest areas focused, (right) X-ray spectra of rubber

Reinforcing filler used in rubber with particles of similar shape and size is finely divided silica. Magnesium oxide is necessary to give scorch resistance during vulcanization, mixed with zinc oxide.

Magnesia is included in the formulation to act as a scavenger for the chlorine atom also. Iron oxides were found to be active fillers which improve mechanical and magnetic properties of the elastomers. Aluminum silicates are good reinforcing fillers, they give comparatively harder vulcanizates than other fillers, such as calcium silicates [8].

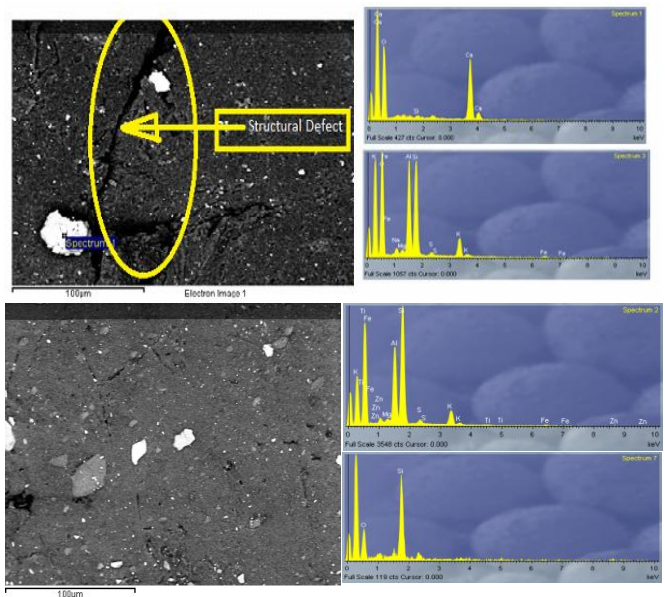


Fig 2. ((left) Micrographs of second rubber with crumb, (right) X-ray spectra of 2nd rubber

The SEM image figure 2 shows the spread of additives on seventh rubber crumb such as calcium, oxide, aluminum, silicon, potassium and other elements in small amounts. We can observe defects in the microstructure of the rubber, presented by holes and microclusters. The BSE image shows the presence of many foreign elements inside the matrix of the second rubber crumb. Chemical analysis over a number of such stains reveals quantities of chemical elements, such as silicon, aluminum, potassium, iron, magnesium, and sulfur. The presence of oxygen shows that additives are added as metal oxides. Titanium and iron oxides are used in many processes as pigments. Microholes and microclusters are present in this sample.

The DSC results generated from the test are displayed in the following figures (see figure 3 to 6). Plots, for all the samples show almost the same shape. By using the program was possible to calculate the characteristics of each curve for first second heating and cooling down.

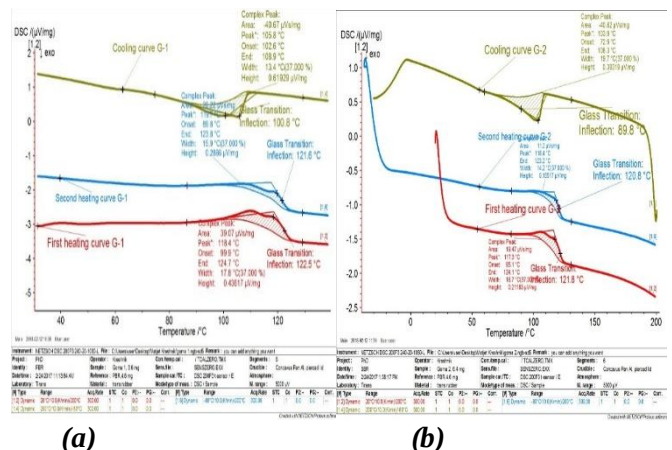


Fig 3: DSC curves of first, second heating and cooling down, for sample G-1. (a), DSC curves of first, second heating and cooling down, for sample G-2

As can be seen from the figure 3 and 4, (for sample G-1 and G-2), the graph show a slight difference in the shape of the curves, between first and second heating, respectively for sample G-1 and G-2. Thus by influencing also on the heat capacity, but not influencing the melting temperatures, which show almost the same value.

