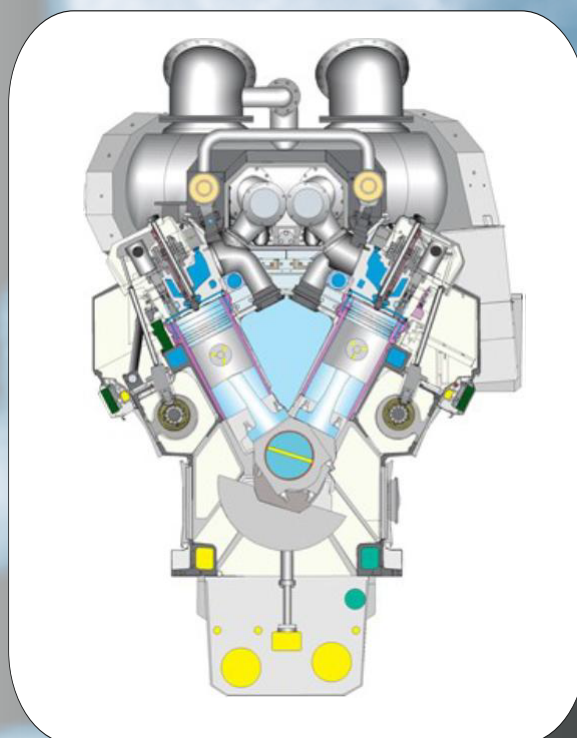


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CONTENTS

MACHINES

Dual fuel four stroke lean burn engine supercharging system operational features Delyan Hristov	263
---	-----

TECHNOLOGIES

The use of machine learning methods to predict the processes and results of high-voltage electric discharge treatment of titanium powder in kerosene Mykola Prystash, Svitlana Prystash, Andrii Torpakov, Yevhen Lypian, Olha Syzonenko, Rasa Kandrotaitė Janutienė	267
Influence of surface laser texturing on surface wettability Janette Brezinová, Miroslav Džupon, Ján Hašul'	270
Mechanical properties of parts fabricated with additive manufacturing: A review of mechanical properties of fused filament fabrication parts Jelena Djokikj, Elisaveta Doncheva, Ognen Tuteski, Bojana Hadjieva	274
Optoelectronic method for optical diagnosis of the state of the vascular system Alexander Gisbrecht, Sergej Mamilov	280
Contactless Determination of the Number and Diameter of Fog Droplets Using Gravitational Separation and Measurement of Electrical Signals Petar Todorov, Zahary Peshev, Nely Ilieva, José Luis Pérez-Díaz, Ognyan Ivanov	283

MATERIALS

The Effect of Vanadium, Niobium and Boron on Microstructure, Mechanical and Corrosion Properties of High-Chromium White Cast Irons Kemal Delijić, Mirjana Filipović	286
Nanodisperse modifiers produced by the shs method for composite materials of automotive equipment Auchynnikau Y., Vozniakovskii A., Vozniakovskii A., Semenov A.	290
New regulations on the formaldehyde emission from wood-based panels Nadir Ayrilmis	293

Dual fuel four stroke lean burn engine supercharging system operational features

Delyan Hristov¹

Nikola Vaptsarov Naval Academy Varna, Bulgaria¹
d.hristov@nvna.eu¹, d.hristov@naval-acad.bg¹

Abstract: In the present publication are considered the features of the dual fuel four stroke lean burn engines supercharging system operational features. The supercharging system control means are analysed and performance data is collected from an engine in operation on an offshore vessel. The data obtained from the engine in operation is analysed, processed and figures of related parameters are obtained. The latter are analysed in relation to the importance of the supercharging technical condition. Conclusions and recommendations are stated as a final outcome.

Keywords: DUAL FUEL LEAN BURN FOUR STROKE MARINE ENGINE, SUPERCHARGING SYSTEM CONTROL, WASTE GATE, MARINE TURBOCHARGER SPEED CONTROL

1. Introduction

With the present energy transition forced changes in the marine industry there are new dual fuel engines introduced in the ship power plants, which have different behavior on gas mode operation, compared with the conventional diesel engines. As a matter of fact, these engines operate on Diesel cycle while operating on liquid fuel and change to Otto cycle while on gas.

There are specifics in the operation of the subsystems of the Lean burn Otto cycle engines such as the gas supply and the supercharging system. The operation of the supercharging system on gas mode is critical for the ability of the engine to run safe and in case of system deteriorated condition it could be even impossible to run on gas.

The information related to the specifics of the supercharging systems on the dual fuel four stroke engines are well known to the engine manufacturers but mainly remain in their envelope. The general knowledge for the supercharging systems of the dual fuel engines on gas mode should be populated and better disseminated.

In this publication the aim is to be presented the features of the supercharging system control components and the logic of the control system dealing with the air-fuel ratio on gas mode of operation. The tasks linked to the aim stated are to be collected data for the charge air system operation on dual fuel engine Wärtsilä 34DF and the data to be analyzed in respect to the features of the charge air pressure control.

2. The dual fuel four stroke engine type Wärtsilä 34DF

The object in the publication is a four-stroke dual fuel engine Wärtsilä 34DF operating in the medium speed range has the characteristics as shown in Table 1 [1].

Table 1: Engine 34DF characteristics

	Wärtsilä 34DF
Cylinder bore	340 mm
Speed	650 - 720 RPM
Power output	5760 kW
Turbocharger maximum RPM	32500

The engine is part of the ship power plant of an offshore supply vessel and operates in the range of 650 – 720 RPM depending on the mode of operation. There are two turbochargers Napier NT 1-10 co-operating with the engine with specific control system components – bypass valve and waste gate system, dealing with the pressure control in two different modes – nominal and low load operation.

A sectional view of the V-type engine is shown on a figure 1 [2]. It is trunk engine, twin bank with scavenge manifold positioned between the two engine blocks.

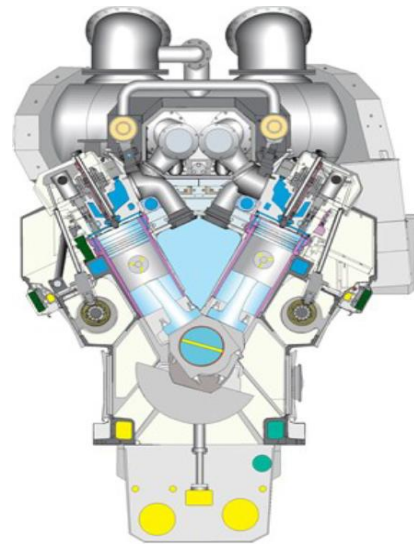


Fig. 1 Sectional view of V34DF [2]

2.1 Engine turbocharging control system

The function of the bypass valve is to increase the pressure of the air charge, supporting the operation of the turbocharger turbine at low engine load. It is positioned before the air cooler of the engine in order to recirculate part of the air flow. By a command from the engine control system to open it, it diverts part of the still uncooled portion of air directly to the inlet of the turbine side of the turbocharger, thereby helping to increase the turbine speed, followed by an increase of the charge air pressure in the receiver. This distinctive feature of the engine improves its performance at low loads by reducing the thermal load and avoids unwanted additional smoke creation.

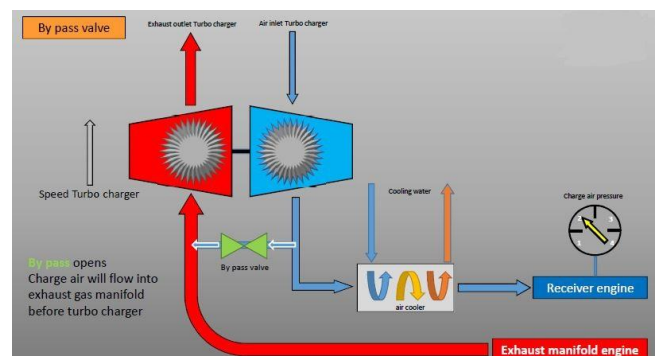


Fig. 2 Charge air bypass valve [2]

The waste gate valve is installed in the exhaust gas flow path before the turbine side of the turbocharger. One of its functions is a safe activation in a high engine load mode [2]. Its function is to be opened for bypassing part of the flow of exhaust gases off the turbine upon reaching the critical values in terms of revolutions per

minute for the turbocharger shaft and charge air pressure in the receiver

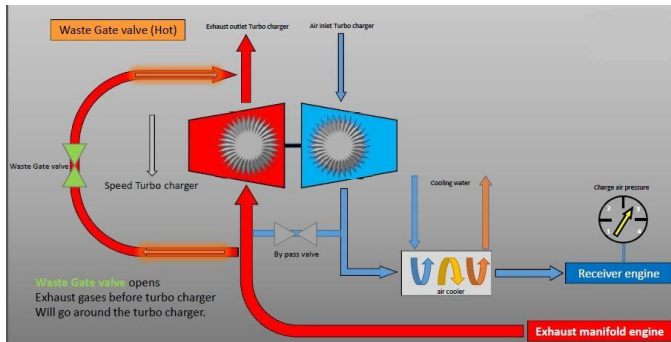


Fig. 3 Waste gate valve [2]

In addition, the main distinguishing feature of the waste gate is the control of the charge air pressure and thus the stability of the fuel ignition. By precisely adjusting its opening, the flow of exhaust gases entering the turbine side of the turbocharger unit is bypassed, by routing them directly to the funnel. In this way, regulation/reduction of the revolutions developed by the turbocharger is achieved, in a large range of the rotation speed and wide range of the engine power. This function determines the waste gate valve as a regulator of the maximum values of λ within the limits of a lean fuel-air mixture, preventing it from exceeding its upper limit, which would lead to problems in the combustion process, increasing the NO_x formation and tending to engine knocking.

The waste gate valve control is carried out by the engine control system which monitors the value of the air pressure in the receiver and if the pressure of the charge air is higher than the set value it sends a command to gradually open the waste gate valve, until the correct pressure value set in the engine map is reached. In the event that the pressure drops below this value, the engine control system commands to gradually close the waste gate valve until the correct value of the charge air pressure is reached again. The control logic is implemented in the engine control system and no external regulators are needed [2].

3. Performance results of the turbocharging system

For the purpose of the task execution in this publication, there are collected the results of the performance of the supercharging system in variable modes from 25% to 100% load modes of the engine with liquid and gas fuel in use in actual operation of the engine, by using the engine monitoring system for data acquisition of the parameters. The condition of the engine could be evaluated as optimal as the data was attained on a mode of sea trials of the ship power plant. Due to the different control approach on both modes, there can be seen the significant differences in the supercharging system behavior. There are differences in the turbocharger performance due to the control action of the charge air bypass valve and the waste gate valve operation by the engine control system.

In table 2 are presented the results of the turbocharger RPM in the variety of the loads of the engine. It could be noticed that the revolutions of the turbocharger are higher on low load mode at gas fuel mode and tend to decrease at higher loads compared to the liquid fuel mode.

Table 2. Turbocharger RPM

Turbocharger RPM					
Load %	25	50	75	90	100
LNG	12315	20290	24340	25855	27045
MDO	8370	21560	25844	27845	29140

In the table 3 are presented the values of the charge air pressure in the scavenge air manifold in the both modes – liquid and gas fuel operation as the gas fuel supply pressure on gas mode of the engine.

Table 3. Charge air and gas pressure

Charge Air Pressure and fuel gas supply pressure (bar)					
LNG	0.4	1.39	2.46	2.93	3.35
MDO	0.15	1.61	2.88	3.64	4.12
GVU	1.4	2.53	3.76	3.94	4.27

The control positions of the waste gate valve and the charge air bypass valve for the liquid and gas fuel mode are shown on table 4 and table 5. It noticeable that the waste gate is utilized mostly on gas fuel mode and the charge air bypass valve is used on both modes mostly to facilitate the smokeless operation in low load operation.

Table 4 Waste gate and charge air bypass valves control positions - gas

Gas fuel mode operation					
Load %	25	50	75	90	100
Waste gate [%]	12	5	6	6	14
CA by-pass [%]	69	33	10	4	0

Table 5 Waste gate and charge air bypass valves control positions - liquid

Liquid fuel mode					
Load %	25	50	75	90	100
Waste gate [%]	0	0	0	0	8
CA by-pass [%]	31	37	20	8	0

3.1 Performance results analysis

A comparison of the RPM's of the turbocharger in both modes – liquid and gas fuel mode are shown on figure 4.

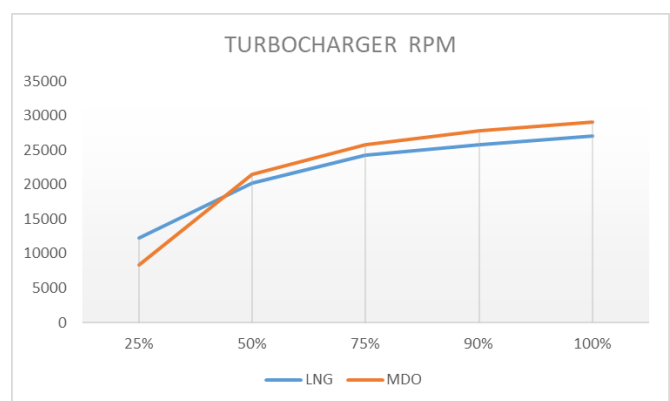


Fig. 4 Turbocharger RPM comparison on gas and liquid fuel mode

As it can be seen, there is a difference in the revolutions in low load of operation and the turbocharger is supported by the charge air bypass with intention to increase the turbine RPM. On the high load range, although the charge air bypass is still opened the waste gate allows part of the gases to go directly to the funnel thus controlling the turbocharger performance with relation to the charge air pressure control for the lean burn concept combustion execution.

On the figure 5 it can be seen the pressure developed by the turbocharger in both modes, compared to the fuel gas pressure supplied in the gas mode.

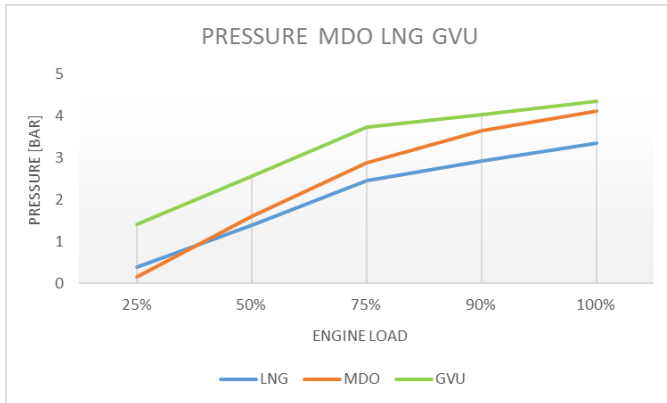


Fig. 5 Charge air and gas pressure development

The comparison of both lines with the orange and blue color on figure 5 shows the influence of the charge air control system on the performance of the system. The orange line representing the pressure development in liquid mode shows the simplified operation of the Diesel cycle engine compared to the gas fueled Otto engine with lean burn concept. Although there is surplus air in the combustion chamber of the engine it is not critical as it is precisely metered to the fuel amount, so to obtain proper fuel-air ratio. Due to the non-homogeneous combustion of the Diesel cycle engines, there would be always rich fuel-air ratio areas in the combustion chamber which cannot be controlled due to the manner of fuel injection. It is the most significant difference with the presented subject engine in the publication. On gas mode the engine operates on homogeneous combustion which requires precise adjustment of the fuel-air ratio.

On figure 5 it could be seen another special feature of the gas fueled engine, the difference in the pressure of the charge air and gas fuel shown with blue and green color lines. There is strong dependence of the pressure difference between both fluids in the entire engine load range. The gas fuel pressure is kept higher with approximately one bar above the charge air pressure. In this relation the charge air pressure is controlled by the waste gate of the exhaust gases around the turbocharger turbine and the gas valve unit of the gas fuel system controls the supply pressure of the gas. Due to the specific mixing approach of the gas fuel and the air on gas mode it is necessary to have positive difference in the gas pressure compared to the air pressure in order to achieve proper routing of the flow of the mixture to the direction of the combustion chamber. The gas fuel is fed to the inlet charge air branch of the air manifold next to the inlet valve of the specific cylinder unit and to be sure that the gas will approach the combustion chamber the dosing gas valve has specific position and additionally the pressure must be kept with the difference described to not change the direction of the gas fuel aside from the combustion chamber to the scavenge manifold. If for any reason this pressure difference cannot be maintained there is direct safety issue with the gas operation of the engine.

On a figure 6 it is shown the opening value of the charge air bypass valve on gas mode of the engine. In an alignment with the intended use of the charge air bypass system the bypass valve is opened mostly in the low range load modes for the purpose of the smokeless combustion of the engine supported by the reverted flow of the hot charge air directly to the turbine side of the turbocharger. The bypass valve is fully closed at high load modes and supports the turbine in the mid and low range mode. It could be concluded that the bypass valve ability to support the turbine operation is similar to the control margin of the turbocharging system. If there is no sufficient air amount to be supplied to the turbine it would lead to smoke operation of the engine, especially in the low load ranges where the turbocharger operates with poor efficiency by default.

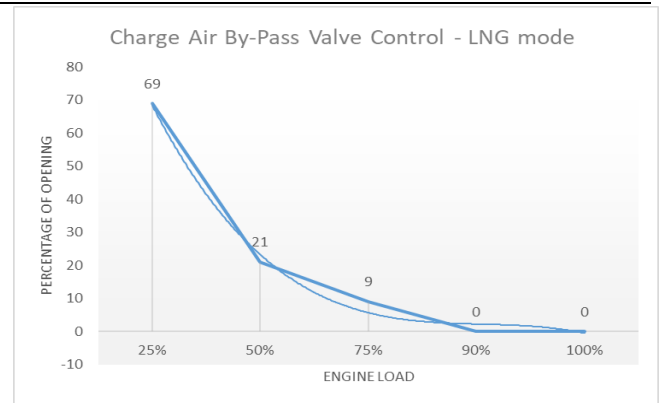


Fig. 6 Charge air bypass valve operation

On figure 7 it is shown the waste gate valve operation in both modes – liquid and gas fuel mode.

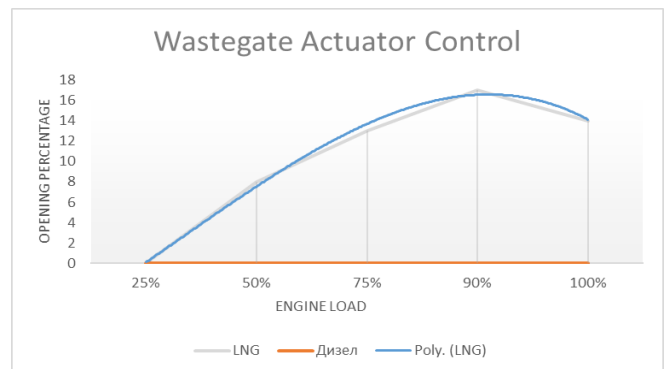


Fig. 7 Waste gate valve operation on liquid and gas fuel mode

The waste gate valve is used exclusively in gas fuel mode by the engine control system. As it was underlined its function is to keep the proper charge air pressure related to the engine load and the gas consumption, so to keep constant fuel-air ratio during gas mode operation. On liquid fuel mode the waste gate valve is closed, and the full capacity of the turbocharger is used to supply the engine with air. There is a possibility to use the waste gate as a safety device to redirect part of the gases on full load on liquid fuel mode in case of specific matching approach of the engine and the turbocharger by choosing smaller turbocharger for better performance in lower range of operation.

The core function of the waste gate is to act as pressure controlling device on gas mode, but it has strong dependence of the turbocharging system technical condition. The turbocharger must be able to keep its operation with control margin determined by the excessive efficiency for the waste gate opening. If there is no margin for opening the waste gate while the engine is operating on gas mode it could be impossible to keep the intended charge air pressure and respectively the fuel-air ratio in the specific mode, so the gas operation would become impossible.

The optimal condition figure of the waste gate valve position could be utilized as a reference condition for the turbocharging system deterioration. If there is excess fouling or there is marginal wear of the turbocharger components and the scavenge air system components it could be impossible to achieve the desired control of the turbocharger performance by opening the waste gate valve. The turbocharger must be kept in optimal condition for the smooth operation of the scavenge air control system. There must be considered variable factors which could influence the turbocharging system operation in different way than the considered in this publication. The margin for control is a must after all considerations.

4. Conclusions

In the publication are stated the special features of the turbocharging system of a dual fuel lean burn four stroke engine. The functions of the waste gate and the bypass valves are described in their critical minimum.

It could be considered that the dual fuel engines operate in two fundamentally different modes. On liquid fuel they are pure diesel engines and on gas fuel they are different engines. While operating on liquid fuel and not only there can be considered significant process of fouling of the turbocharger components. These components need to be in optimal condition for normal operation on gas mode. If there is a contradiction in this direction it must be expected that there will be deviation in the gas operation of the engine. It must be considered the proper maintenance of the engines and their subsystems as a critical requirement for the safe gas operation.

