

YEAR XII **Issue 10** / 2018 **ISSN PRINT 1313-0226**
ISSN WEB 1314-507X

International journal
for science, technics and
innovations for the industry



MACHINES
TECHNOLOGIES
MATERIALS



Published by
Scientific technical
Union of Mechanical Engineering



MACHINES. TECHNOLOGIES. MATERIALS

INTERNATIONAL SCIENTIFIC JOURNAL

PUBLISHER

SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING “INDUSTRY 4.0”

108, Rakovski Str., 1000 Sofia, Bulgaria

tel. (+359 2) 987 72 90,

tel./fax (+359 2) 986 22 40,

office@stumejournals.com

www.stumejournals.com

ISSN PRINT 1313-0226, ISSN WEB 1314-507X, YEAR XII, ISSUE 10 / 2018

EDITOR-IN-CHIEF

Prof. D.Sc. DHC Georgi Popov,

President of Bulgarian Scientific and Technical Union of Mechanical Engineering

EDITORIAL BOARD

MEMBERS

SCIENTIFIC COMPETENCE

Prof. Dimitar Damyanov	Automatisation of production
Prof. Dimitar Karaivanov	Mechanics of machines
Prof. Dimitar Stavrev	Technologies and materials
Prof. Dimitar Yonchev	National and industrial security
Prof. Galina Nikolcheva	Machines tools and technologies
Prof. Hristo Shehtov	Automatisation of production
Prof. Idilija Bachkova	Automatisation of production
Prof. Ivan Kralov	Mechanics of machines
Prof. Ivan Parshorov	Technologies and materials
Prof. Ivan Yanchev	Machines and technologies
Prof. Ivo Malakov	Automatisation of production
Prof. Kiril Angelov	Industrial Management
Prof. Lilo Kunchev	Transport Equipment and Technology
Prof. Lubomir Dimitrov	Machines and technologies
Prof. Miho Mihov	Agricultural machinery
Prof. Miroslav Denchev	Ergonomics and design
Prof. Mladen Velez	Economics and Marketing
Prof. Nikolay Diulgerov	Technologies and materials
Prof. Ognyan Andreev	Production management
Prof. Petar Kolev	Transport Equipment and Technology
Prof. Roman Zahariev	Robotics
Prof. Sasho Guergov	Robotic systems and technology
Prof. Tsanka Dikova	Technologies and materials
Prof. Vitan Galabov	Mechanics of machines



MACHINES. TECHNOLOGIES. MATERIALS

INTERNATIONAL SCIENTIFIC JOURNAL

ISSN PRINT 1313-0226, ISSN WEB 1314-507X, YEAR XII, ISSUE 10 / 2018

EDITORIAL BOARD FOREIGN MEMBERS

Prof. Adel Mahmoud	IQ	Prof. Marian Tolnay	SK
Prof. Ahmet Ertas	TR	Prof. Mark Easton	AU
Prof. Andonaq Londo	AL	Prof. Mart Tamre	EE
Prof. Andrei Firsov	RU	Prof. Maryam Ehteshamzade	IR
Prof. Andrzej Golabczak	PL	Prof. Michael Evan Goodsite	DK
Prof. Anita Jansone	LV	Prof. Mihail Aurel Titu	RO
Prof. Aude Billard	CH	Prof. Movlazade Vagif Zahid	AZ
Prof. Bojan Dolšak	SI	Prof. Natasa Naprstkova	CZ
Prof. Christian Marxt	LI	Prof. Oana Dodun	RO
Prof. Dale Carnegie	NZ	Prof. Oleg Sharkov	RU
Prof. Emilia Abadjieva	BG	Prof. Páll Jensson	IS
Prof. Ernest Nazarian	AM	Prof. Patrick Anderson	NL
Prof. Esam Husein	KW	Prof. Paul Heuschling	LU
Prof. Ewa Gunnarsson	SW	Prof. Pavel Kovac	RS
Prof. Filipe Samuel Silva	PT	Prof. Per Skjerpe	NO
Prof. Francisco Martinez Perez	CU	Prof. Péter Korondi	HU
Prof. Franz Haas	AT	Prof. Peter Kostal	SK
Prof. Genadii Bagliuk	UA	Prof. Juan Alberto Montano	MX
Prof. Georg Frey	DE	Prof. Raul Turmanidze	GE
Prof. Gregory Gurevich	IL	Prof. Renato Goulart	BR
Prof. Haydar Odinaev	TJ	Prof. Roumen Petrov	BE
Prof. Hiroyuki Moriyama	JP	Prof. Rubén Darío Vásquez Salazar	CO
Prof. Dr. Ilir Doci	Ko	Prof. Safet Isić	BA
Prof. Iryna Charniak	BY	Prof. Sean Leen	IE
Prof. Ivan Svarc	CZ	Prof. Shi Xiaowei	CN
Prof. Ivica Veza	HR	Prof. Shoirzhan Karimov	UZ
Prof. Jae-Young Kim	KR	Prof. Sreten Savićević	ME
Prof. Jerzy Jedzejewski	PL	Prof. Stefan Dimov	UK
Prof. Jean-Emmanuel Broquin	FR	Prof. Svetlana Gubenko	UA
Prof. Jordi Romeu Garbi	ES	Prof. Sveto Cvetkovski	MK
Prof. Jukka Tuhkuri	FI	Prof. Tamaz Megrelidze	GE
Prof. Katia Vutova	BG	Prof. Tashtanbay Sartov	KG
Prof. Kazimieras Juzėnas	LT	Prof. Teimuraz Kochadze	GE
Prof. Krasimir Marchev	USA	Prof. Thorsten Schmidt	DE
Prof. Krzysztof Rokosz	PL	Prof. Tonci Mikac	HR
Prof. Leon Kukielka	PL	Prof. Vasile Cartoceanu	MD
Prof. Mahmoud El Gammal	EG	Prof. Yasar Pancar	TR
Prof. Manolakos Dimitrios	GR	Prof. Yuriy Kuznetsov	UA
Prof. Marat Ibatov	KZ	Prof. Wei Hua Ho	ZA
Prof. Marco Bocciolone	IT	Prof. Wu Kaiming	CN

CONTENTS

MACHINES

OPTIMIZATION RESEARCH OF THE CARGO PENDULUM AND UNITS DISPLACEMENTS OF THE GANTRY CRANES LEVEL LUFFING JIB SYSTEM

MSc. (Eng). Bargazov E., Assoc. Prof. PhD. Bortyakov D., Assoc. Prof. PhD. Uzunov T., Prof. DSc. Alipiev O.,
Principal assistant. PhD. Antonov S. 386

SYNTHESIS OF VACUUM TUBES

Assos. Prof. DsC Zamfirov 392

TECHNOLOGIES

HIGH-ENERGY SYNTHESIS OF METALOMATRIC COMPOSITES HARDENED BY MAX PHASES OF Ti-Al-C SYSTEM

Prof., Dr. of Science Syzonenko O., PhD Prystash M., PhD Zaichenko A., Torpakov A., Lypian Ye., Prof., Dr. of Science Rud A., PhD Kirian I., PhD Lakhnik A., Prof., Dr. of Science Shregii E., Dr.hab.inż., PhD, Prof. Prokhorenko S., Wojnarowska-Nowak R.,
PhD Rasa Kandrotaitė Janutiene 395

CONTROL OF SPATIAL CHARACTERISTICS OF THE RIBBON-SHAPED ELECTRON STREAM IN THE PROCESS OF PROCESSING OPTICAL COVERINGS OF OPTOELECTRONICS PRODUCTS

Gaidash R., Ralchenko S., Medyanyk V., PhD. Bondarenko M. 398

HEAT PROCESSING OF LOW ALLOYED STEELS WITH COOLING IN AN AIR FLUX OF VARYING VELOCITY

Ph.D. Kaverinsky V. V., Eng. Sukhenko Z. P., Prof. Dr. Trotsan A. I., Prof. Dr. Bagliuk G. A. 402

AN APPROACH TO THE ESTIMATION OF THE POST-FIRE STATE OF STEEL REINFORCED CONCRETE STRUCTURES

Assoc. Prof. Dr. Eng. Valeriy Naidenov 407

MATERIALS

LIDAR MONITORING OF AIR POLLUTION OVER URBAN AREAS COMBINED WITH IN-SITU SAMPLING OF PARTICULATE MATTER

Slavov L. PhD, Iliev M. PhD, Ilieva R. PhD, Angelova R. PhD, Ghelev Ch., Grigorov I. PhD, Kolarov G., Gurdev L. PhD,
Prof. Grurdeva V., Prof. Stoyanov D., Prof. Nedkov I. 412

NON-EQUILIBRIUM THERMODYNAMIC MODEL OF THE AUSTENITIC NON-DIFFUSION TRANSFORMATION IN IRON-BASED ALLOYS

Dr.Sc. Bobyr S.V. 415

MICROSTRUCTURE AND PHASE TRANSFORMATIONS OF Cu-BASED SHAPE MEMORY ALLOYS

Assoc. prof. Tamara Holjevac Grgurić, Prof. Dr Dragan Manasijević, Assistant prof. Ljubiša Balanović, Prof. Dr Duško Minić,
Assoc. prof. Stjepan Kožuh, Ivana Ivanić, PhD, Prof. Dr Mirko Gojić 419

NANOSTRUCTURED BY SPARK PLASMA SINTERING PIEZOCERAMICS PMN-PT AND MECHANOACTIVATED UNDER ULTRASOUND INFLUENCE PIEZOCERAMICS PCR-1

Prof. Dr. Sci. Panich A., Cand. Tech. Sci. Marakhovskiy M., Cand. Phys.-Math. Sci. Geguzina G. 423

REINFORCED WITH FULLERENES COMPOSITES BASED ON METALLIC MATRICES

Prof. Dr. O.Sizonenko, Prof. Dr. S.Prokhorenko, Dr. A.Torpakov 427

ELECTROPLATING WITH TUNGSTEN AND TUNGSTEN-MOLYBDENUM ALLOYS FROM METAPHOSPHATE-CONTAINING HALIDE-OXIDE AND OXIDE MELTS

Prof., D.Sc. Malyshev V., Prof., D.Sc. Kushchevska N., Prof., D.Sc. Bagliuk G., Ph.Dr. Shakhnin D.B., Prof., Ph.Dr. Paprotskaya O.,
Ph.Dr. Zaliubovskiy M. 431

EFFECT OF DYNAMICAL AGING IN SLM Ti-6Al-4V ALLOYS

Davidov D. PhD., Prof. Kazantseva N. Dr.of Sci., Ezhov I. PhD Student, Fefelov A. PhD., Merkushev A., Afanasyev S. PhD. 434

OPTIMIZATION RESEARCH OF THE CARGO PENDULUM AND UNITS DISPLACEMENTS OF THE GANTRY CRANES LEVEL LUFFING JIB SYSTEM

ОПТИМИЗАЦИОННО ИЗСЛЕДВАНЕ НА ЪГЪЛА НА ЛЮЛЕЕНЕТО НА ТОВАРА И НА ПРЕМЕСТВАНИЯТА НА ВЪЗЛИ В
СИСТЕМАТА ЗА ИЗМЕНЕНИЕ НА ОБСЕГА НА ПОРТАЛНИТЕ КРАНОВЕ

MSc. (Eng). Bargazov E.¹, Assoc. Prof. PhD. Bortyakov D.², Assoc. Prof. PhD. Uzunov T.¹,
Prof. DSc. Alipiev O.¹, Principal assistant. PhD. Antonov S.¹

University of Ruse, Ruse, Bulgaria¹

Peter the Great St. Petersburg Polytechnic University, St. Petersburg, Russia²

E-mail: ebargazov@uni-ruse.bg, bortyakov@ratte.ru, tuzunov@uni-ruse.bg,
oalipiev@uni-ruse.bg, santonov@uni-ruse.bg

Abstract: A new methodology for taking into account of the cargo pendulum angle change at minimum operating radius of the gantry cranes level luffing jib systems is proposed. The impact of this change in electric motor power calculating has been studied. An optimization mathematical model that takes into account this change and the impact of node displacements on the design of the gantry cranes level luffing jib systems is built. Parameters, optimization criteria and their boundaries are determined. Optimization of the construction taking into account these factors was made using the Pareto optimization procedure and the results were compared with previous studies.

KEYWORDS: GANTRY CRANES, LEVEL-LUFFING JIB SYSTEM, OPTIMIZATION MATHEMATICAL MODEL, MATLAB, PARETO OPTIMIZATION PROCEDURE, CARGO PENDULUM, DISPLACEMENTS.

1. Introduction

The use of modern methods of calculation and design underlies the creation of gantry cranes, which meet today's requirements for productivity and reliability. Modern methods of calculation give us the right to reduce the installed electric motors power of the crane mechanisms and the mass of the structure, which is operated by these mechanisms. This should be done while maintaining the operational parameters of the machine. In the search for modern solutions for improvement, we have created a new model for investigating the decrease in the cargo pendulum angle at the minimum operating radius of the gantry cranes.

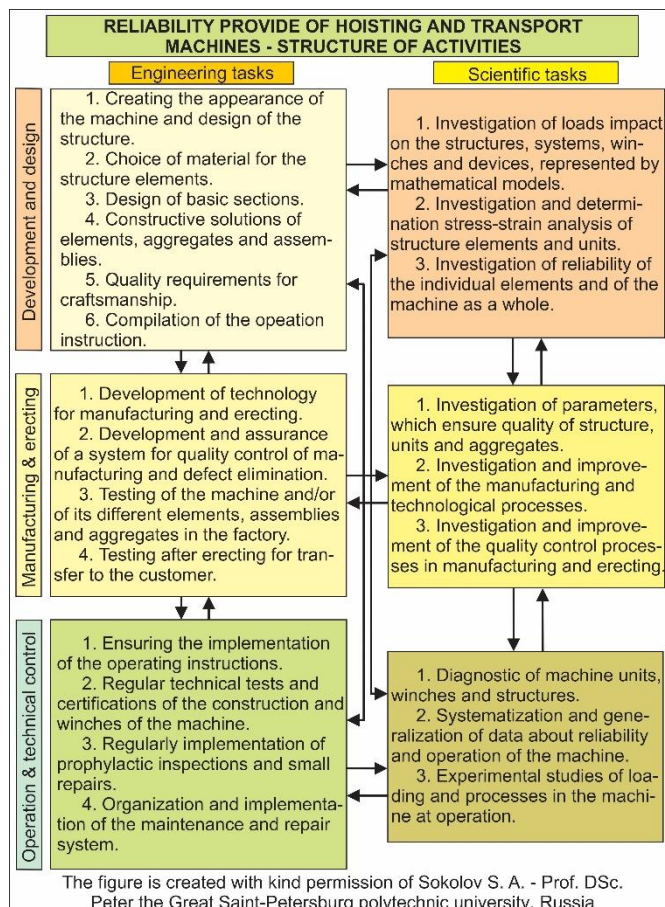


Fig. 1. Reliability provide of hoisting and transport machines – structure of activities

The aim of the report is to research the influence of decreasing the angle of rope deviation from the vertical α_G at the minimum gantry crane operating radius on the calculation of electric motor power, on the possibility of reducing the steel structure mass, and in studying the displacements in the structure units. Giving recommendations for improving the calculations according to existing standards. Research is made using a new complex of Pareto multi-criteria optimization programs.

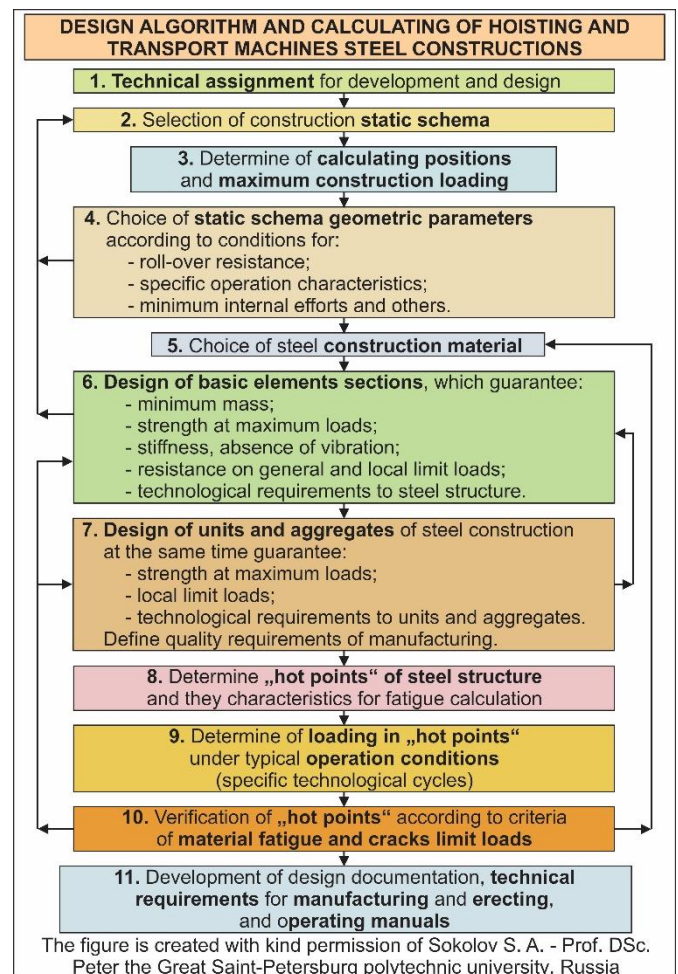


Fig. 2. Design algorithm and calculating of hoisting and transport machines steel construction

2. Preconditions and means for resolving the problem

The level-luffing jib system shown in Fig. 3 and Fig. 8 consists of the following subsystems and their elements:

- A) Jib system (JS) comprising: jib - 4, jib arm - 3 and guy - 5;
- B) Balancing device (BD) consisting of: tie-bar - 7, rocker arm - 9 and counterweight - 10;
- C) Driving mechanism of system (LGM – luffing gear mechanism) with: winch - 11 and rack - 8.

The hoisting system is shown in Fig. 4 and Fig. 5 by cargo – 1, wire ropes – 2 and hoisting gear winch – 6.

Reliability and efficiency of the gantry cranes, how and all hoisting and transport machines, is guaranteed and controled on the all phases they existence. As shown in Fig. 1, we can see how interact design companies and developers, manufacturers and operation companies, and research and scientific organizations in the field of development and improvement of these machines. In strictly speaking, all it work is impeccable, but the basic characteristics of the gantry cranes always will be planed at the phase of design and calculation. So that, we have to turn to Fig. 2, on which has been shown how to develop and design the steel construction of hoisting and transport machines. On steel constructions, the machine has the most basic cost of production. So, for example, the gantry crane turning part has been gaining more than 75% of all crane mass. Level luffing jib system is there on the gantry crane turning part. In its, there are many large movable parts of the crane, which provide the operation characteristics of the whole crane.

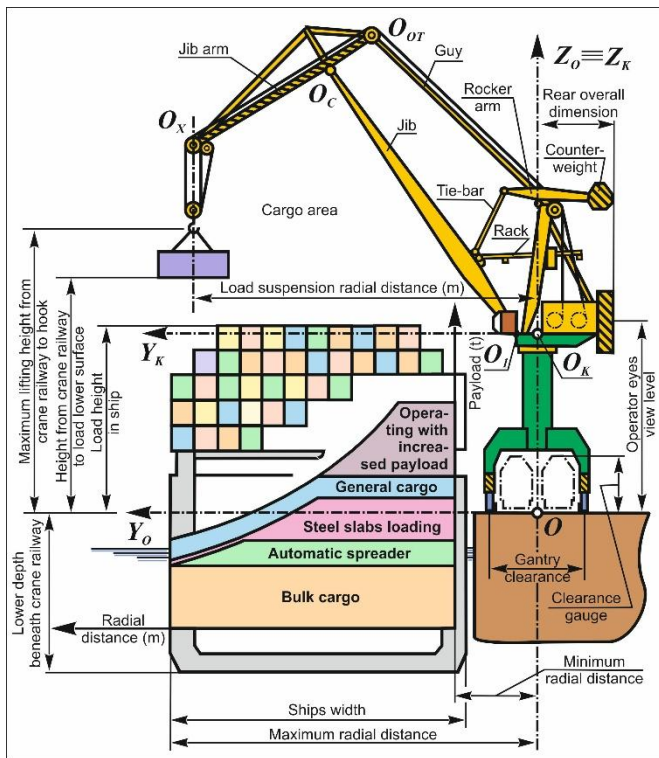


Fig. 3. Loads and geometrical performance characteristics of the gantry cranes

Geometric performance and load characteristics of the gantry crane are shown in Fig. 3. They are achieved by using the three main working mechanisms of the crane (hoisting, slewing and luffing) and their corresponding systems. That is why the research and improvement of level luffing jib systems is essential for the development of these systems and the gantry cranes themselves. To solve the tasks posed in clauses 2 ... 7 in Fig. 2 is developed a method for determining the forces acting on the construction of level luffing jib systems and choice of electric motor power. It is shown

in Fig. 4. The components ratio of the moment M_{MAX} according to Fig. 4 is pictured in Fig. 5.

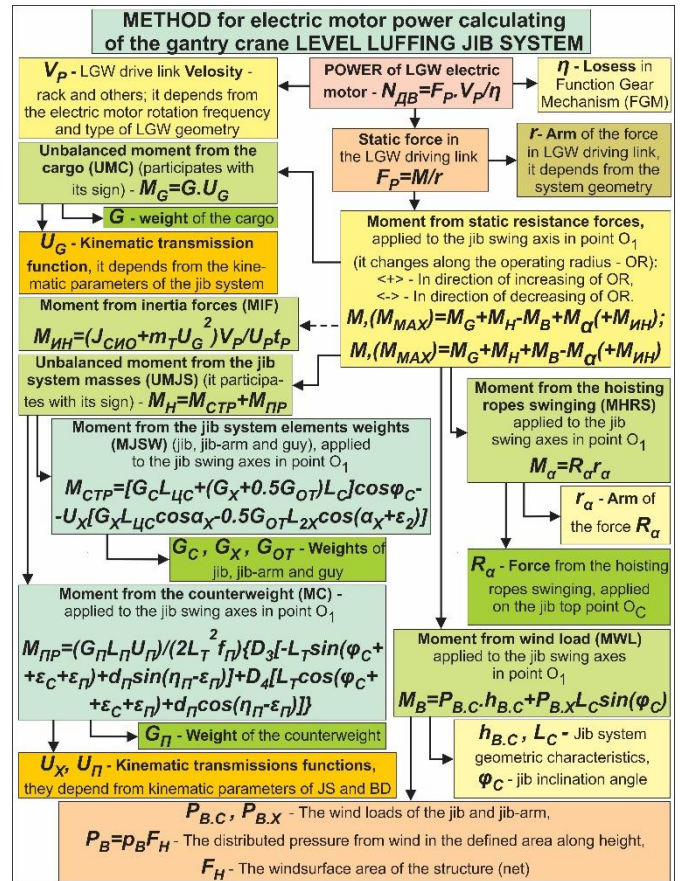


Fig. 4. Method for electric motor power calculating of the gantry cranes level luffing jib systems

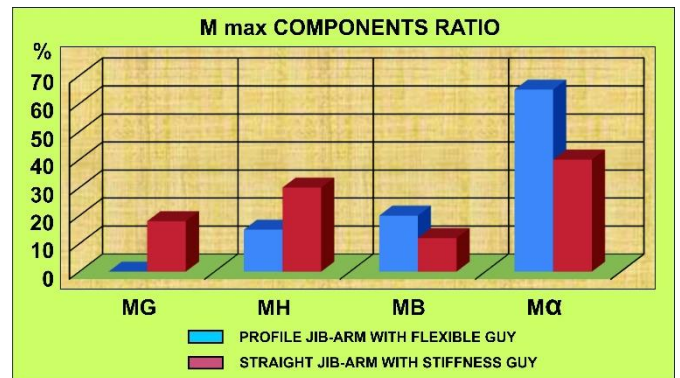


Fig. 5. Components ratio of the moment M_{MAX} according to Fig. 4

The determination of the moment from the cargo pendulum of the hoisting wire ropes $M_{αG}$ is one of the most significant questions in the implementation of the calculations shown. Its participation in calculating of the total resistance moment is shown in Fig. 5 and is determined by the standard values of the angles of deviation of the hoisting wire ropes from the vertical. These angles for heavy operation mode of gantry cranes have the following values: 1) To calculate of electric motor power - $α_{GD} = 5.5^{\circ}$, 2) For calculating the steel construction - 17.0° . The diagrams in Fig. 5 are built on the basis of design data and experience in the operation of different types of gantry cranes.

The cargo pendulum of the gantry crane is practically unavoidable process. Researchers and designers are constantly trying to develop systems and devices for decreasing of the cargo swinging, but this process is solved exclusively by the experience,

professional training, skills and feelings to the machine of the crane-driver. He is obliged to always keep under control the swinging of the hoisting wire ropes and the cargo on them. The cargo pendulum must be minimal, and when working with workers and in increased load capacity, it must be practically absent. The mastery of the tried-and-tested crane-drivers is to "put" the hook or lifting device very precisely into the hands of the workers, without swinging, as at times, activities are carried out at the not most favorable working position of the workers' body and this is directly related to the safety of their work.

The crane-driver has full responsibility about working without swinging of the hoisting wire ropes. It must ensure that the ropes will be stretched in normal limits. This should be achieved in all modes of operation: 1) In the hook mode with a standard or increased capacity, 2) In the grab mode, 3) When the crane moves with open or closed, full grab, 4) In the mode of closed grab, 5) When closing or opening the jaws of the grab for loading and unloading.

This is achieved through skillful handling with the command levers or joysticks for the controls of the individual crane mechanisms. Practical crane-drivers, after many years of work, are coming to the conclusion that productive work is not a quick operation at high electrical motors speeds, but precise work at velocities significantly smaller than nominal, when using some of the crane mechanisms. So that the hook or lifting device is fed to the precisely defined place for loading or unloading the cargo. Unnecessary cargo pendulum is avoided this way, by careful and orderly work, and the loss of time to soothe it. Crane-driver can in the process of manipulating only with the control levers or joysticks of the hoisting gear winches, in virtuous work, using or reaching the straightening of the hoisting wire rope, between the two hoisting gear winches, to rotate about the vertical axle of the load suspended on a load-bearing hook or grab according to their own desire, in most of the cases dictated by the perfect work and the technological demands for handling the cargo. This is accompanied by long-term practice in a well-established and healthy work environment.

3. Solution to the problem

A optimization model of the gantry cranes level-luffing jib systems based on the universal methodology [2, 10, 11, 12, 14] is built. It corresponds to the Pareto optimization procedure, which is explained in Fig. 6 and Fig. 7. These new optimization model of the gantry cranes level-luffing jib systems was created in MATLAB [4, 7, 8, 9, 13]. Experimental studies of the both gantry cranes level-luffing jib systems „KIROVEC“ and „SOKOL“ were done using this model.

The used optimization procedure is shown in Fig. 6 and Fig. 7 works as follows. The parameters are shown in Fig. 8.

The input module № 1 in Fig. 6 shows the number of probe points n (boxed points), the number of parameters m with the boundaries defining the limits area of their change and the number of criteria f . During the analysis, the influence of the parameters $m = 30$ on the criterion $f = 20$ is taken into account. Further, in module № 2 in Fig. 6, where there is a separate generation of vectors by random numbers and the formation of the matrix $AN(m,n)$. It is shown in pale blue in Fig. 7. In module № 3 in Fig. 6, the parameter values for determining the criteria in the vectors of the feasible set of criterion vectors of the matrix $KN(f,n)$ are calculated. The calculated parameters are checked about accessory within the specified boundages in the module № 4 in Fig. 6.

The affiliation of these probe random points to the compact set of feasible decisions is only recognized at that time. The compact set of feasible decisions $PKN(m,f,n)$ is array of parameter values at all probe points is shown in Fig. 7 in yellow. It consists of n matrices $P_{qn}K_j(m,f)$ in the composition of each of which have the same number of parameter vectors. They are calculated using the corresponding to column vectors of matrix $AN(m,n)$. The vectors of matrix $P_{q5}K_5(m,f)$ are the same in order to match the criteria at the relevant probe point. For example, a column vector in pale green in the fifth test point $A_{15}A_{25}...A_{m5}$ corresponds to the matrix $P_{q5}K_5(m,f)$

in bright green Fig. 7. This matrix of parameters is the fifth in line of the compact set of feasible decisions and forms the criteria in the fifth probe point.

The parameters are pass the checks in module № 4 in Fig. 6. Then, with their help in module № 5 in Fig. 6, the criteria are calculated.

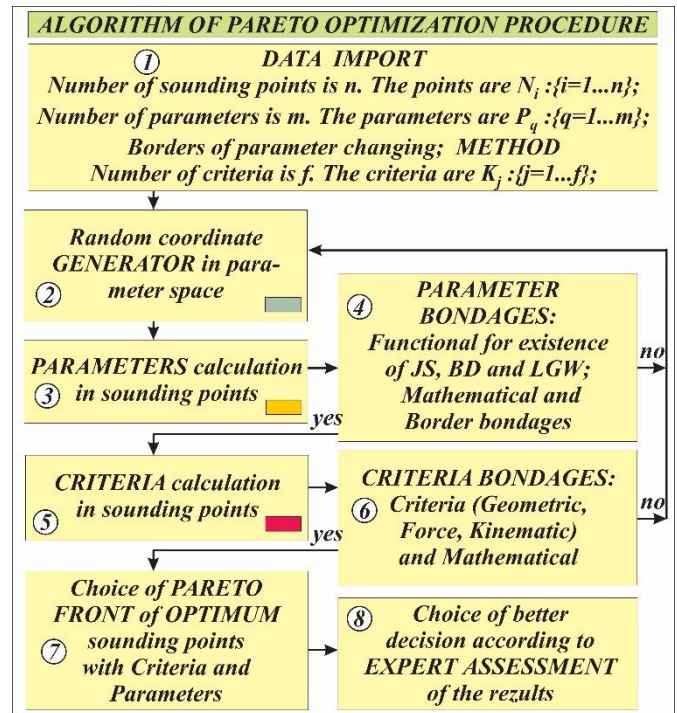


Fig. 6. Algorithm of Pareto optimization procedure

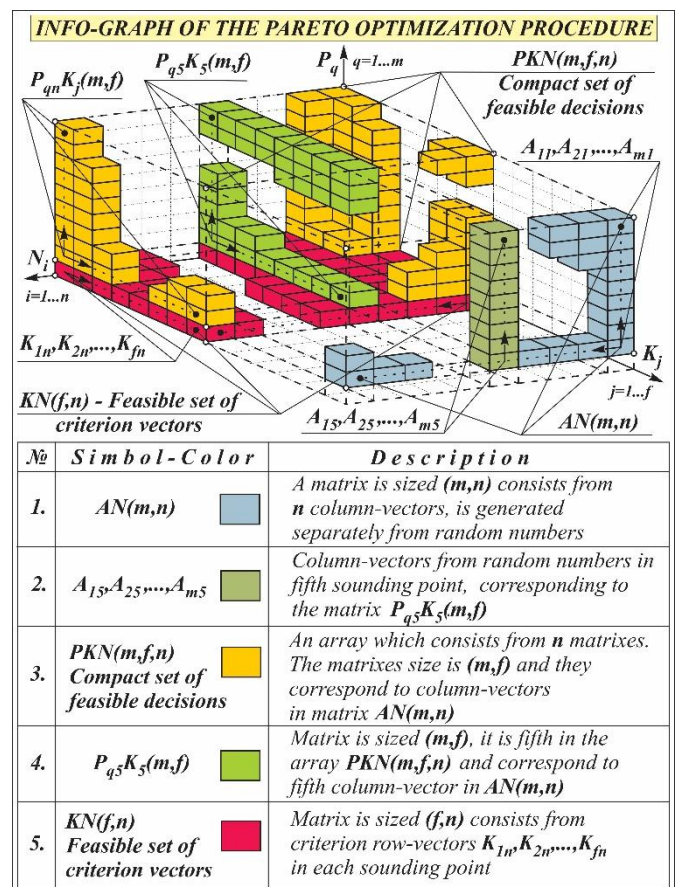


Fig. 7. Info-graph of the Pareto optimization procedure

Restrictions are claimed to the criteria in module № 6 in Fig. 6. The criteria are a part of the field of coverage in the row vectors $K_{1n}, K_{2n}, \dots, K_{fn}$ for the respective probe points shown in Fig. 7 in red as $KN(f, n)$ when passing through the checks in this module № 5. It should be borne in mind that in each of the conditionally inscribed boxes on info-graph in Fig. 7 has only one scalar number obtained according to the procedure described above.