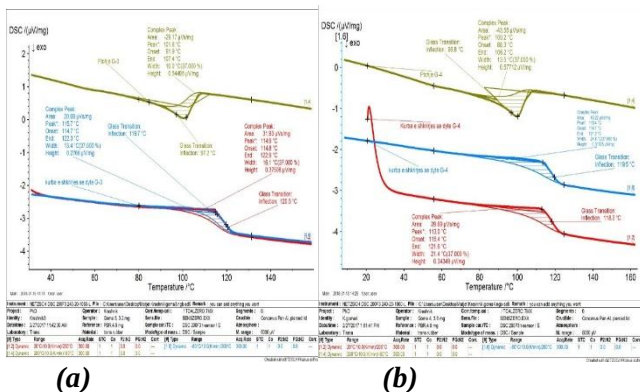


Fig 4: DSC curves of first, second heating and cooling down, for sample G-3. (a), DSC curves of first, second heating and cooling down, for sample G-4

For sample G-3 and G-4, the first and the second heating are almost identical, as the curves overlap on top of each other. The same behavior is noticed also on the samples G-5 and G-6, G-7 and G-8, as presented in the following figures.

The melting characteristics of the tested rubbers, for the first and the second heat, show different values, as expected. However, for sample G-4 the heat capacity is almost at the same value (see fig 4). Interesting is the fact that same samples show higher values of second melting heat, this could be interpreted as a result of re-crystallization of the product. Regarding the results of the cooling curves for all the samples there is a difference, between samples, especially for samples G-3, G-5 and G-8.

From the segment analyses, of the first heating, it is possible to find glass transition, melting temperature and to calculate the total heat flow of melting. For a better view the results are summarized in fig5.

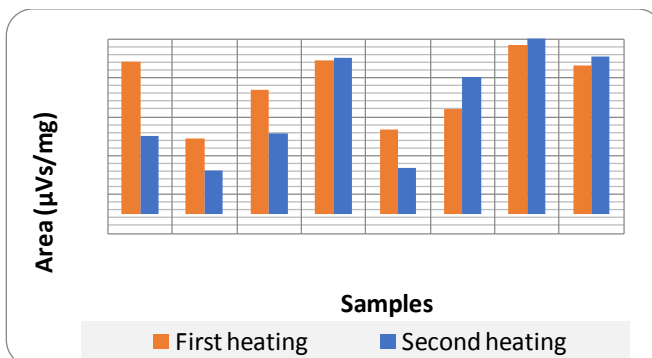


Fig 5. Graphically presented the comparison of the heat capacity of all the tested samples, in first and second heating.

From the spectrum it is noted that the second heating values are higher than the first heat value. this may be related to the restructuring / recrystallization of tire components.

4. CONCLUSION

The present paper aims to investigate the structure and the component of recycled tires, used in artificial turf/ grass as infill materials. From the analysis of BSE images was highlighted the basic matrix of rubber. Different shapes and sizes of particles of additives were spread on the whole surface (and therefore volume) of rubber. Except the chemical analysis of the additives, we can observe defects in the microstructure of the rubber, presented by holes and microclusters. Analyzing the EDX spectra, we identified the main additives, such as them influence the processing of recycled rubbers also, influence the physic mechanical properties, and the appearance of the rubbers

By analysing the received spectra was possible to see the differences between the samples as they show different values of heat capacity. Samples G-4 and G-7 show almost the same values of heat capacity for first heating and for the second heating, differently from other samples, thus due to the fact that there is no difference on the thermal history. Samples G-6 and G-8 show higher values of heat capacity on the second heating compared with first heating. This could be explained by the presence of different additives that may be re-crystallized, however this needs a more detailed analyse which is in the further work of the research. Different shapes and sizes of particles of additives were spread on the whole surface (and therefore volume) of rubber.