The experience with the diesel engines supercharging system could lead to poor results in the case of gas used as fuel [3]. The diesel engine could run in most of the cases even with turbocharging system in poor condition with some smoke and heat tensioning, but the gas fuelled engine cannot run in that way, just because of the engine control concept. The operation of relatively new engines is non problematic, but with the running hours stored there will be deviations of the technical condition which must be handled with the required attention from the engine operators.

5. Acknowledgements

The tasks in the publication to show the specifics of the turbocharging control system of the lean burn dual fuel engine is accomplished. There are shown the differences of the turbocharging system of the Diesel and the Lean burn concept engine with the potential weak points to be considered during the operation of such engines. The data analysis in the publication could be considered as a reference for the expected performance of the newly introduced dual fuel engines.

The data acquired from real ship power plant is the most realistic figure which could be seen in the real practice of the marine engineers working on natural gas fuelled ships.

The outcome of the publication could be beneficial to the marine engineers to better understand, clarify and explain the differences in the operation of the dual fuel and the Diesel four stroke engines in relation with the charge air system.

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The use of machine learning methods to predict the processes and results of high-voltage electric discharge treatment of titanium powder in kerosene

Mykola Prystash¹, Svitlana Prystash², Andrii Torpakov¹, Yevhen Lypian¹, Olha Syzonenko¹, Rasa Kandrotaitė Janutienė³
 Institute of Pulse Processes and Technologies of NAS of Ukraine, Bohoyavlenskyi ave., 43-A, 54018, Mykolaiv, Ukraine¹
 Admiral Makarov National University of Shipbuilding, Heroes of Ukraine ave., 9, 54025, Mykolaiv, Ukraine²
 Kaunas University of Technology, K. Donelaičio St., 73, 44249 Kaunas, Lithuania³
 torpakov@gmail.com

Abstract: The possibility of using machine learning methods to predict the results of high-voltage electric discharge treatment of titanium powder in a hydrocarbon liquid is studied. As a result of the work, distribution surfaces for the average particle diameter of Titanium powder, the amount of Titanium carbide formed during processing, and the number of spherical particles of titanium powder depending on the interelectrode gap and the number of pulses, when using spark discharge and with Titanium powder concentration in kerosene of 0.07 kg / dm³, pulse repetition frequency 0.3 Hz and the energy of single discharge of 1 kJ, were obtained.

Keywords: MACHINE LEARNING, RANDOM FOREST, LOGISTIC REGRESSION, HIGH VOLTAGE ELECTRIC DISCHARGE, TITANIUM.

1. Introduction

Traditional methods of analyzing the composition and properties of materials are time consuming and expensive. On average, modern laboratories need up to 10 years to develop new materials and up to 20 years to mass produce them. However, the use of modeling technologies in the development of new materials can reduce the time, needed for development and implementation of new materials, by almost half due to the high speed of results obtainment, repeatability, safety, rapid error detection and low cost.

Modern methods of modeling and forecasting can be divided into two major groups [1]:

- modeling based on physical models;
- modeling based on large databases (machine learning).

Modeling based on physical models is based on the observation of the studied physical phenomenon to form a correct idea about it, which is then formulated in the form of mathematical equations that can be solved. Accurate engineering calculations give this method physical realism.

The advantages of this method include:

- a solid foundation based on physics and logic;
- they can be easily generalized to similar physical problems.

Disadvantages:

- can be time consuming and expensive;
- have a large error in problems with nonlinearity;
- take the boundary conditions into account;
- with increasing complexity of calculations, their results are difficult to reconcile with real problems.

Modeling based on large databases has emerged with the increasing amount of digital data we receive about the world around us, and high-quality and consistent access to storage and forecasting resources is making this method increasingly popular. Compared to the physical model approach, this method is based on the assumption that, since the data comes from both well-studied and not very well-studied sections of physics related to this issue, the development of a model based on large databases can take into account all the physics of the studied phenomenon together.

The advantages of this method include the following:

- It takes into account data and experience for the previous long period of time.

- The obtained models are stable and make predictions quickly.

Disadvantages:

- poor generalization of unidentified problems;
- deviations of the initial data affect the forecasts created by the model;
- most modern algorithms work as a "black box".

High-voltage electric discharge (HVED) treatment of powder mixtures is one of the modern methods of grinding and changing the phase composition of powders, which is efficient and has low cost of the process if compared to classical grinding methods. But wide usage of HVED treatment is limited by the fact that the physical mechanism of dispersion processes when using HVED in a liquid has not been studied enough. In [2, 3] it was suggested that

the main role in the destruction of particles of material in the discharge zone is played by the shock wave generated by the spark discharge channel. In addition, the process of dispersion to varying degrees involves volumetric microcavitation, the destruction of particles due to their impact with the walls of the discharge chamber and the mutual abrasion of particles during their stirring throughout the chamber. Titanium powder was chosen for studies due the wide possibilities of its use as a filler, modifier, or as a component of metal matrix composites.

The use of methods of modeling on large databases can give more accurate results of forecasting processes and results of HVED treatment. Therefore, the **goal of the work** is to study the possibility of using machine learning methods to predict the results of high-voltage electric discharge treatment of titanium powder in a hydrocarbon liquid.

2. Methodology

In general, the machine learning process consists of input data, algorithm, and results obtained. In addition, data from the previous learning of the model can be added to the process in order to assess the accuracy of the forecast. Such model is called "controlled".

Logistic regression and the Random forest method were chosen as modulation algorithms. The Python programming language and the Colaboratory application, or Colab for short, a product from Google Research, were used as implementation languages. Colab allows writing and executing arbitrary Python code through a browser and is especially well suited for the implementation of machine learning and data analysis.

Logistic regression is a classification algorithm used to relate data to a discrete set of classes. In contrast to linear regression, which outputs continuous numerical values, logistic regression converts the original data using a sigmoid. This is one of the simplest algorithms that can be used to solve classification problems [4], which is both its advantage and disadvantage.

Random forest is a method of machine learning for classification, regression and other tasks, which works by building numerous decision-making trees during model training and produces an average forecast (regression) of constructed trees [5, 6].

Advantages of the Random forest method:

- Ability to efficiently process data with a large number of attributes and classes.
- Insensitivity to scaling and any other monotonous transformations of feature values.
- Both continuous and discrete features are equally well processed.
- There are methods of constructing trees according to data with missing values of signs.
- There are methods for assessing the significance of individual features in the model.
- It has an internal assessment of the model's ability to generalize.

Disadvantages of the Random forest method:

- The algorithm is prone to overtraining on some tasks, which creates an error.

- Large size of the received models, and, accordingly, high requirements to the equipment.

The results and process characteristics of the titanium powder treatment in kerosene using a single-point electrode system, obtained in the period from 2013 to 2021, were used as data for modelling. Single-point electrode systems allow the realization of the spark discharge (SD) in the kerosene-powder system. The results of these experiments are given, in particular, in [7, 8]. The data included information on the number of treatment pulses, results of optical microscopy of titanium powder particles performed according to [9], namely the mean particle size and sphericity of shape, and the amount of synthesized titanium carbide calculated by RIR method [10].

One of the tasks of modeling was to determine the basic characteristics of HVED processing, which can be directly controlled, and which would affect the results of the processing itself. For this purpose, preliminary data processing was performed. This allowed establishing constant values for all selected treatments, which could be excluded from modelling, namely:

- The concentration of titanium powder in the hydrocarbon liquid, which was 0.07 g / dm^3 .
- Energy of a single discharge equal to 1 kJ.
- Discharge frequency – 0.3 Hz.

This allowed determining the main variables that were used as input data, namely the interelectrode gap and the number of treatment pulses that affect the formation of the discharge channel and the characteristics of the environment, and the output data: mean powder particle diameter after treatment, quantity of spherical particles and the amount of titanium carbide formed after HVED treatment.

A controlled machine learning model was used to predict the initial data. To do this, the data were divided at a ratio of 80/20 percent to determine the accuracy of the forecast, for which the Accuracy metric was used. Accuracy is an indicator that determines the overall accuracy of model prediction for all classes. This is especially useful when each class is equally important. Accuracy is calculated as the ratio of the number of correct predictions to their total number [11]. According to the Accuracy metric, the accuracy of used logistic regression and Random forest forecasts is 60% and 70%, respectively.

3. Results and discussion

As a result of hydrodynamic influence and influence of plasma of the discharge channel on titanium powder in kerosene, its grinding, spheroidization of particles and chemical transformations with formation of titanium carbide take place [7, 8].

Fig. 1 shows that according to the logistic regression model, the dispersion process begins with 200 pulses at almost all values of the interelectrode gap and allows reducing the mean diameter of Ti powder to $9 \mu\text{m}$. This is due not only to Ti particles grinding, but also to the formation of free carbon in the process of kerosene pyrolysis. Further increase in the number of impact pulses allows reducing the value of the mean particle diameter to $5 \mu\text{m}$, and in the area with the interelectrode gap from 2 mm to 14 mm and the number of treatment pulses from 2000 to 4000 – obtaining particles with the mean diameter of $\sim 4 \mu\text{m}$.

The mean particle diameter of the powder according to the Random forest model when using SD in kerosene at the interelectrode gap from 2 mm to 8 mm remains unchanged and is $60 \mu\text{m}$ (see Fig. 1, b). Increasing interelectrode gap from 8 mm to 36 mm allows decreasing the mean diameter of particles to approximately $9 \mu\text{m}$ starting with 200 processing pulses.

The number of particles of a shape close to spherical in the original powder was around 20%. According to the logistic regression model, HVED treatment in almost all possible modes increases their number due to the impact of the plasma of the discharge channel (see Fig. 2, a). Thus, at the values of the interelectrode gap from 10 mm to 36 mm, and at the number of

treatment pulses from 200 to 1000, the number of spherical particles increases to 27%. Increasing the number of treatment pulses from 1000 to 4000 allows increasing the number of spherical particles up to 30% at all values of the interelectrode gap. The treatment with the interelectrode gap from 10 mm to 36 mm and the number of treatment pulses from 1000 to 2000 will allow obtaining up to 33% of spherical particles.

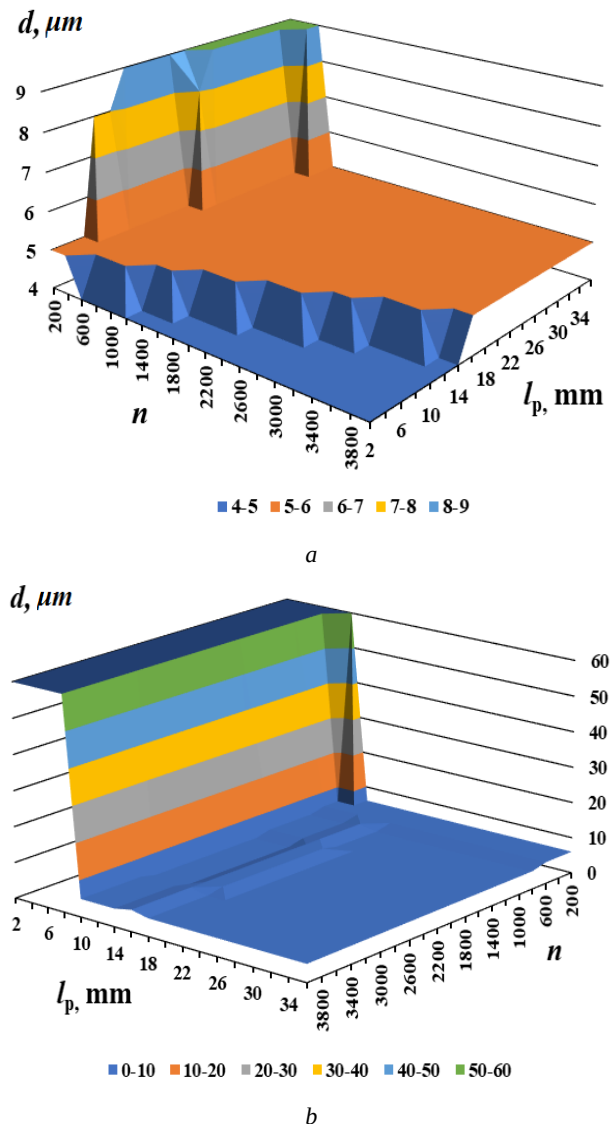


Fig. 1. Distribution of the average particle diameter of titanium powder after HVED treatment depending on the interelectrode gap and the number of treatment pulses, using SD: a – the model of logistic regression; b – Random forest

According to Random forest, the number of spherical particles (see Fig. 2, b) increases from 20% to 30% when the interelectrode gap is in range from 8 mm to 36 mm and the number of treatment pulses is in the range from 200 to 4000. However, in the range of interelectrode gap values from 18 mm to 36 mm and the number of pulses from 500 to 1000, the number of spherical particles is approximately 35%.

Data on the amount of titanium carbide formed during HVED treatment are given on Fig. 3. This process depends on many factors: grinding, the presence of plasma, the presence of free carbon. According to logistic regression models, the amount of synthesized titanium carbide gradually increases during HVED treatment from 0 to 40% with increasing number of processing pulses from 200 to 4000. However, for the interelectrode gap from 20 mm to 36 mm, this process only actively begins at 1000 pulses, and at 4000 pulses the amount of synthesized carbide does not exceed 30%.

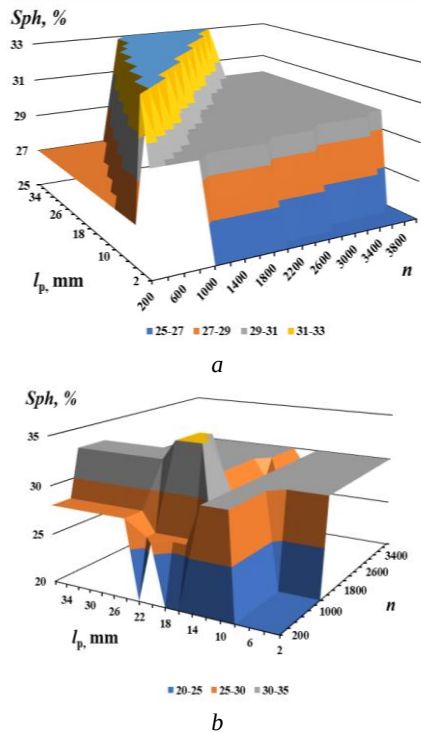


Fig. 2. Distribution of the number of spherical particles of titanium powder formed during HVED processing, depending on the interelectrode gap and the number of treatment pulses, using SD: a – the model of logistic regression; b – Random forest

It should be noted that the simulation results do not take into account the possible change in the interelectrode gap during processing due to the interaction of the powder layer with the hydro flows. And although the data obtained are within the model, it is impossible to draw practical conclusions about the optimal value for carbidization or dispersion of the interelectrode gap in the range above 20 mm from them.

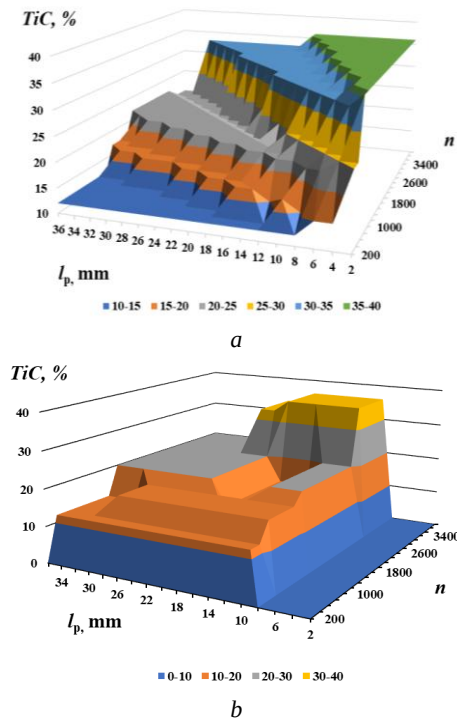


Fig. 3. Distribution of the amount of titanium carbide formed during processing formed during HVED processing, depending on the interelectrode gap and the number of treatment pulses, using SD: a – the model of logistic regression; b – Random forest

4. Conclusions

1. The possibility of using machine learning methods to predict the average particle size of titanium powder, the number of spherical particles and the amount of synthesized titanium carbide as a result of high-voltage electrodischarge treatment of titanium powder in kerosene with SD depending on the interelectrode gap and the number of pulses is shown.

2. It was found that according to the logistic regression, grinding of titanium powder occurs in almost all of studied treatment modes, but the greatest spheroidization of powder particles is characteristic to the treatment with the interelectrode gap of more than 18 mm, while titanium carbidization occurs better in the range of the interelectrode gap up to 18 mm with increasing number of processing pulses.

3. Random forest predictions are more accurate according to the experimental data and show that the average particle size of titanium powder after HVED treatment with the interelectrode interval from 10 mm to 36 mm is almost independent of the number of treatment pulses, and the number of spherical particles is highest at the range of processing pulses number from 500 up to 1500. With the value of the interelectrode gap from 10 mm to 20 mm, and the number of pulses from 2500 to 4000, it is possible to achieve up to 35% of titanium carbide in the composition of powder after treatment.

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Influence of surface laser texturing on surface wettability

Janette Brezinová^{1,*}, Miroslav Džupon², Ján Hašul¹

Technical University of Košice, Faculty of Mechanical Engineering, Košice, Slovakia¹

Slovak Academy of Science, Institute of Materials Research, Košice, Slovakia²

janette.brezinova@tuke.sk, mdzupon@saske.sk, jan.hasul@tuke.sk

Abstract: The paper presents the results of research aimed at determining surface wettability. The research was focused on microtexturing by low-energy laser irradiation of the surface of molded parts using innovative engraved surface treatment methods (LBT and EBT) to ensure a smooth distribution of the separation agent on the surface of high-pressure Al castings. The basic material was Uddeholm Dievar, which is used to make molds. PVD coatings were applied to the base material. The effect of laser texturing surfaces on the contact angle size was determined. Contact angle was evaluated on the base material, on PVD coatings without surface treatment and with the use of two types of separating agents.

Keywords: WETTABILITY, TEXTURING, MOLDS, CONTACT ANGLE

1. Introduction

Contact angle, a quantitative measure of macroscopic surface wettability, plays an important role in understanding liquid-vapor heterogeneous phase change phenomena. Equilibrium contact angle theory was established by Young [1] and refers to a system where a liquid droplet rests on an ideal solid (i.e., a perfectly smooth, non-reactive, chemically homogenous, insoluble rigid surface). Contact angle measured on these ideal surfaces are termed intrinsic contact angles, whilst actual contact angles are the contact angle of 'non ideal' surfaces and apparent contact angles are the angle measured. One of the most difficult aspects of contact angle analysis is the surface roughness, which can have a large impact on the apparent contact angle. This occurs because, as the surface roughness increases, the number of favorable or unfavorable intermolecular interactions increases thus deforming the liquid droplet. Figure 1 shows the classification of the wettability of surface using the contact angle [2].

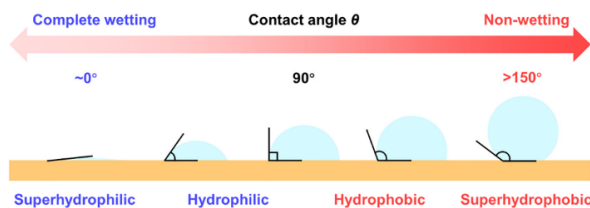


Fig. 1 Classification of the wettability of surface using contact angle

Micro and nanoscale morphology plays a fundamental role in the behavior of both natural and engineered function surfaces. Production of fine surface features has been exploited to modify wettability, tribological performance [3], optical properties and bacterial retention [4]. From a manufacturing point of view, the capacity to produce micro and nanoscale surface features over large areas represents a significant challenge in terms of production technology, throughput, and cost. Amongst the various techniques employed to date, ultrashort pulsed laser irradiation has emerged as an important candidate for texturing metallic surfaces due to its capability of producing surface features smaller than 1 μm via Direct Laser Interference Patterning (DLIP) or Laser Induced Periodic Surface Structures (LIPSS). The ability to transfer micro and nanoscale morphology from metallic molds to polymeric components with standard production processes would not only increase the range of material that could exploit such surfaces, but also greatly improve productivity and economic feasibility [5,6]. Controlled modification of material's surface wettability has been the subject of significant scientific research due to its importance for various applications. In terms of wettability, the water contact angle (WCA) and contact angle hysteresis are affected by both material surface chemistry and topology of surface [7].

The general purpose of surface texturing is to modify and control surface properties, and a key one of these properties is surface wettability. Achieving extreme surface wettability scenarios, including super hydrophobicity and super hydrophilicity has great significance for various industrial and biomedical applications. There are two main methods for fabrication of surfaces

with extreme wettability: one method is by depositing hydrophilic or hydrophobic coatings onto the substrate, which includes crystal growth and electrochemical processing, and the other method directly creates microstructures on the substrate, which includes photolithography, micromachining laser surface texturing and so forth [8]. Surface texture, as an important branch of surface engineering, is the process of creating ordered patterns on the surface of materials, which can significantly improve the tribological properties of materials and improved the adhesion of materials. The surface structure is given as a 3-dimensional topography of a given body surface. It is impossible to obtain a perfectly flat surface topography. Therefore, there is texture on every surface. Surface texturing using ultrashort pulsed lasers is used to apply surface textures with very fine properties and high depth resolution. It allows the creation of small-scale textures that change the functional properties of surfaces, such as surface adhesion, reduction of the coefficient of friction, and the like [9,10]. Some of the textures can be seen as a regular repeating pattern and some of them may be accidental and very difficult to describe in general. In general, texturing involves creating a series of patterns on the surface of parts or on the surface of tools (molds). It can be used to texture complex curved surfaces [10,11]. Advantages of surface texturing are [10]: improvement of adhesion and coefficient of friction of the textured surface, creation of extremely small elements up to 10 μm or less, the possibility of texturing any material, including very hard materials, negligible thermal effects, no melting, burrs, or other damage, contact and forceless process.