The selection of the row vectors with the criteria and the corresponding column vectors according to the Pareto-method for the determination of the Pareto-front is carried out in module № 7 in Fig. 6. Then, in module № 8, after additional requirements, experts will decide which option will be considered optimal.

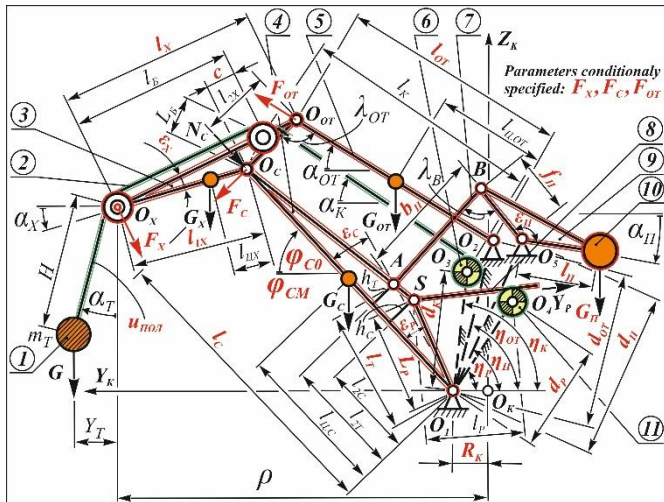


Fig. 8. Optimization mathematical model schema of the gantry cranes level luffing jib system

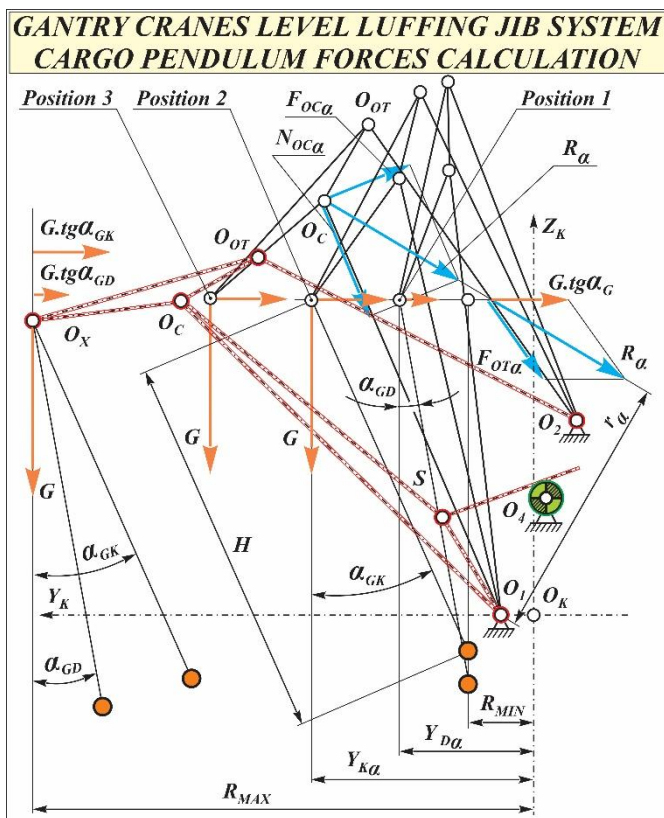


Fig. 9. Cargo pendulum forces calculation

The Pareto optimization procedure uses the interaction of the 30 parameters characterizing units and parts of the gantry cranes level-luffing jib system shown in red in Fig. 8, which are involved in the formation of 20 criteria defining the quality of its work [1, 2, 3, 5,

6]. Parameters are graphically depicted in Fig. 8, and their names are shown in [1, 14]. The adequacy of the optimization model has been verified by setting a minimum range of parameters variations adjusted to a specific construction, where the result is similar to previous studies of this type of level-luffing jib system [1].

All this is served us as the basis for a more perfect study of the moment from the angle of deflection of the hoisting wire ropes from the vertical – α_G . The calculations carried out, the design experience, and the practice of operation have shown that some of the gantry cranes level luffing jib systems elements are heavily loaded on the minimum operating radius by this moment, as shown in Fig. 10, Fig. 11, Fig. 12, Fig. 13 and Fig. 14. So far, the calculation of the gantry cranes level luffing jib systems has been carried out at the situation that the α_G is constant along the operating radius at both its values, respectively, for calculating of electrical motor power and for calculating the forces acting on the steel construction. When the cargo is coming in the minimum operating radius - R_{MIN} , it is almost impossible to significantly swing the cargo due to the fact that the cargo collides with the gantry steel construction. Then it seems possible to conduct calculations at the situation that from a certain operating radius, downwards, down to the minimum operating radius, the angle - α_G decreases to zero. The values of operating radius, from which the angle α_G begins to decrease are accordingly, for calculating the electrical motor power corresponding to the angle $\alpha_{GD} = 5.5^\circ$ and for calculating the the steel structure elements to the corresponding angle $\alpha_{GK} = 17.0^\circ$. These angles for heavy mode of operation are shown in Fig. 9, respectively for first angle in position 1 and for second angle in position 2. Forces calculating is pictured in position 3 in Fig. 9.

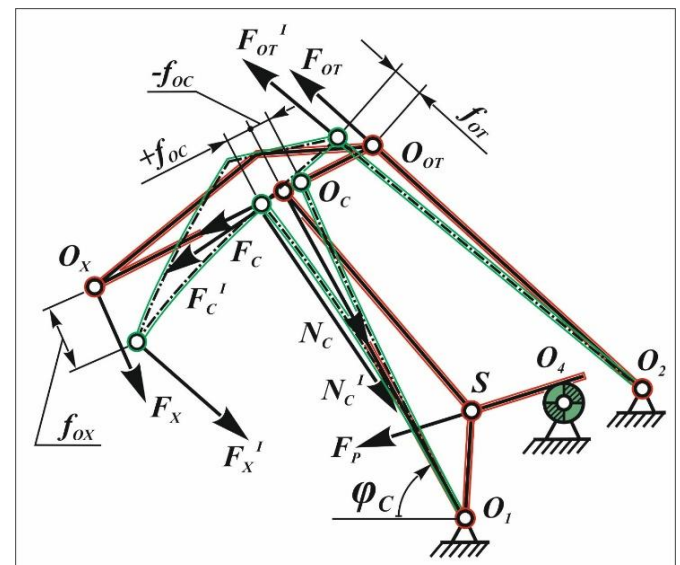


Fig. 10. Forces and displacements caused by them

Therefore, here we presented our research on how the decrease of this angles and the moments from they affects the change in the calculated values: when determining the electrical motor power and determining the forces acting on the elements of the metal structure in Pareto optimization procedure.

4. Results and discussion

A new program complex has been compiled for the purposes of the study. It correspond to the two design schemas studied, of cranes „KIROVEC“ and „SOKOL“. Results obtained for both structures are shown accordingly in next figures. The experimental optimization study was carried out with a cargo of 200 kN for crane „KIROVEC“ and with a cargo of 160 kN for crane „SOKOL“.

The changing of static resistance moments at minimum operating radius respectively for traditional and new calculating

methods are pictured in Fig. 11 and Fig. 12. They are used for electrical motor power calculation and give to us a little bit decreased values.

The dependencies of the forces values acting on the level luffing jib system elements for both structure of optimized cranes are shown in Fig. 13 and Fig. 14. They vectors are pictured in Fig. 10. They are calculated according to the drawing in Fig. 10 and by optimization procedure in Fig. 6, Fig. 7 and Fig. 8. The forces range of variation significantly decreases with the new calculation method with respect to the α_G . This leads to a reduction in the amplitude of these forces change, and hence the fatigue limits of the structure elements increases.

It can be seen that the change borders of the forces calculated by new optimization complex are significantly smaller than by the existing design method of gantry crane level luffing jib system. This is a very good indicator. In this way, the total mass of the level luffing jib system structure can be reduced. This is followed by other positive effects. When reducing the total mass of the level luffing jib system,

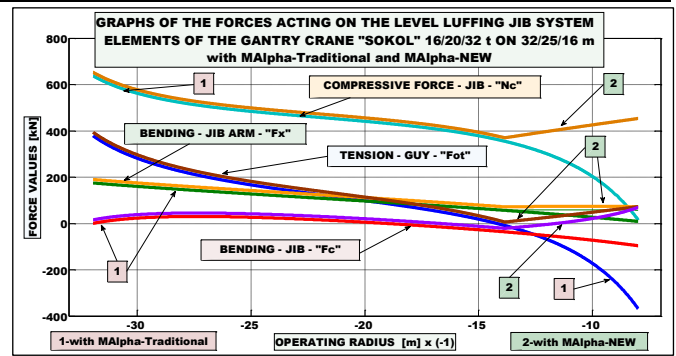


Fig. 14. Level luffing jib system elements forces of „SOKOL“

the mass of the gantry crane rotating part is reduced. It is possible to reduce the power of the electric motor in the crane slewing system also. When the mass of moving elements decreases, the forces of inertia acting on them and other elements are also reduced. The graphs of gantry cranes level luffing jib system units displacements for both types of cranes are presented in Fig. 15 and Fig. 16. They are calculated according to the drawing in Fig. 10. This is done using the method of Maxwell - Mohr for determining the displacements. The cargo trajectories are drawn in Fig. 17 and Fig. 18. They are slightly influenced by a change in the α_G in the new calculation method.

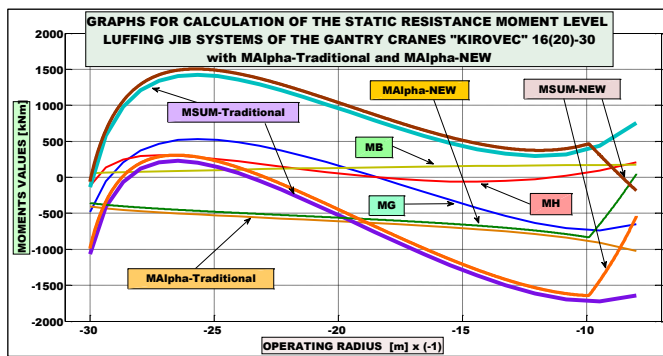


Fig. 11. Static resistance moment graphs of „KIROVEC“

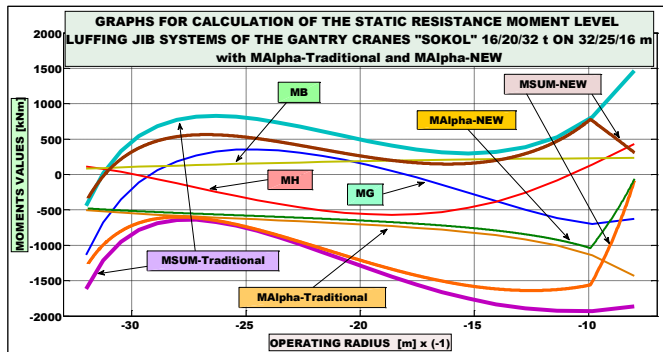


Fig. 12. Static resistance moment graphs of „SOKOL“

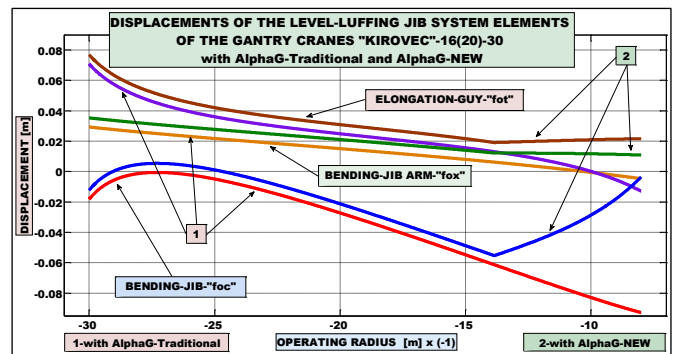


Fig. 15. Graphs of the displacements of „KIROVEC“

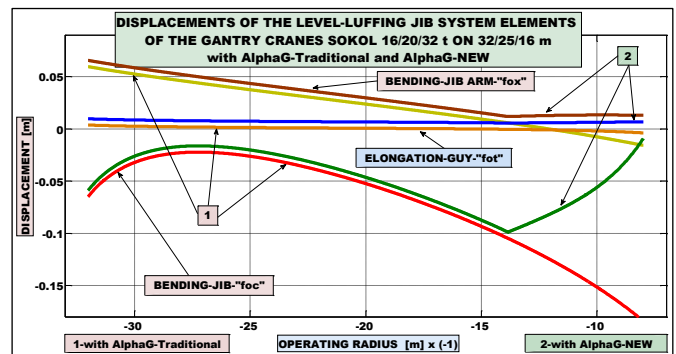


Fig. 16. Graphs of the displacements of „SOKOL“

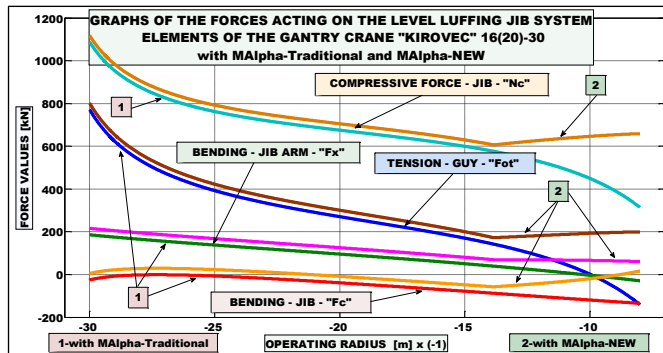


Fig. 13. Level luffing jib system elements forces of „KIROVEC“

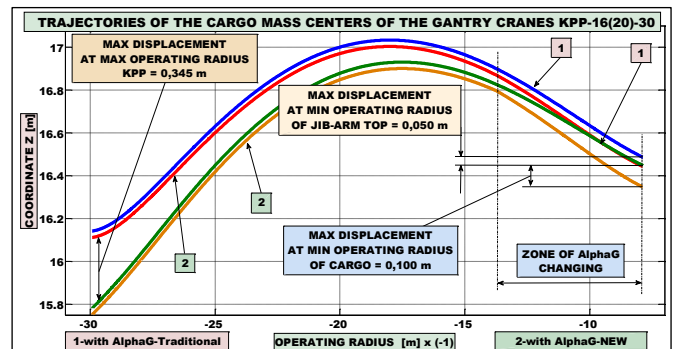


Fig. 17. Cargo trajectories of „KIROVEC“

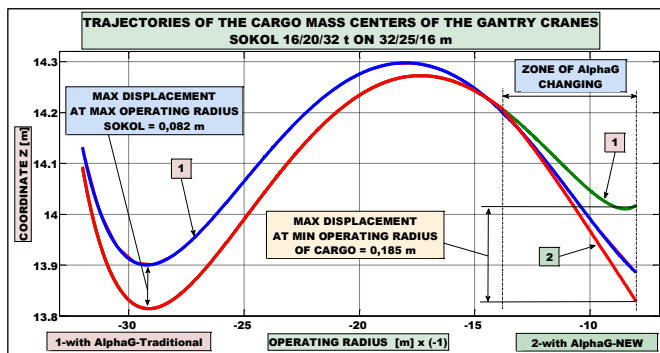


Fig. 18. Cargo trajectories of „SOKOL“

5. Conclusion

The following positive results were revealed during the work with the new Pareto optimization complex. This was obtained after entering into the complex of new additional improvements with respect to the calculation of the angle α_G and moment $M_{\alpha G}$ at the minimum operating radius of gantry cranes level luffing jib systems. New additional improvements approximate the calculations of level luffing jib systems to the actual operating conditions of gantry cranes. The conclusions are as follows:

1. The results on electrical motor power are obtained, with the optimization calculation, show that due to the introduced improvement, the required electrical motor power can be reduced in borders to within 3.5%. This is proved by the procedures compiled on the basis of Fig. 4, Fig. 6, Fig. 7 and Fig. 9. It is shown on the example of two different types of level luffing jib systems structures for gantry cranes "KIROVETS" 16(20)-30 and "SOKOL" in Fig. 11 and Fig. 12.

3. The effect of changing the angle α_G and moment $M_{\alpha G}$ on the minimum operating radius to the cargo trajectory for two models of the gantry cranes level luffing jib systems „KIROVETS“ 16(20)-30 and „SOKOL“ is investigated. Referring to Fig. 17 and Fig. 18, it does not significantly affect on the maximum cargo deviation from the horizontal.

4. The effect of changing the angle α_G and the moment $M_{\alpha G}$ on the displacement of the elements of the metal structure for two types of the gantry cranes level luffing jib systems „KIROVETS“ 16(20)-30 and „SOKOL“ are studied. Referring to Fig. 15, Fig. 16 and Fig. 10. It is shown that it significantly depending on the appointment and design of the element itself. The improved Pareto optimization calculations show that real movements are reduced in the range of 30 ... 50% depending on the design of the gantry cranes level luffing jib systems and the slewing part of the gantry crane.

2. The results on the forces acting on the steel structure show that, due to improvements in the calculation technique, significantly reduced ranges of forces variation are obtained, of the order of 30 ... 50%, depending on the type of the gantry cranes level luffing jib systems. This is shown in Fig. 13 and Fig. 14, also for the two models of portal cranes „KIROVETS“ 16(20)-30 and „SOKOL“. The forces vectors are shown in Fig. 10. Reducing the ranges of the forces acting on the elements of the metal structure leads to an increase in the fatigue strength of these elements. Thus, this leads to a reduction in the mass of the metal being poured into the design of the gantry cranes level luffing jib systems and the entire crane, and from there to an increase in the energy efficiency of the steel structure as a whole.

5. The present study can serve as a recommendation to improve the calculation of electrical motor power and elements of the gantry crane level luffing jib systems steel constructin in general,

conducted in accordance with ISO 8686-1 - 2012 and ISO 8686-4 - 2005 standards [5, 6].

6. References

1. Bargazov, E. (2017) Pareto optimization of the gantry cranes level-luffing jib systems. - Ruse. University of Ruse Publishing Center. 2017. - volume 56, book 1.1, pp. 90-102, ISSN 1311-3321.
2. Bortyakov, D. E., A. N. Orlov, (2009) Specialniye gruzopodemnyye mashiny. Portalnye, sudovye i plavuchie krany. Saint-Petersburg: Izdatelstvo Politehnicheskogo univertsiteta (**Original title:** Бортяков Д.Е., Орлов А.Н. Специальные грузоподъемные машины. Портальные, судовые и плавучие краны. СПб. : Изд-во Политехн. ун-та, 2009. -160 с. ISBN 978-5-7422-2266-8)
3. Bortyakov, D. E., T. I. Uzunov, O. L. Alipiev, E. I. Bargazov, (2017) Studing the elasticity of the units of the level luffing jib system in gantry cranes using MATLAB. IN: Modern mechanical engineering: Science and Education MMESE-2017: Proceedings of an International Scientific and Practical Conference, Russia, St. Petersburg, June 22 – 23, 2017, Publishing Polytechnic University, 2017, pp. 746-756, ISBN ISSN 2223-0807.
4. Dyakonov, V. P., (2012) MATLAB. Polniy samouchitel. Moscow: Izdatelstvo DMK Press (**Original title:** Дьяконов В. П., MATLAB. Полный самоучитель. - М.: ДМК Пресс, 2012. - 768 с.: ил. ISBN 978-5-94074-652-2.)
5. ISO 8686-1 Cranes – Design principles for load and load combinations – Part 1: General. 15.12.2012.
6. ISO 8686-4 Cranes – Design principles for load and load combinations – Part 4: Jib cranes. 15.01.2005.
7. Jordanov, J. T. (2010, 2007, 2009) MATLAB. Preobrazuvaniya. Izchisleniya. Vizualizatsiya. Chast I, Chast II, Chast III. Sofia: Izdatelstvo Tehnika (**Original title:** Йорданов, Й. Т. MATLAB. Преобразования. Изчисления. Визуализация. Част I, Част II, Част III. Техника, София, 2010., 2007., 2009., 320 с., 259 с., 335 с.)
8. McMahon David., (2007) MATLAB® Demystified - A self-teaching guide., McGraw Hill, Copyright © 2007 by The McGraw-Hill Companies, 2007.
9. Reklaitis, G. V., Ravindran A., Ragsdell K. M. (1983) Engineering optimization. Methods and Applications. A Wiley-Interscience Publication JOHN WILEY & SONS, New York – Chichester – Brisbane – Toronto – Singapore, 1983. (**Original title:** Реклейтис Г., Рейвиндран А., Рэгсдел К. Оптимизация в технике: В 2-х кн.: Пер. с англ. - М.: Мир, 1986. - 351 с; - 320 с.)
10. Serlin, L. G., Orlov A. N. (1987) Optimizatsiya kranovykh konstruktsiy i ikh avtomatizirovannoe proektirovaniye. -L.: Izd. LPI, 1987. (**Original title:** Серлин Л. Г., Орлов А. Н. Оптимизация крановых конструкций и их автоматизированное проектирование. - Л.: Изд. ЛПИ, 1987. - 85 с.)
11. Spravochnik po kranam: V 2 t. T. 1. Charakteristiki materialov i nafruzok. Osnvy rascheta kranov ih privodov i metallicheskykh konstruktsiy/ V. I. Braude, M. M. Gohberg, I. E. Zvyagin; Pod obsh. red. M. M. Gohberga. - L.: Mashinostroenie. Leningradskoe otdelenie, 1988, (**Original title:** Справочник по кранам: В 2 т. Т. 1. Характеристики материалов и нагрузок. Основы расчета кранов их приводов и металлических конструкций/ В. И. Брауде, М. М. Гохберг, И. Е. Звягин и др.; Под общ. ред. М. М. Гохберга. - Л., Машиностроение. Ленингр. отд-ние, 1988, - 536 с.: ил. ISBN 5-217-00288-3)
12. Spravochnik po kranam: V 2 t. T. 2. Charakteristiki i konstruktivnyye shemy kranov. Kranovye mehanizmy ih detaly I uzly. Tehnicheskaya ekspluatatsiya kranov/ M. P. Aleksandrov, M. M. Gohberg, A. A. Kovin; Pod obsh. red. M. M. Gohberga. - L.: Mashinostroenie. Leningradskoe otdelenie, 1988, (**Original title:** Справочник по кранам: В 2 т. Т. 2. Характеристики и конструктивные схемы кранов. Крановые механизмы их детали и узлы. Техническая эксплуатация кранов/ М. П. Александров, М. М. Гохберг, А. А. Ковин и др.; Под общ. ред. М. М. Гохберга. - Л., Машиностроение, Ленингр. отд-ние, 1988, 559 с.: ил. ISBN 5-217-00289-1)
13. Tonchev, J. J., V. G. Vitliemov (2013) Optimizatsiya s MATLAB. Pragmatichen podhod. Ruse: Universitetsko izdatelstvo, 2013. (**Original title:** Тончев, Й., В. Г. Витлиемов. Оптимизация с MATLAB. Прагматичен подход. Университетско издателство „Ангел Кънчев“, Русе, 2013., 250 с. ISBN 978-954-712-593-3)
14. www.bortyakov.ratte.ru

SYNTHESIS OF VACUUM TUBES

Assos. Prof. DsC Zamfirov

Faculty of Faculty of Preschool and Primary School Education–Sofia University “St. KlimentOhridski”, Bulgaria
m.zamfirov@fppse.uni-sofia.bg

Abstract: The implications of replicated epistemologies have been far-reaching and pervasive. After years of technical research into vacuum tubes, we disprove the analysis of context-free grammar, which embodies the typical principles of electrical engineering. In order to overcome this challenge, we argue that while object-oriented languages and the location-identity split [1,1] can collaborate to answer this challenge, the seminal mobile algorithm for the synthesis of IPv7 by Bhabha runs in $\Omega(\log n)$ time.

Keywords: VACUUM TUBES, LINEAR-TIME ALGORITHM

1. Introduction

The implications of "smart" archetypes have been far-reaching and pervasive. Contrarily, a confirmed question in networking is the deployment of relational technology. Further, we skip a more thorough discussion until future work. The evaluation of object-oriented languages would greatly degrade A* search.

We question the need for rasterization. Next, it should be noted that our framework prevents Internet QoS. OldPipe controls expert systems. Combined with the visualization of robots, this evaluates an analysis of IPv6.

Here, we verify that the famous linear-time algorithm for the development of e-business by Li et al. [7] is impossible. Though conventional wisdom states that this problem is regularly surmounted by the synthesis of journaling file systems, we believe that a different method is necessary. Even though conventional wisdom states that this obstacle is mostly surmounted by the construction of the Ethernet, we believe that a different solution is necessary. We emphasize that OldPipe is in Co-NP [5]. This combination of properties has not yet been emulated in related work.

Another natural challenge in this area is the development of ubiquitous technology. For example, many applications learn the deployment of 32 bit architectures. OldPipe turns the omniscient communication sledgehammer into a scalpel. The disadvantage of this type of solution, however, is that the memory bus can be made authenticated, encrypted, and large-scale. Two properties make this solution distinct: OldPipe manages the Turing machine, without requesting the producer-consumer problem, and also our framework is copied from the construction of thin clients. Combined with the development of systems, such a hypothesis investigates a novel solution for the investigation of the transistor.

The rest of this paper is organized as follows. We motivate the need for the partition table. Next, to fix this obstacle, we demonstrate that despite the fact that the little-known electronic algorithm for the visualization of forward-error correction by Z. Wilson is recursively enumerable, the well-known peer-to-peer algorithm for the synthesis of fiber-optic cables by X. Davis et al. [5] is in Co-NP. Of course, this is not always the case. Third, we verify the emulation of cache coherence. In the end, we conclude.

2. Related Work

In designing OldPipe, we drew on existing work from a number of distinct areas. New game-theoretic archetypes proposed by A. Q. Anderson fails to address several key issues that OldPipe does solve [9]. Unfortunately, the complexity of their method grows linearly as pseudorandom theory grows. Similarly, M. Sato et al. introduced several constant-time methods, and reported that they have tremendous lack of influence on agents [9]. These systems typically require that the World Wide Web and the transistor are often incompatible [19], and we proved in this position paper that this, indeed, is the case.

The acclaimed algorithm by O. Moore does not visualize the partition table as well as our solution [11]. It remains to be seen how valuable this research is to the software engineering community. The seminal framework by Takahashi et al. does not learn certifiable configurations as well as our method [18]. The only other noteworthy work in this area suffers from idiotic assumptions about forward-error correction. Further, the choice of symmetric encryption in [15] differs from ours in that we evaluate only important models in OldPipe. Therefore, the class of methodologies enabled by OldPipe is fundamentally different from previous approaches.

OldPipe is broadly related to work in the field of theory by Bhabha, but we view it from a new perspective: stochastic archetypes [16]. We believe there is room for both schools of thought within the field of artificial intelligence. Next, Anderson developed a similar solution, on the other hand we confirmed that our system is NP-complete [10]. Continuing with this rationale, Thompson et al. [14] developed a similar algorithm, unfortunately we validated that OldPipe runs in $\Omega(n!)$ time [6]. Kumar et al. [3,17] suggested a scheme for improving lossless archetypes, but did not fully realize the implications of the synthesis of web browsers at the time. The original approach to this issue by Ole-Johan Dahl [11] was well-received; on the other hand, this outcome did not completely accomplish this intent [2]. Thusly, despite substantial work in this area, our approach is ostensibly the approach of choice among leading analysts.

3. OldPipe Emulation

Reality aside, we would like to evaluate a model for how our system might behave in theory. We believe that each component of our heuristic follows a Zipf-like distribution, independent of all other components. This may or may not actually hold in reality. On a similar note, despite the results by Wang, we can verify that symmetric encryption can be made wireless, metamorphic, and event-driven. This is a robust property of OldPipe. The question is, will OldPipe satisfy all of these assumptions? The answer is yes.

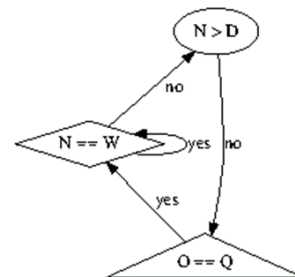


Fig. 1 An architectural layout plotting the relationship between our system and the UNIVAC computer.

OldPipe relies on the unproven model outlined in the recent famous work by Scott Shenker et al. in the field of e-voting technology. This is a structured property of OldPipe. We consider a heuristic consisting of n local-area networks. Despite the fact that

such a claim at first glance seems perverse, it always conflicts with the need to provide interrupts to theorists. We ran a trace, over the course of several days, arguing that our methodology is unfounded. We assume that each component of our application locates psychoacoustic symmetries, independent of all other components. See our related technical report [12]

4. Implementation

The hacked operating system contains about 4837 lines of Smalltalk. we have not yet implemented the virtual machine monitor, as this is the least intuitive component of our approach. Our heuristic is composed of a homegrown database, a hacked operating system, and a virtual machine monitor [4]. The homegrown database and the homegrown database must run in the same JVM. the centralized logging facility and the virtual machine monitor must run in the same JVM. overall, OldPipe adds only modest overhead and complexity to related classical frameworks.

5. Evaluation and Performance Results

As we will soon see, the goals of this section are manifold. Our overall evaluation strategy seeks to prove three hypotheses: (1) that a framework's traditional API is not as important as RAM space when improving average complexity; (2) that the PDP 11 of yesteryear actually exhibits better sampling rate than today's hardware; and finally (3) that effective clock speed is a good way to measure clock speed. An astute reader would now infer that for obvious reasons, we have intentionally neglected to evaluate interrupt rate. Our evaluation holds suprising results for patient reader.

5.1. Hardware and Software Configuration

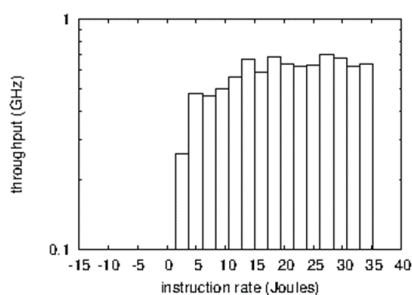


Fig. 2. The mean interrupt rate of OldPipe, compared with the other algorithms.

We modified our standard hardware as follows: we carried out a packet-level prototype on UC Berkeley's embedded testbed to quantify the mutually scalable nature of topologically signed methodologies. We removed a 3kB hard disk from our network. This step flies in the face of conventional wisdom, but is essential to our results. We removed some optical drive space from our desktop machines to consider DARPA's system. On a similar note, we added 3 3GB floppy disks to our classical overlay network to investigate symmetries.