5. References

- [1] Turer A. 2012. Recycling of scrap tires. Material recycling – trends and perspectives, 8: 196. Edited by Dimitris S. Achilias. ISBN 978-953-51-0327-1
- [2] Alessandria L, Scozia D, Bono R, Gilli G. 2013. Artificial turf football fields: environmental and mutagenicity assessment. Arch Environ Contam Toxicol, 64:1–11.
- [3] Adamiak M. 2012. Abrasion resistance of materials. 150. ISBN 978-953-51-0300-4.
- [4] Luz Claudio March 2008 Environmental Health Perspectives • VOLUME 116 | NUMBER 3.
- [5] Adamiak M. 2012. Abrasion resistance of materials. 150. ISBN 978-953-51-0300-4.
- [6] Niyogi UK. 2007. Introduction to fiber science and rubber technology b. Rubber technology natural and synthetic rubber.
- [7] Changwoon Nah, Je Hwan Park, Choon Taxk Cho, Young-Wook Chang Specific Heats of Rubber Compounds Journal of Applied Polymer Science Vol. 72, 1513-1522 (1999).
- [8] Joseph D. Menczel, R. Bruce Prime; Thermal Analysis of Polymers: Fundamentals and Applications, Copyright © 2009 John Wiley & Sons, Inc ISBN: 9780471769170.
- [9] Phywe System GMBH & CO. Kg Laboratory experiments. D-37070 Gottingen, Heat insulation / Heat conduction,(2008), LEP 3.6.03-00 .
- [10] Valerio Causin (2015), Polymers on the Crime Scene Forensic Analysis of Polymeric Trace Evidence ISBN 978-3-319-15494-7 (page 3001 – 320).
- [11] Joseph D. Menczel, R. Bruce Prime; Thermal Analysis of Polymers: Fundamentals and Applications, Copyright © 2009 John Wiley & Sons, Inc ISBN: 9780471769170.

Influence of the rate of cooling on the formation of non-equilibrium eutectics in pre-eutectic alloys of the AL-SI system

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Abstract: Computer experiments were carried out with a simulation model of alloy crystallization in this work. The model was preliminarily calibrated for alloys of the Al-Si system. The presence of a non-equilibrium eutectic in pre-eutectic alloys with a silicon content of 1.0% - 1.6% has been detected. The minimum cooling rates at which the formation of an eutectic in these alloys is possible have been determined.

KEYWORDS: CRYSTALLIZATION, EUTECTIC, NONEQUILIBRIUM EUTECTIC, COMPUTER MODEL OF CRYSTALLIZATION

1. Introduction

One of the ways to improve the competitiveness of foundry products is to develop new technological processes and improve existing ones. The solution of this problem can be significantly facilitated by simulating of the process of the metal's primary structure formation during crystallization, as the primary structure significantly affects the final properties of the alloy. Nowadays methods of simulation are widely used for the construction of models of crystallization. They allow both to create computer models to study the peculiarities of structure formation in castings during crystallization, and to approach consciously the improvement of casting technologies [1, 2].

The methodology of thermodynamics is usually used for theoretical research and for creating models of crystallization. In theoretical physics, thermodynamics is divided into three subsections, depending on the internal state of the physical system, namely: equilibrium thermodynamics, linear non-equilibrium thermodynamics and nonlinear non-equilibrium thermodynamics [3, 4]. The last two subsections aroused and have been developing since about the middle of the twentieth century. However, they have not yet found wide application in applied sciences. There are several reasons for this. First, there is the so-called "inertia of thinking", which makes us to act with the usual, generally accepted methods, abstracting from a thorough analysis of the conditions for their application, even in science. Secondly, there is a certain gap between theoretical, fundamental research and the application of their results in solving specific, applied problems. This gap is a consequence of the shortage of time and of the material resources both among "theorists" to deal with "uninteresting" problems of the applied level, and among "practitioners" to master new achievements of theory. Thirdly, there are still no clear criteria for determining which subsection to refer to in each specific case. Therefore, this situation requires creative development with the involvement of modern knowledge and theories. Therefore, it seems expedient to find out previously which system one has to deal with in each specific case, and, consequently, which physical concepts and theories can be used. To do this, it is necessary to establish the criteria for "equilibrium" or "non-equilibrium" of the process or system. Having such an objective, physically substantiated criterion, it is possible to choose both the method of describing of a specific system, and the corresponding mathematical apparatus with sufficient reliability. To substantiate the choice of such a criterion, first of all, it is necessary to analyze the characteristic features of "equilibrium", "weakly non-equilibrium" and "strongly non-equilibrium" systems.