Laser surface texturing (LST) is a clean and fast surface approach, especially suitable for functional surfaces with high demands on geometric complexity and accuracy on a micrometer scale [12]. The LST application is now emerging in tradition metal forming or functionalization processes. It is stated that special motifs such as grooves and effectively improved tribological performance, such as the distribution of the separating agent in the process of die casting of Al and its alloys. Laser texturing can be used to apply very fine functional textures to the mold surface in high pressure die casting of Al an its alloys, which improve the adhesion of the mold surface and serve as a reservoir for the separating agent applied to the mold. We recognize these basic types of textures [11]:

1. **Dimple textures** (Figure 2) consist of individual small craters arranged in a specific envelope. The wells can be machined either by leaving the focused laser in one place and firing a defined number of pulses (also called hammer drilling) or by moving the dot along a certain path which can be used to created larger round holes.

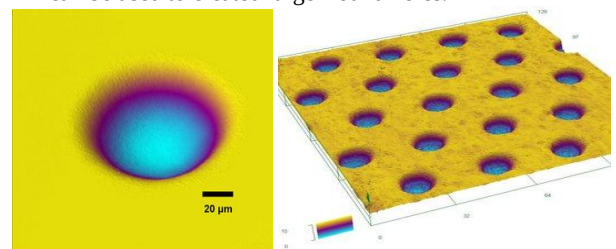


Fig. 2 Example of dimple texture

2. **Free-form textures** (Figure 3) can be machined by laser micromilling, where the material is removed layer by layer according to a given input model. This method allows to process any texture limited only by the size of the point of focus and the depth of one layer. For typical applications, this means a depth resolution below one micrometer and side elements smaller than the size of the point of focus. With this type of texture, the machining time is directly proportional to the depth of the texture. Typical texture depths range from a few micrometers to about 0.1 mm, resulting in machining speeds from a few minutes to one hour to about a centimeter. By using texture mapping with a laser micromilling process, shaped textures can be applied to confined surfaces.

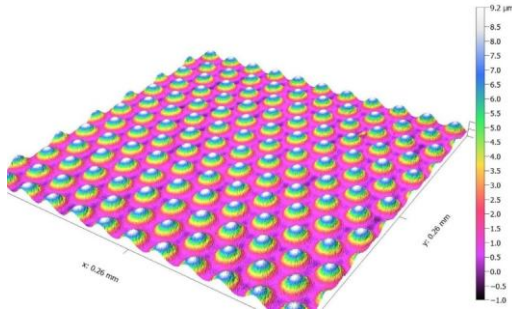


Fig. 3 Free-form texture (height 10 μm)

3. **Crosshatch textures** (Figure 4) they are formed by the application of laser-machined grooves in a square grid. By placing the grooves at a pitch that is close to the diameter of the point of focus, a dense columnar texture resembling the shape of an egg box is created.

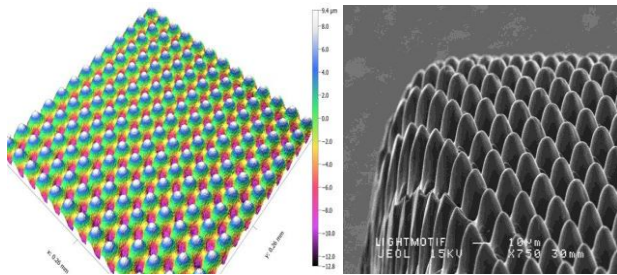


Fig. 4 Example of crosshatch texture

4. **Laser Induced Periodic Surface Structures (LIPSS)** – these LIPSS textures usually form wavy patterns with a pitch in the order of the laser wavelength, resulting in a texture with a properties that are much smaller than the laser spot (Figure 5).

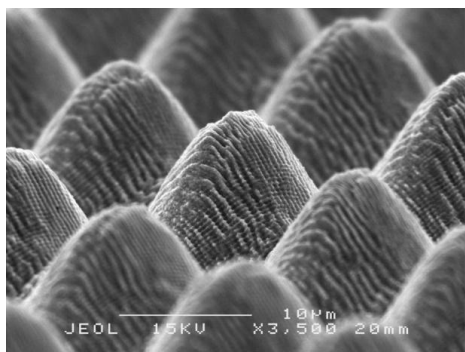


Fig. 5 A sub-micron scale LIPSS texture

Laser microtexturing can be used to apply very fine (functional) textures to the surface and functional parts of a mold for high pressure die casting of Al and its alloys. Figure 6 shows the dimple texture (dark area) applied to the funnel-shaped mold insert (left) and the loose free-form texture applied to the mold insert (right).

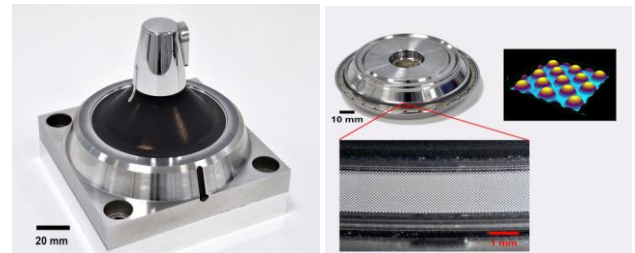


Fig. 6 A dimple texture – dark area (left); Free-form texture (right)

2. Material and methods

Uddeholm Dievar was used as the basic material for the experiment, which is mainly used for molds in high-pressure casting of light non-ferrous metals and their alloys. It is a tool steel alloyed with Cr, Mo, and V. It offers very good resistance to heat control, rough cracking, hot wear, and plastic deformation. The material excels in good toughness and ductility, has good weather resistance, good strength at high temperatures and good dimensional stability during the heat treatment and coating process. The chemical composition of the material is given in Tab. 1.

Table 1: The chemical composition of Uddeholm Dievar

Element	C	Si	Mn	Cr	Mo	V
Weight %	0.38	0.2	0.5	5	2.3	0.6

Main areas of application of the material Uddeholm Dievar in practice are forging, hot sheet metal stamping, metal extrusion, high-pressure aluminum casting.

The surface texturing of the samples was performed by the LBT (laser beam texturing) method. The Yb fiber laser type Piranha II Multi FL205 with a power of 20 W was used. The creation of dimple textures was used, which serves as a reservoir for the separating agent in the process of high-pressure casting of Al and its alloys. Before the coating and texturing process, the surface of the base material was pretreated with wet sandblasting and polishing technologies. Three types of PVD duplex coatings AlTiN G, AlXN₃ and nACRo⁴ were deposited on the surfaces prepared in this way using PLATIT LARC technology. AlXN₃ is a duplex coating composed of: X=Cr; CrN layer + Al/CrN nanomultilayer + AlN layer. The nACRo⁴ nanocomposite coating consists of layers: the first adhesive layer is formed by chromium nitride, on which a gradient AlCrN layer is subsequently deposited. Very thin AlCrN nanolayers are applied to the thus prepared gradient layer. The final top layer of nACRo⁴ is formed by a nanocomposite coating of nc-AlCrN/a-Si₃N₄. AlTiN is a hard coating that solves many tribological problems with components that can be coated at temperatures of 450°C - 475°C. The contact angle on the Advex Instruments was measured by the attached bubble method according to ISO 19403. The following liquids were used: distilled water and 2 types of separating agents Safety Lube 7815 and 8801, which are used in the process of high-pressure casting of Al and its alloys. The samples were cleaned in acetone and ethyl alcohol in the ultrasonic cleaner before the measurements.

3. Results and discussion

3.1 Surface without laser texturing

When measuring the contact angle of the base material and applied PVD nanostructured coatings without texturing, the best results were achieved by separating agent Safety Lube 8801, where the average value of contact angles ranged from 28.4° in the case of duplex nACRo⁴ coating to 32° in the case of base material (polished). Another of the used safety agents Safety lube 7815 reached a slightly higher value of contact angles. The highest average values of contact angles when measuring coated surfaces without texturing were achieved by distilled water in the range from 65.8° to 78.2°. Figure 7 shows examples of the appearance of bubbles when measuring the contact angle without laser texturing of surface.

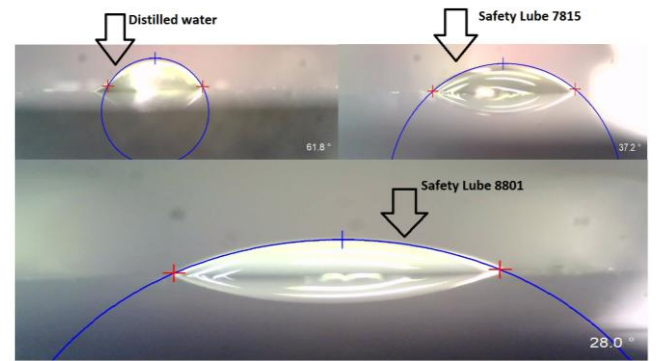


Fig. 7 Appearance of bubbles when measuring the contact angle (without laser texturing)

The measured average values of the contact angles are given in Table 2.

Table 2: Average values of contact angles without laser texture

Used fluid	Average value of contact angles without texture				
	Base material (ground)	Base material (polished)	AlTiN G	nACRo ⁴	AlXN ₃
Distilled water	67.6	65.8	78.2	77	78.6
Safety Lube 7815	45.5	46.8	42.5	38.5	37.2
Safety Lube 8801	29	32	30.4	28.4	28.9

Figure 8 is a comparison of average values of contact angles in the form of a graph of the base material and PVD nanostructured coatings for the type of liquid used (distilled water, Safety Lube 7815, and Safety Lube 8801).

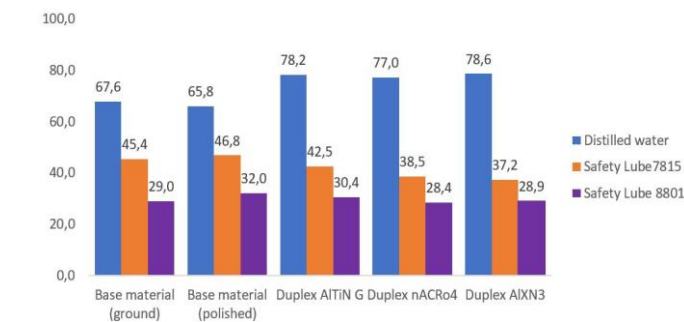


Fig. 8 A comparison graph of average values of contact angles without textured surface

3.2 Surface with laser texturing

The laser used in the texturing process was described in the previous chapter. Dimple textures have been created to serve as a reservoir for the separating agent in a process of repetitive cycles in high-pressure casting of Al and its alloys. AFM images of the textured surface of the base material without and with PVD nanostructured coatings are shown in Figure 9.

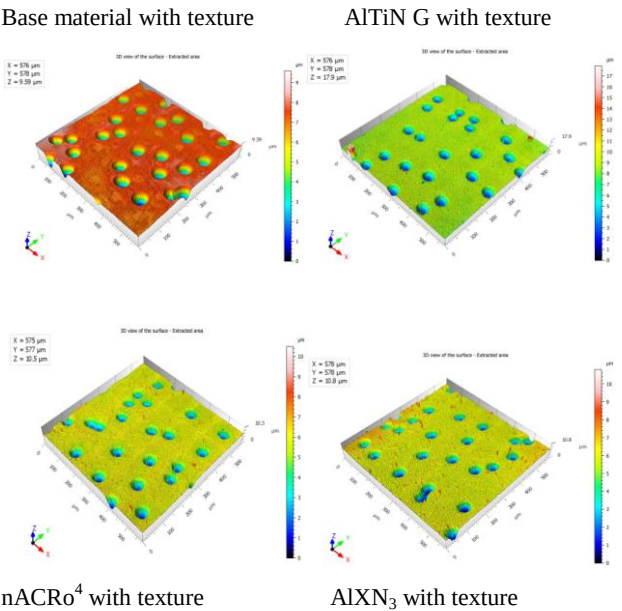


Fig. 9 AFM images of the created textures of the base material and the material with PVD nanostructured coatings

Even when measuring the contact angle of the base material and duplex PVD coatings with texturing, the best values were achieved by the separating agent Safety Lube 8801, where the average values of contact angles was ranged from 27° in the case of nACRo4 coating to 31.9° in the case of Uddeholm Dievar base material with laser random texture. The second separating agent Safety Lube 7815 achieved higher values of contact angles compared to Safety Lube 8801. When evaluating, the contact angles using distilled water, the highest contact angles were measured, which means that the wettability of the surface is insufficient in the case of the base material with the texture. Figure 10 shows examples of the appearance of bubbles when measuring the contact angle with laser texturing of surface.

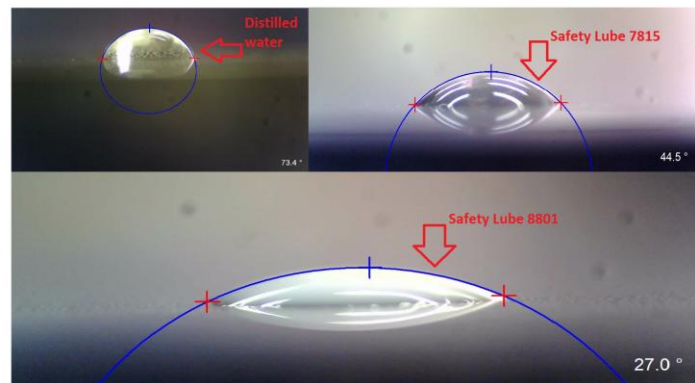


Fig. 10 Appearance of bubbles when measuring the contact angle (with laser texturing)

The measured average values of the contact angles are given in Table 3.

Used fluid	Average value of contact angles with texture			
	Base material	AlTiN G	nACro ⁴	AlXN ₃
Distilled water	73.7	72.3	62.6	64.8
Safety Lube 7815	46.2	46.1	44.8	44.4
Safety Lube 8801	31.9	28.2	27	28.5

Table 3: Average values of contact angles with laser texture

Figure 11 is a comparison of average values of contact angles in the form of a graph of the base material and PVD nanostructured coatings with laser texturing for the type of liquid used (distilled water, Safety Lube 7815, and Safety Lube 8801).

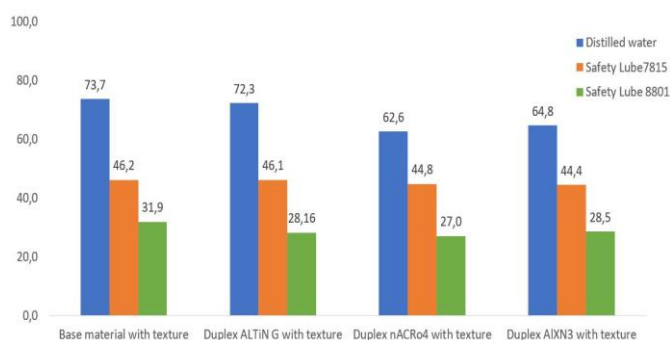


Fig. 11 A comparison graph of average values of contact angles with a textured surface

5. Conclusions

The paper was focused on the evaluation of the effect of the textured surface on the wettability of the surface. The contact angle of the base material Uddeholm Dievar, which is used on the shaped part of molds used in high-pressure casting of Al and its alloys with and without texturing was measured. PVD nanostructured coatings were applied to the base material: AlTiN G, nACro⁴ and AlXN₃. Before the coating process, the base material was pre-treated by wet sandblasting and polishing technologies. Dimple textures were created and served as reservoirs for the separating agent used in the high-pressure casting process of Al and its alloys. Three types of liquids were used during the measurement of contact angle: distilled water and 2 types of separation agent Safety Lube 7815 and Safety Lube 8801. The best surface wettability in both cases was achieved by the separating agent Safety Lube 8801, where small contact angles were measured. When evaluating contact angles using distilled water, the highest values of contact angles were measured, which means that the surface has insufficient wettability. No significant effect of surface texturing was demonstrated, which affected the resulting wettability values of the surface with texturing in comparison to the wettability of the surface of the material without texturing. The importance of texturing should become apparent in the next stages of the experiment, where the tribological properties will be evaluated.

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Mechanical properties of parts fabricated with additive manufacturing: A review of mechanical properties of fused filament fabrication parts

Jelena Djokikj¹, Elisaveta Doncheva¹, Ognjen Tuteski¹, Bojana Hadjieva²

Ss. Cyril and Methodius University, Faculty of Mechanical Engineering, Rugjer Boshkovikj No.18, Skopje, North Macedonia¹

Molior LTD., Hristo Smirnovski No. 25 lok. 1, Skopje, North Macedonia²

e-mail: jelena.djokikj@mf.edu.mk, elisaveta.doncheva@mf.edu.mk, ognjen.tuteski@mf.edu.mk, bojana.hadjieva@molior.mk

Abstract: Additive Manufacturing (AM) Technologies are in constant development since their emergence in the late 80s. However, standardization is still in its infancy, owing to the numerous changing variables in each process. One of the most common are the material extrusion process, in which thermoplastic is extruded, also known as fused filament fabrication (FFF). The popularity of this process is due to the relatively simple method as well as the relatively good mechanical properties of the fabricated parts. There are numerous research studies evaluating mechanical properties because the FFF process allows for the investigation of many variables and the production of many parts with a wide range of characteristics. But how good are those characteristics in reality, and how good do we need them to be? It all depends on the application for which those parts are required.

Keywords: MECHANICAL PROPERTIES, FABRICATION, FUSED FILAMENT FABRICATION (FFF), ADDITIVE MANUFACTURING (AM)

1. Introduction

Additive Manufacturing (AM) technologies are group of processes that build physical model using a three-dimensional Computer-Aided Design (3D CAD), without the need of process planning [1]. Fused filament fabrication (FFF) is an AM process in which the material (most often: thermoplastic) is being extruded through heated nozzle. It is also known under the name fused deposition modeling (FDM), term that is patented by Stratasys. FFF works in the same working manner as all the AM technologies, by building the model layer by layer. This offers many advantages such as geometry complexity, lattice structures, diversify small series and personalized parts fabrication. At the same time, the unique working manner creates challenges for the designers and engineers. One of those challenges are the mechanical properties of the fabricated parts. Mechanical properties of the parts fabricated via FFF differ from the properties of the injection molding parts, even when made from the same material. Determining the cause that influence on the mechanical properties is complex task since it involves many variables, such as: working conditions, process parameters, the material and the machine.

2. Methodology

Determining the mechanical properties of the fabricated parts and what influence the most on them are the concerns for this study. In order to have systematic analysis, two research questions are set: Q1. Which process parameters are taken into consideration for mechanical properties?; Q2. What are the outcomes and findings of these studies and how can they be used in further research?.

In the reviewing process papers from relevant journals and conferences from 1998 to 2022 year were taken into consideration. Papers regarding the mechanical properties of parts fabricated with commercial and open-source FFF machines are analyzed.

3. Analysis

In the text below brief overview of the analyzed paper is given, while in Table 1 detail classification is presented. Bertoldi et al. [2] observed the connection between the mechanical properties and the part orientation. According to their study, the highest values for the modulus of elasticity and the maximum tensile stress were obtained for specimens placed in the y-z plane. The specimens made in the x-z plane have the lowest value for the maximum tensile stress. A critical position is the

vertical placement of the test tube (x-z), due to the high number of layers (> 600), which causes brittle failure. Bellini and Güçeri [3] conducted a similar research with identical results. The samples placed in XZY show the highest values for ultimate tensile stress of 15.99 MPa and Young's modulus of 1653 MPa. While the specimens placed in ZXY show the lowest values for ultimate tensile stress of 7.608 MPa and Young's modulus of 1391 MPa. Ahn [4] takes into consideration the raster width (RW), but report that it has no particular impact on the mechanical properties of the part. Regarding the orientation of the part in the build chamber, the same results are reached by Hussein et al. [5] analyzing pieces of PC (polycarbonate). The highest values for the maximum tensile strength were achieved for the specimens placed in the XZY position, and the lowest for those placed in the ZXY position. In their research, Sood et al. [6] analyze the influence of the part positioning and orientation on the build plate. According to them, the maximum tensile strength and the maximum bending strength decrease with an increase in the angle with respect to the build plate. In later research, Sood et al. [7] investigate the influence of the process parameters on the compressive strength of the parts fabricated with FDM. It is concluded that a maximum compressive strength value of 17.4751 MPa is achieved at the following process parameters: layer thickness 0.254 mm, position 0.036°, screen angle 59.44°, screen thickness 0.422 mm and screen gap 0.00026 mm. Lee et al. [8] analyze the influence of the part positioning and orientation on compressive strength. According to the results, the compressive strength is 11.6% higher when the piece is placed axially than when placed transversely on the build plate. Uddin et al. [9] conduct research in exploring the influence of key printing parameters on mechanical properties of ABS (Acrylonitrile butadiene styrene) specimens. Three parameters were taken into consideration: layer thickness (0.09 mm, 0.19 mm, and 0.39 mm); build plane (XY, YZ, and ZX); and printing orientation (horizontal, diagonal, and vertical). Highest Young's modulus of 1524MPa is noted on specimens with layer thickness of 0.09mm and YZ-H orientation. However, the highest yield strength of 39 MPa is noted in specimens with layer thickness of 0.09mm and YZ-H and YZ-D orientation. In this research it is concluded that the build plane orientation does not have high effect on compressive properties. Slonov et al [10] analyzed the influence of the process parameters on the mechanical properties of PPSU (polyphenylene sulfone) parts. They found out that the best mechanical properties are obtained under the conditions of longitudinal orientation of filaments with a minimum width and negative air gaps between them.