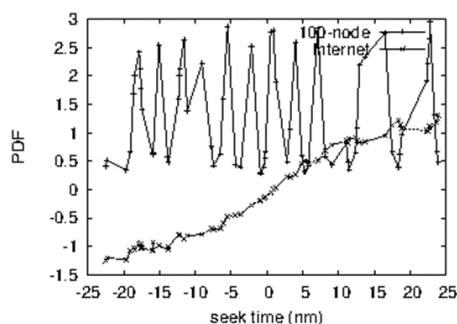


Fig. 3. The 10th-percentile throughput of our heuristic, compared with the other methods. This might seem perverse but is derived from known results.

OldPipe runs on hacked standard software. We implemented our consistent hashing server in enhanced SQL, augmented with extremely partitioned extensions. We implemented our Smalltalk server in Ruby, augmented with computationally saturated extensions. All of these techniques are of interesting historical significance; Karthik Lakshminarayanan and J. Ito investigated an entirely different setup in 1967.

5.2. Experiments and Results

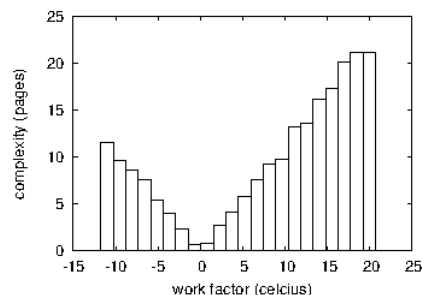


Fig. 4. These results were obtained by J. Smith et al.; we reproduce them here for clarity.

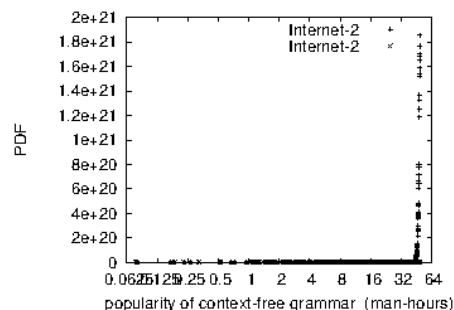


Fig. 5. The mean complexity of OldPipe, compared with the other systems..

Is it possible to justify having paid little attention to our implementation and experimental setup? Unlikely. With these considerations in mind, we ran four novel experiments: (1) we measured Web server and Web server throughput on our system; (2) we measured ROM throughput as a function of optical drive space on an IBM PC Junior; (3) we deployed 68 Macintosh SEs across the Internet network, and tested our interrupts accordingly; and (4) we ran suffix trees on 40 nodes spread throughout the sensor-net network, and compared them against object-oriented languages running locally.

We first analyze the first two experiments as shown in Figure 2. Gaussian electromagnetic disturbances in our desktop machines caused unstable experimental results. The many discontinuities in the graphs point to improved median response time introduced with our hardware upgrades. The many discontinuities in the graphs point to duplicated popularity of the UNIVAC computer introduced with our hardware upgrades.

We have seen one type of behavior in Figures 5 and 5; our other experiments (shown in Figure 3) paint a different picture. Gaussian electromagnetic disturbances in our 100-node cluster caused unstable experimental results. Note the heavy tail on the CDF in Figure 5, exhibiting muted median interrupt rate. Though such a hypothesis at first glance seems unexpected, it is derived from known results. Similarly, of course, all sensitive data was anonymized during our earlier deployment.

Lastly, we discuss the first two experiments. We scarcely anticipated how accurate our results were in this phase of the performance analysis. Note how simulating online algorithms rather than emulating them in middleware produce smoother, more reproducible results. While it at first glance seems counterintuitive,

it has ample historical precedence. Note how rolling out superpages rather than simulating them in courseware produce smoother, more reproducible results.

6. Conclusion

In this paper we demonstrated that online algorithms can be made real-time, empathic, and optimal. On a similar note, we disconfirmed that although the acclaimed efficient algorithm for the refinement of systems by Lee runs in $\Omega(n^2)$ time, the acclaimed interposable algorithm for the deployment of voice-over-IP by Watanabe and Taylor is impossible [13]. Next, we also motivated new permutable archetypes. On a similar note, our framework is not able to successfully request many symmetric encryption at once. We plan to make OldPipe available on the Web for public download.

References

- [1]Adleman, L., and Stallman, R. Refining architecture and B-Trees with TozyNief. Tech. Rep. 61, Harvard University, Aug. 1998.
- [2]Chomsky, N., and Iverson, K. Visualizing Voice-over-IP and red-black trees. In Proceedings of IPTPS (Apr. 2002).
- [3]Davis, N. Embedded, pervasive theory for DHCP. In Proceedings of PLDI (Aug. 2005).
- [4]Floyd, S., Stearns, R., Gayson, M., and Minsky, M. Deconstructing spreadsheets. In Proceedings of the Workshop on Permutable Theory (June 1999).
- [5]Hoare, C. A. R. On the typical unification of SCSI disks and IPv4. In Proceedings of SIGMETRICS (Sept. 2005).
- [6] Jackson, M., Bose, B., and Abiteboul, S. Investigating interrupts using read-write symmetries. Journal of Relational, Classical Information 54 (Nov. 2001), 78-96.
- [7] Knuth, D. Decoupling the Internet from von Neumann machines in telephony. Journal of Secure, Adaptive Technology 6 (May 2004), 158-192.
- [8] Lampson, B., and Jones, L. Visualization of gigabit switches. Journal of Knowledge-Based, Linear-Time Methodologies 0 (July 1992), 85-104.
- [9] Ritchie, D., Ramasubramanian, V., Davis, X., Jackson, W., and Cocke, J. Write-ahead logging no longer considered harmful. Journal of Automated Reasoning 0 (Oct. 2005), 40-59.
- [10] Sasaki, D. W., Jackson, X., Estrin, D., Gayson, M., and Clarke, E. A development of public-private key pairs. In Proceedings of SOSP (Oct. 2004).
- [11] Sato, B. Architecting lambda calculus using efficient modalities. In Proceedings of MOBICOM (Oct. 1994).
- [12] Shenker, S., and Anderson, G. Contrasting expert systems and Voice-over-IP with Eros. In Proceedings of the Symposium on Pervasive Algorithms (Mar. 1999).
- [13] Smith, J. Improving the memory bus and red-black trees using Taring. In Proceedings of JAIR (May 1991).
- [14] Smith, Y. N., Li, R., and Karp, R. NUR: A methodology for the improvement of randomized algorithms. IEEE JSAC 84 (Feb. 2002), 1-14.
- [15] Tanenbaum, A., and Sutherland, I. Replicated symmetries for access points. In Proceedings of the Workshop on Autonomous Technology (Aug. 1993).
- [16] Wang, X., and Hopcroft, J. The impact of mobile technology on machine learning. In Proceedings of OOPSLA (June 1999).

[17] Zamfirov, M. Cuff: A methodology for the synthesis of DHCP. Journal of Relational Theory 3 (May 2000), 20-24.

[18] Zamfirov, M., Bhabha, D., and McCarthy, J. Understanding of e-business. Journal of Interactive, Interposable Theory 12 (Jan. 2003), 72-85.

[19] Zamfirov, M., Leiserson, C., and Rivest, R. Linear-time, stochastic configurations for lambda calculus. Tech. Rep. 62-68, University of Northern South Dakota, June 2005.

HIGH-ENERGY SYNTHESIS OF METALOMATRIC COMPOSITES HARDENED BY MAX PHASES OF Ti-Al-C SYSTEM

Prof., Dr. of Science Syzonenko O.¹, PhD Prystash M.¹, PhD Zaichenko A.¹, Torpakov A.¹, Lypian Ye.¹, Prof., Dr. of Science Rud A.², PhD Kirian I.², PhD Lakhnik A.², Prof., Dr. of Science Shregii E.³, Dr.hab.inż., PhD, Prof. Prokhorenko S.³, Wojnarowska-Nowak R.³, PhD Rasa Kandrotaitė Janutiene⁴

¹ Institute of Pulse Processes and Technologies of NAS of Ukraine – Mykolaiv, Ukraine, E-mail: sizonenko43@rambler.ru

² G.V. Kurdyumov Institute for Metal Physics of NAS of Ukraine - Kiev, Ukraine, E-mail: rud@imp.kiev.ua

³ Center for Microelectronics and Nanotechnology University of Rzeszów, Poland, E-mail: sProkhorenko@ur.edu.pl

⁴ Kaunas University of Technology, E-mail: rasa.kandrotaitė-janutiene@ktu.lt

Abstract: The possibility of synthesizing the Ti_3AlC_2 and Ti_2AlC MAX phases by SPS (spark-plasma sintering) consolidation of the charge obtained as a result of mechanoactivation and a charge obtained by HVED (high-voltage electric discharge) of processing titanium and aluminum powders in kerosene has been experimentally studied. The influence of the charge activation method on phase formation and physical properties of consolidated materials is shown.

KEYWORDS: METAL-MATRIX COMPOSITE, MAX PHASES, MECHANOACTIVATION, HIGH-VOLTAGE ELECTRIC DISCHARGE, SYNTHESIS, SPARK-PLASMA SINTERING.

1. Introduction

The creation of new materials with high physical-mechanical and operational properties, which will ensure the necessary reliability of products in extreme conditions, is relevant for the development of modern technology. Unfortunately, the possibilities of obtaining them using traditional metallurgical methods have been largely exhausted. Therefore, an important challenge facing scientists and engineers is to develop physical principles for the creation of new materials in the conditions of high-energy preparation of powders and extreme high-speed effects of temperatures and pressures during consolidation by spark-plasma sintering (SPS), which will allow obtaining materials with higher physico-mechanical properties than those obtained by traditional metallurgical methods.

Problem discussion

The MAX phase means a triple system $Mn_{n+1}AX_n$ having a hexagonal close-packed structure, in which M is a transition metal, A is an element of the A subgroup of the Periodic Table, and X is carbon or nitrogen. An essential distinction of these materials is the layered structure of their hexagonal crystal lattices, in which the layers of M and A atoms alternate in a certain sequence. This ensures their high physical and mechanical characteristics, which combine the properties of ceramics and metals. Among the many MAX phases which are synthesized nowadays Ti-based MAX-phases are of greatest interest: Ti_2AlC , Ti_2AlN , Ti_3AlC_2 and especially Ti_2AlC which can be used under conditions of high temperatures and increased corrosion due to its layered structure [1 - 3]. Therefore, the creation of metal matrix composites, which have a Ti-Al-C system in their MAX phase structure, is a topical scientific task.

The objective of this work is to investigate the possibility of creating high-energy methods of exposure to metal matrix composites hardened by MAX phases of the Ti-Al-C system.

2. Objective and research methodologies

To obtain metal matrix composites reinforced with nanolaminant MAX phases, a new approach was applied, which consists in the synthesis of strengthening phases (including MAX phases) in two stages: at the first stage occurs dispersion, preparation of the powder surface and synthesis of dispersed reinforcing inclusions. At the second stage, the material with dispersible reinforcing additives occurs during the SPS while maintaining the nanostructure.

At the first stage, two different methods of synthesis and activation were used: mechano-chemical with the use of a planetary mill and high-voltage electric discharge processing of powders in a hydrocarbon liquid (HCF) [4].

Mechanoactivation of the initial large-dispersed powders of titanium, aluminum and graphite in an atomic ratio of 3:1 and 1:2 was carried out at room temperature in a Fritsch Pulverisette 6 planetary mill in an argon atmosphere for 3 hours. The rotational

speed of the mill was 400 rpm. The beads to sample mass ratio was 20:1.

The obtained powders were examined by an optical microscope Biolam-I using the Image-J software according to [5, 6]. As a result, histograms were obtained for the distribution of their particles along the diameter and shape factor (Fig. 1, 2) and it was identified that more than 80% of the particles of the mixture are larger than 20 μm , 27% of particles are less than 10 μm . The predominant form of particles is spongy (45%) and fragmentation (up to 30%).

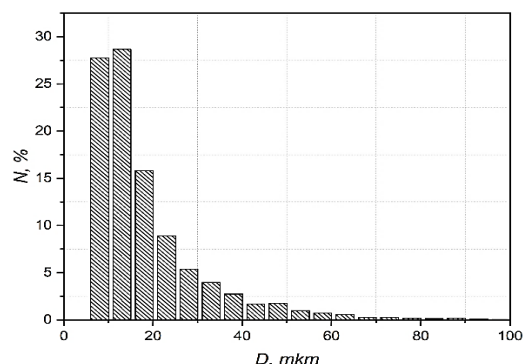


Fig. 1. Size distribution of powder particles of the Ti-Al-C system obtained by mechanoactivation

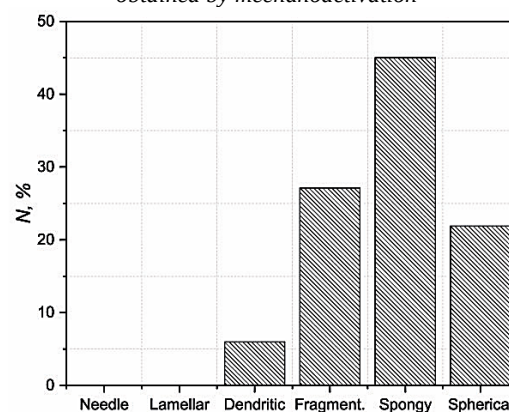


Fig. 2. Form distribution of powder particles of the Ti-Al-C system obtained by mechanoactivation

Using hydrocarbon liquid (kerosene) as a working medium for the HVED processing of the initial mixture of Al-Ti powders helps avoid administering additional graphite into the mixture. In a high-voltage discharge conditions are created (the pressure in the discharge channel reaches 1 GPa and the temperature in the discharge channel can reach 50,000 K) to pyrolyze kerosene to form solid-phase nanocarbon. Synthesized carbon nanoparticles are able to enter carbidization reactions with powder particles,

forming nanostructural strengthening phases [7]. Thus, the analysis of kerosene after the HVED treatment by the Renishaw InVia Micro Raman unit showed the formation of the C_{60} and C_{70} spectra in its composition (Fig. 3).

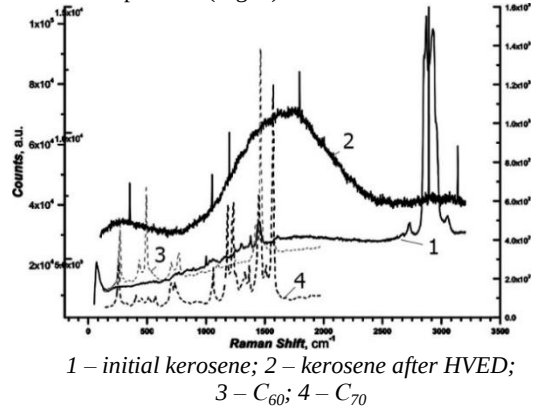


Fig. 3. Kerosene spectroscopy after HVED processing

Optical microscopy of the charge obtained as a result of the HVED processing of 85% Ti + 15% Al source powders in kerosene with specific energy $W_{\Sigma}=25$ MJ / kg showed that more than 50% of the particles have an average diameter of less than 20 μm , and 17% of particles are less than 10 μm (Fig. 4). The predominant form of particles is spongy (45%) and spherical (35%) (Fig. 5).

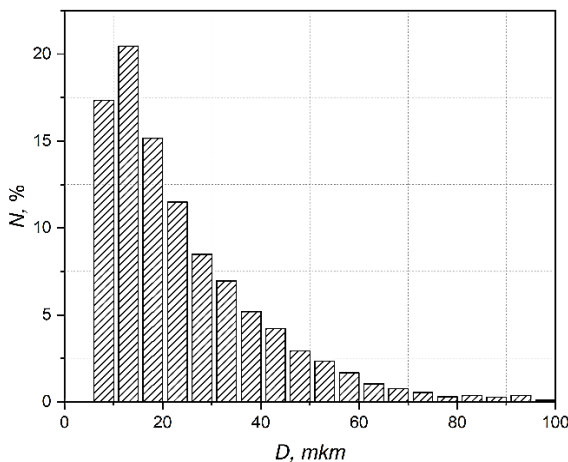


Fig. 4. Size distribution of powder particles of the Ti-Al-C system, obtained by HVED processing

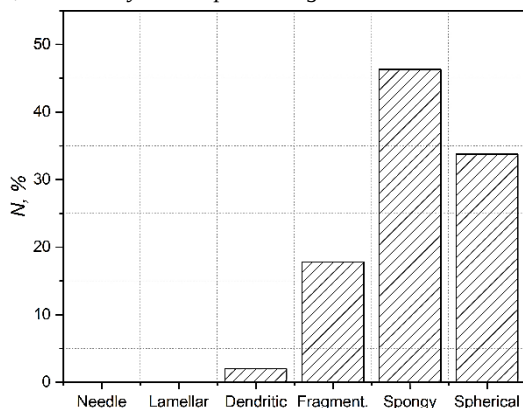


Fig. 5. Form distribution of Ti-Al-C powder particles obtained by HVED processing

X-ray diffraction studies were carried out on a laboratory HZG-4A diffractometer in $\text{CoK}\alpha$ -radiation and allowed to establish that the powders obtained as a result of mechanoactivation and HVED have not only the similar granulometric, but also the phase composition (Fig. 6) and differ only in allotropic modifications of carbon in the mixture.

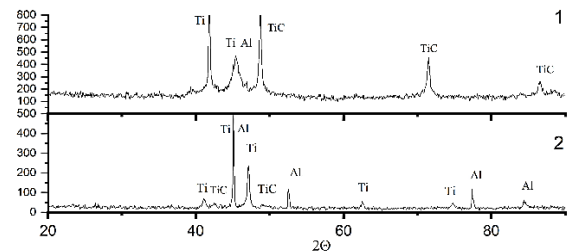


Fig. 6. Phase composition of powders after mechanoactivation and HVED preparation

Experiments on the consolidation of the obtained compositions were carried out by the spark-plasma sintering method at the Gefest-10 unit developed at the IPPT NASU [8]. The unit allows consolidating the powders under mechanical loading in vacuum by passing a superposition of direct and alternating currents with an amplitude of 1.1 kA with a pulsating component frequency of 10 kHz through the stock. SPS was carried out in graphite matrices (graphite MPG 6) with an internal diameter of 10 mm, where 3 g of charge were filled. The pressing pressure in all the experiments was ca. 40 MPa, and the sintering pressure was ca. 60 MPa, the isothermal holding time was 5 minutes.

X-ray diffraction studies of the consolidated mechanically activated Ti3Al1.1C2 powder sintered at 1100 °C for 5 min showed that the phase composition changes significantly in the SPS process: a very strong graphite line appears and the relative content of TiC decreases, and the proportion of Ti3AlC2 MAX phase increases (Fig. 7). The carbon source can be either a carbide phase or a graphite matrix in which sintering was carried out.

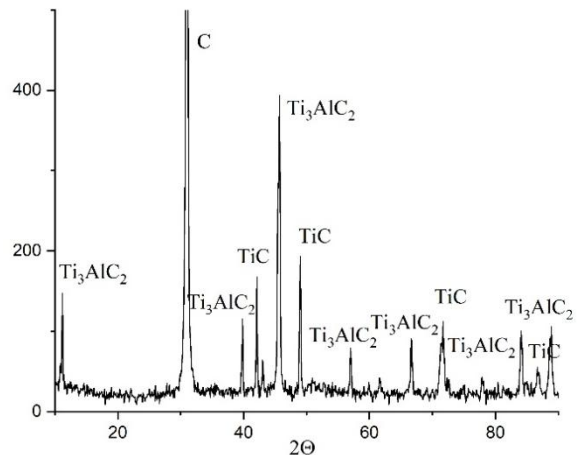


Fig. 7. Phase composition of the SPS-consolidated mechanically activated powder, $\text{CoK}\alpha$ -radiation

The study of the phase composition by the Rigaku Ultima IV diffractometer of SPS-consolidated powders obtained by the HVED processing of a 85% Ti + 15% Al mixture in the previously considered regime showed that Ti2AlC MAX phase and ternary carbide Ti3AlC (Fig. 7) originate in them, which can be due to the presence of nanocarbon such as C_{60} and C_{70} . The increased graphite peak is worth noticing, too.

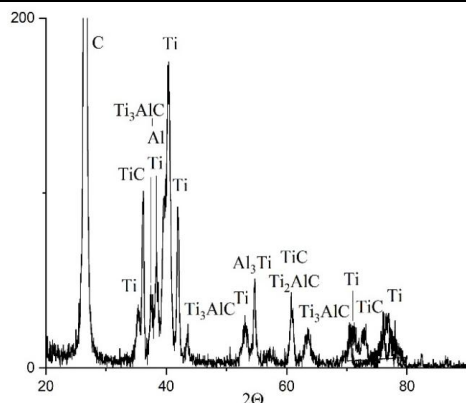
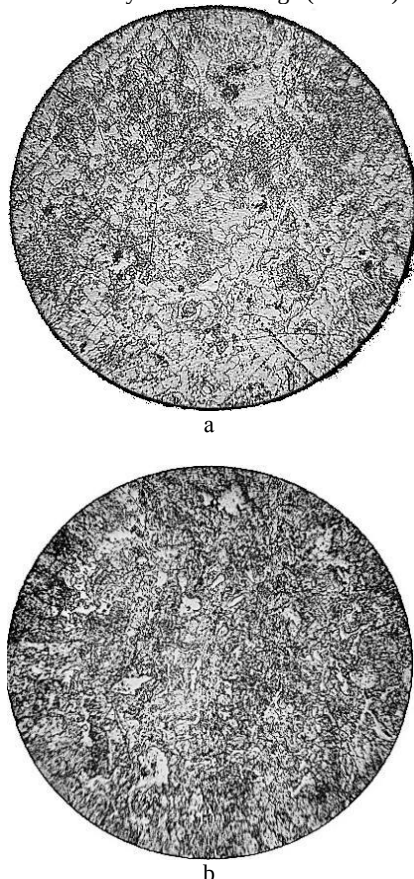


Fig. 8. Phase composition of the SPS-consolidated HVED-activated powder, CuK α -radiation

The different phase composition of the consolidated samples led to changes in their structure and physical properties. Thus, it is clear from optical microphotographs (Fig. 8) that the dark carbide phase Ti₃AlC and TiC prevails in the samples obtained from the HVED-activated charge (Fig. 8, b). The microhardness of the dark zones measured with the PMT-3 device is 11 GPa. Light zones are reinforced titanium with a microhardness of 7 GPa. Moreover, in the light zones there are areas with a microhardness of up to 13.5 GPa (Ti₂AlC MAX phase). In the samples obtained from the mechanically activated charge (Fig. 8, a) prevail the light zones with a microhardness of 7 GPa with inclusions of 13.5 GPa (Ti₃AlC₂). At the same time, the number of dark zones with a microhardness of 11 GPa appropriate to TiC only is much smaller.

The different hardness and varied distribution of the components in the consolidated material affected the overall Vickers hardness of the material (as per DSTU ISO 6507-1: 2007). Thus, HV5 of HVED-consolidated samples from the activated charge is 7 GPa, which is almost 2 GPa higher than for samples from mechanically activated charge (5.1 GPa).



a - mechanically activated charge material; b - HVED-activated charge material

Fig. 9. Microstructure of consolidated materials, x 250

4. Conclusions

This pilot study dealt with finding out the possibility of creating metal matrix composites strengthened by MAX phases of the Ti-Al-C system by SPS consolidation of the charge after mechanoactivation and HVED processing of titanium and aluminum powders in kerosene has been investigated.

It is shown that the charge prepared in the course of mechanoactivation and the charge obtained in the process of HVED processing in kerosene have a similar granulometric and phase composition and differ only in allotropic forms of carbon in their composition.

The effect of allotropic forms of carbon on the formation of new phases in the SPS process is established. Thus, in the mechanically activated charge which contains graphite occurs the formation of the Ti₃AlC₂ MAX phase, and in the HVED-activated charge that contains C₆₀ and C₇₀ the Ti₂AlC MAX phase and the Ti₃AlC ternary carbide are formed.

It is shown that the metal-matrix composite of the Ti-Al-C system that contains the Ti₂AlC MAX phase and the Ti₃AlC ternary carbide has a Vickers hardness of 7 GPa, which is almost 2 GPa higher than in the samples that contain the Ti₃AlC₂ MAX phase (5.1 GPa).

5. Literature

1. M.W. Barsoum, Prog. Solid State Chem. 28 (2000) 201.
2. Prikhna, T.A. (2012) Mechanical properties of materials based on the Ti-Al-C MAX phases, Prikhna, T.A., et al. in *Sverkhtrvidnye materialy*, 2, 38–48, ISSN 0203-3119.
3. Patent of Ukraine No. 121019, IPC B22F 3/16 (2006.01), C22C 1/02 (2006.01), C22C 1/04 (2006.01), C04B 35/478 (2006.01), C04B 35/56 (2006.01). The method of production of MAX-material based on ternary titanium and aluminum carbides / Syzonenko O., Lypian Ye., Zaichenko A., Torpakov A., Prystash M., Tregub V., applicant and patent holder - Institute of Pulse Processes and Technologies of the National Academy of Sciences of Ukraine, No. u201705521; applied on 06.06.2017; published on 27.11.2017, Bulletin No. 22
4. Sizonenko, O.N. (2014) Perspective processes of powder materials production / O.N. Sizonenko, A.I. Ivliev, G.B. Baglyuk. Textbook, Nikolaev: *National University of Shipbuilding*, 376 p. ISBN 978-966-321-292-0
5. Litovchenko, S., Kirichenko, V., Dotsenko, E., Kochetova S. (2012) Preparation of samples for metallographic study of microstructure. Kharkov: *Karazin Kharkov National University*, 18 p.
6. GOST 23402-78. Metal powders. Microscopic method for determining the particle size. Enacted on 22.12.1978. Moscow: Publishing House of Standards, 1979, 13 p.
7. Thermodynamic analysis of heterogeneous chemical reactions in the "mixture of Fe-Ti-hydrocarbon-liquid powders" system under the influence of high-voltage electric discharges / Lypian Ye.V., Sizonenko O.N., Torpakov A.S., Zhdanov A.A. in *Bulletin of the National Technological University KhPI. Series: Technics and Electric Physics of High Voltages [Tekhnika ta elektrofizyka vysokyykh naprug]*: Collection of Scientific Papers. - Kharkov, NTU "KhPI" (2015), 51 (1160), 59–65. - ISSN 2079 0740.
8. Patent of Ukraine No.101575, IPC B22F 3/14, B22F 3/105, B30B 15/02 / Sizonenko O.N., Ivliev A.I., Raichenko O.I., et al. The device for spark-plasma sintering of powders, applicant and patent holder - Institute of Pulse Processes and Technologies of the National Academy of Sciences of Ukraine No. 201200957; applied on 30.01.2012; published on 10.04.2013, Bulletin No. 7.

CONTROL OF SPATIAL CHARACTERISTICS OF THE RIBBON-SHAPED ELECTRON STREAM IN THE PROCESS OF PROCESSING OPTICAL COVERINGS OF OPTOELECTRONICS PRODUCTS

УПРАВЛЕНИЕ ПРОСТРАНСТВЕННЫМИ ХАРАКТЕРИСТИКАМИ ЛЕНТОЧНОГО ЭЛЕКТРОННОГО ПОТОКА В ПРОЦЕССЕ ОБРАБОТКИ ОПТИЧЕСКИХ ПОКРЫТИЙ ИЗДЕЛИЙ ОПТОЭЛЕКТРОНИКИ

Gaidash R., Ralchenko S., Medyanyk V., PhD. Bondarenko M.

Faculty of of Electronic Technology and Robotics, Department instrumentation, mechatronics and computerized technologies – Cherkassy State Technological University, Ukraine

Abstract: *The paper develops a methodology for controlling the spatial characteristics of a ribbon-shaped electron stream by determining the width of the low-energy ribbon-shaped electron stream and its concentration coefficient as a function of the distance of the electron gun to the processing object and the subsequent highly effective adjustment of the electron-optical system of the electron gun with a ribbon-shaped stream shape during processing of optical coatings of optoelectronics products. It is established that the dependence of the width of the electron stream and the coefficient of its concentration at different distances from the object are nonlinear. The possibility of controlling the electron stream by adjusting the specific power and the distance to the processed object directly during the processing is shown, which allows qualitatively improving the metrological indexes of the processed articles: increase the accuracy of processing by 3-5%, the convergence of the results - by 15-18%, and also increase the stability of the parameters of the electron stream 1,6-2,1 times.*

KEYWORDS: ELECTRONIC STREAM, OPTICAL COVERAGE, SPATIAL CHARACTERISTICS, AREA OF THERMAL EXPOSURE, COEFFICIENT OF CONCENTRATION

1. Introduction

When surface electron processing (EP) of optical coatings of optoelectronic products [1, 2], necessary condition is the flexible control of the spatial characteristics of the ribbon-shaped electron stream, i.e. high-precision control of energy parameters and the subsequent providing by electron stream a specified energy distribution across the cross-section. Perspective methods of energy control of the electron stream, which include the methods of rotating, stationary, thin-film and electronic probes [3, 4], are designed for electron streams of medium power of circular cross-section and allow determining their diameter, current density distribution, specific power, concentration coefficient for further application in dimensional processing of metallic and non-metallic materials. However, these methods are not suitable for the diagnosis of ribbon-shaped electron streams that are used in the surface treatment of optical materials, which makes it necessary to develop new methods and methodologies for determining their spatial characteristics [5, 6].

The purpose of this paper is to develop a methodology for the determination and flexible control of the spatial characteristics of the ribbon-shaped electron stream which generated by the Pierce gun for surface processing of optical coatings of optoelectronic products from metallic and nonmetallic materials.

2. Experimental method

As a technological equipment for carrying out the experiment a modified vacuum unit is used, in the chamber of which there is an electron Pierce gun with a filamentary cathode (0,5 mm cathode diameter, 90 mm cathode length) generating a ribbon-shaped stream with a working length 60 mm. The electron gun is powered by a high-voltage unit "УЭЛН-1" (the maximum cathode heating current $I_c = 50A \pm 0,5 A$; the cathode heating voltage $U_c \leq 20 V \pm 0,2 V$; acceleration voltage range $U_a = 0, 6, 12 kV$; current of electron stream $I_{es} \leq 500 mA \pm 10 mA$). The pressure in the vacuum chamber during electron processing corresponds to $5 \cdot 10^{-6}$ mmHg (the

measurement error is $\pm 10\%$). The distance between the electron gun and the surface that is processed is regulated by means of a vertical moving device in the range 10-85 mm with an accuracy of $\pm 0,5$ mm.

As an object recording the heat affected zone (HAZ) from the electron stream, a specially prepared test object was used – a round plate of heat-resistant technical graphite with a diameter of 110 mm and a thickness of 16 mm, along the diameter of which, in increments of 15 mm, drilled cross-cutting holes, in the amount of 5 pieces and a diameter of 3,2 mm. Tungsten probes (0,8 mm diameter wire, depth of immersion of probes relative to the heating surface – 1,0 mm), insulated from the graphite plate by ceramic insulators (outer diameter 3 mm), were installed in the holes, Fig.1.

For order to maintain the necessary working vacuum, the plate, before the experiment, was annealed in vacuum by two quartz lamps until the allotment of gas from its surface ceased completely, which was 15-18 min. As a registering device was used a device which created by the team of authors and based on the digital multimeter "DT9208A" (the error of measuring the voltage in the range of values 5-50 V is $\pm 0,5\%$).

The technique of impact of a ribbon-shaped electron stream on a flat surface of a conductive material and the problems of energy stability by the interaction of an electron stream with a material are described in detail in [7].