2. Preconditions and means for resolving the problem

The study of the behavior of equilibrium systems is the most developed branch of thermodynamics, and historically it is its first stage. Therefore, the theory of the most of the available technological processes is based precisely on its principles. In equilibrium, changes of flows, forces and entropy are equal to zero. Despite the fact that real technological processes occur over a finite period of time (with a finite speed), during which in most cases the system does not have time to come to a state of equilibrium, the use

of the equilibrium theory remains decisive (including in metallurgy). Within the framework of this theory, thermodynamic potentials are determined for typical thermodynamic systems, the extrema of which set states - attractors, to which the system with certain boundary conditions tends. For an isolated system, such a potential is the entropy S , for a closed system under isothermal conditions - free energy F . Linear thermodynamics reflects the stable predictable behavior of systems which are tending to the minimum level of activity, that is typical for most metallurgical processes [4].

In weakly non-equilibrium systems (the area of applicability of linear non-equilibrium thermodynamics), the driving forces of changes (gradients of thermodynamic potentials, which, in turn, can be determined by gradients of concentrations, temperatures, etc.) are small and the flows depend on the magnitude of the driving force linearly. Onsager's reciprocity relations are satisfied. For the field of linear thermodynamics, the theorem on the minimum production of entropy was proved [4], from which it follows that such a system always tends to a stationary state in which the increase of entropy is equal to zero.

That is, such a system exchanges energy with the environment, tends to "forget" the initial conditions and eliminates local fluctuations. The only hint of the area of its existence is the linear dependence of flows on the magnitudes of the driving forces.

Strongly non-equilibrium systems are described by the laws of non-equilibrium, nonlinear thermodynamics. The stay of the system in such a non-equilibrium state is a necessary, albeit insufficient, condition for self-organization (that is, for the formation of dissipative structures). The stationary state in this case is uniquely determined using the properly chosen potential. It is namely this state that must be identified, first of all, using the criterion of non-equilibrium. In other words, it is necessary to determine the presence of a state in which fluctuations can lead to a new regime. Conventionally speaking, the criterion should allow to draw a boundary (threshold) when it becomes possible to enter an unstable state (bifurcation), in which two equally probable results are possible: either the system can remain on the thermodynamic branch, or it will pass into a new structural and energy state which is necessary for maintaining this dynamic structure. When crossing a threshold (bifurcation point), the role of fluctuations and of element of randomness increases sharply, while before this threshold, elements of determinism and predictability prevail [5].

For chemical systems in a strongly non-equilibrium state, there is no universal law from which one could draw a conclusion about the behavior of all systems without any exceptions [6]. However, in the theory, a relation was obtained that makes it possible to relate the conditions of chemical instability with kinetic and thermodynamic parameters [5]:

$$\delta_x P(\lambda_c) = 0 \quad \text{for } t \geq t_0, \quad (1)$$

where: $\delta_x P$ - can be interpreted as an increase of production of entropy by the active part of the system; λ_c - is a measure of distance from equilibrium.

Determining the conditions under which the loss of thermodynamic stability can occur is reduced to determining the sign of the quantity $\delta_x P$, and ultimately, of the quantity [5]:

$$\delta_x P = \delta w \frac{\delta A}{T}, \quad (2)$$

where: w - the reaction rate; A - chemical affinity; T - the temperature.

You can go the other way and develop a criterion for the non-equilibrium of the system by analyzing experimental data. Obviously, the possible variants of the criterion, which determines the degree of non-equilibrium of the system, include the rate of the process, its homogeneity [7, 8], and the desired level of coincidence between theoretical results and experiment. It's clear that such a criterion will not have an exclusively physical and mathematical foundation and will not claim to be universally applicable to all physical laws.