Es-Said et al. [11] investigate the influence of the layer orientation on the mechanical properties. The conclusion is that in the case when the piece is placed horizontally on the bed (0° orientation), with the layers being longitudinal, superior strength and impact resistance is achieved compared to all other positions.

This is also confirmed by other research [12, 13]. Specimens placed along the x axis at an angle of 0° have good maximum bending strength, while specimens placed along the y axis at an angle of 0° have good maximum tensile strength [12]. According to their results, the specimens made along the z axis have significantly the worst results with the highest value of 22.51 MPa for the elongation at a position of 45° in relation to the axis. When it comes to anisotropic features, they are most likely caused by the way the layers are joined [11]. Onwubolu and Rayegani [13] analyze the process parameters (layer thickness, position, raster angle (RA), RW, air gap) to see their influence on the maximum tensile strength. An improvement in the maximum tensile strength is achieved with a minimum layer thickness, minimum RW, a larger RA and a negative air gap [13].

Ahn et al. [4] conducted an investigation on the maximum tensile strength by varying the RA and RW as well as the perimeter to the raster beam. Their research shows that the RA has an effect on the maximum tensile strength, but at a constant RA of 0° and an angle beam perimeter of -76.2 µm, the tensile strength increases by about 30%. The RA has no influence on the tensile strength. Similar results have been reached by Sood and colleagues [14]. In this research, it was concluded that at a positive value for the air gap, the material "flows" between the adjacent layers, which leads to an increased contact area between the layers, and this leads to an increase in the maximum tensile strength of about 15% for thinner layers, for example 0.127 mm.

Shubham [15] came to a conclusion that the layer thickness has influence on the mechanical properties. By increasing the layer thickness, the maximum tensile strength decreases by 46%, the impact force by 54.5% and the flexural strength by 40%. The only exception are the specimens with layer thickness of 0.5 mm, which show deviations in the mechanical properties [15]. This research is followed up by Masood [16] and Hossain [5], considering PC parts. According to Masood [16] the highest value for the maximum tensile strength of 58.8 MPa was achieved at a grid angle of 45°/-45° and a layer thickness of 0.60064 mm. But according to this research, no general rule can be adopted for the maximum tensile stress in relation to the angle of the grid and the layer thickness. Hossain [5] take into account the position, in addition to the RA, RW, air gap and the contour width (CW).

Syamsuzzaman et al. [17] compared the mechanical properties (tensile and compressive properties) of a specimens

fabricated on commercial and open-source low-cost FFF machine. In their research they varied the layer thickness (0.2540 and 0.3302 mm) printing with 100% infill. Their results showed that the layer thickness of low-cost machines has higher effect on the tensile stress of the specimen. This means, in order to get higher tensile stress, the parts fabricated using the low-cost FDM machine must use lower layer thickness setting. Concerning the compression test the results were pretty close which shows that the low-cost FDM machines are reliable in fabricating small parts. For achieving these results the following parameters should be taken into consideration: small layer thickness (< 0.1 mm); orientation of 45°/-45°; and negative air gap. Rajpurohit and Dave [18] also conducted research on an open-source FFF machine. They focused on the flexural strength of PLA (Polylactic acid) parts fabricated on an open-source FFF machine and how it is influenced by the following process parameters: raster angle, raster width and layer height. They concluded that the flexural strength decrease with the increase of the raster angle and the layer height. Regarding the raster width the intermediate values provide the higher flexural strength.

Torres et al. [19] used Design of Experiments (DoE) to explore the tensile and fracture properties of the fabricated PLA part. Following process parameters were taken into account: layer thickness, density or infill percentage, extrusion temperature, speed, infill direction, and component orientation. Layer thickness could then be lowered with little concern to decreased strength, as has been previously shown. Though this would decrease strength, an increase in the number of perimeter layers could be used to reduce the negative effect, decreasing the amount of hollow space. For components which will experience negligible mechanical loading, relative density may be sacrificed to the lower setting as strength will not be an issue and an increase in perimeter layers could be used to prevent it from being too fragile so that mishandling the component would not cause damage. Taylor et al. [20] conducted a research on the mechanical properties (flexural properties, specifically modulus and yield strength) of Ultem 1010 coupons. Build orientation, raster angle and working temperature were varied for the experimental analysis and virtual simulations. The data from the experimental analysis and simulation were found to be within good agreement. For the elevated flexure testing up to 205°C (400°F), as expected, both modulus and yield strength of Ultem 1010 decreased as the testing temperature increased.

Table 1: Classification on researches on mechanical properties of fabricated parts via FFF

Ref	Mater Machine Standard	Variable parameters	Testing	Findings
[2]	ABS Stratasys 1650 ASTM D5937-96	6 build orientations, 4 raster orientations	Tensile testing, thermal expansion,	Build orientation strongly affects the tensile strength, the elastic modulus and the thermal expansion coefficient of fabricated parts.
[11]	ABS 400 Stratasys 1650 ASTM D638, D790, 256-88	5 layer orientations (45/-45, 0, 45, 90, 45/0)	Tensile, flexural and impact testing	Tensile testing showed that the highest UTS and yield strengths are achieved in the 0° orientation, as well as the modulus of rupture. The Izod impact test data indicated that the 0° orientation samples had the highest absorbed energy values.
[21]	ABS P400 Stratasys 1600 ASTM D3039	Mesostructure, air gap	Tensile testing	Mesostructure has a significant influence on the stress-strain response. Modulus values 11-37% lower and strength values 22-57% lower than the ABS monofilament were observed for the fabricated parts. The highest stiffness and strength values were found for an aligned mesostructure with a small negative air gap.
[4]	ABS Stratasys 1650, ASTM D638, D3039	RA, RW, air gap	Tensile and compressive testing vs injection molding	At a RA of 0° and air gap of -76.2 µm, the tensile strength increases by about 30%. The RW does not affect the tensile strength.
[3]	ABS Stratasys 1650 ASTM D5937-96, ASTM D790-96	Build orientation, RA	Tensile and flexural testing	Mechanical properties depend on the build orientation and the RA. The samples placed in XZY show the highest values for the maximum tensile strength and Young's modul. Samples placed in ZXY show the lowest values for peak tensile strength and Young's modul.

[22]	ABS Stratasys 3000	Layer thickness, RA, RW, air gap (3 levels each)	Elasticity testing	All the parameters have heavy influence on the elasticity.
[8]	ABS Stratasys ASTM D695	Build orientation	Compressive testing	Build direction has strong influence in the mechanical properties. Compressive strength is 11.6% higher when the build direction is axial than transversal.
[23]	ABS P400 Stratasys 2000 ASTM D1184-98	Build orientation, envelope temperature	Thermal and flextural testing	Envelope temperature and the cooling conditions have strong repercussions on the flextural properties as well as the accuracy of the final part.
[24]	ABS P400 Stratasys Vantage SE ISO R527:1966, ISO R178:1975, ISO 179:1982	Layer thickness, orientation, RA, RW, air gap	Tensile, flexural and impact testing	Optimized factors for tensile, impact and flexural strength of specimen using the bacterial foraging technique.
[6]	ABS P400 Stratasys Vantage ASTM D638, D790	layer thickness, build orientation, RA, RW, air gap (3 levels each)	Tensile testing, flextural testing	Tensile and flextural strength decrease with the increase of the angle with the build plate.
[14]	ABS P400 Stratasys Vantage ISO R527:1966, ISO R178:1975	Layer thickness, orientation, RA, RW, air gap	Tensile, flexural and impact testing.	By changing the raster angle from 60°/-30° to 90°/0°, the value of the maximum tensile stress decreases. At a positive value of the air gap, the material "flows" between adjacent layers, which leads to an increase in the maximum tensile strength. For flextural strength the parameters were found to be the same, but it differed in factor levels for impact strength.
[16]	PC Stratasys Vantage	RA, RW, air gap (3 levels each)	Tensile testing	Highest values for the tensile strength are achieved with raster angle 45°/-45° and raster width 0.60064 mm.
[25]	ABS P400 Stratasys Vantage ISO R291:1977	Layer thickness, orientation, RA, RW, air gap	Compressive testing	The developed relationship between compressive stress and process parameters is able to explain the 96.13% of variability in the response.
[26]	Ultem 9085 Stratasys Fortus 400mc ASTM D638	RA, CW, air gap (3 levels each), layer thickness (2 levels)	Tensile testing comparison to injection molding	The best results were achieved for all directions by using a negative raster air gap. With thick filaments better mechanical data can be achieved for the X and Z build direction, while a thinner filament improves the strength properties for Y-specimen.
[27]	ABS Stratasys Dimension SST-768	RA (4 levels)	Tensile, flexural and impact testing.	Specimens with raster angle of 45°/-45° (crisscross) had higher strength for deflection, flexural and impact tests. The tensile test result showed higher strength in cross-orientation (0°/90°).
[7]	ABS P400 Stratasys Vantage SE ISO 604-1973, ISO R291:1977	Layer thickness, build orientation, RA, RW, air gap (3 levels each)	Compressive testing (analytical and experimental)	Maximal compressive strength can be achieved with layer thickness of 0.254 mm, orientation of 0.036°, RA 59.44°, RW 0.422 mm and air gap 0.00026 mm. Low part strength is caused by distortion and anisotropy.
[28]	ABS M30 FDM ASTM D638-10	Build orientation, number of contours	Tensile testing, stiffness	The results have been processed for the determination of the Ultimate Strength and of the Young's modulus. Design of an algorithm able to model the rupture event of every single bead and, consequently, to predict the failure of the whole part.
[29]	ABS, ABS+ Stratasys Dimension, Dimension Elite ISO 527-1	Build orientation	Tensile testing for fatigue	ABS+ part's properties were found to be isotropic than properties of ABS parts. The UTS for the ABS specimens ranged from 50-80% of the ABS wire data and for the ABS+ specimens ranged from 75-80% percent (omitting the Z-direction).
[30]	PC Stratasys Vantage SE ASTM D638	Build orientation	Tensile testing, elastic modulus	The results also show a degradation in strength compared to bulk material properties (30%–53%, depending on orientation) and as manufactured properties as reported by the FDM vendor (36%–63%, depending on orientation)
[31]	ABS Stratasys Dimension BST ISO R527:1966, ISO 180:1982	Build orientation (5 levels)	Tensile and compressive testing	The build orientation has more influence on the compressive strength than tensile strength. Compared to the injection molded parts, tensile strength is lower for 48-60 % and compressive strength has a reduction in the range of 57- 64 % for build orientation varying from 0°-90° respectively.
[32]	PLA Bits - Bytes 3DTouch ISO 178:2010, ISO 5271:1996, ISO 180:2001	Build orientation, infill pattern/density, layer thickness, print speed	Tensile, flexural and impact testing	Combination of impact (X oriented) and flexural (Z oriented) tests are more practical for assessing impact strength and flexural modulus when applied to parameter set B specimens, and hence the quality of a build on a FDM machine.
[13]	ABS Fortus 400mc ISO R527:1966, R178:1975	RA, RW, air gap, layer thickness, positioning	Tensile testing	Improvement in tensile strength is achieved with minimum layer thickness and raster width, larger raster angle, and negative air gap.
[5]	PC Fortus 900 mc ASTM D638	RA, RW, CW, air gap, build orientation	Tensile testing	Maximum tensile strength is achieved for the specimens placed in the XZY position, and the lowest for those placed in the ZXY position.
[12]	ABS P400 Stratasys FDM ASTM D638, ASTM D790	Part orientation, layer orientations	Tensile and flextural testing	Maximum flextural strength is achieved with specimens placed at an angle of 0° to the x-axis. Maximum tensile strength is achieved for specimens placed at an angle of 0° to the y-axis have a good maximum tensile stress. The specimens at an angle of 45° with respect to the z axis have the worst results.

[33]	ABS, PLA Lulzbot Prusa, Prusa Mendel ASTM D638	Layer thickner, raster orientation	Tensile testing	Investigated the association between raster pattern and a layer height of open source printers to tensile strength, modulus and strain at tensile strength.
[34]	ABS P430 Dimension 3D Printer ISO 178:2006, ISO 527:1997	RA (5 levels), build orientation (3 levels)	Compressive strength	Smaller raster angles (0°) provide maximum strength because of larger effective raster length.
[17]	ABS low-cost FFF, commerical FDM	Layer thickness, build orientation, air gap	Tensile and compressive testing	FFF open-source parts reached lower values for the tensile strength. For the compressive strength the results were almost same. For optimal results lower layer thickness, orientation 45°/-45° and negative air gap are advised.
[35]	PP (polypropylene), GRPP (glass reinforced PP) Prusa i3 DIN 53504-S3a	infill degree, build orientation, layer thickness	Tensile and compressive testing	The adhesion between adjacent filaments is evident but, and the samples are stiffer in the filament direction. The layer thickness has little influence on the mechanical performance of the samples. The infill degree has a dramatic and linear effect on the mechanical properties. The use of fibers as reinforcement is also effective in 3D printing. The loss in the mechanical performance of the printed samples is 20–30%, depending on the printing parameters values used, when compared to that of samples produced by compression molding.
[36]	ABS Stratasys Vantage ASTM D638, ASTM D7791	raster orientation (4 levels), defined machine default values for parameters	Tensile and fatigue testing	UTS and yield strength are highest for 0° raster orientation.
[37]	PLA Prusa ASTM D638	layer thickness, print orientation (2 levels each), infill percentage (3 levels)	Tensile testing, elastic modulus	The decrease in strength was observed as infill orientation comes closer to 90° and increases when perimeters increase.
[38]	PA12 (polyamide) Fortus 400mc DIN EN ISO 527, DIN EN ISO 178, DIN EN ISO 604, DIN EN ISO 1133	Layer thickness, build orientation (3 levels each)	Tensile, flexural, compressive testing, thermal testing	The highest tensile strength was recorded in X-direction. No anisotropy was visible for the flexural strength but a slight tendency for the flexural modulus. The highest compressive modulus is noticeable in Z-direction with a layer thickness of 254 µm. For the compressive strength, there are only slight differences recognizable. As thermal properties of the Polyamide 12, the flow ability is determined (MVR) and the melting behavior by means of DSC analyze.
[15]	ABS Cubex 3D printer ASTM D-1708, ASTM D-256, ASTM D785	Layer thickness	Tensile, impact and hardnes testing	The layer thickness plays a significant role in the mechanical propertied of ABS fabricated parts. As the layer thickness increases, tensile strength reduced by 46%, impact strength reduced by 54.5% and hardness reduced by 40%; exception is with layer thickness 0.5 mm.
[39]	ABS Lulzbot TAZ 4 ASTM D638-10	Build orientation, raster patterns	Tensile testing	The tensile test results exhibited an equivalency between the vertically printed specimens with horizontal printed specimens. The fracture morphology was also planar in nature and exhibited less plastic deformation than the longitudinal and crosshatched specimens.
[19]	PLA Replicator 2 ASTM D638; D648, E143	layer thickness, build orientation, infill percentage and direction, extrusion temperature, speed (2 levels each)	Tensile and flexural testing	Layer thicknes and infill percentage have highies influence on the tensile and flexural strength.
[40]	Z-ABS, Z-Ultrat, Z-glass-PETG Zortrax EN ISO 527-4 type 5	5 samples for each material	Tensile testing	Results show some distinctions between tensile modulus of the fabricated parts and its base materials, i.e. Z-ABS prints Young modulus have mean value of 1.12 GPa and the encyclopedic value is between 1.7 up to 2.1 GPa.
[9]	Z-ABS Zortrax M200 ASTM D638	layer thickness , build plate, and build orientation (3 levels each)	Tensile testing, compession testing	Specimens with layer thickness of 0.09 mm and YZ-H show the highest Young's modulus of 1524 MPa. YZ-H and YZ-D with layer thickness of 0.09 mm show the highest yield strength of 39 MPa. Compression tests show that XY-H and XY-D have the highest stiffness and yield strength.
[41]	Ninjabflex (5 colors), SemiFlex (4 colors), HIPS (5 colors), T-Glass (5 colors), PC (1 color), Nylon (2 Types), ABS (1 color) Lulzbot TAZ 3.1 and 4 ASTM D638	Different extrusion temperature for different materials, mass	Tensile testing	The study demonstrates that the tensile strength of fabricated specimens depends largely on the mass of the specimen, for all materials. The strongest material among those tested was polycarbonate with a maximum tensile strength of 49 MPa. The most flexible material was Ninjabflex, which did not break after an extension of about 800%. Nylon materials were stronger than Ninjabflex and SemiFlex, and much more flexible than ABS, HIPS, T- Glase, and polycarbonate, which provides a good balance between strength and flexibility.
[20]	Ultem1010 FDM	build orientation, RA, air gaps	Flextural testing	The XYZ 0°/90° build combination was chosen for elevated temperature flexure testing. For the elevated flexure testing up to 205°C (400°F), both modulus and yield strength decreased as the testing temperature increased. Similarly to the elevated temperature tests, the XYZ 0°/90° build combination was chosen for sparse-build flexure coupons. The experimental and simulation data were found to be within good agreement.

[42]	PLA WitBox desktop 3D printer ASTM D638, ASTM D790	Build orientation, feed rate (3 levels each), layer thickness (4 levels)	Tensile and flexural testing	On-edge orientation may be selected for the optimal mechanical performance in terms of strength, stiffness and ductility. If ductile behaviour is desired with the optimal printing time, strength and stiffness, high layer thickness and low feed rate values are recommended for upright and on-edge orientations. Low layer thickness and high feed rate values are recommended for on-edge and flat orientations. If minimum printing time is desired, high layer thickness and high feed rate are recommended.
[18]	PLA FFF open-source	Layer thickness, RA, RW	Flexural testing	A higher flexural strength was observed at 0° RA and decrease with higher angle and higher layer thickness. At the intermediate value of the RW, a higher flexural strength is achieved.
[10]	PPSF FDM	Build orientation, RA, RW, air gap	Tensile and flexural testing	The best physical and mechanical PPSF characteristics, are achieved by printing in a longitudinal filament orientation, with minimum width and negative air gaps between them.
[43]	PLA, PC, PETG Prusa Mk3S ISO 527-1:2019, ISO 178:2019	100% infill, change in material	Tensile and flexural testing	PLA specimens have the highest tensile strength, largest mean Young's modulus and flexural stress. PETG showed the largest elongation before breaking in both test cases. PC specimens have the highest UTS.

4. Discussion

As can be noted from Table 1, most of the researches are conducted for ABS parts, as this material is most widespread. But in the last few years studies on different materials emerge, such as: PLA and Ultem. As can be seen from the Table 1 there is not unified standard used for testing of the fabricated specimens, since the standardization for AM is still in its infancy. This is one element that really makes it difficult for the researchers not being able to compare results, working under different standards. ASTM and ISO has joined forces into creating standards faster, but AM technologies are consisted on many different processes that use different materials and consequently work under different working conditions.

Most of the presented studies focus on the tensile and flexural properties of the specimens, but not all of them concentrate on the same process parameters. From Table 1 can be concluded that there is high connection between the mechanical properties and the part or layer orientation as well as the layer thickness. There are also important parameters such as: working temperature, speed, which are not subject of concern in many studies.

5. Conclusion

In this study more than 40 paper dealing with the mechanical properties of the fabricated parts with FDM and FFF were reviewed. From the stated facts and analyzed papers it can be concluded that FFF process has come a long way since its beginnings, the materials and the machines are more advanced capable of fabricating parts with decent mechanical properties. Although it should be noted that many elements such as working environment, process parameters, used material, machine have influence on the mechanical properties of the final part. This is why the application of the part should be taken into consideration in the design phase and according to that the appropriate process and process parameters will be chosen.

It is important to be noted that these processes are not meant to substitute the conventional technologies such as injection molding and there for comparison is not necessary. These processes are meant to create new opportunities and enable application in areas that were not expected.