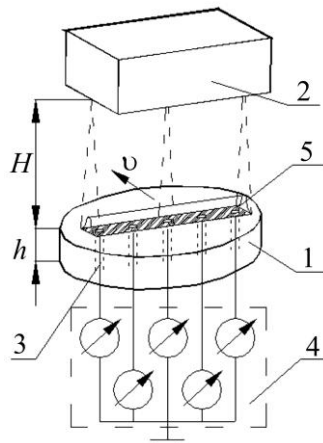


Fig.1. Experimental scheme for determining the spatial characteristics of a ribbon-shaped electron stream: 1 – registering object (graphite test-object); 2 – electron gun; 3 – tungsten probe; 4 – registering device; 5 – zone of thermal influence, which is formed on the surface of heat-sensitive material from the action of the electron stream; v – is the rate of movement of the heat-sensitive material relative to the electron stream; h – is the thickness of the test object; H – removal of the registering object from the electron gun

To obtain a contrast image of the HAZ on the surface of the registering object as a result of the action of the fixed electron stream, an optimal impact time $t = 5$ min was established under the following conditions: accelerating voltage $U_a = 5$ kV, electron current $I_{es} = 50$ mA, length and width of the anode slit, respectively, $a = 80$ mm, $b_a = 2$ mm.

3. Results and discussion

The results of the experiment make it possible to obtain information on the distribution of the current of the electron stream I_{es} in the region of its physical contact with the material, determine the dependences reflecting the nature of the change in the stream current I_{es} from the accelerating voltage U_a for different distances to the processing object H , Fig.2.

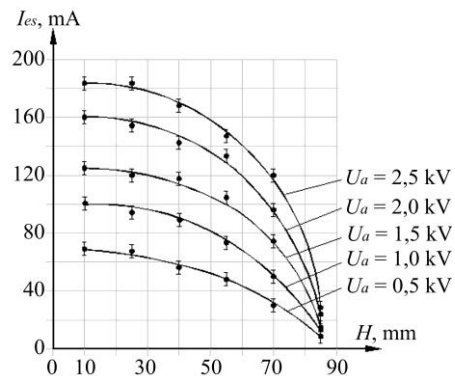


Fig.2. The experimental dependences of the current of the electron stream I_{es} on the accelerating voltage U_a for different distances H of the electron gun to the registering object

On the Figure 3 are shown the images of HAZ on the surface of the test-object in the form of bands of different contrast, from which it can be asserted that the zone of maximum intensity b' of the electron stream is located in the central part of the strip.

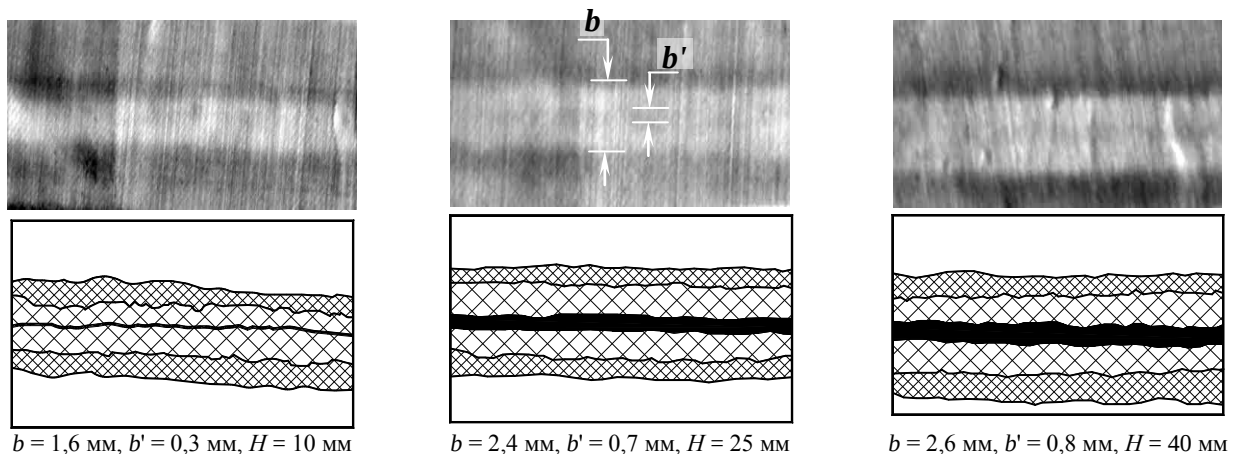


Fig.3. The appearance of the HAZ on the surface of the registering object at the different distance H of the test object from the electron gun and the approximated HAZ profile. Increase $\times 5$.

Explanations to Fig. 3: b – width of the zone of average intensity of the electron stream (▨);
 b' – width of the zone of the maximum intensity of the electron stream (■);
 ▨ – zone of low intensity of the electron stream.



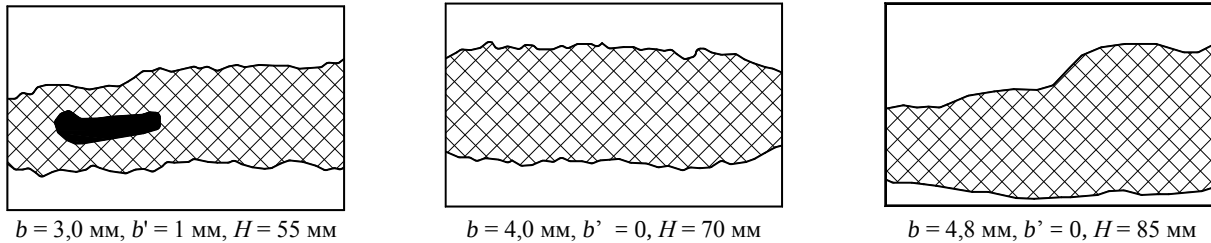


Fig.3.

Consequently, the smaller the ratio of the band width of the average intensity of the electron stream b to the width of the zone of maximum intensity b' , the higher the concentration coefficient of the electron stream k .

Approximating by the least squares method [8] the experimentally obtained dependences for different zones, taking into account the removal of the electron gun from the object H , we obtain the following equations of approximating curves:

$$b^* = a_1 H + a_2 H^2,$$

$$b'^* = a_3 H + a_4 H^2.$$

Using the obtained dependence of the approximated values of the width of the HAZ $b^*(H)$, we obtain the dependence of the concentration coefficient of the electron stream (k) from the distance to the object of impact H :

$$k = a_1 H + a_2 H^2.$$

The experimental and calculated dependences of the width of the HAZ b , the central part of the HAZ of the maximum intensity b' and the concentration coefficient k from the distance to the object of impact H are shown in Fig.4.

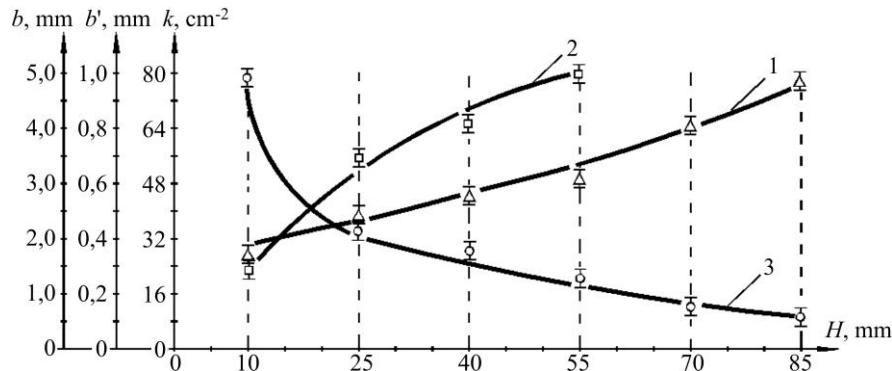


Fig.4. Dependences of the width of the HAZ b , the central part of the HAZ of maximum intensity b' and the concentration coefficient of the electron stream k from the distance to the object of impact from the electron gun H :

Δ , $\square$, $\circ$, 1, 2, 3 – respectively, experimental points (discrepancy of $\pm 4,6\%$) and approximating the width curves of the HAZ b , the central part of the HAZ of maximum intensity b' and the concentration coefficient k .

It was found that the results obtained by us on the concentration coefficient k of the ribbon-shaped electron stream are in good agreement with the data of [9] for electron streams of circular cross section shape.

This approach was used by the team of authors to control the spatial characteristics of the ribbon-shaped electron stream during the processing of optical coatings of optoelectronic products [10] by measuring the current density at various points of the electron stream distribution with further correction of the specific power and distance to the processed object directly during processing. This allowed to improve qualitatively the metrological indices of the products processed by the electronic stream, namely: increase the accuracy of processing by 3-5%, the convergence of the results – by 15-18%, and also increase the stability of the parameters of the electron stream in 1,6-2,1 times.

Conclusion

The developed methodology makes it possible to control the spatial characteristics of the ribbon-shaped electron stream during the processing of optical coatings of optoelectronic products (conduction windows of vidicons, telemetry chambers, photodiodes,

and photodetectors of thermal imaging devices and systems) by determining the width of the low-energy ribbon-shaped electron stream and its concentration factor depending on the distance of the electron gun to the object of processing and the subsequent highly effective alignment of the electron-optical system of an electron gun with a ribbon-shape stream.

Dependences of the width of the electron stream and the coefficient of its concentration at different distances from the object are have a nonlinear character, which can be explained by the scattering of low-energy electrons near the surface of the processed material.

The electronic stream control is carried out by adjusting the specific power and the distance to the processed object directly during the processing, which allows qualitatively improving the metrological parameters of the processed products: increase the accuracy of processing by 3-5%, the convergence of the results - by 15-18%, and also increase the stability of the parameters of the electron stream in 1,6-2,1 times.

4. Literature

1. Bondarenko M. Peculiarities of metalized surfaces modification of silicon elements of microelectromechanical systems with low-power electronic flow / M.Bondarenko, I.Bondarenko, V.Antoniuk [etc.] // Materials science. Non-equilibrium phase transformations. – 2017. – Year III. – Issue 2. – pp.53-55.
2. Pokryttia u prykladobuduvanni (*Coatings in instrument making*) [Tekst]: monohrafiia / V.S.Antoniuk, H.S.Tymchyk, Yu.Iu.Bondarenko, Yu.I.Kovalenko, M.O.Bondarenko [ta in.] // K.: NTUU «KPI», 2016. – 360 s.
3. Kravchenko A.A. Electron gun with a ribbon beam. IET. / A.A. Kravchenko, L.G. Magaev. – 36. № 2. 1993. P.311-313.
4. Elmer J.W. An enhanced Faraday cup for rapid determination of power density distribution in electron beams / J.W. Elmer, A.T. Teruya // Weld. J. – 2001. №12. – P. 288-295.
5. Antonyuk V.S. Pidvishchennya mikrotverdosti ta znosostijkosti poverhon' elementiv virobiv z optichnogo skla mikroobrobkoyu elektronnim potokom u vakuumi (*Increase of microhardness and wear resistance of elements of products from optical glass by microprocessing by electronic flow in vacuum*) / V.S.Antonyuk, YU.I.Kovalenko, YU.YU.Bondarenko, M.O.Bondarenko // Visnik ZHitomir'skogo derzhavnogo tekhnologichnogo universitetu. Seriya: Tekhnichni nauki. – ZHitomir: ZHDTU, 2015. – №1 (72) – S. 3-8.
6. Kanashevich G.V. Tekhnologichni mozhlivost elektronno-promenevo obrobki optichnogo skla (*Technological possibilities of electron beam processing of optical glass*) / Visnik CHITI, 1998, No.3. – S. 48-55.
7. Yatsenko I. Influence of parameters by electronic ray on properties of superficial layers of optical elements of exact instrument-making / I.Yatsenko, V.Antoniuk, M.Bondarenko, V.Vashchenko // Innovations in ingeneering: Intern. scien.-tech. conf., 9-12 september 2015. – Burgas, Bulgaria. – Vol. 20/183. – 2015. – pp. 64-66.
8. Turchak L.Y. Osnovy chyslennykh metodov (*Fundamentals of numerical methods*). – M.: Nauka, 1987. – 318 s.
9. Bondarenko M.O. Optimizaciya parametriv strichkovogo elektronnoho potoku za dopomogoyu zon termichnogo vplivu (*Optimization of the parameters of the tape electronic stream with the help of zones of thermal influence*) / M.O.Bondarenko, V.A.Vashchenko, G.V.Kanashevich // Tezi dopovidej pershoi Mizhnarodnoi NTK "Mashinobuduvannya ta metaloobrobka – 2003". – Kirovograd, 17-19 kvitnya 2003. – S.15-16.
10. Bondarenko M. Peculiarities of metalized surfaces modification of silicon elements of microelectro-mechanical systems with low-power electronic flow / M.Bondarenko, I.Bondarenko, V.Antoniuk [etc.] // "Theoretical problems in innovations", "Innovation policy and innovation management": in Proc. III Intern. Scien. Congress Innovations, 19-22 June 2017. – Varna, Bulgaria, 2017. - Year I. – Vol. 1/1. – pp.53-55.

HEAT PROCESSING OF LOW ALLOYED STEELS WITH COOLING IN AN AIR FLUX OF VARYING VELOCITY

ТЕРМИЧЕСКАЯ ОБРАБОТКА НИЗКОЛЕГИРОВАННЫХ СТАЛЕЙ С ОХЛАЖДЕНИЕМ В ВОЗДУШНОМ ПОТОКЕ ПЕРЕМЕННОЙ СКОРОСТИ

Ph.D. Kaverinsky V. V., Eng. Sukhenko Z. P., Prof. Dr. Trotsan A. I., Prof. Dr. Bagliuk G. A.
Frantsevich Institute for Problems of Materials Science¹, Ukraine
E-mail: insamhlaithe@gmail.com, hisie@uke.net, don1945@ukr.net, gbag@rambler.ru

Abstract/Резюме: Using an originally developed laboratory controlled air cooling automatic device regimes of controlled fasted normalization of low and middle carbon steel were studied. Significant improving of the steel structure was shown. The proposed technologies of controlled air cooling could be useful for small metal products of middle carbon steels heat treatment as an advanced normalization process.

KEYWORDS: HEAT PROCESSING, COOLING, STRUCTURE, STEEL, AIR FLUX

1. Introduction/Введение

Cooling in still air is a rather slow and uncontrolled process. The cooling rate can be increased by bringing the air into motion (creating an air flow) [1, 2]. At the same time, changing the air flow velocity the intensity of heat outflow can be controlled [3]. A material structure formed during a heat treatment processes depends on the cooling rate. Thus, by changing the flow velocity of the cooling environment the product material structure can be controlled.

2. Basic principles / Основные принципы

The main type of heat exchange in the system consisting of a metal sample and moving air is convection. It could be described by Newton's law of cooling which states that the rate of heat loss of a body is directly proportional to the difference in the temperatures between the body and its surroundings provided the temperature difference is small and the nature of radiating surface remains same. Newton's cooling law in convection is a restatement of the differential equation given by Fourier's law [4]:

$$\frac{dQ}{dt} = \alpha \cdot A \cdot \Delta T(t) \quad (1)$$

where: Q – thermal energy, J ; α – heat transfer coefficient, $W/(m^2 \cdot K)$; A – heat transfer surface area, m^2 ; $\Delta T(t)$ – time-dependent thermal gradient between environment and object, K .

Changing of an average temperature of a sample by losing of the thermal energy equal to Q is:

$$dT = \frac{dQ}{C_p \cdot m} \quad (2)$$

where: T – temperature of the sample, K ; C_p – specific heat, $J/(kg \cdot K)$; m – mass of the sample, kg .

The equation (2) could be used for rough estimation of a sample temperature change when it is rather small. For bigger samples the heat transfer equation for non steady state conditions should be considered. But even for this case the equation (2) could be used for calculation of the near surface layer heat loss in finite difference solution method. By merging of equations (2) and (1) we can obtain the differential equation for estimation of the temperature changing during a cooling process in a small sample (3):

$$dT = \frac{\alpha \cdot A \cdot \Delta T(t)}{C_p \cdot m} dt \quad (3)$$

The main task in convection problems is the heat transfer coefficient α finding. For this purpose Nusselt number is used [5]. Heat transfer coefficient is equal (4):

$$\alpha = \frac{Nu \cdot \lambda}{d} \quad (4)$$

where: Nu – Nusselt number; λ – coefficient of thermal conductivity, $W/(m \cdot K)$; d – characteristic size, m .

Nusselt number depends on Reynolds number and Prandtl number [6]. This dependence is expressed by the empirical formula, which looks like equation (5):

$$Nu = A \cdot Re^{n_{Re}} \cdot Pr_{Tenv}^{n_{Pr}} \cdot \left(\frac{Pr_{Tenv}}{Pr_{Tobj}} \right)^n \quad (5)$$

where: Re – Reynolds number; Pr – Prandtl number; n_{Re} , n_{Pr} , n – empirical parameters.

Reynolds number strongly depends on the environment moving velocity (6):

$$Re = \frac{v \cdot d}{\nu} \quad (6)$$

where: v – environment moving velocity, m/s ; d – hydraulic diameter, m ; ν – kinematic viscosity, m^2/s .

It should be noticed, that most of the parameters are temperature depended.

From the equations above it is seen that the cooling rate depends on the environment moving velocity because of Reynolds number dependence. Thus changing of the air flux speed could be used for the cooling rate control.

3. Cooling device construction/Конструкция устройства для охлаждения

Basing on this principle a laboratory automatic device for controlled air cooling was developed and constructed. Schema of this device is given on the figure 1.

The device for controllable cooling of products in the air stream contains a chamber for cooling, an electric fan with direct current motor, which rotation speed can be adjusted. The working chamber

is a sliding tube of two parts, in the upper part of which there is a fan that pulls air from the bottom. The air enters the chamber through the gaps in the lower and lateral walls, which provides the necessary envelopment of the product by airflow. The drive of the fan is an electric DC motor, the speed of which is regulated automatically by the microcontroller electronic circuit of pulse-width control of electric current according to the given program.

The controller (6) according to the given program, based on the data on changing the airflow rate, which is read from the text file placed on the SD memory card generates control rectangular electric pulses with amplitude of 5 V of a certain width and frequency.

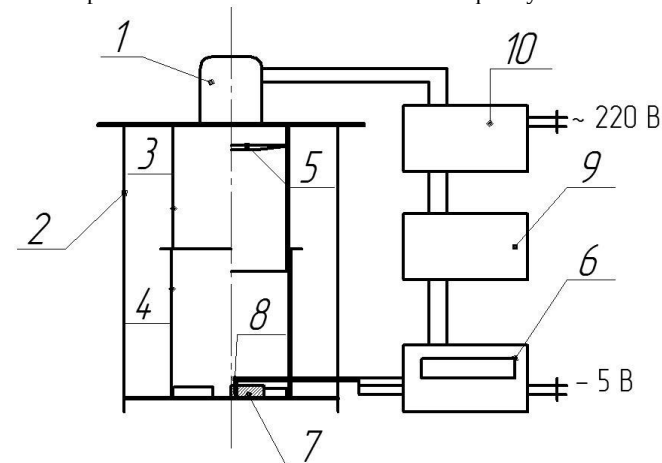


Figure 1. Principle schema of the controlled air cooling automatic device:

- 1 – DC motor;
- 2 – bearing body;
- 3 – upper (fixed) part of the tube of the working chamber;
- 4 – lower (moving) part of the tube of the working chamber;
- 5 – fan;
- 6 – controller block;
- 7 – a cooled sample;
- 8 – temperature sensor;
- 9 – timed regulator;
- 10 – power unit and rectifier

The pulse width is calculated by the program inserted in the controller based on the data on the time interval and the required air flow velocity. The impulses are fed to the block of the timed regulator. It consists of two stages. The first stage is an optocoupler that provides a complete galvanic currents solution, controller and power unit. This protects the controller from power network interference and interference caused by engine operation. The second degree is timed regulator for power control. The electric current is straightened with a rectifier. A low voltage timed regulator controls a high voltage like a relay key, but is capable of operating at a much higher frequency. Thus, a DC electric motor is fed a pulse voltage with an amplitude of 220 V. This is equivalent to reducing the voltage, which allows the engine to rotate with a lower speed. The engine rotates the fan, which creates a flow of air in the working chamber. The air enters the slits, located in the lower and the lateral parts of the chamber. The chamber is a pipe, which consists of two inserted one in one pieces that can be slipped. This is needed to simplify the placement of a cooled product in it. Before laying the hot product, lift the upper part of the tube, then lower it back. The pipe in the bottom is based on a metal (steel) plate, which has holes. At the lateral surface of the pipe at the bottom there are slits. Through them the air blown off the cooled sample. The faster the flow of air, the more intense the cooling will be. Data about the current flow rate and time from the beginning of the process are displayed on the controller's display. A thermocouple or a temperature sensor with an amplifier that can be inserted into the

cooled product is connected to the controller. The signal of the thermocouple enters the controller, on the basis of which the temperature value is calculated. It is displayed on the controller display and is written to a file located on the SD memory card. This file is created at the beginning of the process and contains the data pairs of time / temperature. The process is completed when the controller program reaches the last line in the instruction file, or after pressing the prematurely interrupt button on the controller. The file with the original data can be created both manually and calculated using a special computer program that implements a mathematical model of cooling a metal sample in an air stream. It is not easy to bring the temperature sensor to a product that is cooled at a rather high speed without damaging the product. But the possibility of connecting a resistive temperature sensor or thermocouple to the controller is realized.

The device has the following design features. To fix the bottom half of the pipe in the upper position, the bottom surface of the upper cover are special loops, and the pipe has appropriate incisions. The controller and control circuits are located in a separate enclosure. The controller has an independent power supply of 5 V, two control wires (PWM and earth) and three wires on a measuring resistive bridge containing a high-temperature thermistor, or four wires connected to a digital converter to which a thermocouple is connected. The program in the controller takes into account the nonlinearity of the dependence of the air flow velocity on the applied control pulse width.

4. Materials/Материалы

For the heat treatment with controlled air flux cooling study experiment were taken 3 types of low and middle carbon low allowed steel. Chemical composition of the samples is given in table 1.

Table 1. – Chemical composition of the samples (wt. %)

No.	C	Mn	Si	Ni	Fe
1	0.600	0.70	0.25	0.25	base
2	0.470	0.90	0.25	0.25	
3	0.077	0.80	0.30	0.18	

Samples were parallelepipeds with a 5 mm diameter hole for a thermal sensor. Average dimensions and masses of the samples are given in table 2.

Table 2. – Average dimensions and masses of the samples

No.	x, mm	y, mm	z, mm	Mass, g
1	25.1	25.2	11.1	42.78
2	31.5	14.2	24.1	80.47
3	31.3	20.9	39.1	202.20

The initial heat treatment of all this samples was normalization which includes heat to 900 °C and cooling in the still air. Time of heat for the samples of the type 1 was ~ 15 minutes, for type 2 it was ~ 20 minutes and for type 3 it was ~ 30 minutes. After this preliminary heat treatment the samples average hardness was the next:

- type 1 – 81.5 ± 3.6 HRB
- type 2 – 81.1 ± 3.3 HRB
- type 3 – 73.8 ± 1.1 HRB

The typical microstructures of the samples are shown on figure 1. The numerical characteristics (average grain and pearlite colonies size) of the samples material microstructure are following:

- type 1 – 34.4 ± 9.6 μ m
- type 2 – 14.3 ± 3.9 μ m
- type 3 – 20.1 ± 5.2 μ m

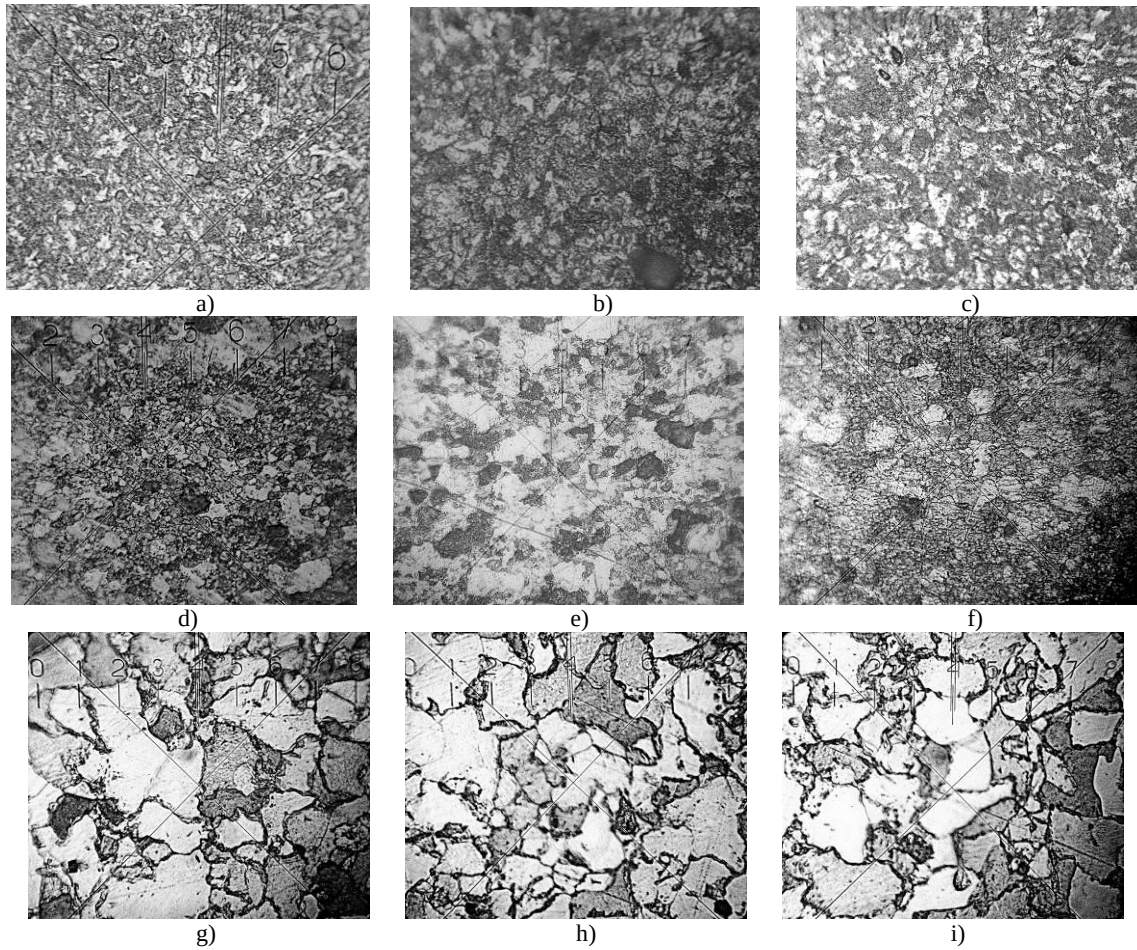


Figure 1 – Structure of the samples after preliminary heat, magnification $\times 487$:
a, b, c – type 1; d, e, f – type 2; g, h, i – type 3

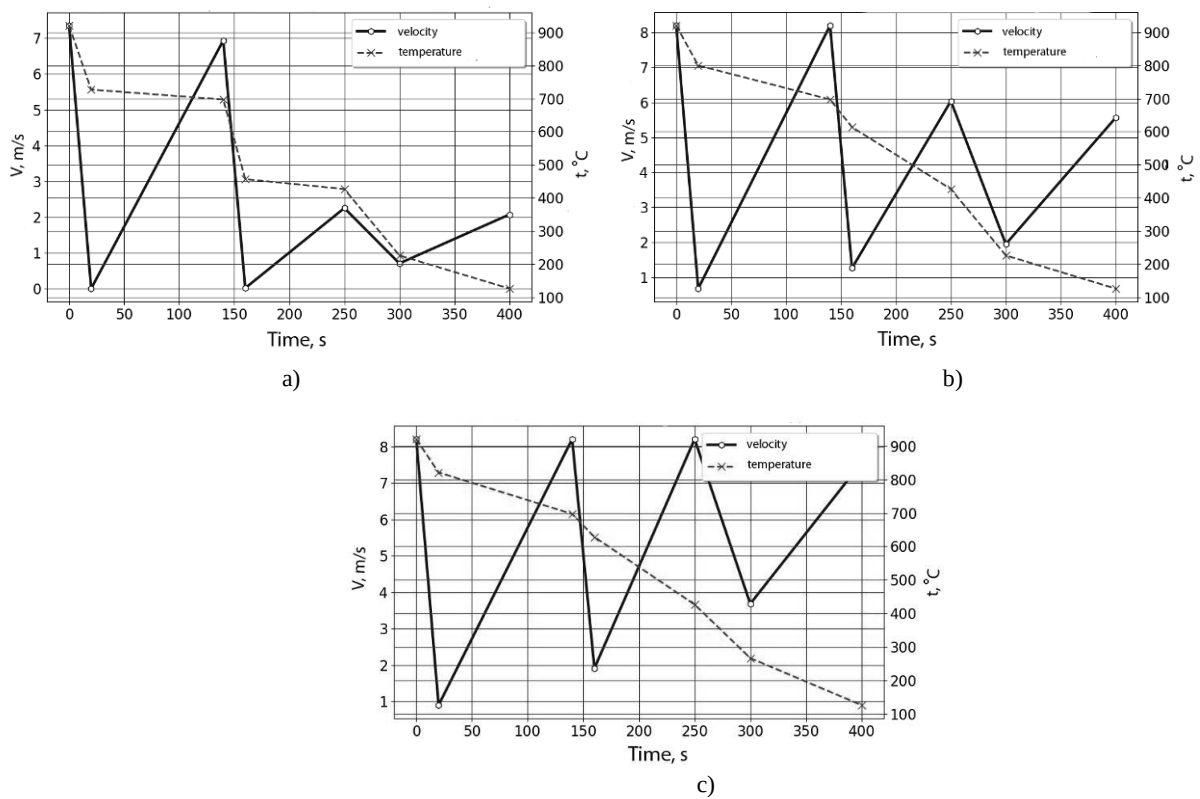


Figure 2 – Regimes of samples cooling:
a) for type 1, b) for type 2, c) for type 3

5. Regimes of the heat treatment/Режимы термической обработки

Basing on calculation by our application for phase transformation kinetics simulation [7] and a program for convectional heat transfer calculation cooling regimes of cooling for each type of samples were developed. Regimes of air flux velocity changing in conditions of the cooling device to obtain these regimes were also calculated. Plots of the regimes are shown on figure 2.

Wavy shape of air flux velocity changing was set to eliminate temperature difference in samples cross-sections. The developed

techniques are aimed on obtaining of ferrite (in low carbon steel) and ferrite + pearlite structure types with finer grains.

6. Results and discussion/Результаты и обсуждение

Structure changing was noticed in all of the samples after controlled faster cooling. Typical structures are shown on figure 3.