State diagrams can be considered as peculiar models of alloy crystallization. However, they are constructed in the approximation of equilibrium conditions. At the same time, it is known that with an increase of the cooling rate, the lines of the diagrams shift, and phases appear that should not exist at such compositions and temperatures [8; 9], the structure of the alloys changes. Thus, it means that the conditions of crystallization in this case cease to be equilibrium. Therefore, one of the possible criteria for non-equilibrium during crystallization can be the cooling rate at which non-equilibrium phases appear.

The aim of this work is to study the effect of the cooling rate on the formation of a non-equilibrium eutectic in alloys of the Al-Si system.

The studies were carried out within the framework of a computer experiment using a simulation model of alloy crystallization [1], which allows registering the formation of a non-equilibrium eutectic.

3. Solution of the problem under consideration

The method of preparing of a simulation model for research is based on the selection of model's parameters in order to maximize the coincidence of the simulated cooling curves and structural elements of the macro-grain with those ones obtained in a real experiment [10]. The model was calibrated on the Al + 8.2% Si alloy (by weight).

First, in a natural experiment, the cooling curve was recorded and a thin section was made to study the structure of the alloy. Then, the thermo-physical characteristics of the alloy were introduced into the model: density, specific heat, specific heat of crystallization, and coefficient of thermal conductivity. The simulation model was calibrated in three stages. At the first stage, the cooling rate during the solidification of the melt was set by selecting the heat transfer coefficients in such a way that the initial sections of the experimental and calculated cooling curves coincide. At the second stage, the coincidence of the experimental and calculated cooling

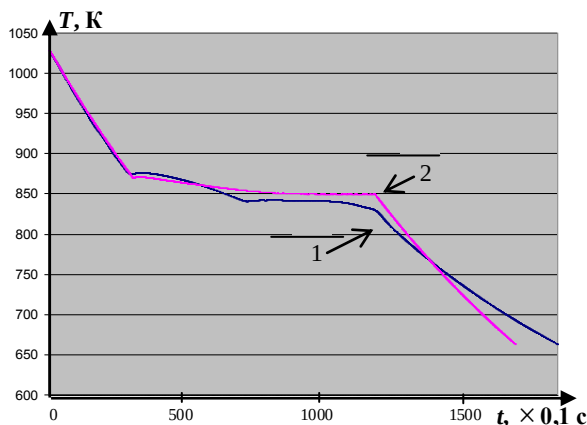


Fig. 1. Comparison of the real cooling curve of the Al-8.2% Si alloy (1) with the cooling curve (2), modeled using a simulation model

curves was achieved by adjusting the value of the adaptation coefficient. At the third stage of setting up the model by selecting its parameters, we sought out a match between the modeled alloy structure with that one, which was obtained in a real experiment.

The real and modeled cooling curves of the Al + 8.2% Si alloy are shown in fig. 1 [11]. The initial sections of the cooling curves practically coincide. Small discrepancies are observed only upon cooling after the end of crystallization. This is due to the fact that in a real experiment, after solidification, the volume of solid metal decreases due to shrinkage, and its contact with the mold wall worsens. As a result, the real heat transfer coefficient decreases and the temperature decreases more slowly.

In the areas corresponding to the formation of a solid solution of the Al + 8.2% Si alloy, there are also some differences between the real and simulated curves. These differences are explained by the constant change of the content of the second component in the liquid. As a result, the value of the latent heat of crystallization changes, which was not taken into account in the mathematical formulation of the heat conduction problem for this model.

A small deviation in the value of the eutectic temperature (5 - 7 °C) is due to the presence of impurities that always exist in a real alloy. If they are present, complex eutectics ((α + Si) + FeAl₃ and (α + Si) + Al_xFe₉Si₂ [12]) can be formed, the formation temperature of which is slightly lower than the temperature (α + Si) of the eutectic.