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Optoelectronic method for optical diagnosis of the state of the vascular system

Alexander Gisbrecht^{1*}, Sergej Mamilov²

Institute of Electronics, Sofia, Bulgarian Academy of Sciences¹

Institute of applied problems of physics and biophysics, Kiev, NAS of Ukraine²

agiz@abv.bg

Abstract: In the present work we have investigated the parameters of peripheral blood flow by using a non-invasive method for processing photoplethysmograms (PPGs). The developed original technique allows us to register a photoplethysmogram, isolate the pulse wave and determine the duration of cardio intervals, the duration of the anacrotic and dicrotic phases, the duration of fast and slow blood filling, the expulsion period, the dicrotic and diastolic indices, temporal and amplitude parameters of vascular tone, etc. We observe three types of PPGs after taking medicaments Corvitol-50 and nitroglycerin. The analysis of the amplitude-temporal characteristics of PPGs allows the determination of key diagnostic parameters.

KEYWORDS: PULSE WAVE, VASCULAR SYSTEM, PHOTOPLETHYSMOGRAMS

1. Introduction

Optical diagnostics of biological objects has gained wide application in recent years. The advantages of optical diagnostic methods consist primarily in noninvasiveness, rapidness and high accuracy. Unlike radiological and ultrasonic methods, optical irradiation is natural for the organism and does not cause any side effects with the powers used. Determination of the relative saturation of arterial blood with oxygen (SaO₂) - pulse oximetry has become the gold standard in resuscitation and intensive care. The spectral range between 600 and 1000 nm (near IR) is well suited for optical tissue oximetry because at these wavelengths, the absorption spectrum of hemoglobin is closely related to its oxygenation state. Moreover, the penetration depth of biological tissues is high in this spectral range.

Today, cardiovascular diseases are the leading cause of death and disability. The most important tasks are the improvement of methods for diagnosing and monitoring, the development of effective methods for prevention. Doctors need non-invasive research methods that could record the main indicators of central and peripheral hemodynamics and would characterize the contractile activity of the heart. At the present stage of the development of medicine, it is no longer enough to take only electrocardiographic and blood pressure measurements to make a comprehensive diagnosis. In assessing the adaptive abilities of a person (physiology of labor and sports medicine, etc.), determination of basic hemodynamic parameters is necessary to establish rational modes of work and rest, optimal and maximum levels of physical activity.

There are many methods of measuring cardiac output, both invasively and non-invasively; each has advantages and drawbacks. Invasive methods are well accepted, but these methods are quite complicated, traumatic and often lead to changes in heart rate. Consequently, the focus on development of non-invasive methods is growing [1]. Ultrasound Dopplerography is most used by these methods. Being accurate and inexpensive, Doppler ultrasound is a routine part of clinical ultrasound; it has high levels of reliability and reproducibility, but it does not measure blood volume and is complicated to use. This method is most suitable for large clinics [2]. Electrical impedance plethysmography and electrical cardiometry are similar methods based on the model of electrical velocimetry, and non-invasively measures stroke volume, cardiac output and other hemodynamic parameters through the use of 4 surface ECG electrodes. The disadvantage of rheoplethysmography to determine the parameters of peripheral blood flow is the placement of current and measuring electrodes at a great distance. At the same time, the signal is influenced by the properties of vessels throughout the pathway.

Photoplethysmography (PPG) is a simple and low-cost optical technique that can be used to detect blood volume changes in the microvascular bed of tissue. It is often used non-invasively to make measurements at the skin surface. A PPG is often obtained by using a pulse oximeter which illuminates the skin and measures changes

in light absorption. The PPG waveform comprises a pulsatile physiological waveform attributed to cardiac synchronous changes in the blood volume with each heart beat [3-5]. PPG offers significant potential for data mining and a range of innovative pulse wave analysis techniques.

The aim of our study is to determine the parameters of peripheral blood flow using an optoelectronic method for processing photoplethysmograms.

2. Materials and Methods

The photoplethysmogram is a change in the transmittance of light by a biological tissue under the influence of a pulse wave. The sensor for recording photoplethysmography is a light-emitting diode and a photodetector, between which biological tissue is placed. Taking into account the absorption spectra of blood and tissue, the use of near-infrared emitters is most appropriate. The use of photoplethysmogram allows local research of peripheral blood flow.

Similar to the analysis of the rheoplethysmogram proposed in [6], the information parameters of the photoplethysmographic pulse curves can be divided into primary (amplitude and time) and derivatives of the primary, obtained by simple mathematical operations. The pulse curve depends on the systolic ejection, blood flow intensity, blood viscosity, condition of the vascular walls, the ratio of precapillary and postcapillary pressure, etc.

The pulse wave has the following main components (Fig. 1): a steep systolic ascent - the anacrotic phase and the descending part, which corresponds to the catacrotic phase. On the anacrot there are two sections - the period of rapid blood filling from the beginning of the anacrot to the point of maximum steep rise (maximum of the first derivative of the pulse wave) and the period of slow blood filling. On the catacrot is the so-called dicrotic wave.

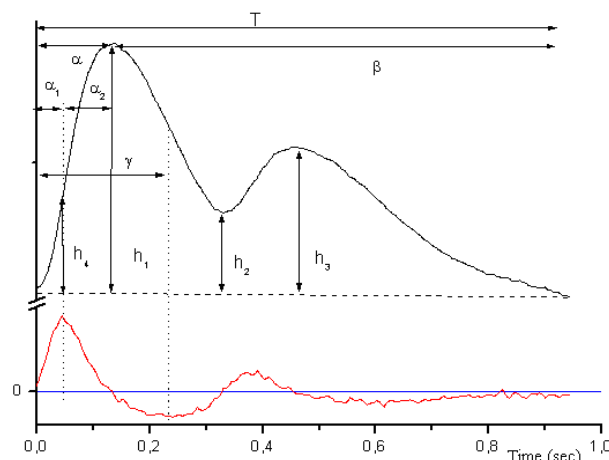


Fig.1 Pulse wave (upper curve) and its first derivative (lower curve)

Primary characteristics of the pulse wave:

T - the duration of the cardiac cycle.

α - the duration of the ascending part of the wave (anacrotic phase)

α_1 - the duration of rapid blood filling.

α_2 - the duration of slow blood filling.

β - the duration of the catacrotic phase

γ - the ejection period.

h_1 - the maximum amplitude of the pulse wave, the indicator of the magnitude of the pulse of blood.

h_2 - the amplitude of the pulse wave at the level of the incisura.

h_3 - amplitude of the pulse wave at the level of a dicrotic wave.

h_4 - amplitude of the pulse wave at the level of the projection of the maximum of the first derivative.

There are other secondary indices that are left out of our study.

In medical practice, the averaging of the SaO_2 value over 8 or 16 heartbeats is used, which simplifies the requirements for recording a photoplethysmographic signal. However, when we developed methods for determining changes in the relative volume of peripheral blood [7], the relative concentration of carboxyhemoglobin in arterial blood [8], and the relative oxygen concentration in venous blood [9], to reduce the error we need a lot of points, so it is necessary to record a photoplethysmogram with a frequency of 200-250 Hz [10]. Due to our original method of data processing, the accuracy of measurements is 3-4 times higher compared with standard systems. The system allows continuous photoplethysmographic monitoring, recording and data storage. Data acquisition was executed by a measuring block with a microcontroller connected to PC. The microcontroller includes a microprocessor, RAM, ROM, decoder, timer, quartz-stabilized clock generator, and input/output ports. The sampling frequency was 348 Hz, the LED flash pulse duration - 160 μs , the interval between pulses of red and IR emission 200 μs . Calculations were made on interval lengths of 200 to 400 points with a shift of 100 points. This procedure provides a measurement with a smaller increment than the cardiac cycle length. This system enables to implement the diagnosis of the cardiovascular system by analyzing the volume pulse wave. The developed original technique allows us to register a photoplethysmogram, isolate the pulse wave and determine the duration of cardio intervals, the duration of the anacrotic and dicrotic phases, the duration of fast and slow blood filling, the expulsion period, the dicrotic and diastolic indices, temporal and amplitude parameters of vascular tone, etc. All results are given as mean $\pm$ (SD). The Student's test for connected sampling was used for the statistical calculations. Statistical results with a value of $p < 0.05$ were viewed as being significant. The evaluation was carried out using the program "Origin 7.5".

3. Results and discussion

Measurements of these parameters were carried out with a medicament impact on a 51-year-old volunteer with coronary heart disease. The registration was carried out in a calm state with a satisfactory state of health. The measurements were carried out 30 minutes after taking "Corvitol-50" and 2-3 minutes after taking nitroglycerin. The analysis revealed photoplethysmograms of several types (Fig. 2). The y-axis are arbitrary units, because we are only interested in the shape of the signal. We attributed the first type of photoplethysmogram (Fig. 2a) to a curve with a well-expressed dicrotic wave, the maximum of which is located approximately in the middle of the catacrotic phase. The difference between the amplitudes of the wave at the level of incisura and dicrotic wave is small. Photoplethysmograms of the first type were observed in a calm state and after taking Corvitol-50. The photoplethysmogram shown in Fig. 2b was attributed to the second type. In this type the dicrotic wave is also well expressed, but is shifted closer to the end of the catacrotic. Incisura has a much smaller amplitude than in the previous case and the difference between the amplitudes of the wave at the level of incisura and the dicrotic tooth is very significant. Such photoplethysmograms were observed after taking nitroglycerin. The third type of photoplethysmogram (Fig. 3b) is characterized by the absence of a expressed dicrotic wave. This leads to the fact that it is impossible

to isolate the incisura and dicrotic prong and measure their amplitudes. This type of photoplethysmogram was also observed after taking nitroglycerin.

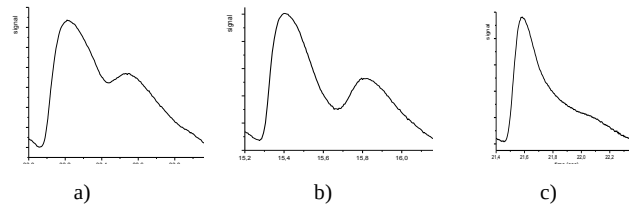


Fig. 2 Photoplethysmograms: a) first, b) second, c) third type.

After taking nitroglycerin, the second type of photoplethysmogram mainly occurs at the beginning of the recording, and the third is closer to the end.

3.1. Temporal characteristics

During the experiments, the following primary properties were determined: the duration of the cardio intervals, the duration of the anacrotic phase, the duration of the fast and slow blood filling, the ejection period. In a calm state, the temporal characteristics were: $\alpha_1 = 0.053 \pm 0.006$ sec., $\alpha_2 = 0.089 \pm 0.007$ sec., $\alpha = 0.142 \pm 0.008$ sec., $\gamma = 0.279 \pm 0.018$ sec., $T = 0.945 \pm 0.023$ sec. Changes in temporal characteristics after taking medications are shown in Fig. 3 and Fig. 4.

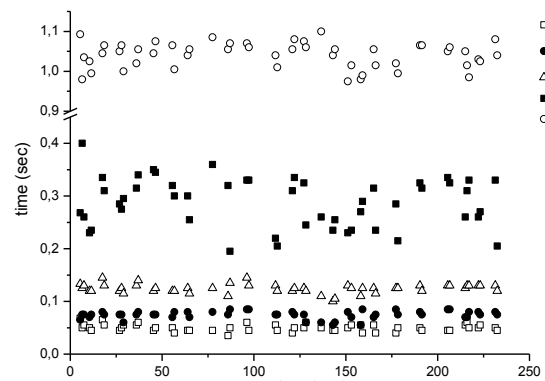


Fig. 3 Temporal characteristics after taking "Corvitol-50".

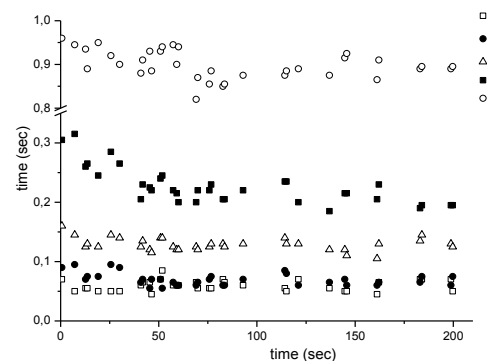


Fig. 4 Temporal characteristics after taking nitroglycerin

After taking Corvitol, the duration of cardio intervals increased ($T = 1.040 \pm 0.031$ sec), which corresponds to a decrease in heart rate. The duration of the anacrot decreased, the durations of the fast and slow blood filling were respectively $\alpha_1 = 0.050 \pm 0.007$ sec., $\alpha_2 = 0.075 \pm 0.007$ sec., $\alpha = 0.124 \pm 0.009$ sec. The ejection period increased slightly - $\gamma = 0.287 \pm 0.040$ sec., the spread of its values also increased.

The correlation characteristics between these parameters were determined. High correlation is observed between α_1 and α and between α_2 and α (0.53 and 0.67, respectively). The correlation of these values with the ejection period was 0.02 for α_1 , 0.31 for α_2 and 0.29 for α . With the duration of the cardio interval, the correlation was 0.13 for α_1 , 0.01 for α_2 , 0.11 for α and 0.23 for γ .

After taking nitroglycerin, the duration of cardiointervals decreased ($T = 0.899 \pm 0.026$ sec.), which corresponds to an increase in heart rate. The duration of anacrotic and the duration of slow blood supply decreased, but the duration of fast blood filling increased. They amounted to, respectively, $\alpha_1 = 0.059 \pm 0.007$ seconds, $\alpha_2 = 0.070 \pm 0.008$ seconds, $\alpha = 0.129 \pm 0.008$ seconds. It is noted, unlike other experiments, the excess of the duration of fast blood filling over the duration of slow blood filling. The ejection period significantly decreased - $\gamma = 0.227 \pm 0.023$ sec.

The correlation between α_1 and α and between α_2 and α is slightly lower than in the previous case, but quite high (0.43 and 0.64, respectively). The correlation of the duration of fast blood filling with the ejection period became negative and amounted to - 0.17, while the correlation between the duration of slow blood filling and the length of anacrot with the ejection period was high - 0.74 for α_2 and 0.59 for α . With the duration of the cardio interval, the correlation was 0.06 for α_1 , 0.26 for α_2 , 0.31 for α , 0.55 for γ .

The secondary temporal characteristics were determined: the temporal index of the vascular tone and the specific time of the anacrot. The temporal index of vascular tone was 0.60 ± 0.10 for a calm state, 0.68 ± 0.11 after taking Corvitol and 0.88 ± 0.18 after taking nitroglycerin, and the specific anacrot time was 0.15 ± 0.01 for a calm state, 0.12 ± 0.006 after taking Corvitol and 0.14 ± 0.01 after taking nitroglycerin.

3.2 Amplitude characteristics

The amplitudes h_1 , h_2 , h_3 , h_4 and secondary characteristics were determined: dicrotic index, diastolic index, amplitude index of vascular tone. At calm state, the dicrotic index was 0.48 ± 0.06 , the diastolic index was 0.59 ± 0.03 , and the amplitude index of vascular tone was 0.40 ± 0.04 .

After taking Corvitol all parameters slightly increased and amounted to a dicrotic index - 0.53 ± 0.10 , diastolic index - 0.67 ± 0.05 , amplitude index of vascular tone - 0.43 ± 0.03 . Taking nitroglycerin leads to a decrease in the dicrotic and diastolic indices and is characterized by the appearance of a pulsogram without a dicrotic wave. The mean values were respectively: dicrotic index - 0.20 ± 0.06 , diastolic index - 0.35 ± 0.11 , amplitude index of vascular tone - 0.45 ± 0.04 .

4. Conclusion

The method of optoelectronic determination of the characteristics of the cardiovascular system allows the analysis of the amplitude-temporal characteristics of the photoplethysmographic curve to determine such interesting diagnostic parameters as the duration of the anacrotic and dicrotic phases, the duration of fast and slow blood filling, dicrotic and diastolic indices, temporal and amplitude vascular tone. In contrast to the other methods, the use of photoplethysmography allows us to conduct local research, to determine changes in the state along the vessels, excludes electrical effects on the patient when conducting research.

Acknowledgments

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Contactless Determination of the Number and Diameter of Fog Droplets Using Gravitational Separation and Measurement of Electrical Signals

Petar Todorov^{1,*}, Zahary Peshev², Nely Ilieva¹, José Luis Pérez-Díaz³, Ognyan Ivanov⁴

Georgi Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria¹

Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, Bulgaria²

Escuela Politécnica Superior, Universidad de Alcalá, 28805 Alcalá de Henares, Madrid, Spain³

Institute of Mechanics, Bulgarian Academy of Sciences, Block 4, Acad. G. Bonchev St., Sofia -1113, Bulgaria⁴

pv_todorov@abv.bg

Abstract: A method was developed for contactless evaluation of the number and diameter of droplets in a jet, by means of gravitational separation and measurement of an electrical signal from a laser-induced electromagnetic echo effect (EMEE), at several points of the jet. With it, only with modulated laser radiation, an electrical signal is induced. The measured value of the signal from this EMEE depends on the parameters of the fog (number and sizes of droplets). This signal is measured at several points of the jet, as the droplets must be in laminar flow. After measuring the signal at the first point, the signals at the previous points are subtracted from its value at each subsequent point, in order to separate the measured signal at each point and determine the change in fog parameters. The method represents an affordable and reliable alternative to existing fog characterization techniques.

Keywords: FOG PARAMETERS, ELECTROMAGNETIC FIELD-MATTER INTERACTIONS, SENSOR

1. Introduction

Characterization of airborne particles or droplets is crucial for research in a number of fields, such as air quality research, cloud and fog characterization, cleanroom monitoring, jet research, etc. Nowadays, there are various methods for determining the number and size of particles, including droplets. Some of them use separation to segregate the particles by size, but they are not suitable for the study of droplets, as they are only applicable to solid particles [1]. There are many instruments that use optical methods based on Fraunhofer diffraction and various forms of light scattering (dynamic, static, etc.), such as laser diffraction, to determine the number and spectrum of particle diameter distribution. Optical techniques require specific statistical processing of the results, and they are greatly influenced by the specific statistical method used for the purpose [2]. More modern technologies are based on the use of high-resolution cameras and image analysis, which are also used to determine particle velocities [3]. Other imaging techniques include optical and electron microscopy, holography, and photography. With these methods, the main problem is the overlapping of the particles, they are also quite expensive.

2. Prerequisites for solving the problem

We have developed an alternative method for contactless determination of the number and diameters of droplets in a jet, by means of gravitational separation and measurement of electrical signals from laser-induced electromagnetic echo effect (EMEE), at several points of the jet. The signals are generated using only modulated laser radiation, and their values depend on the fog parameters (number and sizes of droplets). These signals are measured at several points of the jet, in which the droplets are required to be in laminar flow. After measuring the signal at the first point, at each subsequent point the signals obtained at the previous points are subtracted from the measured value, in order to separate the signal at each point and determine the change in fog parameters.

It was experimentally established that during the generation of fog, at a certain distance from the nozzle, the flow of drops is turbulent, after which the flow becomes laminar. It is from this moment on that a gravitational separation of the droplets by size is observed. The largest droplets of the stream fall to the ground first, and the rest continue forward. Then the next largest drops fall, and only the finest droplets reaching the furthest. The presented method and the corresponding device are protected by a patent issued by the Patent Office of the Republic of Bulgaria in 2020 [4].

3. Methodology for non-contact measurement of fog parameters in an artificially generated jet

Consider a small cloud of fog, for which we are interested in the spectrum of the distribution of the diameter d of the drops by the number N_d for each diameter. Let us assume that a force F acts on the cloud in the direction indicated in Fig. 1. Such a force can be created in various ways - for example, by a constant airflow or an electrostatic field. As a result of the acting force, the drops will begin to move in the indicated direction, and at the same time they will also begin to fall. The heaviest drops will travel the shortest way. They will reach point 1. All drops of size up to d_1 will settle there. Accordingly, drops of sizes up to $d_2, d_3, d_4, \dots d_n$ will reach points 2, 3, 4, etc. We can measure with a suitable instrument the number N_d of drops for each point.

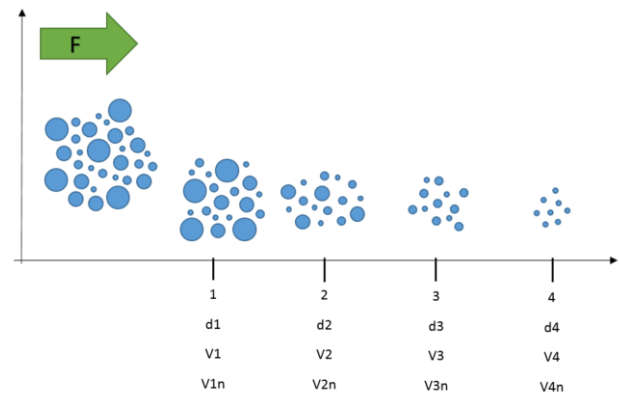


Fig. 1 Gravitational separation of drops in laminar flow.

Fog Detector 6 is a device that we developed and through which we implement our method. It works on the basis of EMEE and is very sensitive to the number and diameter of the drops (Fig. 2).



Fig. 2 Device for measuring the number and diameter of fog drops (Fog Detector 6).