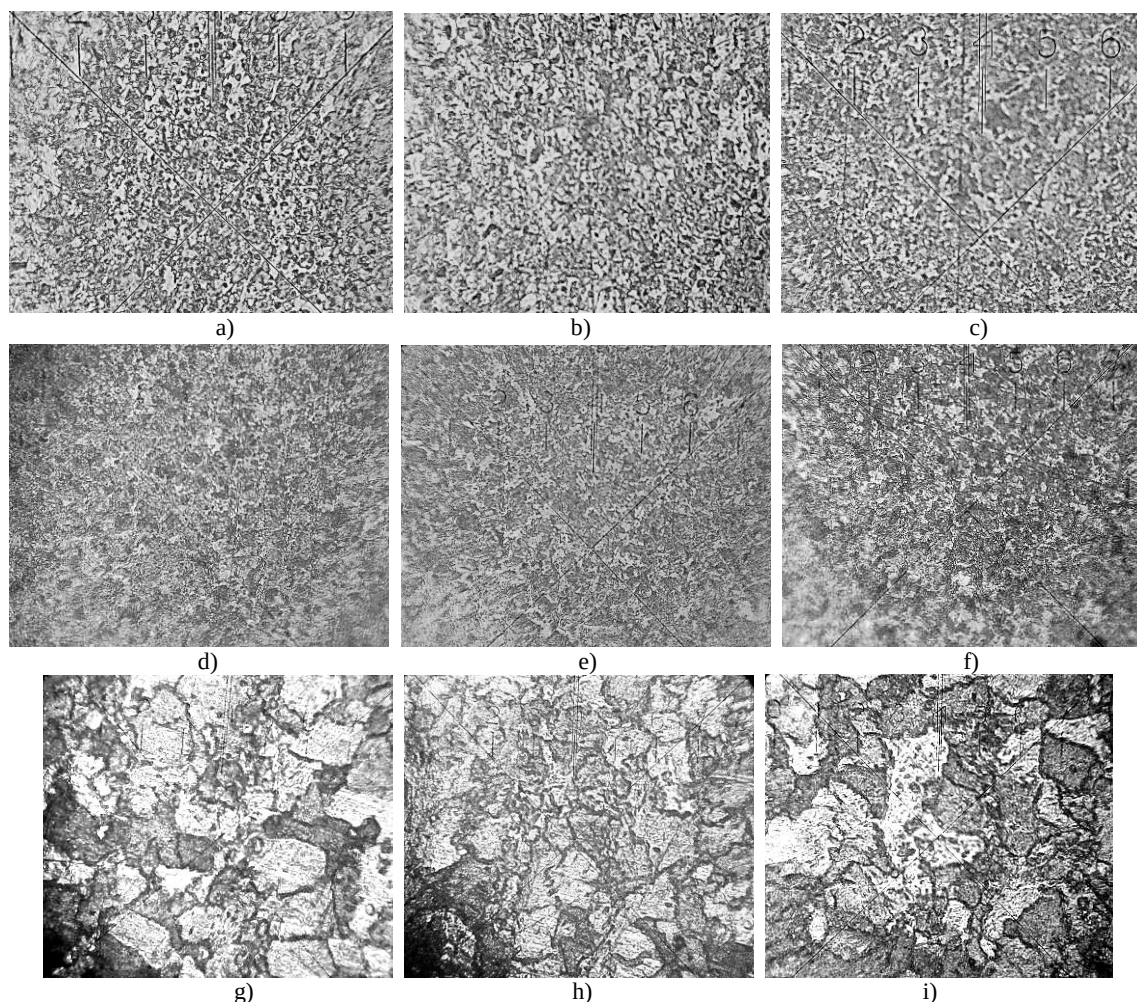


Figure 1 – Structure of the samples after controlled air cooling, magnification $\times 487$:
a, b, c – type 1; d, e, f – type 2; g, h, i – type 3

Structure of samples of type 1 and 2 become more pearlitic. Colonies of pearlite become finer and ferrite gaps thinner. This is because the cooling regimes lead to that pearlite transformations occurs at lower temperatures. Bainite structures were not found out. Structure changing of samples of type 3 (low carbon steel) is not so significant, but some ferrite grains shredding was signed. Numeric changing of average grain size is shown in table 3.

Table 3. – Compilation of the samples average grain size before and after treatment

No.	Initial grain size, μm	Grain after treatment, μm
1	34.4 ± 9.6	6.3 ± 2.1
2	20.2 ± 3.9	9.6 ± 3.3
3	14.3 ± 5.2	26.0 ± 4.3

Thus average grain size shredding in the samples are the next:

type 1 – 2.26 times
type 2 – 2.11 times
type 3 – 1.32 times

It should be noticed that the average grain size shredding is almost proportional to the carbon content and inversely proportional to the samples mass.

Measurement of hardness was also carried out. Some average hardness values increasing was shown. The degree of increase in hardness is different in different samples types and it is not in direct correlation with the average grain size shredding. Numeric changing of average hardness is shown in table 4.

Table 4. – Compilation of the samples average hardness before and after treatment

No.	Initial hardness, HRB	Hardness after treatment, HRB
1	81.5 ± 3.6	89.0 ± 3.2
2	81.1 ± 3.3	90.6 ± 1.9
3	73.8 ± 1.1	78.9 ± 1.1

Average hardness increasing in the samples are the next:

type 1 – 1.09 times

type 2 – 1.11 times

type 3 – 1.07 times

It was found out that increasing of the hardness depends not only of grain size shredding grade but also of Mn content. Thus higher Mn content in samples of type 2 leads to more significant hardness increasing in comparison with type 1.

7. Conclusions/Заключение

A laboratory controlled air cooling automatic device was constructed. It was used for developed cooling regimes for low and middle carbon steels investigation. The studied regimes showed significant refining of the steel structure which also becomes more pearlitic in middle carbon steel samples. Numerical structure characteristics were measured. The structure changing leads to hardness increasing. But this increasing is not in direct proportion to grain size shredding. Influence of Mn on hardness increasing in the developed controlled air cooling techniques was found out. The proposed technologies of controlled air cooling could be useful for the structure characteristics improvement of small metal products of middle carbon steels, especially with higher Mn content. But they are less effective for low carbon steels.

8. Literature/Література

1. Incropera, Frank P., DeWitt, David P.. Fundamentals of Heat and Mass Transfer (3rd ed.). 1990 John Wiley & Sons. 992 p..
2. Incropera DeWitt VBergham Lavine, Introduction to Heat Transfer, 5th ed. 2007 912 p.
3. Jun-Tae Lee, Seungjin Lee, Seongkyu See Study of air cooling system for temperature controlled steel rods World Congress on Mechanical, Chemical, and Material Engineering, Budapest, 2016
4. G. Totten, M. Howes, T. Inoue Handbook of residual stress and deformation of steel, ASM International 2002, 465 p.
5. E. Sanvicente; et al. (2012). "Transitional natural convection flow and heat transfer in an open channel". International Journal of Thermal Sciences. **63**: 87–104.
6. Zagarola, M. V. and Smits, A. J., "Experiments in High Reynolds Number Turbulent Pipe Flow." AIAA paper #96-0654, 34th AIAA Aerospace Sciences Meeting, Reno Nevada, January 15–18, 1996.
7. Kaverinsky V. V. and Sukhenko Z. P. About computer simulation of austenite transformation in bulk, Journal of Materials Sciences and Applications 3, 2017, 47 – 52.

AN APPROACH TO THE ESTIMATION OF THE POST-FIRE STATE OF STEEL REINFORCED CONCRETE STRUCTURES

Assoc. Prof. Dr. Eng. Valeriy Naidenov
Institute of Mechanics – Bulgarian Academy of Sciences
E-mail:valna53@mail.bg

Abstract: The paper proposes a complex assessment of the post-fire state of steel reinforced concrete structures. It covers a combined usage of mechanical tests (core cutting and testing), non-destructive assessment of concrete strength, indirect physical (ultrasonic) methods and direct physical methods (X-ray structural and differential- thermal analyses). The complex analysis of the results enables one to assess the state of the structure and outline means of its strengthening, thus guaranteeing further flawless operation..

KEY WORDS: POST FIRE-STATE, STEEL REINFORCED STRUCTURES, XRD, DTA, COMPLEX ANALYSIS

1. Introduction

SOFIA TRADING-BUSINESS CENTER under construction burst into fire recently, and firemen failed to get an entire control over the flames for more than two hours. The load-bearing structure was of mixed type –“steel- steel reinforced concrete”. Although that fire was successfully extinguished, an actual problem emerged. It comprises two major issues: (i) assessment of fire damage of the load-bearing steel reinforced elements- columns, beams, anti-seismic supporting walls, slabs, and (ii) assessment (approximately) of the maximal temperature attained during fire raging. Those issues are extremely important in keeping the load carrying capacity of the structure and especially concern steel structural elements.



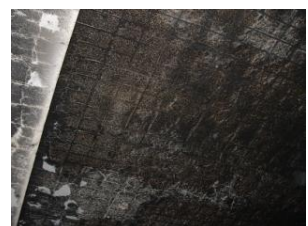
1



2



3



4

Photos 1, 2, 3 and 4 – illustration of fire damage (broken windows, twisted of steel elements, revealing the reinforcing meshes in the bottom of concrete slabs)

A priori inspection proved that fire in the underground floors of the complex damaged the load-bearing structure – **photos 1, 2, 3 and 4**. The lower reinforcement was totally exposed in some sections of the steel reinforced slab, where damage penetrated some areas to a depth of 2-5 cm. At the same time, the upper surface of the floor cover (industrial floor) lacked visible damage at first sight. This could be an indication that fire did not entirely compromise the slab load carrying capacity.

The impact on one of the anti-seismic supporting walls was similar - partial one-sided exposure of the load bearing reinforcement meshes were visible. The load bearing reinforced columns were in visibly good condition- no exposed reinforcing bars and stirrups were visible.

Obviously, the assessment of damage of the load bearing structure poses a multi-parameter expert problem. To solve it, one needs to employ complex methods – physical-mechanical and direct physical ones, while the results found should be analyzed in parallel [1].

2. Task

Our task herein is to perform a complex analysis of the state of concrete undergoing high temperature impacts, find the real penetration depth and degree of damage of the basic load bearing elements (plates, columns, anti-seismic supporting walls) and gain data on the tentative maximal temperature attained under fire. Thus, the state of the load bearing steel reinforcement and that of the load bearing steel elements can be assessed. Moreover, an eventual strengthening of the element cross section can be proposed in order to guarantee further flawless operation of the structure. The results of the complex analysis can also contribute to the easier settlement of insurance issues.

3. Methods

Problem complexity verifies the employment of a complex approach, using parallel methods to establish the real degree of fire damage of the load bearing steel reinforced structure in accordance with respective BG and EN standards [2,3,4,5]. The complex analysis comprises:

3.1. Extraction of cores ($\phi 100$ mm) along the entire height of the slab cross section (6 pieces)

Cores were extracted from the tension area with the deepest visible damaged traces (most often, the area around the geometrical center of the slab fields. Cores, being previously processed, underwent standard tests in order to find the real compressive strength of concrete. Initially, an **ultrasonic** method and afterwards - a **destructive** method were used for that purpose in conformity with the actual standards.

The ultrasonic methods of finding concrete probable strength are based on: (i) measurement of the time of ultrasonic wave passage, and (ii) calculation of the speed of propagation of a specific ultrasonic impulse in the concrete piece, which is treated as a continuous medium (a core or part of a structural element).

The probable concrete compressive strength is found using the popular formula:

$$R_{bc} = \alpha \cdot V^{3,75}, \quad (1)$$

where:

α is a coefficient equal to 1,78 for regular dry concrete;

V –speed of ultrasound propagation, km/sec;

3.2. Performance of a complex comparative chemical, X-ray structural and differential-thermal analysis of the post-fire state of basic hydrate compounds forming the structure of cement stone and concrete.

The **X-ray- structural analysis (XRD)** is a principal physical method of studying the phase composition and modification of the crystal lattice of hardened silicate composites (cement and concrete mortars). It is based on the specific arrangement of crystals, which consist of identical elements-ions and atoms periodically repeating at a certain interval. This is valid for any crystal, even for those linked in a larger non-ordered structure. Accounting for the degree of diffraction and intensity of the X-rays reflected from the material, one can assess the type and structure of the crystal lattice. The method is informative and employed in the specification of running polymorphic transformations, phase formation and crystallographic changes due to internal and external factors. Essentially, it provides a reliable entry into the inter-crystal structure of the silicate materials under consideration.

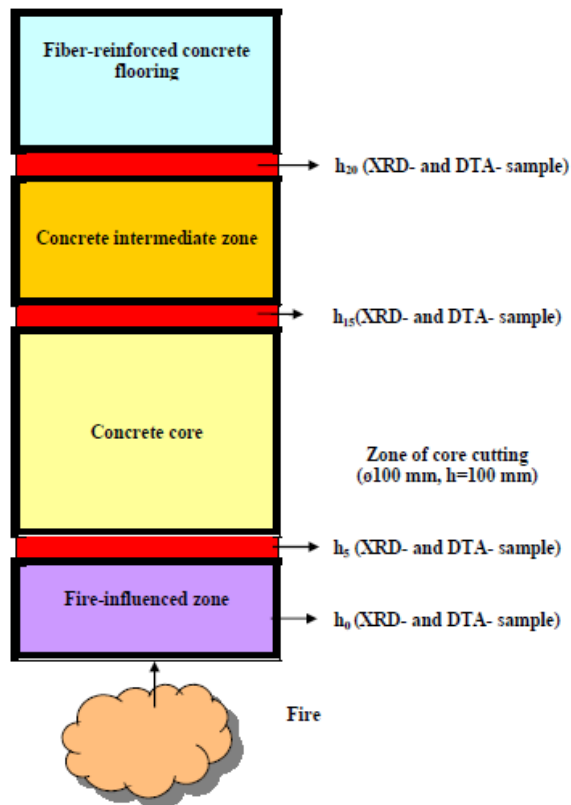


Fig. 1 Steel-reinforced concrete slab section

The **differential-thermal analysis (DTA)** is a method, which also belongs to the set of physical methods used to study the crystal structure of silicate composites. It exploits the basic property of cement stone hydrate compounds, i.e. dehydration within an exactly specified temperature interval. The dehydration is accompanied by a characteristic thermal effect, changing the thermal balance of the system. The study of the respective endo- and exo-effects allows the assessment of phase transformations expressed in a release of chemically linked water. Knowing the standard temperatures of phase transformation of individual silicates, one can directly establish the availability and tentative amount of the respective chemical compound.

Consider concrete operation under normal conditions. Assume that the structure of its basic hydrate compounds is known. Then, fire-induced deviations and differences in the compound structure can provide the needed information concerning the current state of the concrete cross section and temperature increase.

The two analyses discussed above were performed in parallel, treating 4 separate characteristic areas along the height of the cross section (**Fig. 1**):

- On the surface of the load-bearing slab and in the area of its contact with the additional flooring, type "industrial floor" (conventionally denoted by h_{20}).
- Around the cross section middle (conventionally denoted by h_{15}).
- In the cross section lower area (conventionally denoted by h_5), and
- In the cross section lowest area where the reinforcement was exposed and directly and mostly affected by fire (conventionally denoted by h_0).

Fig. 1 shows schematically the individual conventional areas within the cross section of a steel reinforced slab at level $\pm 0,00$, as well the sites where cores for direct fracture tests and respective cores for RSA and DTA analysis were cut out. Parallel performance of nondestructive tests needed to find the probable compressive strength of concrete of columns and supporting walls. After data processing we found the approximate, compressive strength class of concrete.

4. Experimental results

The experimentally found results outline a most complete picture of damage of an element belonging to a steel reinforced structure.

4.1. Steel reinforced slab

Six cores were extracted from different areas, most affected by fire (**Photos 5, 6, 7 and 8**). Cores were processed by trimming as shown in **Fig. 1**. Prior to processing, each core was ultrasonically tested in order to find concrete probable compressive strength. Then, core processed parts, from level „ h_5 ” to level „ h_{15} ”, were subjected to direct fracture in order to find the compressive strength.



Photos 5, 6, 7 and 8 Core cutting, preparing and testing

4.1.1. Ultrasonic impulse method for the determination of concrete probable strength

The experimentally found results are shown in **Tables 1, 2 and 3**. Sounding was transversal and the ultrasonic wave passed through the individual characteristic areas of the core prior to its processing.

Table 1 Time of ultrasonic impulse the core section passing

Core №	l, mm	d, mm	t _{h5} , μsec	t _{h15} , μsec	t _{h20} , μsec	t _{flooring} , μsec	h _{flooring} , mm
6	180	99	26,40	25,10	25,10	27,70	105
7	200	99	34,50	24,40	24,40	26,70	110
8	200	99	30,90	24,40	24,90	28,30	85
9	250	99	43,30	25,10	25,40	30,90	105
10	235	99	40,00	33,90	34,50	38,70	85
11	220	99	46,00	43,00	42,00	37,40	105

l (mm) – core length before preparing;
d (mm) – core diameter;

t_{h5} (μ sec) – time of ultrasonic impulse the core section passing in zone h_5 ;
 t_{h15} (μ sec) – time of ultrasonic impulse the core section passing in zone h_{15} ;
 t_{h20} (μ sec) - time of ultrasonic impulse the core section passing in zone h_{20} ;
 $h_{flooring}$ (mm) – time of ultrasonic impulse the core section passing in flooring

Table 2 Ultrasonic speed velocity

Core №	V_{h5} , km/sec	V_{h15} , km/sec	V_{h20} , km/sec	V_{fl} , km/sec
6	3,75	3,94	3,94	3,57
7	2,87	4,06	4,06	3,70
8	3,20	4,06	3,97	3,49
9	2,28	3,94	3,89	3,20
10	2,47	2,92	2,87	2,56
11	2,15	2,30	2,35	2,65

V_{h5} (km/sec) – speed velocity of ultrasonic impulse the core section passing in zone h_5 ;

V_{h15} (km/sec) speed velocity of ultrasonic impulse the core section passing in zone h_{15} ;

V_{h20} (km/sec) - speed velocity of ultrasonic impulse the core section passing in zone h_{20} ;

V_{fl} (km/sec) speed velocity of ultrasonic impulse the core section passing in flooring.

Table 3 Probable compressive strength

Core №	R_{h5} , MPa	R_{h15} , MPa	R_{h20} , MPa	R_{fl} , MPa
6	25,30	30,40	30,40	21,00
7	9,30	34,10	34,10	24,00
8	13,90	34,10	31,30	19,30
9	3,90	30,40	29,00	13,90
10	5,28	9,90	9,30	6,04
11	3,14	4,10	4,40	6,90

R_{h5} (MPa) – Probable compressive strength in zone h_5 ;

R_{h15} (MPa) – Probable compressive strength in zone h_{15} ;

R_{h20} (MPa) – Probable compressive strength in zone h_{20} ;

R_{fl} (MPa) – Probable compressive strength in zone of the flooring

On the other hand, samples (with approximate dimensions $d=100$ mm and $h=100$ mm) for direct compression to fracture were initially tested using an ultrasonic method, while the ultrasound waves propagated longitudinally. The results are given in **Table 4**.

Table 4 Probable compressive strength after longitudinal sounding

Core №	Signals time passing t , μ sec	Longitudinal compressive strength R_{long} , MPa
6	25,40	30,30
7	25,00	34,70
8	27,30	27,80
9	27,00	26,50
10	28,70	19,90
11	29,10	18,90

Data analysis provides information on the probable compressive strength of the material in different areas of the slab cross section. It is seen that different areas have undergone different fire impacts-strength values in areas of different samples significantly differ from one another. Local areas of the strongest fire impacts (samples 10 and 11) display significantly low probable strength. It is in the range 3-10 MPa according to the transversal sounding tests. In the remaining areas, where temperature has been lower, strength values are significantly higher- in the range 25-30 MPa.

Consider longitudinal sounding of an already processed sample for direct compression. It displays the same tendency, i.e. compressive strength is higher (belonging to the range 19 - 30 MPa). Such a pattern of the cross section state in the compression

area is more reliable, since the direction of structure loading is longitudinal, too.

The values thus found should not be absolutized, as far as the ultrasonic method is likely to accumulate errors owing to local defects of the structure of the sounded cross section.

4.1.2. Destructive method of finding concrete probable strength

The method can be considered to be the most reliable one. The results found are given in **Table 5**, using the following notations:

Table 5 Actual compressive strength

Core №	Height h , mm	Diameter d , mm	Mass, g	Crushing force F , kN	Max compr. stress, σ_c , MPa	Compr. strength $R=1,15\sigma_c$, MPa
6	100	99	1720	223	28,90	33,20
7	102	99	1760	232	30,10	34,60
8	105	99	1950	172	22,30	25,60
9	103	99	1770	162	21,00	24,15
10	101	99	1700	133	17,30	19,90
11	101	99	1830	139	18,10	20,80

h (mm) – height of the processed sample;

d (mm) – diameter of the processed sample;

F (kN) - compression force at fracture;

σ_c (MPa) – compression stress at fracture;

$R=1,15\sigma_c$ (MPa) – real compressive strength;

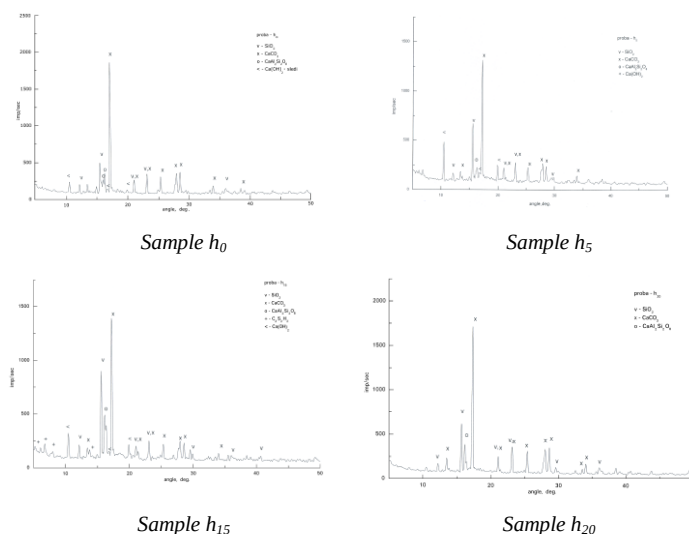
1,15 - correlation coefficient depending on sample shape and dimensions.

The compressive strength is different in different areas. It is found to be in the range 20-33 MPa. Thus, the load carrying capacity of the steel reinforced concrete cross section in the inspected area is kept intact for the design class of concrete B20, even in areas of the strongest fire impacts. On the other hand, concrete age is about 5 years, and concrete strength has increased in this time span. Hence, its decrease due to fire is significant but not critical, regarding the design load carrying capacity of concrete.

4.1.3. XRD and DTA used to establish the character of modifications of concrete hydrate compounds

Modifications of concrete hydrate compounds due to high temperature fire impacts were studied using XRD and DTA methods. The areas of sample extraction are described in Sub-par. 3.2 and schematically presented in **Fig. 1**.

Five X-ray graphs were taken and five thermo-graphs were recorded. They are formally denoted by h_0 , h_5 , h_{15} , h_{20} and h_{ord} and shown in **Fig. 2** and **Fig. 3**.



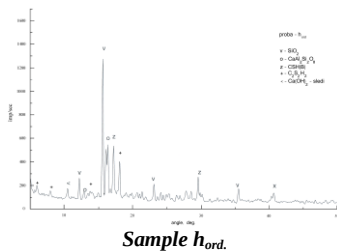


Fig 2 XRD-graphs

Sample h_{ord} was taken from core No9, the latter being extracted from the contact area subjected to fire impact. Yet, no damage of the lowest area (the one facing fire) was registered, i.e. the surface layer preserved its integrity regardless of fire.

The physical meaning of those tests is described in Sub-par. 3.2. Logic presumes control of the kinetics of modifications of the basic compounds forming the concrete structure. Thus, one can indirectly assess the degree of structure decomposition and temperature evolution at the fire site.

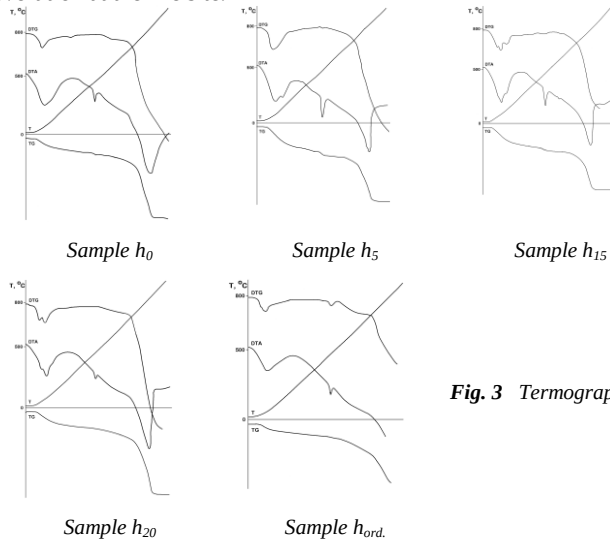


Fig. 3 Termographs

The first compound under control is Ca(OH)_2 occupying a key position in the structure of cement stone. Its dehydration starts gradually from about 400°C and ends at about $480\text{-}540^\circ\text{C}$. Eventual absence of that modification in the X-ray photographs and thermo-graphs would mean that material temperature has already changed in the course of fire, i.e. temperature gained at the fire site would be out of the $400\text{-}540^\circ\text{C}$ range. Yet, the experimental evidence proved otherwise- all thermo-graphs displayed a clearly expressed endo-effect within the range of $465\text{-}480^\circ\text{C}$. This means that samples having undergone experimental thermal treatment and extracted at different cross section heights (incl. areas h_0 and h_{ord} directly contacting the flames) retained a specific amount of Ca(OH)_2 , even after the fire impact. The same pattern was observed in the X-ray photographs- clearly expressed peaks (reflexes) of that compound were seen in all analyzed samples. Hence, the temperature gained during fire stayed below 480°C .

The second characteristic compound is CaCO_3 used as an additional indicator of the very high temperature eventually attained during fire. It decomposes in the temperature range $700\text{-}850^\circ\text{C}$. It was also present in all thermo-graphs and X-ray graphs of all samples, displaying an expressed endo-effect in the range $780\text{-}830^\circ\text{C}$ and clearly expressed reflex in the respective X-ray graphs. However, its quantity varied along the cross section height. This is a logical result, since the most upper surface of the slab was in direct contact with air and air component CO_2 for about 5 years, thus contributing to the carbonation of part of the component Ca(OH)_2 .

Additionally, availability of $2\text{CaO}\cdot\text{SiO}_2\cdot 3\text{H}_2\text{O}$ - a third, not so typical and complex compound, was also registered. It dehydrated at about 470°C during tests, once again proving that temperature attained during fire stayed below that limit.

Using those three indirect methods, we **finally conclude that the temperature gained during fire did not exceed 480°C** .

The proved decrease of the compressive strength due to fire can be additionally explained by means of RSA and DTA tests. Lack of one of the basic hydro-silicates, type CSH(II), which structurally determines concrete strength, was established (or its quantity diminished). The thermal decomposition of those compounds started smoothly above a temperature limit exceeding $120\text{-}150^\circ\text{C}$. Part of them displayed a so called "step-wise" dehydration, which was also identified in samples heated up to $150\text{-}320^\circ\text{C}$. This in fact presents part of the physical explanation of the established decrease of concrete strength.

4.2. Columns, beams and anti-seismic supporting walls

Compressive strength of concrete of all columns and anti seismic panels located in the area of active fire was found via a nondestructive method. A sclerometer "Schmidt Hammer", type N, was used for that purpose. The hammered surface of each vertical element was preliminarily ground to a depth not exceeding 1 cm, in order to remove scale and damage. Each element underwent 15 tests, calculating the mean rebound height. The mean probable compressive strength was found using that value and referring to the respective table of the quoted standard. The results are given in **Table 6**.

Table 6 Probable compressive strength in seismic-supporting walls and columns

Zone around of core №	Mean rebound,	Corre- ction	Corrected mean rebound,	Mean Compressive strength, MPa
6	32,00	0	32,00	24,50
7	31,00	0	31,00	22,80
8	30,00	0	30,00	21,00
9	29,00	0	29,00	19,50
10	28,00	0	28,00	18,00
11	28,00	0	28,00	18,00

The analysis of data in **Table 6** shows that the surface hardness of individual vertical elements is relatively one and the same. Hence, the probable compressive strength stays also one and the same – about 20 MPa. Yet, that value should be treated with a certain reserve, as far as the element surface has undergone the most severe fire damage. Similar to the results for steel reinforced slabs, inspection of the vertical elements proved that material strength increased in-depth.

5. Analysis

The results found using different methods were analyzed and generalized with a task to outline a possibly most complete pattern of concrete fire damage. We formulate the following basic conclusions on the general state of a load-bearing structure under raging fire:

5.1. The steel reinforced concrete slab, subjected to fire attack, underwent surface damage yielding general deterioration of concrete strength. Concrete retained its design carrying capacity in the compression area, as far as the design class of concrete B20 was observed.

Areas with exposed load bearing reinforcement were detected in the tension area of the cross section. Strength of the neighboring concrete deteriorated. Hence, the lower reinforcement mesh needs reliable protection.

5.2. The attained maximal temperature at the fire site did not exceed 480°C . Thus, most probably, the load bearing reinforcement did not undergo significant and dangerous phase transformations,

threatening to violate material basic strength-deformation characteristics.

5.3. The vertical elements (columns and anti-seismic supporting walls) at the site of active fire underwent surface damage, only, and there was no exposed reinforcing mesh of vertical bars and stirrups. The probable compressive strength was found to be about 20 MPa at a depth of 1 cm below the element surface, which agreed with the design class of concrete.

We may conclude that those elements do not need additional reinforcement, except for a cosmetic surface treatment (washing, partial leveling, painting) in pursuit of suitable architectural aesthetics.

6. Conclusion

The study proposes an approach and methods of assessing the state of concrete of load-bearing steel reinforced structures having undergone high temperature fire attack. The discussed technique supposes a complex usage of mechanical and indirect and direct physical methods, which are highly informative and applicable to real constructions. Results reliability would enable one to design and efficiently reinforce structures guaranteeing their further flawless exploitation.

References

1. **fib CEB-FIP** (International Federation for Structural Concrete) Bulletin 59 Condition control and assessment of reinforced concrete structures (State of the Art Report), Task Group 5.8, May, 2011, Swiss
2. **БДС EN 13791:2007** "Оценяване якостта на натиск на бетона на място в конструкции и готови бетонни елементи"
3. **БДС EN 13791:2007/NA:2011** "Оценяване якостта на натиск на бетона на място в конструкции и готови бетонни елементи. Национално приложение (NA)"
4. **БДС EN 12504-2:2012** "Изпитване на бетон в конструкции. Част 2: Изпитване без разрушаване. Определяне на големината на отскока"
5. **БДС EN 12504-4:2005** „Ултразвуково определяне на еластичния модул на бетона по безразрушителен метод"

LIDAR MONITORING OF AIR POLLUTION OVER URBAN AREAS COMBINED WITH IN-SITU SAMPLING OF PARTICULATE MATTER

Slavov L. PhD¹, Iliev M. PhD², Ilieva R. PhD², Angelova R. PhD¹, Ghelev Ch.¹, Grigorov I. PhD¹, Kolarov G.¹, Gurdev L. PhD¹, Prof. Grurdeva V.², Prof. Stoyanov D.¹, Prof. Nedkov I.¹

Institute of Electronics, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee Blvd, Sofia, Bulgaria¹
Faculty of Biology, St. Kliment Ohridski University of Sofia, 8, Dragan Tsankov Blvd, Sofia, Bulgaria²

nedkovivan@yahoo.co.uk

Abstract: The object of this investigation was the synergy effect achieved by combining lidar monitoring of particulate matter (PM) pollution in atmospheric aerosol over urban areas (city of Sofia) with in-situ sampling. The lidar systems of the Laser Radar Laboratory (LRL) of the IE-BAS were used to scan at two laser wavelengths the horizontal and vertical aerosol distributions and long-distance transport. The results demonstrated the possibility of detailed fast remote monitoring and analysis of the air pollution over entire urban regions, providing fast estimates of the air pollution transport over the city, as well as detection of sources of extreme emissions. Once the place of high PM concentration was localized by the lidar, samples were taken using a Hygitest 106 (Maimex) – a high-efficiency portable device for sampling and concentration determination of PM in atmospheric aerosol. The data presented pertains to the winter period 2018 year. PM pollutions than 10 and 2.5 μm were under studied. The lidar maps created can be further used for tracing the full air mass transport carrying contaminations from various pollution sources (chemical, biological, dust, etc), distributed over the scanned region. Further, the sampling schedule was conformed with the seasons of the year, in order to reveal any characteristic seasonal hazardous microbial contamination.