4. Results and discussion

The presence of a non-equilibrium eutectic is fixed on the dependence of the rate of formation of solid phase centers $\frac{dN}{dt}$ on

time t . Figure 2 shows: the cooling curve, the number of formed centers of the solid phase and the rate of their appearance during the crystallization of the Al-4.4% Si alloy. An alloy of this composition

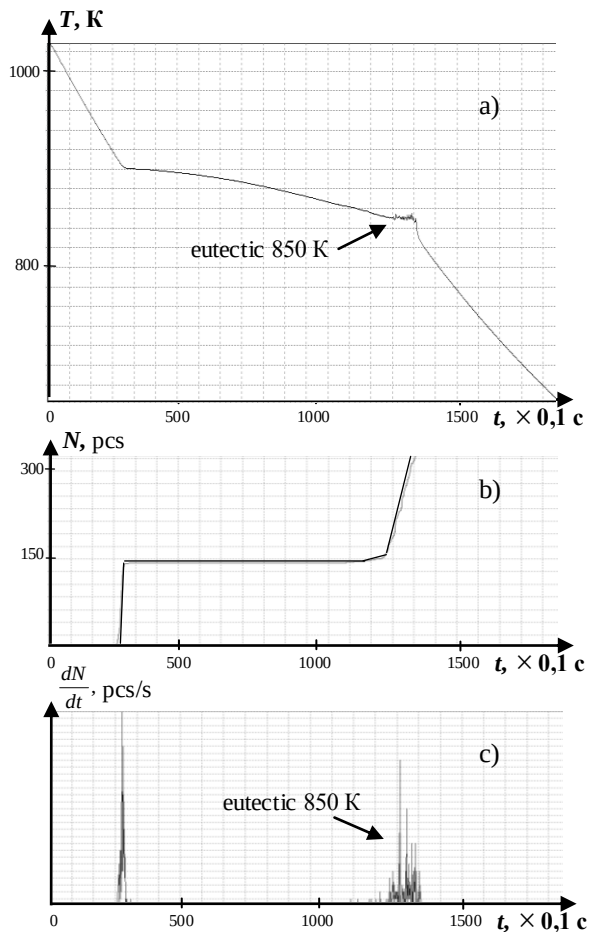


Fig. 2. Cooling curve (a), the number of centers of the solid phase (b) and the rate of their formation (c) during the crystallization of the alloy Al-4.4%Si

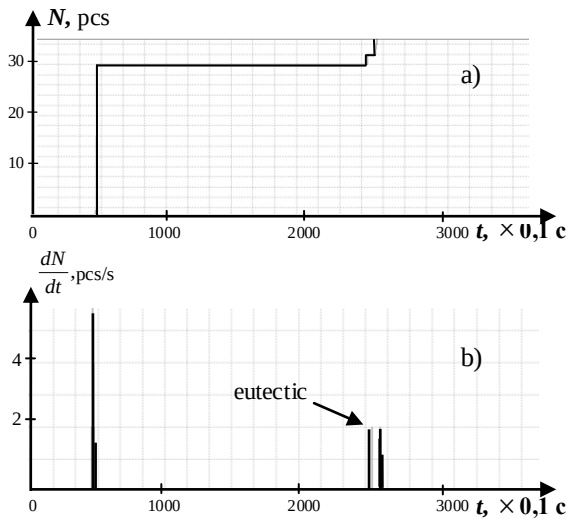


Fig. 3. The number of centers of the solid phase (a) and the rate of their formation (b) during the crystallization of the alloy Al-1.2%Si

forms a solid solution and an eutectic (at 850 K), which is recorded on the cooling curve. At that, the centers of the solid phase appear in two stages (Fig. 2 b). The first stage corresponds to the onset of crystallization and of the formation of a solid solution. The second stage is connected with the beginning of the formation of the eutectic. These stages are more clearly manifested by the dependence of the rate of formation of solid phase centers on time (Fig. 2 c). Thus, using this crystallization model, it is possible to record the presence of a non-equilibrium eutectic during the crystallization of pre-eutectic alloys.

Computer experiments were carried out for alloys of the Al-Si system with a silicon content of 1.0%; 1.2%; 1.4% and 1.6%. All these alloys are pre-eutectic ones and do not form an eutectic under equilibrium conditions. In the experiments, the rate of cooling of the sample (size 0.025m×0.025 m), at which a non-equilibrium eutectic began to form, was recorded. Figure 3 shows the fixation of a non-equilibrium eutectic on the dependence of the rate of formation of centers of the solid phase during crystallization of the Al-1.4% Si alloy. A small amount of eutectic is recorded at the temperature of 850 K and the cooling rate of 0.37 deg/s. The results for the investigated alloys are shown in Table 1.