The idea is to compare the signals it measures at the various points with the results of a laser particle analyzer. In this way, we

can calibrate it by the number of drops so that at each point we have a signal proportional to that number. It should be taken into account that in each point there will be an admixture from the number of drops in the following points. To neutralize this additive, we must subtract from the signal at a given point the signal at the next point. Thus, we will obtain an electrical signal that is proportional only to the number of drops that have settled to that point.

For example, through point 1 all the drops from the following points will pass. We will measure a common signal V_{1n} . To obtain a signal V_2 that is proportional only to the number of drops that have settled between points 1 and 2, we must subtract the signal from drops that have passed through point 2 from V_{1n} . In other words, $V_2 = V_{1n} - V_{2n}$. In this way, we obtain information about the number of drops with diameters between d_1 and d_2 . The same is repeated for all subsequent intervals. The diameter distribution will appear simultaneously on the display.

4. Experimental setup

To realize the idea, we performed a series of experiments. We used an automated fog generation system and measured the number and diameter of droplets at various distances from its nozzle, with a laser particle size analyzer. Thus, we established the presence of gravitational separation of the drops after the jet has travelled a certain distance from the nozzle in the direction in which it is fired, i.e. when the flow changes from turbulent to laminar. The laminar flow zone is actually also our working zone where we can evaluate droplet separation. We then selected five specific distances from the nozzle at which we made measurements with a laser particle analyzer to determine the actual parameters of the generated fog and thus to be able to calibrate our device Fog Detector 6.

The block diagram of the experimental setup for carrying out the measurements is given in Fig. 3. From a water source (1) water with a pressure of 6 bar is supplied to a nozzle (4), and the fog generation is carried out on pulses set by a control module (3), which controls a solenoid valve (2). The produced jet passes through several Fog Detector 6 devices, consisting of an emitter (5) and a receiver (6), located along the jet. The measured signals from the electromagnetic echo effect at these several points are passed through a preamplifier (7) and transmitted to a measuring module EMEE Meter 1 developed by us. It forwards the detected values of signal amplitudes to a VLC-1 amplifier (9), after which they reach a processing and visualization module (10).

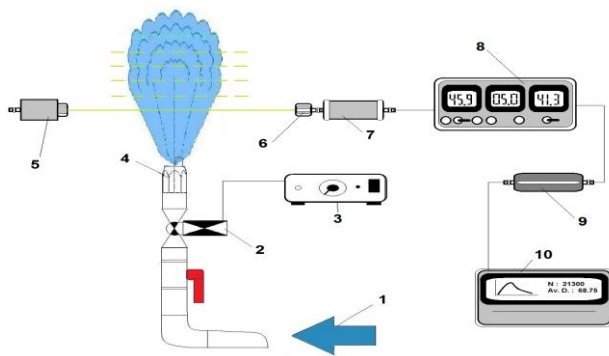


Fig. 3 Block diagram of the fog generation system, measurement and visualization of its parameters: 1. water source (6 bar); 2. electromagnetic valve; 3. device for setting the duration of fog generation; 4. atomizing nozzle; 5. laser module; 6. sensor; 7. preamplifier; 8. measuring module (EMEE Meter 1); 9. amplifier (VLC-1); 10. signal processing and visualization module.

5. Experimental results

We conducted measurements with several nozzles from the company BETE Fog Nozzle, Inc. (<http://www.bete.com>). Here we present the results of the P40 nozzle (with an orifice diameter of

1.07 mm). We experimentally found that the working area for the mist generation system starts at 120 cm from the nozzle, i.e. at this distance the droplet flow becomes laminar. We selected five points at 140, 160, 180, 200, and 220 cm from the nozzle, respectively, and measured the average droplet size with a laser particle analyzer. For each distance, 100 measurements were taken within 100 seconds, which were then averaged. The results of these measurements are given in Fig. 4. The average droplet diameters for these distances are 69.415, 67.283, 61.156, 60.780 and 53.509 μm , respectively.

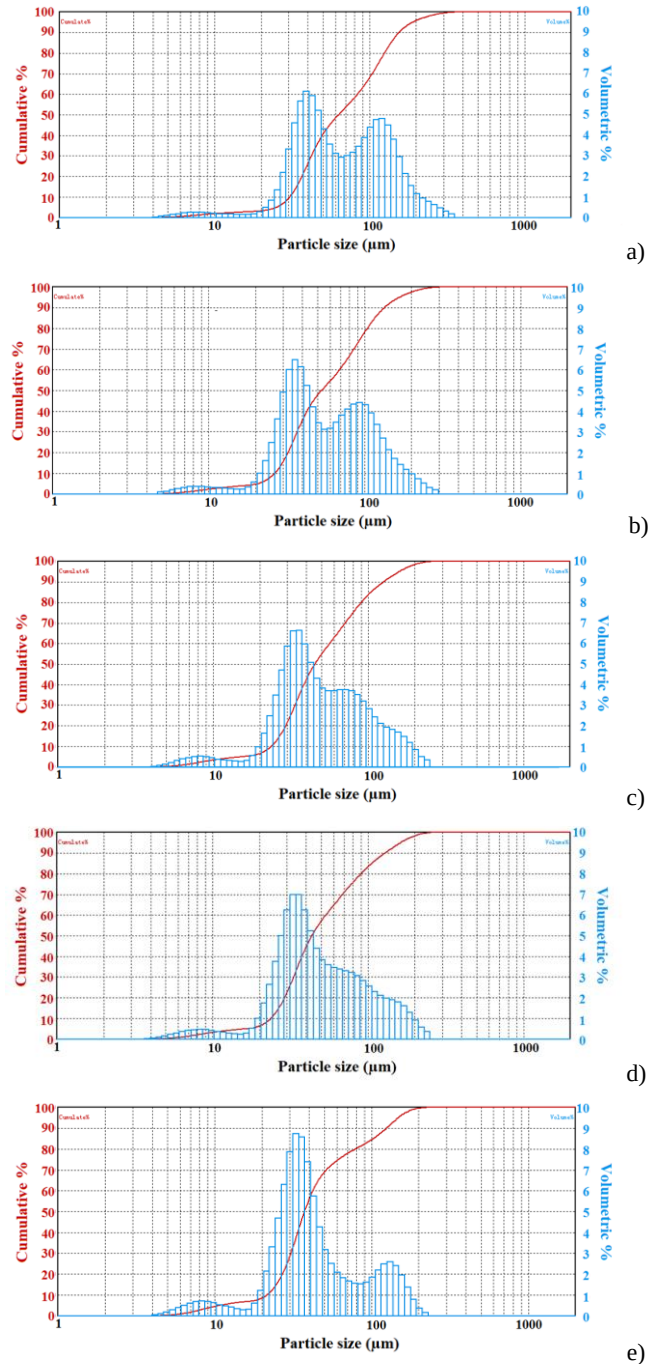


Fig. 4 Droplet diameter distributions produced by nozzle P40 at distances: a) 140 cm; b) 160 cm; c) 180 cm; d) 200 cm; e) 220 cm.

A decrease in mean as well as maximum measured droplet diameter was observed as the distance from the nozzle increased. For the aforementioned distances, it is 354.020, 297.890, 250.660, 229.932 and 193.476 μm , respectively (Fig. 5).

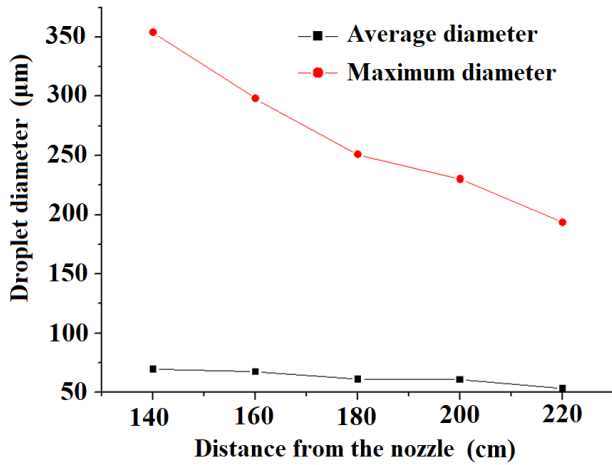


Fig. 5 Average and maximum diameter of fog drops as a function of distance from the nozzle.

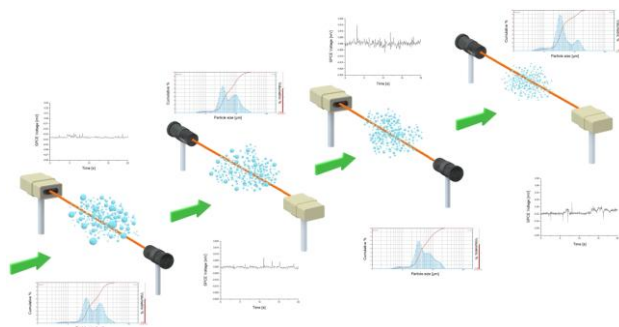


Fig. 6 Visualization of the method for non-contact measurement of fog parameters by matching EMEE signals with laser particle size analyzer results.

6. Conclusion

The results confirm the presence of drop size separation at distances greater than 120 cm from the nozzle. It can be concluded that it is quite possible to calibrate our Fog Detector 6 device in each of the five points using the results of the laser analyzer. In fact, a real implementation of non-contact drop measurement involves several such devices located at each point (Fig. 6). As the fog cloud moves from one point to the next, the drops begin to fall under their own weight. Naturally, at first the largest fall, at the next point the next largest, and thus a division by size is obtained. The second point, for example, will be missing the drops that fell between the first and second points. Accordingly, the signal must change. This change gives us the number of drops of that diameter. The difference in the processed signals between the individual points corresponds to the changes in the size distribution.

The advantages of the method include high accuracy, quick access to results and the possibility of real-time measurements, without the need for complex equipment. Research on this development continues to improve the devices and optimize their operation.

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The Effect of Vanadium, Niobium and Boron on Microstructure, Mechanical and Corrosion Properties of High-Chromium White Cast Irons

Kemal Delijić^{1,*}, Mirjana Filipović²

University of Montenegro, Faculty of Metallurgy and Technology, (MNE)¹

University of Belgrade, Faculty of Technology and Metallurgy, (SRB)²

kemal@ac.me

Abstract: The influence of the vanadium, niobium and boron addition on properties of high-chromium white cast iron alloys for grinding balls is investigated in this paper. These alloying elements were individually added to the high-chromium white cast iron alloys with monitoring of changes in microstructure, corrosion rate, and mechanical properties in the as-cast conditions. The microstructure in all tested alloys consists of primary austenite dendrites and eutectic colonies, which consist of M_7C_3 carbides and austenite. The addition of V, Nb or B affects, to a greater or lesser extent, the size, morphology and volume fraction of both primary austenite dendrites and eutectic colonies. Samples of iron alloyed with vanadium and boron have a much finer structure than unmodified (base) alloy and niobium alloyed iron sample. Vanadium affects the decrease in the volume fraction of the primary austenitic phase, and the increase in the volume fraction of eutectic colonies, and thus the eutectic carbide phase in hypoeutectic alloys of high-chromium iron. The tested alloys have a comparable values of average hardness in the cross section of cast balls, as well as compressive yield strength, noting that the addition of vanadium increases the hardness, while boron addition increases the compressive yield stress. The single addition of all of three tested alloying elements shifts the corrosion potentials (and Tafel curves) of modified high-chromium white irons toward less negative values. The most favorable values of mechanical and corrosion properties were measured for the iron modified with 0.021 % of boron.

Keywords: HIGH-CHROMIUM WHITE CAST IRON, GRINDING BALLS, VANADIUM, NIOBIUM, BORON, CORROSION

1. Introduction

High-chromium white irons represent the third generation of wear-resistant white irons, developed after unalloyed white cast and nickel-alloyed type of irons, with a favorable ratio of abrasion wear and toughness, which makes them very attractive for use in the most demanding conditions of grinding and crushing of various materials [1,2]. This class of alloys have a wide range of applications in mining, metallurgy, cellulose and paper production, construction industry or wherever is a need for grinding huge quantities of material by crushing or milling. The properties of these irons are influenced by the type, hardness, morphology, distribution, volume fraction and orientation of eutectic carbides, as well as the matrix microstructure, which supports the carbide phase-[3].

One of the possibilities of improving the performance of high-chromium white cast irons is alloying with carbide-forming elements, such as vanadium [4, 5, 6], niobium [4, 6, 7, 8], and boron [10, 11, 12]. These alloying elements bind carbon in the form of carbides different from cementite, with higher hardness and a much more favorable morphology, and reduce the carbon content in the matrix enabling the simultaneous improvement of both impact toughness and resistance to abrasion wear [4, 13, 14]. Refining the eutectic carbide structure by creating finer, more globular carbides, is also a possible strategy to improve the toughness of white iron alloys, as well as the wear resistance [15, 16]. The influence of certain alloying elements, which are the subject of the analysis in the paper, can be briefly described as follows. Increasing in carbon and chromium content in white cast iron causes the change of eutectic carbide from M_3C to M_7C_3 [17]. Niobium has a limited solubility in M_7C_3 carbides. The formation of NbC before M_7C_3 carbide [7] causes a decrease in the carbon content of the melt. Since carbon mainly determines the volume fraction of the carbide phase in the structure of high chromium iron, the amount of M_7C_3 carbide will decrease with increasing of niobium content in the alloy. Concentration of vanadium and boron in M_7C_3 carbides increases with the increase of their content in the alloy. Increase in vanadium content in high-chromium iron, affects the changes in volume fraction of eutectic M_7C_3 carbides [5, 6, 18], although the data in the literature are not consistent: according to [6] increasing of vanadium content decreases the amount of eutectic M_7C_3 carbides, but according to others [5, 18], it increases. Boron changes the morphology, size and volume fraction of M_7C_3 carbide [11, 20]. By adding up to 0,15% boron to high-chromium iron, the structure becomes much finer and the volume fraction of the eutectic, or M_7C_3 carbide, increases.

The corrosion behavior of these materials does not depend only on the content of Cr and C individually, but primarily on the ratio of

their content Cr/C, as well as on the ratio of Cr content in carbides, and in the matrix ($Cr_{M_7C_3}/Cr_{matrix}$) [21]. The addition of other alloying elements, such as Si, Mo, Ni, Cu, V, Ti, etc., also affects the corrosion behavior. The microstructure of white cast iron consists of a ductile γ -Fe phase and various carbides (M_7C_3 , $M_{23}C_6$), which provide an extremely high level of hardness. Wear resistance depends on the volume fraction of carbide in the structure, while the Cr content in the Fe-base affects corrosion behavior and corrosion resistance [21]. When the matrix contains a sufficient amount of chromium ($Cr > 12\%$), a very thin layer of passivating oxide nano-film (Cr_2O_3) is formed on the surface, which protects these alloys from corrosion [23]. Increasing the carbon content provides a higher proportion of carbides in the structure, but at the same time worsens the corrosion characteristics of white cast iron [21]. If the Cr/C value decreases, the amount of Cr bound in the carbides is significant, the chromium-depleted zone around the carbide particles expands, due to which the sensitivity to corrosion increases [22]. The improvement of corrosion resistance of this type of alloys can be also achieved when the particles of the secondary phases in the structure are approximately spherical, and when their content/volume fraction in the structure, is optimal [23]. In this way, the formation of a micro galvanic cell becomes difficult, or pitting corrosion is prevented.

The aim of this paper is to present some results and considerations related to the influence of the single addition of vanadium, niobium and boron on microstructure, corrosion and mechanical properties of high-chromium white cast iron alloys for grinding balls.

2. Experimental procedure

The chemical composition of tested alloys is listed in Table 1. The melting of high chromium white irons, individually alloyed with vanadium, niobium and boron, was performed in induction furnace. Grinding balls with 60mm of diameter were cast in water cooled permanent molds. The casting temperature was 1470 °C - 1490 °C and the mold temperature was 130 °C -140 °C. The balls were kept in the mold for 3 minutes, the mold was subsequently opened, cast balls were taken out and further cooled in ambient air. The samples were tested in the as-cast conditions. The microstructure of the samples was investigated by conventional optical microscopy and scanning electron microscopy. Corrosion behavior was evaluated by linear and potentiodynamic polarization electrochemical methods in fresh water, using the potentiostat/galvanostat Princeton Applied Research PAR 273 with the software SoftCorr 352 II (standard saturated calomel electrode; auxiliary graphite electrodes.). Properties of fresh water: pH=7,78; Fe <0,003mg/l; chlorides 6,54 mg/l; nitrates (NO_3^-) <1,00 mg/l;

sulphates (SO_4^-) 3,12 mg/l; potassium (K^+) 0,562 mg/l; magnesium (Mg^{++}) 3,1 mg/l; sodium (Na^+) 0,798 mg/l; calcium (Ca^{++}) 55,86 mg/l; Fe < 0,003 mg/l.

Table 1. Chemical composition of tested alloys

Element, wt%	Base alloy ¹	HCCI balls alloyed with vanadium	HCCI balls alloyed with niobium	HCCI balls alloyed with boron
C	2,91	2,91	2,86	2,64
Si	0,83	0,92	0,95	1,28
Mn	0,79	0,81	0,71	0,80
P	0,029	0,030	0,034	0,047
S	0,016	0,017	0,016	0,013
Cr	17,83	17,95	16,42	14,28
Mo	1,15	1,14	1,13	1,08
Cu	0,84	0,87	0,95	0,92
Ni	0,11	0,10	0,12	0,10
B	<0,002	<0,002	<0,002	0,021
V	0,041	1,23	0,074	0,072
Ti	0,021	0,045	0,068	0,109
Nb		0,011	2,43	0,056
W	<0,001	<0,001	<0,001	<0,001

¹ high chromium cast white iron, chemical composition ASTM A532-IIIE

Mechanical properties were analyzed by: measuring of Rockwell hardness and calculating the average values for the cross-section of the grinding balls; determining the compressive yield stress on cylindrical samples of 7mm of diameter and 14mm of height, using the FPZ-100 universal tensile/compressive testing machine.

In order to compare the properties of novel cast balls, casting and testing of high chromium white iron "base alloy" balls (chemical composition defined by ASTM A532-IIIE) were performed under the same conditions.

4. Results

Microstructures of tested as-cast balls, at the surface and in central zones on the cross-sections, are presented in Fig. 1. The microstructure of the base high chromium white iron balls is also shown with the aim of more clearly observing the changes caused by alloying with different carbide-forming elements, Fig. 1.a. The structure consists of primary austenite dendrites and eutectic colonies, which consist of M_7C_3 carbides and austenite in all tested alloys. The alloying elements, vanadium, niobium and boron affect to a greater or lesser extent the size, morphology and volume fraction of both primary austenite dendrites and eutectic colonies. Niobium affects the smallest influence on the size of the micro-constituents present in the structure, noting that it affects the morphology of the primary austenite dendrites, and thus the morphology of the eutectic colonies, Fig.1.c. Significantly finer structure is noticeable in vanadium alloyed irons if compared to the base alloy and the alloy with niobium. There is a difference in the size of the micro-constituents in the structure from the surface to the center of the balls, but it is much less pronounced in the alloys with vanadium compared to the base alloy, Fig.2. Niobium affects the volume fraction of phases present in the structure, changes the morphology of both primary dendrites and eutectic colonies (Fig. 1.c). The shape of the eutectic colonies is determined mainly by the volume fraction and morphology of the dendrites of the primary austenite. The size of the particles increases from the surface to the central zone of balls, with the largest changes in their size in the region from the surface to a distance of 5 mm from the surface, Fig. 3. The volume fraction of dendrites of primary austenite is higher, while the amount of eutectic, and thus of M_7C_3 carbide, is lower in Nb-alloyed iron if compared to the base alloy. The presence of NbC carbide particles, of different morphologies and sizes, in the microstructure of niobium-alloyed iron can also be indicated (Fig. 3 and Fig. 4). NbC particles are mostly located in the surface zone of austenite dendrites, or precisely at the border of dendrites and eutectic M_7C_3 carbides, and very rarely in the central zone of

dendrites. In certain regions, accumulations of large NbC carbide particles can be observed.