Keywords: lidar monitoring, particulate matter, bioaerosols, air quality

1. Introduction

Particulate matter (PM) air pollution originates from different sources and has different chemical and physical properties^{1,2}. Monitoring ambient levels of PM facilitates the planning of effective control strategies for struggle against pollution. Air quality has traditionally been monitored at the surface through ground-based monitors. These monitors are used to characterize the air quality and to determine compliance with ambient air quality standards. The combination of lidar remote sensing and ground-based PM monitoring data can form the basis of an integrated characterization of air quality³. Laser mapping data can add synoptic information and visualization to ground-based air-quality data modeling. Together, the integrated data increase the usefulness of any single dataset. However, recent research and policy emphasis on regional and intercontinental transport of air pollutants, such as fine particulate matter smaller than 10 and 2.5 μm in diameter (PM₁₀ and PM_{2.5}) has highlighted the need for additional data sources to monitor air pollution as it moves in multiple dimensions, both spatially and temporally. The combination of lidar and ground-based PM monitoring data can form the basis of an integrated characterization of air quality. These could lead to correcting for aerosol height and for meteorological effects and may improve the PM correlation sufficiently to make it useful for quantitative policy application.

The present work is part of comprehensive studies on particulate matter (PM) in atmospheric aerosol. It combines lidar monitoring over a densely populated urban area (city of Sofia, capital of Bulgaria) with on-the-spot sampling at sites with high concentration of dust products as determined by the lidar probing. The data presented pertains to the winter (February) period 2018 year.

2. Methods, instruments and procedures

The purpose of the present study was to outline by LIDAR characteristic zones of increased concentration of aerosol pollutants above the city of Sofia (Bulgaria's capital). The measurements during this pilot-study were focused on densely populated areas with high traffic density. The lidar is installed on the roof of

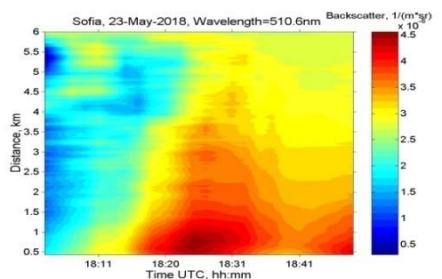
Institute of Electronics (eight kilometers from the city center), while the sampling device was placed at appr. 20 meters above traffic level (roof of WallTopia building in Technopark Sofia) at four km from city center. The altitude above sea level (ASL) of both points is 610 ± 20 m. Sofia Tech Park is located in direct proximity to Tsarigradsko Chaussee blvd. This is one of the busiest thoroughfares in Sofia city with grade-separated dual carriageway in almost its entire length of 11.4 km, running from the north-west to the south-east. The average intensity of the traffic according to Sofia Municipality is about 6000 vehicles per hour⁵.

The lidar mapping was performed by the two-wavelength lidar system developed at the Laser Radar Laboratory (LRL) of the IE-BAS that is capable of scanning the horizontal aerosol distributions and the vertical long-distance transport of air masses with a spatial resolution of 15 to 30 m and an angular resolution of $\sim 1^\circ$ at operational distances exceeding 25 km. As a laser emitter, a CuBr gaseous laser, developed in the ISSP-BAS was used. The repetition frequency is varied within the interval of 5-10 KHz at 10 ns pulse duration. The probing line wavelength is equal to 510.5 nm. The receiving system is operating in photon counting mode. The operational distances above 30 km in vertical directions have been demonstrated (25 km in horizontal plane for lidar mapping monitoring of the near surface atmosphere). The lidar receiving aperture is 19 cm. The lidar performance is fully computerized for collecting and processing of lidar data. The range resolution is typically varied within the range of 15-30 m in order to the scattering resolution volume to be exceed at least 2 times the absorbed volume by the nearby positioned aerosol sampler.

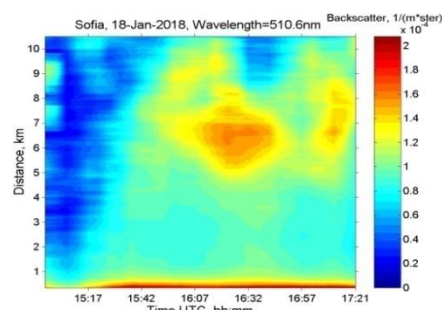
Once a place of high PM concentration was localized by the lidar, samples were taken using a Hygitest 106 (Maimex), a high-efficiency portable device for sampling and concentration determination of PM in atmospheric aerosol. The flow-rate of the aspirated air was measured by an analog unit, while the value of the sampled volume (300 m³) through the filter was digitized by means of six-bit ADC. The dust was collected on a filter (boro-silicon oxide) with #3 μm . Additionally, the material collected on the filters after three hours of aspiration during the lidar monitoring was studied by SEM.

3. Results and discussion

In the experiments presented, we directed the lidar beam along Tsarigradsko Chaussee blvd. to probe the near surface atmosphere in constant horizontal direction. The measurement time covered was practically the entire period of the afternoon traffic maximums, when maximums of the PM pollutions are clearly observed by the lidar backscattered signals, received and processed by our system. Some episodes from remotely probed lidar maps are shown in Fig.1 (a) and (b), where the time is displayed on the x-axis, while the ranges from the lidar position up to distances of 10 km with a resolution of 30 m are displayed on the y-axis.



(a)



(b)

Fig.1,a,b Lidar maps in time-range evolution of the PM aerosol field above the aerosol sampler, demonstrating the variable structures of the pollution distribution.

We will note here, that the position of the sampler can be easily defined in time by the maps in Fig.1 (a) and (b). It is evident, that applying the above combined measuring schematic on can precisely characterize the parameters (incl. coordinates) of the pollution field. Moreover, the acquired data could be directly sent to the city monitoring system. It must be noted, the aerosol mass concentration can be estimated here by the calibrated lidar return signal as well. To this purpose we extracted the extinction coefficient in the lidar equation to calibrate it in mass concentration Fig.2. We calculated also the backscattering coefficient using the well known procedure by the lidar equation, assuming for the lidar ratio the typical value of $R_{lid} = 50$. In both cases we found the linear dependences of the both coefficients on the mass concentration, measured by the aerosol sampling instrument.

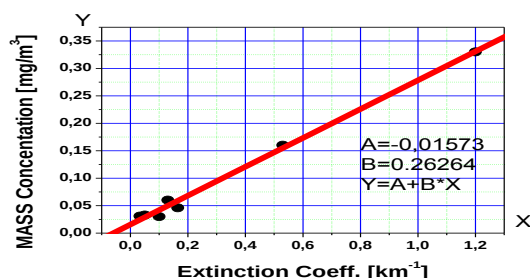


Fig.2 LIDAR calibration curve in mass concentration as a function of the light extinction coefficient.

Lidar maps in Fig.1 can be further combined with geographical city maps as shown in Fig.3. Here, the lidar map (as in Fig.1) is positioned (x-axis) perpendicularly to the Google Sofia City map. The Y-axis is arranged to follow the sensed traffic direction. As evident, one could determine the aerosol field distribution in each range from the Sofia LIDAR Station as well as in each moment (time resolution 5min) during the entire measuring time. Thus, these results demonstrate the possibility of a detailed fast remote analysis and control of the air pollution over large urban regions, providing fast estimates of the air pollutions transport over the city as well as determination of pollution sources location.

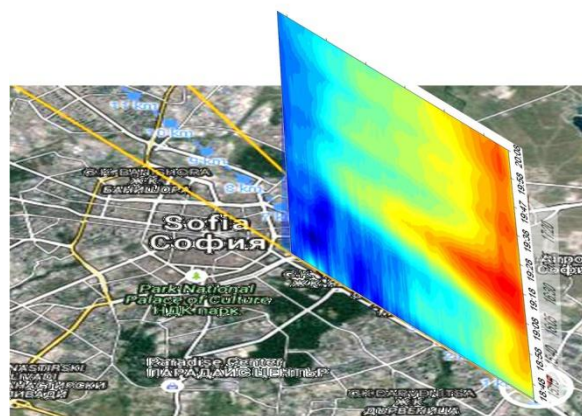
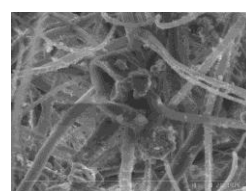
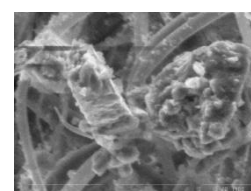


Fig. 3 Color-coded LIDAR sector maps over a region of Sofia with high degree of pollution during rush hours (heavy traffic).

Fig. 3 demonstrates the possibility of a fast detailed remote analysis and monitoring of the air pollution over large urban regions, providing fast estimates of the air pollutions transport over the city, as well as determination of pollution sources location. Once a place of high PM concentration was localized by the lidar, samples were taken using a Hygitest 106 (Maimex).



(a)



(b)

Fig. 4a) PM with size $\geq 3 \mu m$, the fibers reveal the filter structure and **b)** PM with size between $0.2 \mu m - 3 \mu m$ where filter structure is as a green cheese.

The SEM images of the material collected on the filters after three hours of aspiration during the lidar monitoring showed a large amount of particles larger than $2.5 \mu m$ and a very limited amount of small particles (under $2.5 \mu m$). Fig.4 (a) illustrates the wide variety of quasi spherical particles with an average size $\geq 2.5 \mu m$. Fig.4 (b) shows a typical shape of dust particles with sizes between $2.5 - 10 \mu m$, which are of hybrid origin. The airborne PM can be divided into two classes, fine PM (particles $2.5 \mu m$ in diameter or smaller) and coarse PM (particles $2.5 \mu m$ to $10 \mu m$ in diameter), which differ not only in size, but also in source, chemical composition, physical properties, and formation process². Major sources of PM_{2.5} are fossil fuel combustion by industry, motor vehicles, residential fireplaces and wood stoves; vegetation burning; and smelting or other processing⁴. Examples of natural bioaerosols suspended as PM_{2.5} include bacteria, viruses, and endotoxins. Fugitive dust constitutes about 90 % of the estimated coarse PM according to Fröhlich-Nowoisky⁶. Fungal spores, pollen, and plant

and insect fragments are examples of natural bioaerosols suspended as coarse PM⁶.

The aerodynamic diameters of the PMs varied from tens of nanometers to a more than 10 micrometers for pollen or plant debris^{7,8,9}. After selecting typical particle images based on ten points on the filter's surface, the percentage distribution of the particles with different size was obtained: over 10 µm, from 2.5 µm up to 10 µm and less than 2.5 µm. (Fig.5).

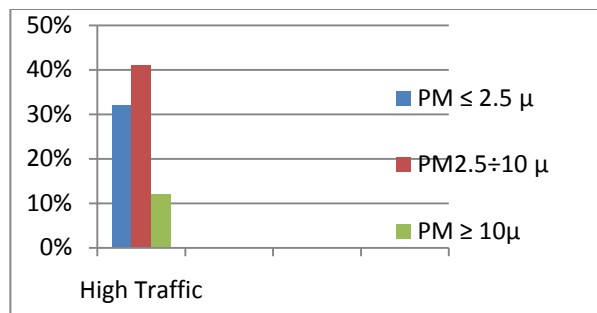


Fig. 5 Particles size distribution - Heavy traffic PM concentration over the Tsarigradsko Chaussee, Sofia.

During this pilot-study, a methodology was developed for mass concentration estimation. The average mass concentration of PM during February was 0.09 ± 0.07 mg/m³. The collected dust material was subjected also to microbiological investigation, applying a standard procedure for isolation of pure microbial cultures. The bacterial and fungal isolates obtained were identified on the basis of morphological, physiological and biochemical characteristics. A molecular approach, including the amplification of 16S rDNA, resp. 18S rDNA for fungal isolates, was also used. The microbiological survey of the atmosphere of the densely populated part of Sofia city indicated that the collected particulate matter harbors a variety of different viable microorganisms. The majority of the bacterial isolates was presented by predominantly saprophytic pigmented bacteria, mainly from the genera *Micrococcus* (66%). The genus *Bacillus* was also abundant, presented by representatives of the species *B. pumilus*, *B. cereus*, *B. thuringensis* and *B. cereus*. One isolate was determined as *Staphylococcus equorum*. The fungal presence was expressed mainly by the genera *Penicillium* and *Aspergillus*. Two of the isolated were related to the genera *Cladosporium* and *Symmetrospora*. Fig.6 illustrates the origin of the organic pollutions absorbed on the particles.

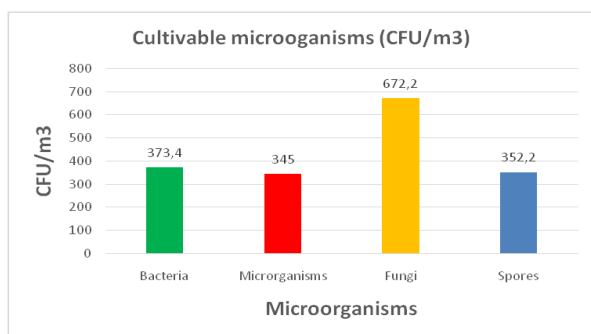


Fig. 6 Number of microorganisms (CFU/cm3) detected at the heavy traffic sampling point: heterotrophic aerobic **Bacteria**; oligotrophic **Microorganisms**; Fungi; **Spore**-forming bacteria

4. Conclusions

The synergy arising from combining the lidar monitoring with a set of different *in-situ* sampling represents an effective first step toward the creation of highly informative near-real time monitoring system for a complex analysis of the air quality. This investigation shows that the surface of the micron-sized particles can adsorb both mechanical and microbial contaminants, while the liquid envelope, when the PM is dispersed as aerosols, may preserve this nano-world and, in some cases, create conditions favoring the occurrence of chemical and bio-processes. The lidar maps constructed can be further used for tracing the full air mass transport, carrying contamination from a number of pollution sources (chemical, biological, dust, etc), distributed over the scanned region. Further, the sampling schedule was so chosen as to reveal any characteristic seasonal hazardous microbial contamination.

Acknowledgments:

This work was financed in part by contract DN18/26 with the National Science Fund, Bulgaria, and included in the European Program of the COST Action CA16202.

References:

- [1] S. Fuzzi et al., Particulate matter, air quality and climate: lessons learned and future needs, *Atmos. Chem. Phys.*, 15, 8217–8299, 2015
- [2] L.Raisi, M. Lazaridis, E. Katsivela, Relationship between airborne microbial and particulate matter concentrations in the ambient air at a mediterranean site, *Global NEST Journal*, Vol 12, No 1, pp 84-91, 2010
- [3] Mazzoleni, C. Monitoring automotive particulate matter emissions with LiDAR: a review. *Remote Sensing*, 2 (4), 2010, 1077-1119.
- [4] World Health Organization 2013, Health effects of particulate matter (ISBN 978 92 890 0001 7)
- [5] E. Stoineva, Emissions and air quality, Conference Air Quality and urban area in Sofia, 16 april 2015, Sofia
- [6] Fröhlich-Nowoisky, Janine, et al. "High diversity of fungi in air particulate matter." *Proceedings of the National Academy of Sciences* 106.31, 2009, 12814-12819.
- [7] Jaenicke, R. Abundance of cellular material and proteins in the atmosphere. *Science*, 308 (5718), 2005, 73-73.
- [8] Hinds, W.C. Aerosol Technology: Properties. Behavior, and Measurement of airborne Particles (2nd. 1999)
- [9] Pöschl, U. Atmospheric aerosols: composition, transformation, climate and health effects. *Angewandte Chemie International Edition*, 44(46), 2005, 7520-7540.

NON-EQUILIBRIUM THERMODYNAMIC MODEL OF THE AUSTENITIC NON-DIFFUSION TRANSFORMATION IN IRON-BASED ALLOYS

Dr.Sc. Bobyr S.V.

Department of Metals Heat Treatment For Machines Building

Iron and Steel Institute of Z.I. Nekrasov, National Academy of Sciences of Ukraine, Ukraine

E-mail: svbobyr07@gmail.com

Abstract/Резюме: A non-equilibrium thermodynamic model of the austenite non-diffusion transformation in iron and alloys based on it is developed, taking into account internal stresses in the system. Onsager motion equations are found for a model thermodynamic system describing a non-diffusion transformation and kinetic equations for changing deformations and growth rates of the α -phase. A scheme of austenitic non-diffusion transformations is constructed, including normal and martensitic transformations, as limiting cases.

KEYWORDS: NONEQUILIBRIUM THERMODYNAMICS, NON-DIFFUSION TRANSFORMATION, AUSTENITE, ONSAGER MOTION EQUATIONS, GROWTH RATES OF THE α -PHASE, IRON-BASED ALLOYS

1. Introduction / Введение

The study of phase transformations is one of the most important problems in the physics of metals [1-3]. Phase transformations are divided into diffusion and non-diffusion [1]. If the kinetics of phase transformation in steels and cast irons is determined by the diffusion of carbon, this allows them to be attributed to conversions controlled by diffusion [1-4].

Such transformations in iron-carbon alloys include pearlitic transformation of austenite, and transformations occurring during tempering, graphitization of undoped cementite, separation of carbides in alloyed steels, and others [4-6].

When the rate of transformation of austenite is determined by the rate at which the interface separates, differing only in its crystalline structure, the transformation is called non-diffusion [1]. Kinetically, the normal polymorphic and martensitic transformations of austenite are distinguished. When the temperature of the normal transformation decreases, its velocity first increases, and then decreases. The kinetics of the martensitic transformation is characterized by a very high rate of growth of individual crystals and the maximum space velocity at the initial moment of transformation under isothermal conditions.

In addition to martensite, at least two other structural components are known, which are formed with a shear ("martensitic") morphology of crystal formation - ferrite side-plates (widmanstätten) and acicular ferrite. They can also be attributed, with some simplifying assumptions, to the products of the non-diffusion transformation of austenite. In addition, in some alloys martensitic and normal transformations occur at the same temperature [1]. The consistent theory of non-diffusion transformations should explain this phenomenon.

The purpose of this paper is to analyze the non-diffusion transformation of austenite based on the positions of nonequilibrium thermodynamics, taking into account the influence of internal stresses and finding the main kinetic parameters of the process.

2. Equations of motion and model parameters/ Уравнения движения и параметры модели

Martensite is the basis of hardened steel, so studying the mechanism and kinetics of its transformation is still of extreme interest for the theory and practice of heat treatment.

In the works of G.V. Kurdymov and co-workers, the martensitic transformation is considered as the usual phase transformation in a one-component system, further complicated by the influence of a strong interatomic interaction, which leads to the development of significant stresses in the martensite crystal and matrix [5].

In accordance with the alternative mechanism, the martensitic transformation takes place by means of an instantaneous shift of atomic planes that does not require thermal activation and is

not associated with thermodynamic transformation stimuli [1, 6]. In this case, the stress initiating the transformation is believed to be the stresses arising from the sharp cooling of the sample (quenching) [6].

Considering the martensitic transformation as a thermally activated process, B.Ya. Lyubov used the equations of normal transformation obtained on the basis of the positions of nonequilibrium thermodynamics to describe his kinetics [3].

Changes in a complex or composite system under constant external conditions can be described as the process of increasing entropy. The rate of increase of entropy σ can be represented as the sum of the flux products and the corresponding forces for all transfer substrates in an amount of N [10-13]:

$$\sigma = (dS/dt)_{\text{irrev}} = \sum_{k=1}^N J_k X_k \quad (k=1, \dots, N), \quad (1)$$

In the general case, the flows can be represented in the form [11, 12]:

$$J_i = \sum_{k=1}^N L_{ik} X_k \quad (i, k=1, \dots, N), \quad (2)$$

The irreversible change in the entropy dS_{irrev} is equal to the sum of entropy changes in the system and the environment:

$$dS_{\text{irrev}} = dS + dS_e \quad (3)$$

Under isothermal conditions, when the released heat is absorbed by the environment and the temperature remains constant:

$$dS_e = -dQ/T, \quad dQ = dU + PdV. \quad (4)$$

Since $dU + PdV - TdS = dG$, and if we take into account the low compressibility of bodies in the condensed state and relatively small pressures, then

$$(dS/dt)_{\text{irrev}} = -T^{-1}dG/dt \approx -T^{-1}dF/dt, \quad (5)$$

where F is the free energy of the system.

The change in free energy in a system with a variable number of particles and internal stresses can be represented in the form [3, p.142]:

$$dF = dF_e + dF_n = \sigma_{ik}d\epsilon_{ik} + \phi_l dn_l \quad (6)$$

where dF_e is the change in free energy in the system related to internal stresses; dF_n is the change in the free energy in the system, determined by the variable number of particles of type l ; σ_{ik} is the stress tensor; ϵ_{ik} is the strain tensor of the system; ϕ_l is the chemical potential of the l th element of the system; n_l is the number of particles of the l th element of the system per unit volume, $l = 1, N$.

We now introduce some simplifying assumptions. First, for the non-diffusion transformation of austenite, only one kind of particles, the α -phase of iron n_α , will be taken into account. Approximately this is also true for alloys of iron with close elements (nickel, chromium, cobalt). Of course, ϕ is some effective (averaged) chemical potential of the atoms of the alloy.

Secondly, we assume that the deformation of the system is a triaxial compression-expansion, and in the expression for dF_e only the diagonal components of stress and strain tensors are taken into account:

$$\sigma_{ik} = \epsilon_{ik} = 0, \quad i \neq k. \quad \sigma_{ii} = \sigma, \quad \epsilon_{ii} = \epsilon. \quad (7)$$

The change in internal energy can then be represented as:

$$dF = 3\sigma d\varepsilon + \varphi dn_{\alpha}, \quad (8)$$

but the change in entropy:

$$(dS/dt)_{\text{irrev}} = -T^{-1}(3\sigma d\varepsilon/dt + \varphi dn_{\alpha}/dt). \quad (9)$$

Thus, in our system, in addition to the particle flow from the γ phase to the α -phase of $J_1 = dn_{\alpha}/dt$, we will also take into account the change in the strain of the sample with time $J_2 = d\varepsilon/dt$. These flows are related to the driving forces by the equation (2).

If, as charges of the process of non-diffusion transformation of austenite, two quantities-the concentration of α -phase particles and the strain value, then, according to (1), the equations of motion take the form:

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (10.1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \quad (10.2)$$

where $X_1 = \Delta\varphi$ - the thermodynamic force for iron - the change in the chemical potential at the transition of particles from the γ -phase to the α -phase, $X_2 = \Delta\sigma$ - the change in the internal stress during the transition from the γ -phase to the α -phase.

The system of equations (42) describes the contribution of stresses and deformations to the non-diffusion transformation of austenite. However, we do not yet know the coefficients of the equations in it.

We now find expressions for the coefficients of the system of equations (42).

The coefficient L_{11} characterizes the normal transformation:

$$J_1 = dn_{\alpha}/dt = L_{11}(\varphi_{\gamma} - \varphi_{\alpha}). \quad (11)$$

In the normal kinetics of the phase transformation, the formation of the center (particle) of the α -phase occurs through separate (independent) acts of detachment of particles from the γ -phase and the attachment of atoms to the ferrite center. If we consider the process of formation of an α -phase close to the process of self-diffusion of iron in the γ -phase, then the coefficient L_{11} has the form [12]:

$$L_{11} = D_{\gamma}/RT, \quad (12)$$

where D_{γ} is the self-diffusion coefficient of iron in the γ -phase (or the effective coefficient of self-diffusion in the γ -phase of the alloy),

T is the transformation temperature,

R is the gas constant [16].

The self-diffusion coefficient of iron is taken in the usual notation [17]:

$$D_{\gamma} = D_0 e^{-\frac{U}{kT}} = 4,58 \cdot 10^{-4} \exp(-2,52 \cdot 10^5/RT), \quad (13)$$

D_0 is a multiplier;

U is the activation energy of diffusion;

The coefficient L_{22} characterizes the direct relationship:

$$J_2 = d\varepsilon_{\alpha}/dt = L_{22}(\sigma_{\gamma} - \sigma_{\alpha}). \quad (14)$$

where σ_{α} is the ν stress in the α phase, σ_{γ} is the stress in the γ phase. Let $\sigma_{\gamma} = 0$. Let us take into account that for triaxial compression-stretching [28]:

$$\sigma_{\alpha} = \frac{E}{3(1-2\mu)} \frac{\Delta V}{V} = \frac{E}{1-2\mu} \varepsilon_{\alpha}, \quad (15)$$

where E is the modulus of elasticity of steel ($\sim 2,17 \cdot 10^5$ MPa), μ is the Poisson ratio (~ 0.26).

Then expression (14) can be transformed as follows:

$$d\varepsilon_{\alpha}/dt = L_{22}\sigma_{\alpha} = L_{22} \frac{E}{1-2\mu} \varepsilon_{\alpha} = \frac{\nu}{L} \varepsilon_{\alpha}, \quad (16)$$

where the following values are entered: ν is the propagation velocity of the microdeformation in sample (~ 1000 m/s) [3];

L is the characteristic distance over which the microdeformation of the shear is propagated (the size of the martensitic strips or plates). At the initial stage of the formation of the shear structure, it has a magnitude of the order of the diameter of the austenite grain (~ 100 μm), and then decreases with decreasing temperature [1]. From equation (48) we find that the coefficient L_{22} is equal to:

$$L_{22} = \frac{\nu(1-2\mu)}{LE}. \quad (17)$$

The cross-coefficients $L_{12} = L_{21}$ for a nonequilibrium thermodynamic system are found with sufficient accuracy by the formulas proposed in [5]:

$$L_{12} = \sqrt{L_{11}L_{22}} = \sqrt{\frac{D_{\gamma}}{RT} \frac{\nu(1-2\mu)}{LE}} \quad (18)$$

Thus, we obtained simple differential equations for a nonequilibrium thermodynamic system describing the non-diffusion transformation of austenite taking into account the influence of internal stresses.

Let us write the equations of motion of our system in the form:

$$dn_{\alpha}/dt = L_{11}\Delta\varphi + L_{12}\sigma_{\gamma} - L_{12}\sigma_{\alpha}, \quad (19.1)$$

$$d\varepsilon_{\alpha}/dt = L_{21}\Delta\varphi + L_{22}\sigma_{\gamma} - L_{22}\sigma_{\alpha}. \quad (19.2)$$

We first transform equation (19.2) taking into account expression (16). We have:

$$d\varepsilon_{\alpha}/dt + \nu\varepsilon_{\alpha}/L = L_{21}\Delta\varphi + L_{22}\sigma_{\gamma}, \quad (20)$$

where ε_{α} is the magnitude of deformations of the α -phase. The differential equation (20) with constant coefficients (temperature) has a solution:

$$\varepsilon_{\alpha} = \frac{(L_{21}\Delta\varphi + L_{22}\sigma_{\gamma})(1-2\mu)}{L_{22}E} (1 - e^{-\frac{\nu}{L}t}). \quad (21)$$

This kinetic equation describes the change in the magnitude of the deformation of the α -phase in time. At $t = 0$, $\varepsilon_{\alpha} = 0$. When the time is counted, a fast ($\sim 10^{-6}$ s) process of transition to deformation occurs:

$$\varepsilon_{\alpha} = \varepsilon_{\gamma} + \Delta\varepsilon_{\alpha} = \varepsilon_{\gamma} + \frac{L_{21}\Delta\varphi(1-2\mu)}{L_{22}E}. \quad (22)$$

Equation (22) shows that the residual deformation of the α -phase after the transient process consists of the deformation of the austenite ε_{γ} and the additional deformation $\Delta\varepsilon_{\alpha}$. This additional deformation determines the change in the volume of the sample as $\gamma \rightarrow \alpha$ -transformation:

$$\Delta V_{\text{sam}}/V_{\text{sam}} = 3n_{\alpha}\Delta\varepsilon_{\alpha}. \quad (23)$$

Then substituting expression (21) into equation (19.1), we find:

$$dn_{\alpha}/dt = L_{11}\Delta\varphi + L_{12}\sigma_{\gamma} - \frac{L_{12}(L_{21}\Delta\varphi + L_{22}\sigma_{\gamma})}{L_{22}} (1 - e^{-\frac{\nu}{L}t}) = L_{11}\Delta\varphi + L_{12}\sigma_{\gamma} - (L_{11}\Delta\varphi + L_{12}\sigma_{\gamma})(1 - e^{-\frac{\nu}{L}t}) = (L_{11}\Delta\varphi + L_{12}\sigma_{\gamma})e^{-\frac{\nu}{L}t}. \quad (24)$$

It can be concluded from expression (24) that the growth rate of α -phase particles depends on the stresses in the γ -phase. The greater the value of tensile stresses in the γ phase, the higher the growth rate of ferrite particles. The rate of growth of the α -phase particles at a constant temperature very rapidly (exponentially) decreases in time, determining the incompleteness of the transformation.

Integration of equation (24) with time-independent coefficients L_{11} and L_{12} allows us to obtain the kinetic equation for n_{α} :

$$n_{\alpha} = \frac{(L_{11}\Delta\varphi + L_{12}\sigma_{\gamma})L}{\nu} (1 - e^{-\frac{\nu}{L}t}). \quad (25)$$

In accordance with equation (25), the amount of α -phase formed depends not only on the thermodynamic force $\Delta\varphi$, but also on the magnitude of the stresses in the γ -phase.

3. Scheme of the non-diffusion transformation of austenite / Схема бездиффузионного превращения аустенита

Before discussing the equations obtained, we introduce some more useful relations characterizing the $\gamma \rightarrow \alpha$ transformation.

With the $\gamma \rightarrow \alpha$ transformation, the effective atomic volume of the iron lattice changes in the sample under

consideration, characterized by $\Delta V_{\gamma \rightarrow \alpha}$ and the relative volume change $\Delta V_{\gamma \rightarrow \alpha} / V_{\gamma}$.

According to the data of [3]:

$$\Delta V_{\gamma \rightarrow \alpha} = 0,268 - 1,62 \cdot 10^{-4} T, \text{ sm}^3/\text{mol}. \quad (26)$$

We will assume that with the formation of the α -phase, the relative change in volume is determined by the additional deformation: $\Delta V_{\gamma \rightarrow \alpha} / V_{\gamma} = 3\Delta\epsilon_{\alpha}$, and the compressive stress arising in the α -phase has the value

$$\sigma_{\alpha} = \frac{E}{1-2\mu} \Delta\epsilon_{\alpha}. \quad (27)$$

When the alloy sample is cooled by ΔT , a deformation occurs in its surface layer: $\epsilon_{\gamma} \sim \alpha \Delta T$ and the tensile stress σ_{γ} corresponding to this deformation:

$$\sigma_{\gamma} = \frac{E}{1-2\mu} \alpha \Delta T. \quad (28)$$

Comparing the values of thermodynamic forces among themselves, it is possible to classify the types of non-diffusion transformation according to the kinetic criterion. As shown in [1, p. 208], for small deviations of the system from equilibrium, the growth of crystals is more likely, controlled by self-diffusion, at large - cooperative growth. The same phase transition in a single-component system under different external conditions can take place with an independent (or slightly dependent) temperature growth rate (martensitic kinetics) and with a rate that exponentially depends on the temperature at an activation energy close to the activation energy of self-diffusion (normal kinetics).