The presence of a non-equilibrium eutectic in these alloys can be explained by the formation of local regions of the melt with an increased silicon content at certain values of the growth rate of the

Table 1 - Dependence of the cooling rate on the silicon content with the appearance of a nonequilibrium eutectic in Al-Si alloys

Content Si,%	1,0	1,2	1,4	1,6
Cooling rate, °C/s	3,80	2,00	0,37	0,12

solid phase.

To test the possibility of the formation of a non-equilibrium eutectic, which was established in the computer experiment, a full-scale natural experiment was carried out with an alloy of the Al-Si system. The temperature of the melt was recorded during its cooling at a rate of 0.5 - 0.7 deg/s. The mass of the alloy under study was 20 - 22 g, the diameter of the crucible, in which the melt was located, was 21 mm. With a silicon content from 0.1% to 0.3%, the melt crystallized as a solid solution. A non-equilibrium eutectic appeared at a silicon content of 0.3% and higher. It was reliably fixed both on the derivative of the cooling curve and in the structure of the alloy.

5. Conclusions

1. Non-equilibrium eutectic in alloys of the Al-Si system is formed even at low cooling rates, which is connected with the formation of local areas with an increased silicon content, which are formed due to incomplete equalization of the liquid composition after separation diffusion at the "liquid - solid" interface.
2. In a full-scale experiment, a non-equilibrium eutectic appears starting at a silicon content of 0.3% and above.

6. References

1. Donii O. Modeling of Metal Crystallization by Means of Cellular Automation // Materials science. Non-equilibrium Phase Transformations. 2017. Vol. 4. P. 150–153.
2. Donii A.N. Physical principles of construction of a simulation model of crystallization // Bulletin of SevNTU. Issue 148: Mechanics, energy, ecology: a collection of scientific papers / Sevastopol. nat. tech. un-t. Sevastopol: SevNTU Publishing House, 2014. P. 112–116. (Russian)
3. Bazarov I.P. Thermodynamics. Moscow: Higher School. 1991.376 p., Petrov N., Brankov Y. Modern problems of thermodynamics. Moscow: Mir, 1986. 285 p. (Russian)
4. Bazarov I.P., Gevorkyan E.V., Nikolaev P.N. Non-equilibrium thermodynamics and physical kinetics. Moscow: Moscow University Publishing House, 1989. 240 p. (Russian)
5. Prigogine I., Kondepudi. D. Modern thermodynamics. Moscow: Mir, 2002. 461 p. (Russian)
6. Prigogine I., Stengers I. Order from chaos. New dialogue between people and nature. Moscow: Progress, 1986. 432 p. (Russian)
7. Semenov V.I. Difficulties in the kinetic theory of crystallization of metals and alloys // Metallurgy of mechanical engineering. 2005. No. 1. P. 16 –21. (Russian)
8. Semenov V.I. Influence of temperature and cooling rate on the change of the structure of the melt // Metallurgy of mechanical engineering. 2005. No. 3. P. 24–27. (Russian)
9. Karzhavin V.K. Thermal effects and concentration of magmatic melt impurities during the formation of intrusions. Vestnik MGTU. 2002. Vol. 5. No. 1. P. 133–140. (Russian)
10. Donii A.N. Computer model of crystallization of metals and alloys // Acta Universitatis Pontica Euxinus. Dnipropetrovsk; Varna, 2015. Volume 2. P. 388–393. (Russian)
11. Donii O.M. Simulation modeling of homogeneous and heterogeneous crystallization of Al and Al-Si alloy // Bulletin of NTUU "KPI" Mechanical Engineering. 2011. № 61. Volume 2. pp. 72–78. (Ukrainian)
12. Kuzin O.A., Yatsyuk R.A. Metallurgy and thermal processing of metals. Kyiv: Osnova, 2005.324 p. (Ukrainian)