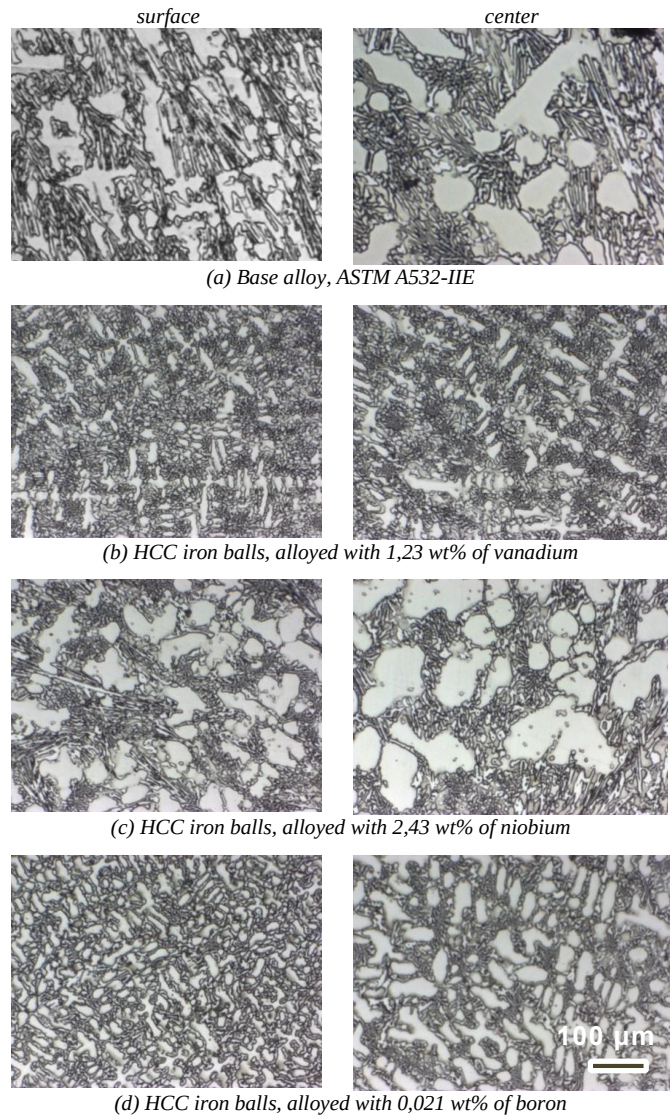


Fig. 1. Optical micrographs of as-cast grinding balls structure (in the surface and in the center of balls): base alloy and high chromium alloys modified by individual addition of vanadium, niobium and boron

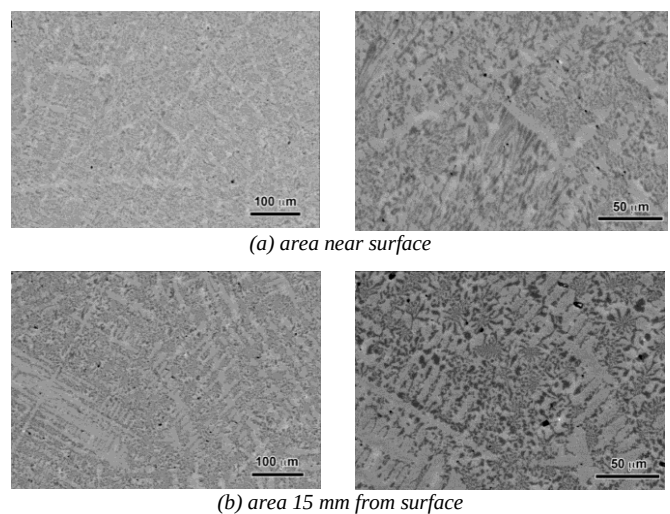


Fig. 2 SEM micrographs of as-cast grinding balls structure, containing 1,23 wt% of vanadium: (a) near surface and (b) central region 5 i 15mm

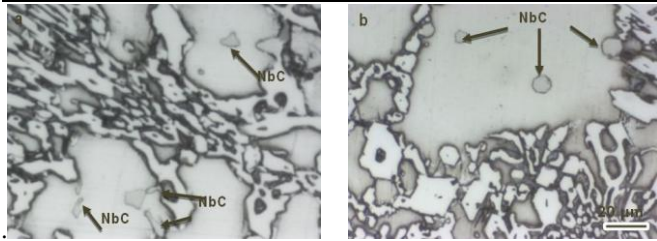


Fig. 3. Optical micrographs of as-cast grinding balls structure, containing 2.43 wt% of niobium: (a) near surface and (b) central region

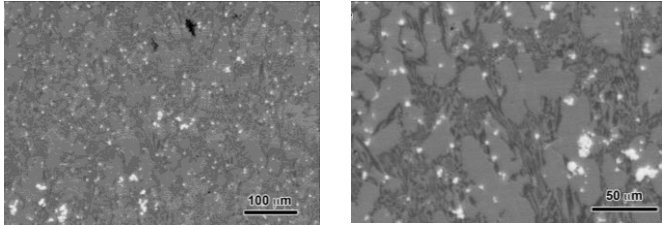


Fig. 4. SEM micrographs of the microstructure of iron with the addition of 2.43 % Nb at a distance of 5 mm from the surface of the ball.

Irons alloyed with boron have a significantly finer structure, if compared to the base alloy and iron alloyed with niobium, Fig. 1 (d). The size of micro-constituents is comparable to the size of those present in the irons alloyed with 1.23 % of vanadium. The size of the particles increases from the surface to the central zone of the balls, with the largest changes in its size being observed in the zone 15 mm from the surface. The morphology of dendrites in boron alloyed irons generally does not change on the observed cross-section from the edge to the center of the balls, in contrast to iron alloyed with vanadium.

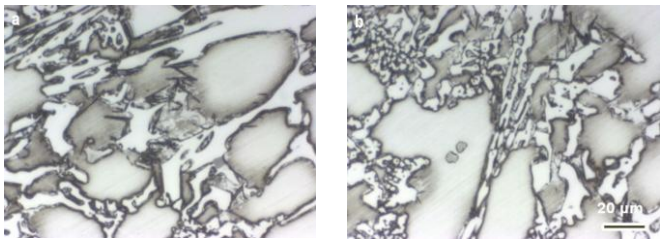


Fig. 5. Optical micrographs of as-cast grinding balls structure, containing 0.021 wt% of boron: (a) near surface and (b) central region

Boron affects not only the way of crystallization of high chromium irons, but also the transformation of austenite during cooling after solidification. The degree of transformation of austenite into martensite, both eutectic and primary, is higher than in irons modified with the addition of niobium, and on the other hand, it is somewhat lower compared to irons with the addition of 1.23 wt%V.

Mechanical properties

The results of hardness tests and examination of compressive yield stress are presented in Fig. 5. and 6. The hardness of grinding balls was determined by the Rockwell hardness testing method, and the calculated average measured values for the cross-section of the balls are given in Fig. 5. All tested alloys have a relatively comparable values of the average hardness in the cross section of cast balls, noting that high chromium iron modified with vanadium

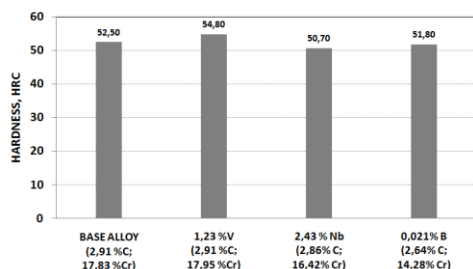


Fig. 5. Rockwell hardness of tested high chromium white iron balls

has the highest hardness, which is a consequence of the largest volume fraction of eutectic M_7C_3 carbides and a relatively high degree of martensitic transformation in the structure, Fig. 2.

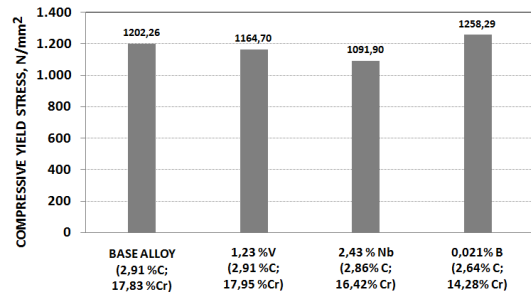


Fig. 6. Compressive yield stress of tested alloys in as-cast condition

The highest compression yield stress is measured on samples of high-chromium iron alloyed with the 0.021 wt% of boron, noting that the measurements were made on cylindrical samples taken from the central zone of the casting, Fig. 6.

Corrosion properties

The corrosion properties were evaluated by electrochemical methods, followed by microstructure analysis, in order to detect the relationship between the different alloying elements content and corrosion behavior of grinding balls. Two techniques have been used for testing corrosion properties of cast balls: linear polarization and Tafel extrapolation technique (potentiodynamic polarization). Corrosion parameters of as-cast balls of base alloy and irons containing vanadium, niobium and boron, obtained by linear polarization measurements are illustrated in Fig. 7.

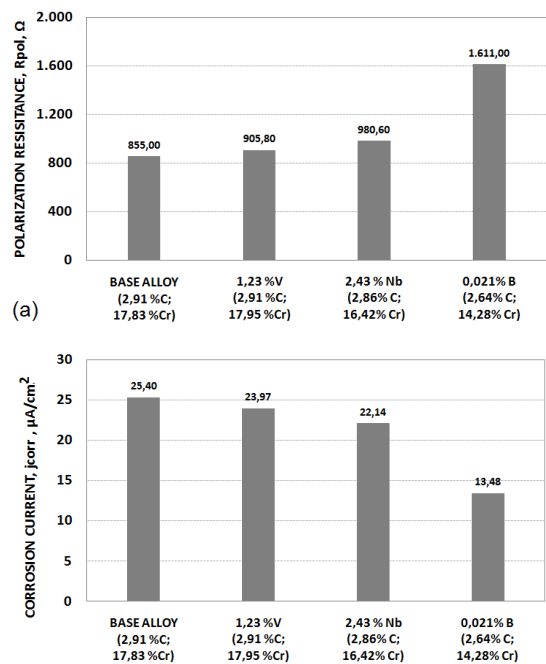


Fig. 7. Polarization resistance (a) and corrosion current (b) obtained from linear polarization measurements; corrosion ambience fresh water

From the figures it can be seen that individual addition of all of three used alloying elements cause an increase in polarization resistance and a decrease in corrosion current under the given test conditions. Linear polarization measurements have shown that boron containing high chromium white iron grinding balls have the highest R_{pol} and the lowest j_{corr} compared to the base alloy and alloys containing the vanadium and niobium.

Tafel curves of high chromium white iron cast grinding balls, containing different alloying elements are given in Fig. 8. The single addition of all of three used alloying elements shifts the Tafel curves of modified high-chromium white irons toward less negative values. Corrosion potentials, $E_{(j=0)}$, of alloyed irons, if compared to

the non-alloyed ones, are less negative in any analyzed case. The value of $E_{(j=0)}$ of boron alloyed iron is less negative by about 80 mV if compared to the base alloy, Fig.8 and Fig. 9.a. Under the potentiodynamic polarization conditions, as well as in linear polarization conditions, the lowest corrosion current density was measured for the boron-modified alloy, Fig. 9.b.

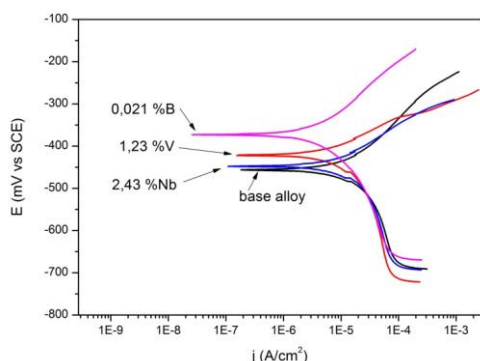


Fig.8. Tafel curves for high chromium white iron cast grinding balls, containing different alloying elements; corrosion ambience fresh water

The shift of the Tafel curves towards less negative values of the potential due to alloying with V, Nb and B, is also followed by a decrease in the values of the corrosion current densities, compared to the basic unmodified base alloy; Fig 9.b.

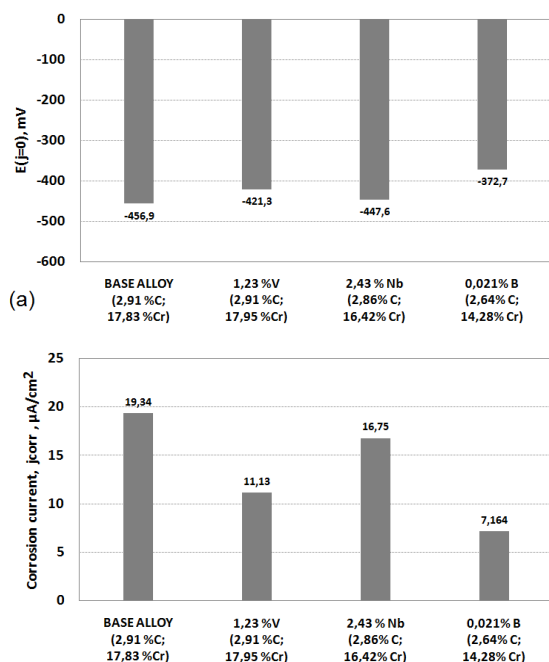


Fig.9. $E(j=0)$ (a) and j_{corr} (b) obtained from potentiodynamic polarization measurements; corrosion ambience fresh water

The results of both techniques indicate the less active corrosion of boron modified high chromium white iron grinding balls in tested conditions if compared to base alloy and niobium and vanadium alloyed irons.

3. Conclusion

The alloying elements, vanadium, niobium and boron affect to a greater or lesser extent the size, morphology and volume fraction of both primary austenite dendrites and eutectic colonies in high chromium white irons. The addition of vanadium produces significantly finer microstructure compared to base and niobium alloyed irons. The addition of boron also produces finer microstructure, noting that the size of micro-constituents is comparable to the size of the constituents present in the vanadium alloyed irons. Iron modified with vanadium has the highest hardness, as a consequence of the largest volume fraction of eutectic M_7C_3 carbides and a relatively high degree of martensitic

transformation. The highest compression yield stress is measured on samples of boron alloyed iron. Boron containing high chromium white iron have the highest R_{pol} and the lowest j_{corr} , compared to the base and vanadium/niobium containing irons. The single addition of all of three used alloying elements shifts the Tafel curves toward less negative values. The lowest corrosion current densities were measured for the boron-modified alloy. Based on the obtained results it can be concluded that the most favorable combination of mechanical and corrosion properties were obtained for the high chromium white iron modified with 0,021 % of boron.

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Nanodisperse modifiers produced by the shs method for composite materials of automotive equipment

Auchynnikau Y.¹, Vozniakovskii A.², Vozniakovskii A.³, Semenov A.¹

Faculty of Innovative Mechanic Engineering ¹ – Yanka Kupala State University of Grodno, Belarus

Sector of Polymer Nanostructured Materials, Institute of Synthetic Rubber, Saint-Petersburg, Russian Federation²

Laboratory "Physics for Cluster Structures", Ioffe Institute, Saint-Petersburg, Russian Federation³

Abstract: The object of the study was carbon particles obtained by the method of self-propagating high-temperature synthesis. The purpose of the work is the development of compositions and technologies for obtaining competitive composite materials modified with low-dimensional carbon modifiers based on vegetable raw materials.

KEYWORDS: CARBON, STRUCTURE, PROPERTIES, COMPOSITES, SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS.

1. Introduction

According to the literature data, the formation of nanodispersed particles by the method of self-propagating high-temperature synthesis makes it possible to obtain low-sized particles with properties that differ from those of bulk carbon materials. The resulting nanosized particles have a high adsorption activity, large specific surface area. The studies performed have shown that, depending on the technology for the formation of these particles in the reactor, it is possible to control the morphology and lateral sizes of the particles, which in the future will make it possible to purposefully change the activity of these particles.

The activity of nanosized particles obtained by self-propagating high-temperature synthesis is due to the imperfection of the formed nanocrystals.

So, for example, if we consider a zero-dimensional, point defect located in a crystal at a distance of no more than 5–7 atomic layers, then an area with mechanical stresses appears on the surface due to violations of atomic mutual configurations. In connection with this, a region with a changed potential appears on the crystal surface. The appearance of these surface defects leads to the appearance of surface active centers (SACs). The interaction of PACs with the molecules of the substance adjacent to them are electromagnetic in nature. The presence of an electric charge is not a prerequisite for the appearance of surface active centers.

At present, one of the promising classes of modifiers for polymeric materials is carbon nanomaterials (CNMs). This classification includes the following substances: detonation nanodiamond, graphene, graphene oxide, graphene nanoplates, single-walled carbon nanotubes, multi-walled carbon nanotubes, fullerenes [1] - [4] of unique properties. In particular, detonation nanodiamonds have thermal conductivity and hardness close to single-crystal diamond. Single-walled carbon nanotubes and multi-walled carbon nanotubes have high physical and mechanical characteristics. The values of the modulus of elasticity for these substances can reach 1.7 - 3.8 TPa, depending on the type of material, and the values of thermal conductivity along the axis of the tube are estimated

~ 3000 W/m K. Graphene has similar physical and mechanical characteristics: thermal conductivity - 5000 W/m K, Young's modulus - 1 TPa, specific surface area - 2630 m²/g.

Detonation diamonds were first synthesized in the USA in 1961. In the USSR, this class of materials was obtained at UNITF in 1962. Detonation diamond particles are geometric objects with a lateral size of about 10 nm. The production of this class of substances can be carried out both by blasting technology with a negative oxygen balance, and by mechanical grinding of natural and synthetic diamonds.

Fullerenes were discovered in 1985, but the theoretical justification for the existence of these particles was given back in the 70s of the last century. This class of materials represents molecules of composition C_n, where n>20, which consist of closed convex polyhedra with pentagonal and hexagonal faces. Fullerenes are synthesized by the electric arc method, which is characterized by a low yield of the product required for industrial use, which determines a rather high cost per gram of material.

In 1991, single-walled carbon nanotubes were synthesized. This allotropic form of carbon is hollow rods consisting of hexagons, at

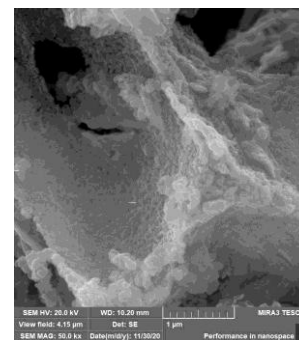
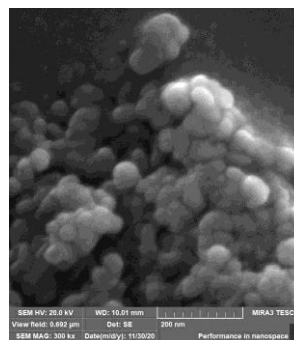
the tops of which there are carbon atoms and up to several tens of nanometers in diameter. The main methods for obtaining this class of materials are laser dispersion of a graphite target, the effect of electric spark discharges on a carbon material, and the formation of nanotubes in vacuum using plasma-chemical methods. However, the above methods are inefficient. Therefore, to obtain nanotubes on an industrial scale, the method of chemical deposition of carbon tubular particles from the gas phase is used [1] – [7]. Multi-walled carbon nanotubes are obtained by a similar method.

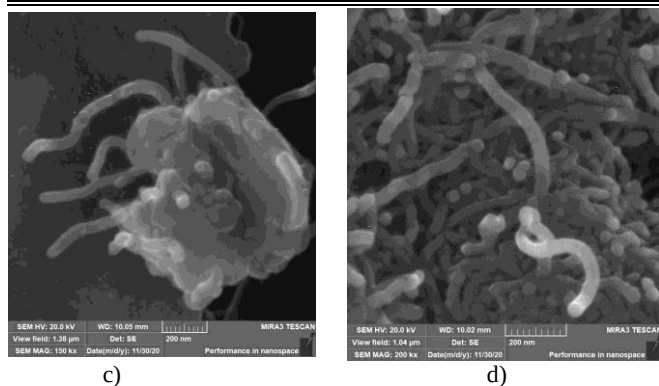
Graphene was obtained in 2004 by exfoliation and subsequent deposition on the surface of silicon oxide. Graphene is a flat layer of sp²-hybrid carbon atoms one atom thick, forming a hexagonal lattice. Graphene nanostructures are understood as materials consisting of 2 – 100 graphene layers. For the synthesis of graphene nanostructures, the following technological approaches are used: "bottom-up", "top-down" [1-7].

2.1. Preconditions and means for resolving the problem

In the course of the studies, the morphology of carbon nanoparticles obtained using the technology of self-propagating high-temperature synthesis from various raw materials was evaluated. It has been established that the technology of obtaining and the prehistory of the sample has a significant impact on the morphology of the formed carbon nanoparticles.