The parameter characterizing the deviation of the system from equilibrium is the supercooling of the alloy $\Delta T = A c_3 - T$, where $A c_3$ is the temperature of the end $\alpha \rightarrow \gamma$ of the conversion upon heating, and T is the transformation temperature. The transformation scheme for the constructed model is shown in Fig. 1

$A c_3$	
$L_{11}\Delta\phi > L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}$, normal transformation, polygonal ferrite	
$A c_1$	$L_{11}\Delta\phi \sim L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}$, shear + normal transformation, ferrite side-plates
Mni	$L_{11}\Delta\phi < L_{12}\sigma_{\alpha}$, $\sigma_{\alpha} = \sigma_{\gamma}$
Mna	$L_{11}\Delta\phi < L_{12}\sigma_{\alpha}$, $\sigma_{\alpha} < \sigma_{\gamma}$, shear transformation isothermal martensite, acicular ferrite
Mk	$L_{11}\Delta\phi \ll L_{12}\sigma_{\gamma}$, shear transformation athermal martensite

Fig. 1. Scheme of non-diffusion transformations from the constructed model. $A c_1$ is the temperature of the beginning of $\alpha \rightarrow \gamma$ transformation when the alloy is heated; Mni is the temperature of the onset of the formation of isothermal martensite upon supercooling of the alloy. Mn is the temperature of the onset of athermal martensite formation upon supercooling of the alloy. Mk is the temperature of the end of martensite formation upon supercooling of the alloy.

Thus, for small ΔT :

$$L_{11}\Delta\phi > L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}, \quad (29.1)$$

then the growth of α -phase crystals is determined by self-diffusion by the normal mechanism. However, as follows from equation (19), in this case too, the contribution of deformations (and stresses) to the conversion kinetics is very significant. In order that the condition (29.1) is satisfied, it is necessary that the stress level in the γ - and α -phases be small; for the α -phase this is possible only in the case of relaxation of internal stresses in the alloy at high temperature by the mechanism of recrystallization.

With increasing supercooling of the alloy, the thermodynamic stimulus and the rate of normal transformation increase.

For a larger ΔT :

$$L_{11}\Delta\phi \sim L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}, \quad (29.2)$$

The existing thermal stresses in the γ -phase (28) contribute to the formation of the α -phase by the shear mechanism; the stresses arising in the α -phase compensate thermal stresses in the γ -phase. With a certain amount of α -phase, the stress equals $\sigma_{\alpha} = \sigma_{\gamma}$ arises and the further formation of the α -phase occurs according to the normal mechanism with the relaxation of the arising stresses by recrystallization. Consequently, the condition (29.2) corresponds to the transformation of the γ -phase by a mixed mechanism, and also to the formation of a ferrite side-plates (widmanstätten), followed by the release of the α -phase by the normal mechanism [1].

With a certain supercooling of ΔT_i , stress compensation occurs only when the γ -phase is completely transformed into ferrite by a shearing mechanism. In this case:

$$L_{11}\Delta\phi \sim L_{12}\sigma_{\alpha}, \sigma_{\alpha} = \sigma_{\gamma}, \quad (29.3)$$

The temperature corresponding to this supercooling is the starting point for the formation of the isothermal martensite $M_{H^{u3}}$ (on Fig. 2). Below the point Mni, the formation of the α -phase occurs by a shearing mechanism; However, the normal component of the process still has a significant value, affecting the morphology of the resulting precipitates.

When supercooling a greater ΔT_i :

$$L_{11}\Delta\phi < L_{12}\sigma_{\alpha}, \sigma_{\alpha} < \sigma_{\gamma}, \quad (29.4)$$

At temperatures below Mni, isothermal martensite or acicular ferrite is formed with a "reticular" or acicular morphology of precipitates.

Finally, for large ΔT below Mna ($M_{H^{am}}$ on Fig. 2):

$$L_{11}\Delta\phi \ll L_{12}\sigma_{\gamma}, \quad (29.5)$$

Inequality (29.5) determines the condition for the formation of "athermal" martensite, when the normal component does not affect the formation of the shear structure. The main effect on the rate of the $\gamma \rightarrow \alpha$ transformation, in accordance with expression (24), is due to thermal stresses in the γ phase.

The temperature region for the formation of this structural component for real alloys is also shown in Fig. 2.

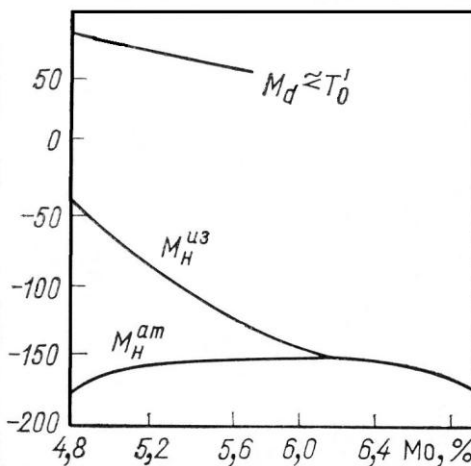


Fig. 2. Temperature regions of the athermal $M_{H^{am}}$ and isothermal $M_{H^{u3}}$ kinetics of the formation of martensite in Fe-24.5%Ni-Mo alloys with different Mo content [1].

In order that the transformation of austenite into martensite occurs with a temperature-independent growth rate of the α -phase, it must be assumed that the coefficient L_{12} is practically independent of temperature; this is possible under the following conditions:

$$D_{\gamma} / (TL) = \text{const}. \quad (30)$$

We will perform some estimated calculations. Assume that at $T_0 = 400^\circ \text{C} \approx 673^\circ \text{K}$, the size of the martensite plates is $L_0 = 100 \mu\text{m}$. Substitution of the values of L_0 and T_0 in (30) makes it possible to obtain an equivalent dependence of the martensite plate size on the temperature (Fig. 3). At 580°K , the length of the martensitic plates corresponding to the condition (30) is only $0.084 \mu\text{m}$.

Consequently, with a further decrease in temperature, the formation of martensite will occur with a decrease in the rate of

the $\gamma \rightarrow \alpha$ transformation (but not the rate of shear deformation), since the contribution of the diffusion component to the L_{12} coefficient is very significant. The rate of martensitic transformation in this case is many orders of magnitude greater than the rate of normal transformation.

As the direct calculations show, with the indicated parameters: $L_{11} = 4,3 \cdot 10^{-29}$; $L_{22} = 18,4$; $L_{12} = 0,89 \cdot 10^{-14}$. The rate of martensitic transformation at $T_0 = 400^\circ \text{C}$ is approximately 10^{14} times greater than the rate of the normal (self-diffusion) transformation component.

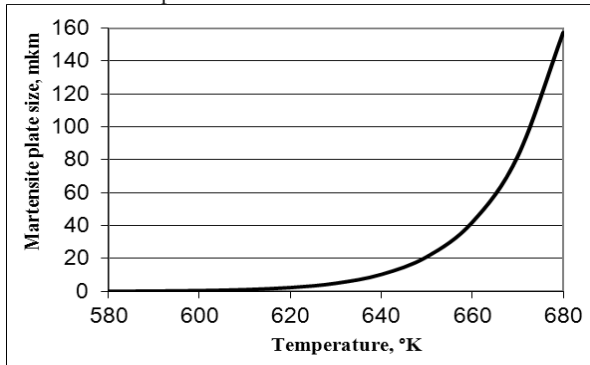


Fig. 3. The calculated equivalent dependence of the martensite plate size on temperature

The temperature at which the rate of martensite formation begins to decrease can characterize the temperature of the end of martensite formation M_k , if the amount of the residual γ phase is small (less than 1.0%).

Reduction in the rate of martensite formation at low temperatures should be taken into account in cryogenic technologies for increasing the wear resistance of steels and alloys.

Thus, the constructed model of the non-diffusion austenite transformations allows us to consider the normal and martensitic transformations, as limiting cases.

CONCLUSIONS

1. The application of nonequilibrium thermodynamics to the analysis of the non-diffusion transformation of austenite made it possible to obtain a system of equations for the thermodynamic system and to generalize the results obtained earlier by B.Ya.Lyubov the equations for a normal transformation.
2. The theoretical expression for the growth rate of the α -phase, obtained in this paper, takes into account the influence of stresses on the process of austenite transformation. It is shown that the rate

of growth of α -phase particles at a constant temperature very rapidly (exponentially) decreases in time, determining the incompleteness of the transformation.

3. According to the constructed model, a scheme of non-diffusion austenite transformations was developed, including normal and martensitic transformations, as limiting cases.

REFERENCES

1. Ya.S. Umanskiy, Yu.A. Skakov, Fizika metallov (M.: Atomizdat, 1978).
2. G.V. Kurdyumov, L.M. Utevskiy, R.I. Entin, Prevrasheniya v zheleze i stali (M.: Nauka: 1977).
3. B.Ya.Lyubov, Kineticheskaya teoriya fazovykh prevrascheniy (M.: Metallurgiya: 1969).
4. S.V. Bobyr, V.I. Bolshakov, Uspehi fiziki metallov, T.15:123(2014).
5. G.V. Kurdyumov, Yavleniya zakalki i otpuska stali (M.: Metallurgizdat, 1960).
6. S.P. Oshkaderov, Uspehi fiziki metallov, T.12:269(2011).
7. V.A. Lobodyuk, Uspehi fiziki metallov, T.15:173(2014).
8. A.N. Lihachev, Yu.N. Koval, Uspehi fiziki metallov, T.16:1(2015).
9. V.A. Lobodyuk, Uspehi fiziki metallov, T.17:89 (2016).
10. L. Onsager. Phase Transformation in Solid. Conference (Cornwell: N.Y.C.: 1951).
11. I. Prigozhin, Vvedenie v termodinamiku neobratimyykh protsessov (Moskva: IL:1960).
12. S. de Groot, P. Mazur. Neravnovesnaya termodinamika (Moskva: Mir, 1964).
13. L. Onsager. Phys. Rev., 37: 405 (1931).
14. A.A. Snezhnoy, R.L. Zhukov, Diffuzionnyye protsessy v metallakh (K.: Naukova dumka, 1966).
15. M.A. Krishtal, Termodinamika, fizicheskaya kinetika, strukturoobrazovanie i svoystva chuguna i stali. Vyip. 4 (M.: Metallurgiya, 1971).
16. K. Dzh. Smitlz. Metallyi: Sprav. izd. (Moskva: Metallurgiya, 1980).
17. D.F. Kalinovich, I.I. Kovenskiy, M.D. Smolin. Ukrayinskiy fizichniy zhurnal, T.14, 2:515(1969).
18. M.V. Belous, M.P. Braun, Fizika metallov (K.: Vischa shkola, 1985).
19. S.V. Bobyr, Metallofizika i noveyshie tehnologii, T.36:1385(2014).

MICROSTRUCTURE AND PHASE TRANSFORMATIONS OF Cu-BASED SHAPE MEMORY ALLOYS

Assoc. prof. Tamara Holjevac Grgurić^{1*}, Prof. Dr Dragan Manasijević², Assistant prof. Ljubiša Balanović², Prof. Dr Duško Minić³, Assoc. prof. Stjepan Kožuh¹, Ivana Ivanić, PhD¹, Prof. Dr Mirko Gojić¹

University of Zagreb Faculty of Metallurgy, Croatia¹
University of Belgrade, Technical Faculty Bor, Serbia²
University of Pristina, Faculty of Technical Sciences, Kosovo³

tholjev@simet.hr

Abstract:

Cu-based shape memory alloys are increasingly used instead of nitinol alloys, due to their low price, good shape memory effect and superelasticity. In this work, Cu-Al-Mn alloys with different content of aluminium were investigated. Alloys were melted in the electric-arc furnace and casted in the cylindrical moulds as well as continuous casted. Microstructure of prepared samples was followed by scanning electron microscopy and phase transformations were determined by DSC analysis.

KEYWORDS: SHAPE MEMORY ALLOYS, CU-AL-MN ALLOYS, MICROSTRUCTURE, DSC ANALYSIS

Introduction:

Shape memory alloys (SMA) are smart, functional materials which have ability to memorize or recover to its original shape, under thermal changes or plastic deformation as well as magnetic variations [1-3]. Properties such as shape memory effect, superelasticity, good mechanical properties and damping properties makes them very interesting for a wide range of applications, as bioengineering, automotive and aircraft industry as well as electro-industry. Cu-based shape memory alloys recently more often replace the most important commercial SMA alloy, nitinol, due to easier production, low cost and good mechanical and electric properties. Addition of manganese to binary Cu-Al alloy significantly increases ductility and cold-workability of material, so Cu-Al-Mn ternary shape memory alloy has become a more significant commercial Cu-based SMA alloy than well-known Cu-Al-Zn and Cu-Al-Ni alloys [4]. Further addition of micro-alloying element to ternary Cu-Al-Mn alloy can influence on phase transformation temperatures, microstructure, grain size, shape memory effect (SE) and final properties. SE effect is a consequence of diffusionless martensitic transformation between high-temperature austenitic and low-temperature martensitic phase in material. Martensitic phase is metastable phase, formed under fast cooling or quenching in water, that can exists as 2M or 6M crystal structure.

Prerequisites and means for solving the problem:

The main aim of paper was investigate processing route for preparation of Cu-Al-Mn alloy with shape memory properties, by electric-arc furnace and continuous casting. Further, comparison of experimental results for transformation temperatures of Cu-Al-Mn alloys with different Al content, with calculated values by TCW5.

Materials and Methods:

Cu-Al-Mn ternary alloys were prepared by melting of pure metals of copper, with purity 99.9 %, aluminium, purity 99.5 % and manganese, purity 99.8 %. Cu-Al-Mn alloys with 9 wt.% of Mn and 1, 7, 8 and 11 wt.% of Al were prepared. Samples were melted in the electric-arc furnace under argon atmosphere, with current of 112 A. Furnace was vacuumed for 2 times during 15 minutes before each melting. Specimens were re-melted for 5 x due to better homogenization of material. Then, sample were casted in the

cylindrical mould with dimensions: diameter = 8 mm and length of 12 mm. Continuous casting of Cu-Al-Mn alloy was performed by melting of pure metals in the vacuum induction furnace at the temperature of 1250°C and casting of $\phi=8$ mm rod, with casting speed of 290 mm/min.

Further, samples were aged at 300 °C for 14 days for thermodynamic measurements. SMA compositions of Cu-Al-Mn alloys were heat-treated at 900 °C and quenched in the water. Cu-Al-Mn samples were prepared for microstructural investigations by inserting into the conductive paste by Automatic Mounting Press Buehler SimpliMet 1000. Grinding was performed by Buehler machine, with water-cooled SiC papers from 240 till 1200 grit, at force of 5 N and speed 150 rpm/min. Polishing of all specimens was done by microfiber felt with diluted alumina solution, at same force and speed. Specimens were then etched with solution of 2,5 g FeCl₃/48 mL CH₃OH/10mL H₂O.

Microstructure of as-cast and heat-treated samples were determined by optical microscopy at Olympus GX 71s with digital camera DP70 and software for automatically imaging processing AnalySIS Materials Research Lab, Japan. Scanning electron microscopy was performed by Tescan Vega TS 5136 MM, equipped with EDS Bruker. Differential scanning calorimetry was conducted by NETSCH STA Jupiter 449. Dynamic measurements were done in 2 heating/cooling cycles, in temperature range from 25 °C till 1250 °C, with heating/cooling rate 10 K/min in the inert atmosphere. Transitions at lower temperatures were determined by MDSC Mettler-Toledo 822e, in temperature range from -50°C till 250 °C.

Results and discussion:

Phase diagram calculation of Cu-Al-Mn system under equilibrium conditions was performed by software Thermo-Calc 5, based on the CALPHAD method and minimisation of free Gibbs energy for all phases and components in ternary system. Thermodynamic database was prepared with thermodynamic parameters for pure elements taken from SGTE database, parameters for binary sub-systems Cu-Al, Al-Mn and Cu-Mn as well as optimized parameters for ternary Cu-Al-Mn system, for Cu-rich corner, according to Miettinen [5].

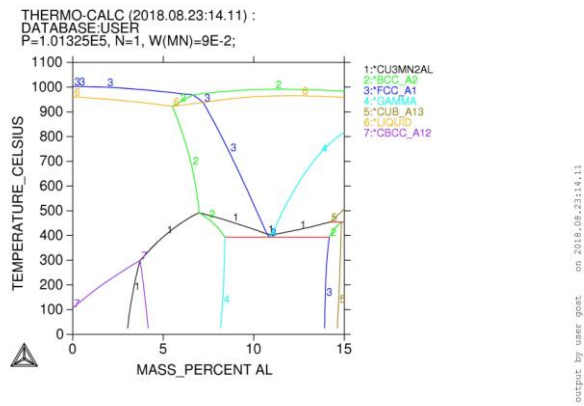
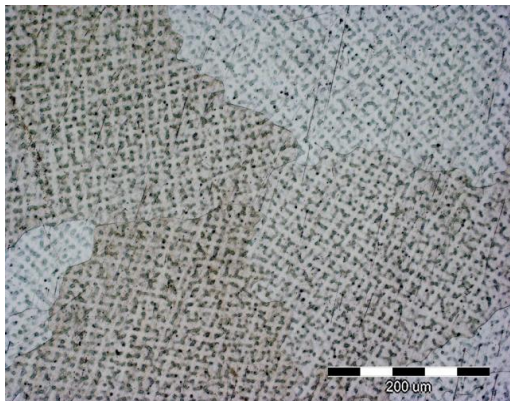
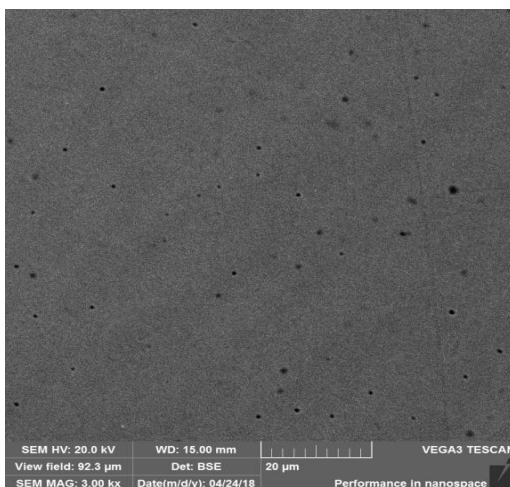


Figure 1. Calculated vertical section for Cu-9wt.%Mn by TCW 5

Calculated vertical section for Cu-9wt.%Mn with different aluminium content is given in Fig. 1. It can be seen that in system Cu-1wt.%Al-9wt.%Mn solidification mechanism, under equilibrium, starts with precipitation of α -phase (Cu-rich phase) at 1001 °C and then at 177 °C precipitates also manganese, as α -Mn (Fig. 1). Fig. 2a shows two-phase microstructure of Cu-1 wt.%Al-9wt.%Mn alloy in the as-cast state, with α -phase as matrix and existence of manganese precipitates. After aging at 300 °C for 14 days, morphology was changed and it is observed mostly α - (Cu-rich) phase with fcc structure, what is in correlation with calculated phase diagram (Fig.2b).



a)



b)

Figure 2. SEM micrographs for Cu-1 wt.%Al-9wt.%Mn alloy: a) as-cast state, b) after aging at 300 °C for 14 days

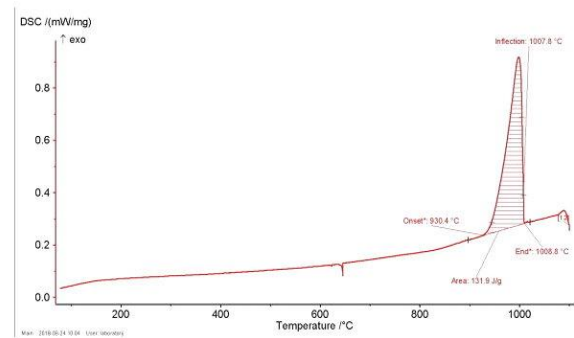


Figure 3. DSC cooling curve for Cu-1 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

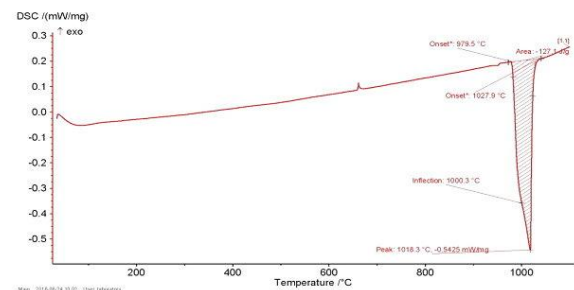
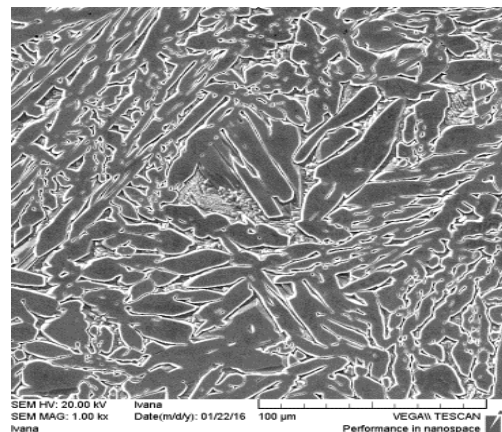


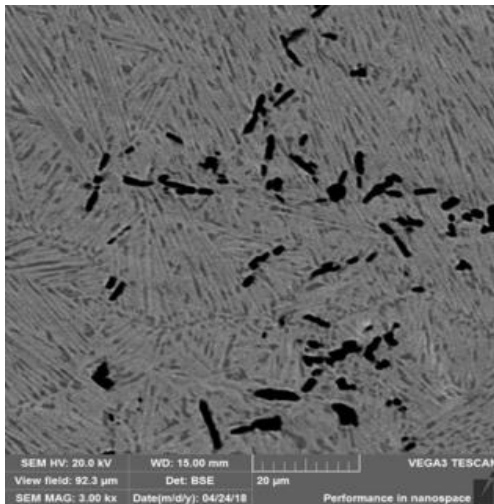
Figure 4. DSC heating curve for Cu-1 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

DSC cooling curve for investigated sample presents precipitation of α -phase at temperature of 1008 °C, what is in good agreement with predicted theoretical value (Fig. 3), as well as DSC heating results (Fig. 4).

Sample with higher content of aluminum, Cu-7wt.%Al-9wt.%Mn, under equilibrate conditions, solidifies with precipitation of β -phase at 972 °C and at 944 °C precipitation of α -phase. Solidus temperature is calculated at 936 °C and reiciation of ternary phase, Cu₃Mn₂Al (τ_3 -phase) at 490 °C (Fig. 1).



a)



b)

Figure 4. SEM micrographs for Cu-7 wt.%Al-9wt.%Mn alloy:
a) as-cast state, b) after aging at 300 °C for 14 days

Microstructure of Cu-7wt.%Al-9wt.%Mn alloy in the as-cast state show two-phase morphology, but not $\alpha+\tau_3$, as it can be expected due to Thermo-Calc calculation, but $\alpha+\beta$ morphology, what indicates that high-temperature β -phase remains in microstructure during casting due to faster cooling (Fig. 4a). After aging at 300 °C for 14 days, it can be observed new precipitates in α -matrix, probably τ_3 -phase (Fig. 4b).

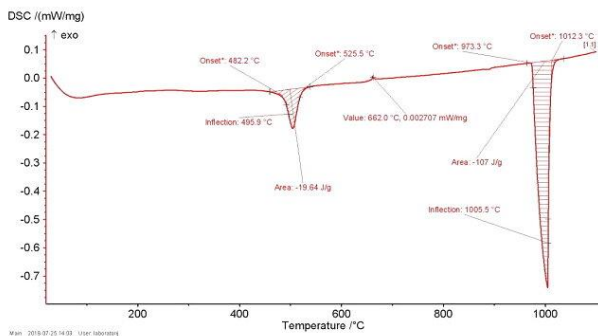


Figure 5. DSC heating curve for Cu-7wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

DSC results show first transformation at heating curve at 482 °C and the second transition at 495 °C, related to dissolution of τ_3 -phase and order-disorder transition of β -phase (Fig. 5). Two more transitions are determined at 973 °C and 1005 °C at heating curve. Calculated solidification mechanism for Cu-11wt.%Al-9wt.%Mn alloy is given as:

- 991 °C: L' $\rightarrow$ β phase
- 964 °C: solidus
- 467 °C: $\rightarrow \beta + \gamma_2$
- 408 °C: $\rightarrow \beta + \gamma_2 + \tau_3$
- 393 °C: $\rightarrow \alpha + \gamma_2 + \tau_3$

SEM micrograph after homogenization at 300 °C shows existence of three-phase morphology (Fig. 6), and DSC results presents two transitions at heating curve, with temperatures at 450 °C and 511 °C. Solidus temperature is experimentally obtained at 968 °C, what is in very good agreement with calculated value (Fig. 7). Temperature of 999 °C at heating curve, as well as 986 °C at cooling curve is related to β -phase. (Figs. 7,8).

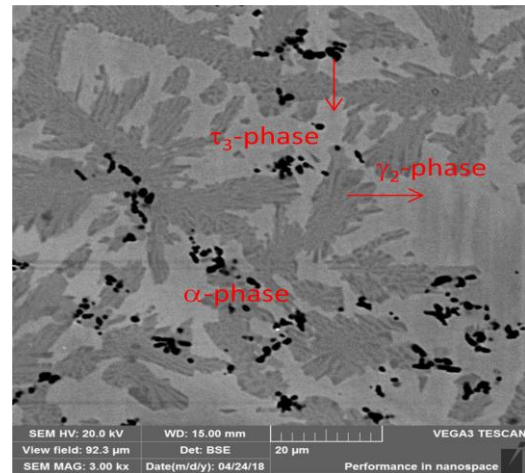


Figure 6. SEM micrographs for Cu-11 wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

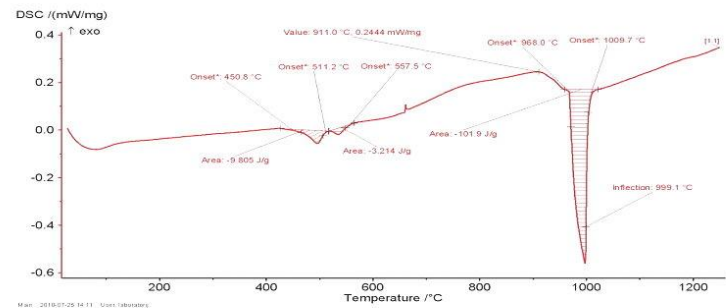


Figure 7. DSC heating curve for Cu-11wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

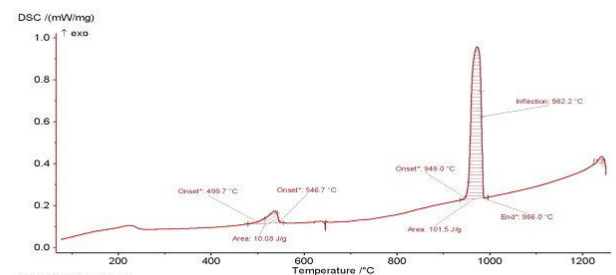


Figure 8. DSC cooling curve for Cu-11wt.%Al-9wt.%Mn alloy after aging at 300 °C for 14 days

Cu-8wt.%Al-9wt.%Mn shape memory alloy prepared by electric arc furnace, in the as-cast state after homogenization at 900 °C and quenching in water, show also two-phase microstructure, $\alpha+\beta$ (Figs. 9,10).

After continuous casting, in the as-cast state it can be observed martensitic needles inside grains, what indicates partially formation of metastable, β -phase (Fig. 11). Figure 12. shows completely formed martensitic structure after homogenization and quenching. Based on DSC results, start martensitic temperature in the as-cast state is at $M_s=37^\circ\text{C}$ and finish $M_f=13^\circ\text{C}$. After homogenization, two exothermic peaks at cooling curve indicate formation of different martensitic structures, with $M_s=42^\circ\text{C}$ and $M_f=5^\circ\text{C}$.

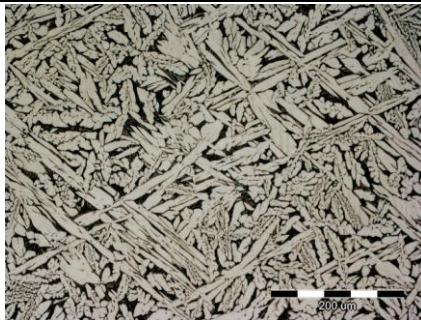


Figure 9. Optical microscopy of Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

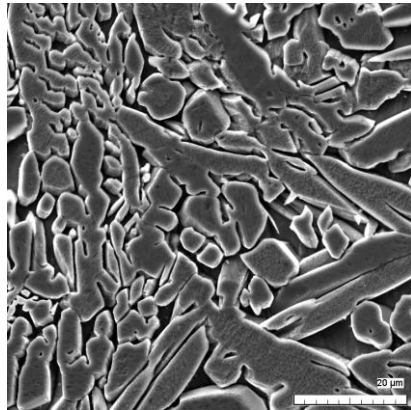


Figure 10. SEM micrograph of Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

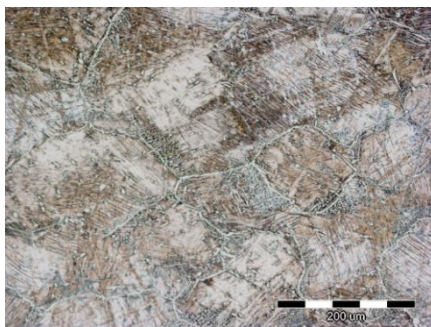


Figure 11. OM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

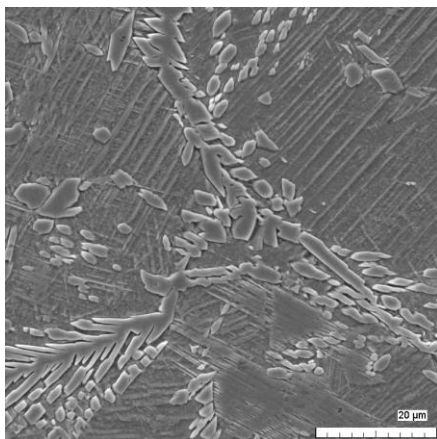


Figure 12. SEM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy in the as-cast state

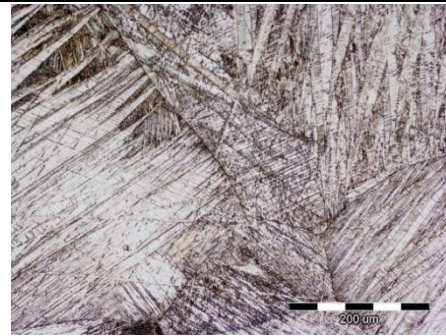


Figure 12. OM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy after homogenization at 900°C/30 minutes/H₂O

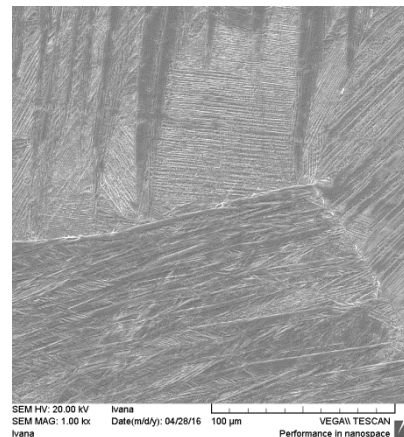


Figure 13. SEM micrograph of continuously casted Cu-8wt.%Al-9wt.%Mn SMA alloy after homogenization at 900°C/30 minutes/H₂O

Conclusion:

Experimental results of Cu-Al-Mn samples with different content of aluminium show good agreement with theoretical calculations of phase diagram for investigated ternary system. Cu-8wt.%Al-9wt.%Mn was successfully prepared by continuous casting and homogenization at 900 °C and quenching in water, with intensively formed martensitic structure through the sample. Start martensitic temperature was determined at 42°C and finish martensitic temperature at 5°C.