In most cases, nanodispersed carbon particles obtained by the SHS method, due to their high activity, form agglomerates that are quite stable. These formations are in the micron range of dimensions, which is confirmed by the data of scanning electron microscopy. Thus, these objects can be studied by optical microscopy. Figures 1 - 3 show agglomerates of carbon particles produced by the SHS method from various materials with different content of combustible matter.





a – ultrafine diamond-containing graphite, b – graphene nanoplates, c – nanodispersed carbon particles obtained from starch, d – multilayer carbon nanotubes

Figure 1 - Morphology of nanodispersed carbon particles obtained by the method of self-propagating high-temperature synthesis

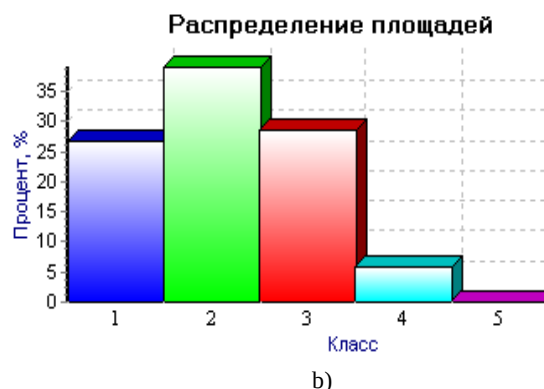
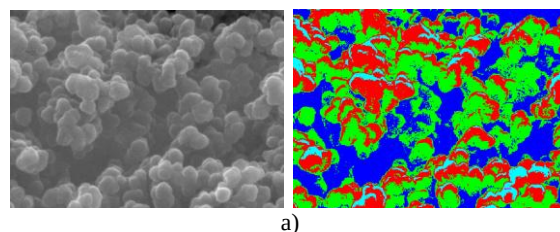
Carbon nanodispersed particles were obtained by the method of self-propagating high-temperature synthesis (SHS). This technology for obtaining nanocarbon particles is exothermic due to the occurrence of chemical processes such as combustion. The combustion process is autowave, flowing through a mixture of reagents with the formation of solid carbon end products of various dispersion. An exothermic reaction occurs in the process of supertemperature self-propagating synthesis, and this process is localized in a narrow range. The heating temperature of the initial material for the implementation of structural transformations in the initial mixture can reach 2000–3000 °C, depending on the initial raw material and combustible materials that make up the mixture for SHS synthesis. As a result, the high-temperature front of SHS synthesis passes from layer to layer of the initial charge. This is an advantage of the technology of self-propagating high-temperature synthesis, which consists in using the heat of chemical reactions released in the heating zone of a substance, instead of volumetric heating of the entire material from an external source. This technological feature of the SHS method makes it possible to successfully compete with the widespread energy-consuming technologies for obtaining nanosized carbon particles.

The studied nanodispersed carbon particles were obtained on the basis of the principle of nanoparticle formation known as "bottom-up". As a result of applying this approach, the structure of the organic material changes with the formation of various carbon structures: graphite, diamond, fullerene, graphene, graphane, nanotubes, etc. The existing alternative technology for creating carbon nanoparticles is the "top-down" technology, the advantage of which is the low cost of the process, relative technological simplicity, and the ability to obtain large volumes of synthesized material.

The application of the principles of formation of carbon nanodispersed structures "bottom-up" makes it possible to obtain carbon structures of various dispersity. Usually, dispersion is understood as the reciprocal of the average geometric dimensions of the object under study. According to one of the classifications of the geometric dimensions of objects, they can be divided into molecular, highly dispersed and coarsely dispersed. Based on this classification, it can be seen that these systems will differ significantly in their physical, mechanical, and chemical characteristics. Thus, the study of the dispersity distribution of formed nanodispersed carbon particles by the SHS synthesis method will make it possible to predict the properties of both the obtained nanocarbon particles themselves and composite materials using this type of substances as a modifier.

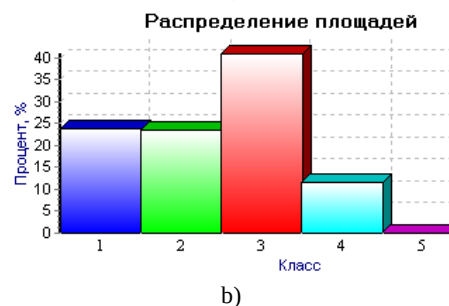
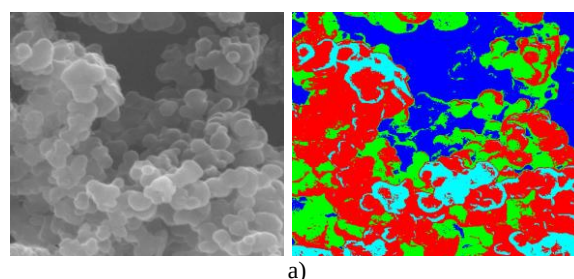
As objects of research, the dispersion composition of the following carbon particles was studied: carbon agglomerates obtained by the method of self-propagating high-temperature

synthesis from cellulose with a percentage of the starting material to a combustible substance of 30:70% wt.; carbon agglomerates obtained by the method of self-propagating high-temperature synthesis from starch with a percentage of the starting material to a combustible substance of 30:70% wt. The research results are presented in figures 1 - 3.



a – SEM image of the test substance, including after the analysis; b - percentage distribution of carbon particles by size in the test sample

Figure 2 - The results of the dispersion analysis of carbon particles obtained by the method of self-propagating high-temperature synthesis from cellulose with a percentage of the starting material to the combustible substance of 30:70% wt.



a – SEM image of the test substance, including after the analysis; b - percentage distribution of carbon particles by size in the test sample

Figure 3 - The results of the dispersion analysis of carbon particles obtained by the method of self-propagating high-temperature synthesis from starch with a percentage of the starting material to the combustible substance of 30:70% wt.

To carry out dispersion analysis of nanodispersed carbon particles obtained by SHS synthesis, we used the method of scanning electron microscopy, which makes it possible to obtain images of particles with a resolution in the nanometer region. For image processing, a specialized program "AutoScan" produced by CJSC "Spectroscopic Systems" was used. According to the size of carbon nanoparticles, they were divided into 5 classes: class 1 - from 300 nm to 400 nm, class 2 - from 200 nm to 300 nm, class 3 - from 100 nm to 200 nm, class 4 - from 50 nm to 100 nm, Class 5 - less than 50 nm.

In the course of the conducted studies, it was found that as a result of the use of self-propagating high-temperature synthesis for the processing of organic raw materials, particles of the nanometer range with different dispersion distributions are formed. The dispersity of the studied samples depends on the organic raw materials used.

It is shown that, depending on the methodology for the formation of carbon particles, various structures are formed with characteristic properties inherent only to them. Thus, the formation of diamond-like structures, fullerenes, fullerites, carbon nanotubes, rods, disks, graphenes, etc. is possible. These materials differ significantly in properties from each other. The disadvantage of the considered technologies is, in most cases, the high cost of the obtained particles, as well as the low yield of carbon nanocluster structures. In some cases, environmentally harmful technologies are used. In this connection, the use of the technology of self-propagating high-temperature synthesis will make it possible to obtain carbon nanoparticles of various nomenclature in large quantities. The use of the SHS method will make it possible to obtain nanosized cluster structures not only of carbon, but also of materials consisting of other chemical elements of the periodic system of D.I. Mendeleev. The main advantage of the SHS method is its sufficient simplicity and environmental safety. Using the method of self-propagating high-temperature synthesis, it is possible to obtain low-sized particles with properties different from those of bulk carbon materials. The resulting nanosized particles have a high adsorption activity, large specific surface area. The studies performed have shown that, depending on the technology for the formation of these particles in the reactor, it is possible to control the morphology and lateral sizes of the particles, which in the future will make it possible to purposefully change the activity of these particles. The activity of nanosized particles obtained by self-propagating high-temperature synthesis is due to the imperfection of the formed nanocrystals. So, for example, if we consider a zero-dimensional, point defect located in a crystal at a distance of no more than 5-7 atomic layers, then a section with mechanical stresses appears on the surface due to violations of atomic mutual configurations. In connection with this, a region with a changed potential appears on the surface of the crystal. The appearance of these surface defects leads to the appearance of surface active centers (SACs). The interaction of PACs with molecules and substances adjacent to them are electromagnetic in nature. It is shown that in the process of self-propagating high-

temperature synthesis, the formation of combined particles of the DND-CNT, CNT-CND (carbon nanodiscs) type occurs; in some cases, the formation of structures such as graphene and graphene nanoplates, lonsdaleite is possible.

In the course of the conducted studies, it was found that as a result of the use of self-propagating high-temperature synthesis for the processing of organic raw materials, particles of the nanometer range with different dispersion distributions are formed. The dispersity of the studied samples depends on the organic raw materials used.

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New regulations on the formaldehyde emission from wood-based panels

Nadir Ayırlım

¹Department of Wood Mechanics and Technology, Forestry Faculty, Istanbul University-Cerrahpasa, Bahçekoy, Sariyer, 34473, Istanbul, Turkey
nadiray@istanbul.edu.tr

Abstract: Formaldehyde is considered a health hazard, hence the wood-based panels must be within the limits imposed by the strictest regulations regarding the formaldehyde release. New national and international regulations of formaldehyde emission from wood-based panels widely used in furniture industry were investigated in this study. The results of the study can be useful for the wood-based panel factories to follow the standards and regulations in terms of formaldehyde emission.

KEYWORDS: FORMALDEHYDE EMISSION, WOOD-BASED PANEL, ADHESIVE, FURNITURE, PARTICLEBOARD, MDF

1. Introduction

Wood-based panel and furniture industries have already reduced formaldehyde emission of raw panels by more than 80% over the past twenty years to minimize indoor air contaminants [1]. Wood based panels such as medium-density fiberboard, particleboard (MDF) and particleboard are increasingly being specified for residential and office furniture applications, especially the use of particleboard in inexpensive bookshelves and similar items. MDF uses more adhesive than particleboard, which causes higher initial formaldehyde emission of MDF than particleboard. Li [2] determined the amount of volatile organic compound (VOC) emission and its composition of six kinds of commercial wood-based panels in a period of time for 28 days. It was found that the formaldehyde emission level from high to low was high-density fiberboard (HDF), MDF, plywood, veneer-faced MDF, and oriented strand board (OSB).

Most of the adhesives currently used in the particleboard industry are formaldehyde-based adhesives (UF, MUF), which have a molar ratio of formaldehyde to urea (F:U) between 1.00 and 1.10. The majority of thermosetting resins used in the wood-based panel industry are based on the formaldehyde-based resins. Among them, the UF resin is the most used resin. Due to its significant advantages such as cheaper, colorless, easy-supply, shorter hot pressing time and temperature than others, good mechanical properties of particleboard in dry conditions. The disadvantages of the UF resin are higher formaldehyde emission from other resins and lower water and moisture resistance. Off-gassing of formaldehyde from wood-based panels can be one of the main contributors to the elevated formaldehyde levels and exposure in the homes. Sensitive people against the formaldehyde start to experience irritation at 0.6 mg/m^3 and most of us will be irritated at 1.2 mg/m^3 . This range of 0.6 to 1.2 mg/m^3 is the official IARC (International Agency for Research on Cancer) threshold for eye, nose and throat irritation [3]. A correlation was determined between the formaldehyde emission of the resin and the formaldehyde emission factor of the wood-based panel. That is, the higher the content of formaldehyde in the adhesive, the higher the level of formaldehyde emission from wood-based panel, and there is a good linear relationship between them [4].

Urea-formaldehyde is classified according to its formaldehyde emission from the wood-based panels (from the lowest to highest level):

1. Super E0
2. E0
3. E1
4. E2
5. E3

For indoor and furniture applications, a lower formaldehyde content is required, if classified under the E1 emission class. Formaldehyde emission classes in finished panels, defined in Annex B of EN 13986:2014+A1:2015 standard are as follows:

- Class E1: $\leq 8 \text{ mg/100g}$ dry board according to EN 120 or $< 0.124 \text{ mg/m}^3$ according to EN 717-1;

- Class E2: > 8 to $< 30 \text{ mg/100g}$ dry board according to EN 120 or > 0.124 to $< 0.3 \text{ mg/m}^3$ according to EN 717-1.

Formaldehyde emission values (perforator value) of various materials (MDF, particleboard, blockboard, laminate flooring, and parquet) characterized by the perforator extraction method of the Chinese national standard GB 18580 is given in Figure 1.

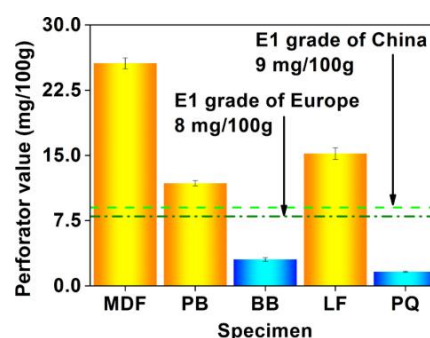


Figure 1. Formaldehyde emission values (perforator value) of various [5].

According to the International Composite Board Emission Standards (ICBES), there are three European formaldehyde classes, which are E0, E1 and E2, respectively. This classification is based on the measurement of formaldehyde emission levels from the wood-based panels. For example, E0 is classified as having less than 3 milligrams of formaldehyde out of every 100 grams of the glue used in particleboard and plywood fabrication. E1 and E2, conversely, are classified as having 9 and 30 milligrams of formaldehyde per 100 grams of the panel, respectively. All around the world variable certification and labeling schemes are there for such products that can be explicit to formaldehyde release, like that of Californian Air Resources Board (CARB). In addition, the production of wood-based panels is increasingly influenced by product emission quality standards applied outside Europe, most importantly CARB standards, originating from Californian legislation. The emission limit values in the wood-based panels used in furniture applications are at levels much lower than the corresponding lowest emitting standard in the EN standards. Formaldehyde emission classes defined by ATCM (Airborne Toxic Control Measure) 93120:

- CARB phase 2 standard for MDF: 0.11 ppm;
- CARB phase 2 standard for particleboard: 0.09 ppm.

2. Formaldehyde emission methods and regulations

There are different standardized methods used in the determination of formaldehyde emission from the wood-based panels such as chamber, gas analysis, perforator, desiccator, and flask. These methods can be classified as “measurable emission” (really emitted amount of formaldehyde under the test conditions) and the “emittable potential” of formaldehyde in the panel (maximum emittable formaldehyde under conditioning at forceful conditions) [6]. Each method measures the formaldehyde released

from wood panels (covered and uncovered) and frequently produces results in different and non-interchangeable units. Standard methods and differences between general conditions used for formaldehyde determination from the wood-based panels are presented in Table 1.

Table 1. Standard methods and differences between general conditions used for formaldehyde determination.

Test method/Standard	Equipment characteristics	Sample dimensions/total surface area	Test conditions	Sample conditioning	E1 class limit
Chamber/ EN 717-1	0.25, 1, 40 (12-52)m ³	Loading ratio: 1m ³ /m ³ Edge sealing	Temperature: 23±0.5°C RH: 45±3% Air velocity: 0.1-0.3m/s Time: 1-4 weeks	No (0.225L) T: 20 °C, RH: 65%	≤0.124mg /m ³ , or 0.1ppm
Gas analysis/ EN 717-2	4L cylindrical chamber	400x50mm Edge sealing	Temperature: 60±0.5°C RH: ≤3% Air velocity: 1L/min Time: 4 hours	Varied T: 20 °C, RH: 65%	≤3.5mg/ m ³ h
Perforator/ EN 120	Extractor apparatus	25x25mm (110g) No edge sealing	Extraction with 600ml toluene at 110°C Time: 3h	T: 23°C RH: 45%	≤ 8 mg /100 g o.d. board
Flask/ EN 717-3	500 ml flask	25x25mm (20g) No edge sealing	Temperature: (40 ± 1) °C Time: 3 hours	No	No official limit are stated
Desiccator / JIS A1460	40L - 240 mm nominal dimension; 120mm outside diameter crystallizing dish/ 60-65mm depth	150x50mm±1mm close to 1800 cm ² No edge sealing	Temperature: 20°C±0.5°C Time: 24h±5min.	7-10 days 65%RH/20°C	F**~E1- ≤1.5mg/L F*** ≤0.3mg/L (SE0)

The formaldehyde emission shows a big challenge for wood-based panel industry because of new regulations concerning the limits of formaldehyde release. Emission databases reveal the interest of consumers for low emitting products in the future. These will lead to an increased requirement for the testing of products to determine the level of formaldehyde emission. To measure the levels of FE, many different methods have been used and the most reliable is the chamber method.

A new class (SE0 and EO) of low formaldehyde emitting panels was established by Japanese standards and European Panel Federation (EPF) launch its own formaldehyde standards that corresponds to a perforator value below 4 mg/100 g oven dry board for particleboard 5 mg/100 g oven dry board for MDF, which is half of the actually limit stated in the EN standard. These new trends force the wood panels' manufacturers and the glue producers to look for alternatives for formaldehyde free wood panels.



Fig. 2. Typical formaldehyde chamber based on EN 717-1 standard (Guangdong grande automatic test equipment limited, China).

Formaldehyde scavengers, often called formaldehyde catchers, are chemical compounds added to the glue mix in order to decrease the formaldehyde emission from the finished wood panels. They are widely used today in the European particleboard and MDF industry. Mostly, aqueous solutions of urea (40% or 45% solids content) are applied. Furthermore, some scavengers such as sodium metabisulfite (Na₂S₂O₅), ammonium bisulfite ((NH₄)HSO₃), or ammonium phosphates, are also applicable in the European panel industry [7]. Formaldehyde scavengers are also added directly on the wood chips ahead of gluing. In some particleboard manufacturers, urea is added as a solid material ahead of blending

to keep moisture content of chips as low as possible. They are used up to a maximum 10-15% on the liquid resin, achieving thus reduction in the formaldehyde emission up to 50% [8]. Experience in Europe has shown that instead of using a very low F:U ratio adhesive, a plant can achieve better results by using a system of an equivalent F:U ratio, which is a combination of a higher F:U ratio UF, and a formaldehyde scavenger. Further developments to address these problems included the addition of a small quantity of melamine (usually 1-4%). Although the addition of melamine increases the production cost, it results in quite successful. Another approach to overcome the negative side effects of the low-emission UF adhesives is the addition of small amounts of PMDI (polymeric diphenylmethane diisocyanate) in the UF binder, in the core layer of particleboards [9].

Table 2. Standards for determining formaldehyde emission from wood-based panels in China, USA, Europe, and Japan.

Standard	Limit value	Grade	Testing method	Application scope
EN13986:2005	≤3.5 mg/(m ² ·h)	E ₁	Gas analysis	Plywood
	≤8 mg/(m ² ·h)	E ₂		
	≤8 mg/100 g	E ₁	Perforation	MDF PB
	≤30 mg/100 g	E ₂		
Formaldehyde Emission Standards for Composite Wood Act (S.1660, H.R.4805)	≤0.05 ppm		Chamber	Plywood PB MDF ≤8 mm MDF
	≤0.09 ppm			
	≤0.11 ppm			
	≤0.13 ppm			
JIS A 1460:2001	≤0.3/0.4 mg/L	F****	Desiccator	Plywood PB MDF PB
	≤0.5/0.7 mg/L	F***		
	≤1.5/2.1 mg/L	F**		
GB/T9846.3-2004	≤0.5 mg/L	E ₀	Desiccator	Plywood
GB18580-2001	≤1.5 mg/L	E ₁	Desiccator	Plywood
	≤5.0 mg/L	E ₂		
	≤9 mg/100 g	E ₁	Perforation	MDF PB
	≤30 mg/100 g	E ₂		

Some regulations in Europe is given in Table 3. As the French labeling system Decree 2011-321 used as construction material. volatile organic compound of many materials used keeps its emissions at a certain standard.

Table 3. VOC regulations used in Europe

EU	Construction Product Regulation (CPR)	CEN/TS 16516:2013 ISO 16000-9
FR	Decree 2011-321 French labelling	ISO 16000-9 ISO 16000-3, 6
DE	Health-related Evaluation of Emissions of Volatile Organic Compounds (VOC, VOC and SVOC) from Building Products	AgBB ISO 16000-9
BE	Royal Decree establishing the threshold levels of emissions to the indoor building products for specific intended use	CEN/TS 16516:2013 ISO 16000-9

3. Formaldehyde scavengers

Main parameters affecting formaldehyde emission from wood-based panels produced using UF resin are as follows:

1. Tree species and wood acidity
2. F/U molar ratio of UF resin
3. The amount of resin used
4. Density and thickness of of fiberboard
5. Hardener type and content
6. Free-formaldehyde content in the UF resin
7. Moisture content of mat
8. Moisture content of finished panel
9. Hot pressing parameters (temperature, time, and pressure)
10. Environmental conditions (humidity and temperature) for finished of fiberboard
11. Overlaying of fiberboard

Formaldehyde scavengers, capable of capturing formaldehyde either physically or chemically and forming stable products, are added to UF resins or to wood particles before pressing. These additives should provide long-term FE reduction, in principle along the panel's service life. Examples used in industry include addition of urea in aqueous solution or powder form, organic amines, scavenger resins such as UF resins with F/U well below 1.0), sulfites, and functionalized paraffin waxes. In the last decades, F/U values in resins for WBP production have decreased from about 1.6 to a range between 0.9 and 1.1. In addition to the F/U ratio, the synthesis process has a relevant role in the final resin properties, including formaldehyde emissions. One strategy to counteract the negative effects of decreasing F/U ratio is resin modification with co-monomers, like melamine or phenol [10].

Industrial use of wood adhesives obtainable from natural resources (also called bioadhesives or bioresins) has been researched since 1970's, but industrial implementation is still restricted due to the production costs, limited availability and consistency of raw materials, and land use issues. Some significant advantages of bio-based adhesives are lower toxicity, renewability, sustainability, and biodegradability. Three materials, tannins, lignins, and vegetable proteins, have found commercial success in the industrial applications.

4. Conclusions

The legal regulations on the formaldehyde emission from wood-based panels will help to increase awareness for the consumers and panel manufacturers. Although the legal regulations can be different in different regions on the world, recently most of them have been updated. Especially, furniture industry is strictly affected by the formaldehyde emission issue due to panel-type furniture has been widely used in the market. It is important for customers to know the meaning of the formaldehyde emission class label from panel type furniture.

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