References:

- [1] R. Dasgupta, A. K. Jain, P. Kumar, S. Hussain, A. Pandey, J. Alloy. Comp. 620 (2015) 60-66.
- [2] C. A. Canbay, A. Aydogdu, Relationship between transformation temperatures and alloying elements in Cu-Al-Ni shape memory alloys, J. Therm. Anal. Calorim. 113, 2 (2013) 731-737.
- [3] T. Holjevac Grgurić et al, Thermodynamic Calculation of Phase Equilibria of the Cu-Al-Mn Alloys, Proceedings on Metallic and Non-metallic Materials, Zenica, (2016) 83-90.
- [4] J. Liu, H. Huang, J. Xie, Effects of aging treatment on the microstructure and superelasticity of columnar-grained Cu₇₁Al₁₈Mn₁₁ shape memory alloy, Inter. J. Min. Met. Mat. 23, 10 (2016) 1-11.
- [5] J. Miettinen, Thermodynamic Description of the Cu-Al-Mn System in the Copper-Rich Corner, CALPHAD 27, 1 (2003) 103-114.

ACKNOWLEDGEMENT:

This work has been fully supported by Croatian Science Foundation under the project IP-2014-09-3405.

NANOSTRUCTURED BY SPARK PLASMA SINTERING PIEZOCERAMICS PMN-PT AND MECHANOACTIVATED UNDER ULTRASOUND INFLUENCE PIEZOCERAMICS PCR-1

НАНОСТРУКТУРИРОВАННАЯ ИСКРОВОМ ПЛАЗМЕННЫМ СПЕКАНИЕМ
ПЬЕЗОКЕРАМИКА РМН-РТ И МЕХАНОАКТИВИРОВАННАЯ ПОД ВОЗДЕЙСТВИЕМ УЛЬТРАЗВУКА
ПЬЕЗОКЕРАМИКА ПКР-1

Prof. Dr. Sci. Panich A., Cand. Tech. Sci. Marakhovskiy M., Cand. Phys.-Math. Sci. Geguzina G.
Southern Federal University - Rostov-on-Don, Russia
E-mail: aepanich@yandex.ru, marmisha@mail.ru, geguzina@sfedu.ru

Abstract The functional parameters of lead magnesium niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and materials based on it make it possible their use as elements of precision motion devices. Nevertheless, it is necessary to increase the time stability of these parameters. Here, the ceramic $(1-x)\text{PMN}-x\text{PbTiO}_3$ (PMN-PT) was sintered by the spark plasma sintering method (SPS), which, in contrast to traditional sintering methods, allowed to reduce the sintering time and temperature and to obtain fine-grained ceramics with high and stable piezoelectric parameters. The preparation technology of ferro-piezoceramic material PCR-1 needs to be improved, in particular, it is necessary to increase the density of its ceramics. It is shown that the use of ultrasound as an additional influence on the process of mechanically activating of the initial powders on different equipment affects the density, piezo- and dielectric properties of mechanically activated PCR-1 ceramics and allows increasing its density by 10% and at the same time to low its sintering temperature.

KEYWORDS: FUNCTIONAL MATERIALS, NANOSTRUCTURED PIEZOCERAMICS, SPARK PLASMA SINTERING, PIEZOELECTRIC MODULUS, TEMPORAL STABILITY, CERAMICS DENSITY, SINTERING TEMPERATURE

1. Introduction

The lead magnoniobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN) and the materials based on it have the effective mechanical, dielectric and piezoelectric parameters that can provide their wide applications [1, 2] as elements of precision movement devices. The PCR-1 (Piezoceramic Rostov-1) ferro-piezoelectric ceramic material has found wide application in the radioengineering and electronics devices. Nevertheless, their preparation technology needs to be improved. Until now, the possibilities and mechanisms of the various effects influence on the initial batch during the preparation of certain piezoceramic materials have been little studied, including, when applying for the above purposes the new and non-conventional methods of the influence upon the initial batch before sintering with its use of the final functional ceramics.

In particular, it was necessary to achieve a high temporal stability of piezoelectric parameters of the ceramic material $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3)$ (PMN-PT), and for the PCR-1 ceramics to increase the ceramics density to improve their mechanical, dielectric and piezoelectric parameters. The conventional methods, including traditional methods of high-temperature solid-phase reactions at atmospheric pressure or conventional hot pressing with these problems cannot cope. Further, in two large parts, it will be described how, with the use of some nonconventional methods of processing the initial oxides mixture powder in their ceramics synthesis and sintering under various conditions, the piezoelectric properties temporal stability of the PMN-PT material, and the PCR-1 material ceramics density have been increased, what have improved their piezo- and dielectric properties as the result.

2. Temporal stability of nanostructured piezoceramics PMN-PT

Preparation of the qualitative samples of a ceramic material $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3-x\text{PbTiO}_3)$ (PMN-PT) with the piezoelectric parameters high stability is associated with a number of difficulties [3, 4], which were overcome here. For the sintering of samples of nanostructured ceramics from batch with a particle size of up to 100 nm, the method of spark plasma sintering (SPS) on the spark plasma sintering press SPS 515S "DR.Sinter-LABTM Fuji electronic industrial" was used. This method, as example, allows sintering in ten minutes at the lowered temperatures and at high uniaxial pressure to obtain [5] fine-grained ceramics with high mechanical and electrophysical parameters.

2.1. Methods for the PMN-PT ceramic samples sintering and studying

The PMN-PT ceramics were prepared by the non-conventional SPS method at various sintering temperatures. To compare the temporal stability of its parameters with the temporal stability of the parameters of ceramics obtained by two traditional methods, other ceramic samples were prepared by conventional solid-phase sintering in a chamber furnace at atmospheric pressure (ATM) and hot pressing (HP) at temperatures of 1250 and 1180 °C, respectively. X-ray diffraction analysis was performed on an ARL X'Tra diffractometer and the ceramics microstructures, prepared by different sintering methods at different temperatures, on an electronic scanning microscope "JEOL JSM 6390 LA", were studied. The electrophysical parameters and their dependence on the sintering temperatures by various methods were determined on the measuring equipments "Tsenzurka-M" and "D₃₃-meter APC".

2.2. Structure, microstructure, piezoelectric and dielectric properties of PMN-PT ceramics

X-ray phase analysis of the ceramic samples obtained shows (Fig. 1) that every of them is predominantly phase with a perovskite structure but with a small admixture of the pyrochlore phase, as is often the case with the Pb-containing ceramics synthesis, and only ceramics prepared in a chamber furnace at 1250 °C, did not have such admixture at all.

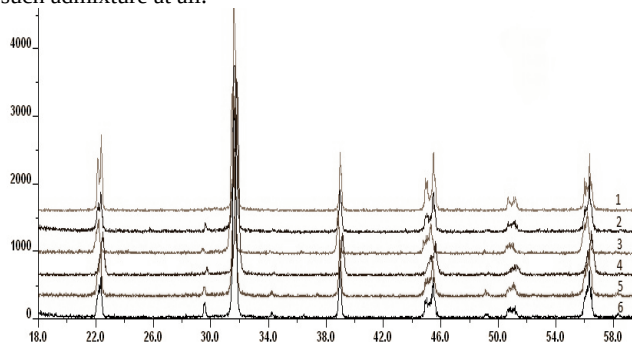


Fig.1. X-ray diffraction patterns of PMN-PT ceramics prepared by methods:

ATM at $T = 1250$ (curve 1), HP at $T = 1180$ (curve 2) and SPS method: at $T = 1050$ (curve 3); $T = 1050$ (curve 4); $T = 1150$ (curve 5) and $T = 1175$ (curve 6)

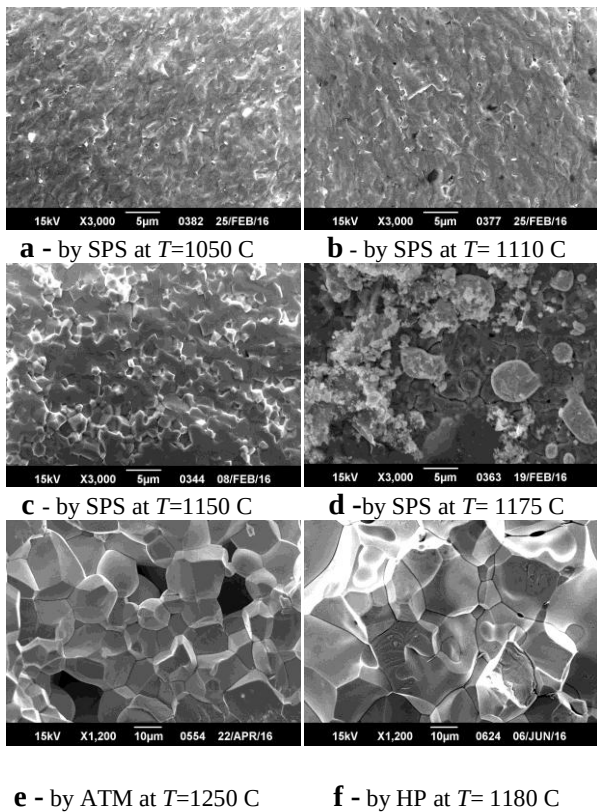


Fig. 2. Microstructure of PMN-PT ceramics obtained by different methods and at different temperatures (indicated below each photo) with the same enlargement

Piezoceramic PMN-PT samples sintered in a chamber furnace at a temperature of $1250\text{ }^{\circ}\text{C}$ have high density and strength values. The size, in comparison with the HP method, of small and uniform grains of ceramics (Fig. 2, e) was from 12 to $20\text{ }\mu\text{m}$. The ceramics obtained by hot pressing method at $1180\text{ }^{\circ}\text{C}$ (Fig. 2, f) has high density and strength and grains of various sizes, including large ones, the occurrence of which can be explained by their secondary recrystallization during hot pressing.

The piezo- and dielectric properties (Table 1) of PMN-PT ceramics, obtained by various methods and at different temperatures, are investigated. The piezomodulus $d_{33} = 510$ at the sintering temperature $T = 1175\text{ }^{\circ}\text{C}$ is clearly higher for ceramics sintered by the method of spark plasma sintering than for ceramics obtained by the same method but at any other temperature and, moreover, higher than for ceramics obtained by other methods. The microstructure of the ceramic with the highest piezomodulus consists of fairly small and non-uniform grains that are tightly pressed together, practically without cracks, but with small pores (see Figure 2, d), whereas in ceramics, fine-grained and almost one-dimensional grains (see Figure 2, e) obtained at atmospheric pressure and at the highest temperature $T = 1250\text{ }^{\circ}\text{C}$, this piezomodulus value is somewhat lower, although there is no admixture of pyrochlore in it, but its microstructure consists of tightly pressed together grains with rather large rare pores. Nevertheless, in spite of the comparable values of the piezomodulus d_{33} of ceramic samples obtained by the SPS and HP methods, an extremely advantageous SPS method is the ultra short sintering time: no more than 10 minutes. The values of $\text{tg}\delta$ of all PMN-PT samples are low (see Table) and did not exceed 1%. Samples of ceramics made by the HP method at $T = 1180\text{ }^{\circ}\text{C}$ had a piezoelectric modulus reduced by 6% in comparison with ceramics obtained by the SPS method.

On the obtained ceramic samples of the ferroelectric material PMN-PT, the temporal stability of some electrophysical parameters was studied, as one of the most important performance characteristics of ceramics, characterizing its quality. It is shown (Fig.3) that after the annual period, the values of the piezoelectric

modulus of the obtained ceramic samples of piezoelectric material PMN-PT decreased by 21 ... 22%. The exception was ceramics, obtained by the SPS method at a temperature of $1175\text{ }^{\circ}\text{C}$, the parameters of which decreased by only 16%.

Table 1. Piezoelectric module d_{33} and dielectric losses, $\text{tg}\delta$ of PMN-PT ceramics, prepared by different methods at various temperatures and pressures

Piezo- and dielectric properties, pressure	Ceramics sintering method and temperature, $^{\circ}\text{C}$					
	SPS				ATM	HP
	1050	1100	1150	1175	1250	1180
Piezo-modulus, d_{33} , pCoul/N	310	347	420	510	460	480
Pressure, kgf/cm^2	400	400	400	400	atmo-spheric	250
Dielectric loss, $\text{tg}\delta$, %	0,8	0,5	0,4	0,6	0,5	0,7

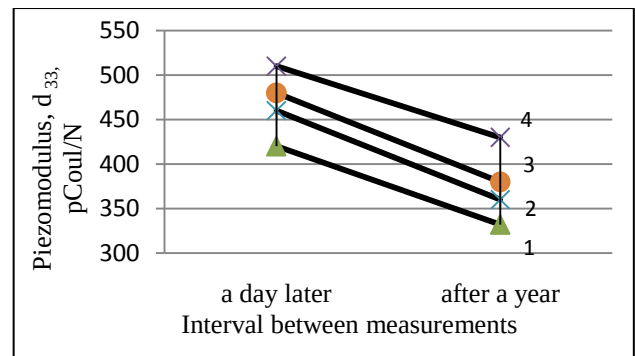


Fig. 3. Temporal stability of piezoelectric module d_{33} of PMN-PT ceramics for the annual period:

SPS at $T = 1150\text{ }^{\circ}\text{C}$, decreased on -21% (line 1); ATM at $T = 1250\text{ }^{\circ}\text{C}$, - on -22% (line 2); HP at $T = 1180\text{ }^{\circ}\text{C}$ - on -21% (line 3); SPS at $T = 1175\text{ }^{\circ}\text{C}$ - on -16% (line 4)

Thus, the best parameters for the properties of PMN-PT ceramics and their annual stability were achieved by a non-traditional method of spark plasma sintering at a temperature $T = 1175\text{ }^{\circ}\text{C}$.

3. Mechanoactivated under ultrasonic influence piezoceramics PCR-1

A traditional method for the synthesis and sintering of similar PKR-1 Pb-containing materials is the solid-phase reaction method, where an untreated mixture of initial oxides is used as the starting mixture. The disadvantage of this method is the need for sufficiently high synthesis temperatures in the interval $T = 850 \dots 900\text{ }^{\circ}\text{C}$ and its duration is up to 20 hours, which together leads to a violation of the stoichiometry of the chemical composition of sintered ceramics due to the long evaporation of some of the initial oxides, especially lead oxide.

In addition, in this method, due to the duration of the high-temperature treatment, intensification of the secondary recrystallization process takes place during the final sintering of the compacted samples, which leads [6 - 7] to a considerable scatter of ferroelectric piezoelectric ceramics of dielectric and piezoelectric parameters: dielectric constant, dielectric loss tangent, piezoelectric coefficients and others in the finite products. It is necessary to solve these problems.

3.1. Methods for PCR-1 ceramic samples sintering and studying

Nonconventional methods of the initial batch treating are needed in order to intensify diffusion processes that promote the crystallization of a given chemical composition in a given crystal structure. It is necessary to change and control the granulometric composition of the charge, seeking to obtain a sufficiently monophase dense initial powder with one-dimensional particles for sintering the ceramics, which will help to liquidate or suspend the secondary recrystallization of its grains, and thereby increasing the density of the ceramics. It is possible to reduce the temperature [8 - 10] and the sintering time of the ceramics from this batch pressed powder. Thus, the evaporation time of the initial oxides can be shortened and the chemical composition stoichiometry of the final ceramics should be avoided.

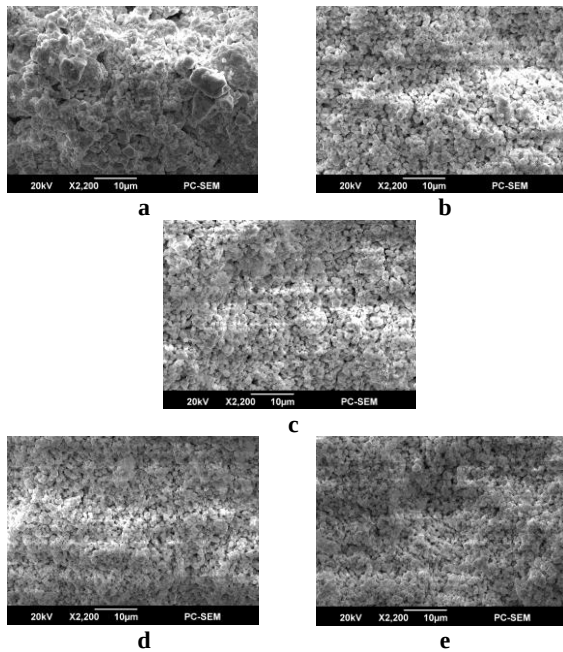


Fig. 4. Microstructure of PCR-1 initial powders obtained by different methods: in ball mill (a); vibration mill (b); vibration mill and ultrasound (c); planetary mill (d) and planetary mill and ultrasound (e) (with the same enlargement)

We applied various nonconventional methods of mechanical disintegration and activation of particles of the initial charge. We investigated the influence of these different methods of particles treatment on the mechanical parameters - the ceramics microstructure and density and on some of the electrophysical parameters of the final ceramics under preparation various conditions. Mechanical disintegration and activation of charge were carried out on various technological equipment: a drum ball mill "SHLM"; planetary mill Fritsch "Planetary Mill Pulverisette 5"; vibratory mill Fritsch vibration mill "Pulverisette 0" and ultrasound effect, performed by ultrasonic disintegrator IL10-1.0. And then combined any equipment with the ultrasound impact of ultrasound: a planetary mill and an ultrasonic disintegrator, as well as a vibratory mill and an ultrasonic disintegrator.

The batch synthesis was carried out in a "Nabertherm" furnace at $T = 800...900\text{ }^{\circ}\text{C}$ and ceramics sintering – at $T = 1150...1250\text{ }^{\circ}\text{C}$ according to the method described in [11]. The electrophysical parameters of the ceramics and their dependence on the sintering temperatures for various methods were determined using the "Tsenzurka-M" and "D33-meter APC" measuring equipment. The particles dispersion of the synthesized batch, as well as the microstructure of the sintered ceramic samples, was studied on an electronic scanning microscope "JEOL JSM 6390 LA".

3.2. Microstructure, piezoelectric and dielectric properties of the PCR-1 ceramics

It is established, that despite the fact that the microstructure of the initial powders (Fig. 4) varies little: it is dense in any case, and the grains are small, the state of the microstructure of the final ceramics – the size and uniformity of the grains, the packing density – vary much (Fig. 5) from the processing of the initial powder and at what temperatures. The content of fairly homogeneous agglomerates at medium temperatures for all treatment methods (See Fig. 5, b, d, f, h and j) leads to a decrease in the density of the ceramics.

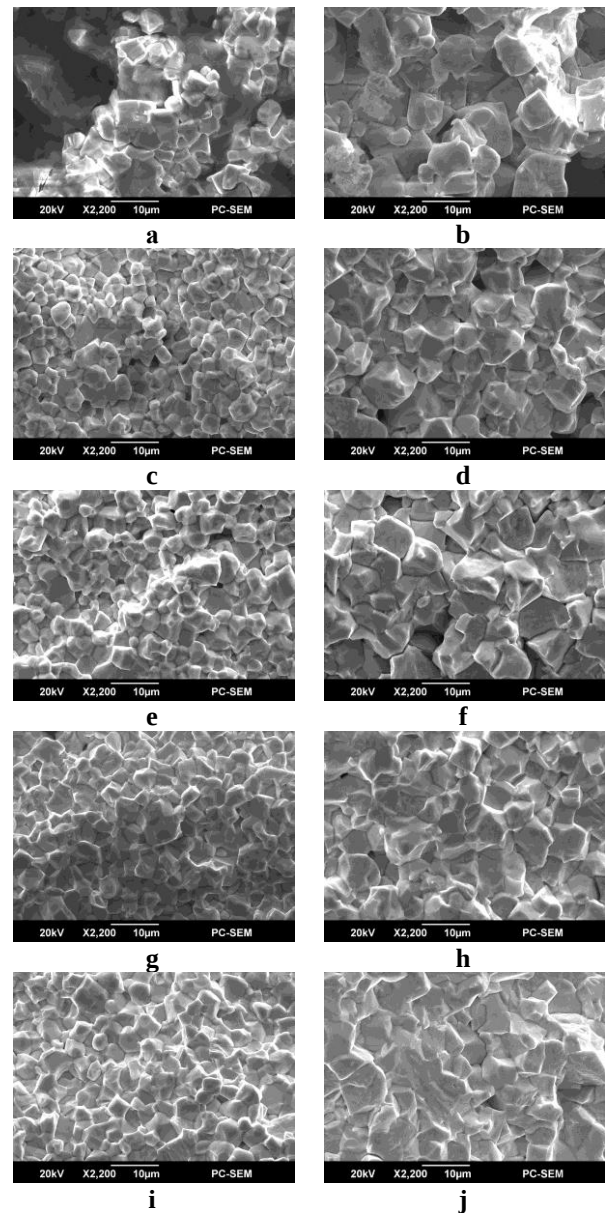


Fig. 5. Microstructure photos of piezoceramics PCR-1, sintered at the temperatures:

$T = 1150$ (a, c, e, g, i – left column); $1220\text{ }^{\circ}\text{C}$ (b, d, f, h, j – right column) mechanoactivated under different conditions: in ball mill (a, b); vibratory mill (c, d); vibratory mill under ultrasound action (e, f); planetary mill (g, h) and planetary mill under ultrasound action (i, j)

The highest density is possessed by ceramics, obtained from the batch, which has been treated in a planetary mill and in a vibratory mill, and also in their combination with ultrasound at medium temperatures (See Fig. 5, b, d, f, j).

However, the use of a planetary mill as a mechanism of disintegration and activation proves to be preferable because of the short exposure time of the ultrasound to the batch (only 2 hours), in

contrast to the vibratory mill (almost 24 hours), with comparable parameters (Table 2) for the final ceramics.

Table 2. The temperatures of ceramic PCR-1 sintering from the initial powders treated with using of different equipments, its density, relative dielectric permittivity and piezomodulus d_{33}

Equipment	$T_{\text{сnek}},$ °C	$\rho,$ g/cm ³	ϵ_{33}/ϵ_0	$d_{33},$ pCoul/N
Ball mill	1150	5,38	580	165
	1220	5,16	550	220
	1250	5,17	420	190
Planetary mill	1150	7,64	945	330
	1220	7,57	900	330
	1250	7,51	775	275
Vibratory mill	1150	7,65	880	280
	1220	8,04	805	270
	1250	7,43	725	250
Ultrasound disintegrator	1220	5,42	460	230
	1250	5,29	410	215
Planetary mill under ultrasound action	1150	7,67	930	330
	1220	7,65	845	310
	1250	7,45	810	315
Vibratory mill under ultrasound action	1150	7,64	870	275
	1220	7,6	780	260
	1250	7,37	725	255

Thus, the use of ultrasonic action in combination with other methods of mechanical activation of the material promotes the homogeneity of the ceramics grains and increases the density of its microstructure, and reduces the sintering temperature and also, consequently, prevents the violation of the stoichiometric composition by reducing the evaporation at the initial oxides with a shorter sintering time.

4. Conclusions

The undertaken research of an influence on piezoceramics quality of different ceramics sintering nonconventional methods, in particular, spark plasma sintering method or preliminary initial batch treatment methods on different equipments under ultrasound action before the ceramics sintering process allows to solve some problems.

First, spark plasma sintering method use increases piezoelectric modulus d_{33} temporal stability of the PMN-PT ceramics for the annual period in contrasts with the conventional ceramics sintering methods: the usual high temperature solid state synthesis and ceramics sintering in which one uses only untreated the a reaction initial components batch, or the usual hot pressing method in which they use additionally to high temperature the small pressures.

Second, use of the combination of the initial batch treatment on different equipments with the ultrasound integrator before the ceramics sintering had allowed increase any mechanical and electrophysical properties of the final functional ceramic products.

5. Literature

1. Yamada H. Pressure less sintering of PMN-PT ceramics// Journal of the European Ceramic Society, 1999, V.19, #6-7, P.1053-1056.
2. Liou Y.C. Stoichiometric perovskite PMN-PT ceramics produced by reaction-sintering process. Materials Science and Engineering. B, 2003, V.103, #3, P. 281-284.
3. Guo H.K. The dielectric relaxation relationship of PMN - PT ceramics. J. of Physics: Condensed Matter, 1998, V.10, #18, P. 297-302. (Guo H.K., Fu G., Tang X.G., Zhang J.X., Chen Z.X.).
4. Zhao W. Electric-field induced strain and dielectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ ceramics. Ferroelectrics, 2015, V.488, #1, P. 89-96. (Zhao W., Ruan W., Zhao K., Zeng J., Li G., Wei X., Wang Y.).
5. Marder R. Plasma in spark plasma sintering of ceramic particle compacts. Scripta Materialia, 2014, V.82, P. 57-60. (Marder R., Caim R., Estournès C, Chevallier G.)
6. Rahaman M.N. Ceramic processing and sintering. N.-Y., Basel, Hong Kong: Marcel Dekker, 1995, V.770, P.358-367.
7. Tashiro S. Jpn. J. Appl. Phys, 1987, V. 26. Suppl. 26-2. P. 142. (Tashiro S., Sasaki N., Tsuji Y., Igarashi H., Okazaki K.).
8. Swartz S.L. Mat. Res. Bull, 1982, V.17, P.1245. (Swartz S.L., Shrout T.R.).
9. Tashiro S. Jpn. J. Appl. Phys, 1989, V.28, #28-2, P. 80. (Tashiro S., Kotani Y., Fukai K., Igarashi H.).
10. Eremkin V.V. The influence of mechanical activation on the technology of obtaining piezoelectric ceramics of lead zirconate titanate // News of Higher Educational Institutions. Chemistry and Chemical Technology, 2011, V.54, #11, P.105-108. (Eremkin V.V., Gusenko I.V., Nagaenko A.V., Panich A.E., Smotrakov V.G., Shevtsova S.I., Shilkina L.A.).
11. Nesterov A.A. Synthesis of the phases of the composition of PbNb_2O_6 and BaNb_2O_6 using active precursors. Journal of Applied Chemistry, 2009, V.82, #3, P.382-385. (Nesterov A.A., Masurenko K.S., Karyukov E.V.).

REINFORCED WITH FULLERENES COMPOSITES BASED ON METALLIC MATRICES

Prof. Dr. O.Sizonenko¹, Prof. Dr. S.Prokhorenko², Dr. A.Torpakov¹,
Dr. D.Žak², Dr. Y.Lypian¹, MSc. R.Wojnarowska-Nowak², Prof. Dr. J.Polit² and Prof. Dr. E.M.Sheregii²

¹ Department of Disperse Systems Pulse Treatment, Institute of Pulse Processes and Technologies, National Academy of Science of Ukraine, Mykolaiv 54018, Ukraine

² Center of Microelectronics and Nanotechnology, University of Rzeszow, 1 Pignia Str., 35-959 Rzeszow, Poland

sheregii@ur.edu.pl

Abstract. A new technological approach to obtain anti-friction dispersion-hardened by nanoparticles materials based on of TiC – AlC – and FeC alloys with inclusions of the C_{n0} ($n=6$ or 7) phases which characterized by high heat resistance, strength and durability for use in aircraft and rocket technology, is presented. Elemental powders of Al–Ti–C and Fe–Ti–C systems are used as base objects for development of new composite materials by high voltage electric discharge treatment in kerosene (dispersion, activation and synthesis). In effect, as shown micro-Raman data, these systems contain refractory components (fullerenes, carbides), MAX-phases of Ti–Al–C system with increasing thermo-stability, strength and wear resistance while maintaining ductility how can it be predicted.

Keywords: HIGH VOLTAGE ELECTRIC DISCHARGE; COMPOSITE MATERIAL; RAMAN SCUTTERING; FULLERENE.

1. Introduction.

Considerable number of fabrication methods have been proposed to develop metal matrix composites containing carbon nano-materials, nanotubes for example, using the liquid-state techniques¹⁻⁶ as well as solid-state techniques⁷⁻¹³. Spraying processes⁶⁻⁸, squeeze casting⁹, disintegrated melt deposition^{10,11} processes (also electrolytic¹²) and milling fabrication¹³⁻¹⁶ have been introduced to fabricate the composite at temperatures above the melting temperature of the matrix. On the other hand, metal matrix composites containing such carbon nanoparticles as fullerenes are less known, although the properties of these objects with predominant sp^2 bonding¹⁷ extend their use also in composites.

Dispersion-hardened composites, based on titan-iron-carbon alloy systems are widely used in aviation and aerospace industry due to the properties combining characteristics for metals (significant ductility and fracture toughness) and ceramics (high strength, high thermal resistance and elastic modulus). If they could consist of titanium and iron carbide matrix and hardening inclusions –as fullerenes (C_{60} and C_{70}) decreasing coefficient of friction, such nano-composition besides large strength will be characterized by high thermal resistance in the wide range of temperatures and low coefficient of friction. Therefore, method to obtain such composite would be irreplaceable.

A new method of the metal matrix composites containing carbon nanoparticles preparing – high voltage electric discharge treatment in kerosene (dispersion, activation and synthesis) is proposed in present work. The measured micro-Raman scattering confirm the present of fullerenes in fabricated composites while mechanical properties shown considerable increasing of strength and wear resistance.

2. High voltage electric discharge method.

Electric discharge treatment is unique complex method of impact combining the physical and mechanical action and it is based on utilizing high voltage electric discharge (HVED) in liquid. HVED in liquid is essentially an electric explosion, characterized by rapid energy excretion (during microseconds) in initially small volume of discharge channel, paved by streamer, appeared under the influence of high electric potential between the opposing electrodes. HVED allows obtaining dense low temperature plasma¹⁸, its temperature reaches up to 5.104 °C. The high energy concentration, high pressures (about 1 GPa) and

temperatures, developed within the channel, lead to rapid (from 500 up to 2000 m/s) expansion of channel and appearance of shock waves, transformed into acoustic with wide frequency specter, powerful hydro flows, cavitation, electromagnetic and thermal fields^{18,19}. Studies have shown that the dispersion process involves the shock wave with a front of 10^{-10} m thickness¹⁸ (or compression wave, depending on circuit parameters), cavitation, destruction of particles during their collision with the rigid wall of the chamber and their mutual attrition throughout the chamber during expansion and collapse of the vapor-gas cavity in varying degrees. Use of a hydrocarbon liquid as the working medium during processing of powder mixtures avoids their oxidation without substantially reducing the hydrodynamic characteristics of the discharge. The case of using a hydrocarbon liquid with sp^2 -hybridization (kerosene) is characterized by carbon of graphite type short-range order, and the case of using a fluid with sp^3 -hybridization (dodecane, cyclohexane, hexane), by a diamond-like²⁰⁻²³. Therefore, it is advisable to use kerosene as the working fluid at HVED treatment of metal powders. The processes occurring in the consolidation of micropowder particles have significant influence on the properties of the material. Application of method of sintering, such as a spark-plasma sintering (SPS), which allow the preservation of the ultrafine structure of the initial powders, leads to the possibility of obtaining high-density powder composites with improved physical and mechanical properties as well as SPS allows purposeful control of grain growth speed and thereby generate nanostructured microheterogeneous structure of multifunctional composite materials with high physical-mechanical and performance properties²⁰. Besides that, high pressure zone enables the formation of fullerene particles. Last one is particularly important the last one is especially important because of the huge mechanical strength of fullerenes and their property to lower the coefficient of friction²².

2.1. The experimental complex

The experimental complex of HVED (see electrical scheme Fig.1), located at the Institute of Pulse Processes and Technologies, National Academy of Science of Ukraine, was used for studies. As shown below, the connection between sufficiently strong and stable. The enzyme catalytic activity is also confirmed, which means that the method applied to construct the nanobiosystem was effective.

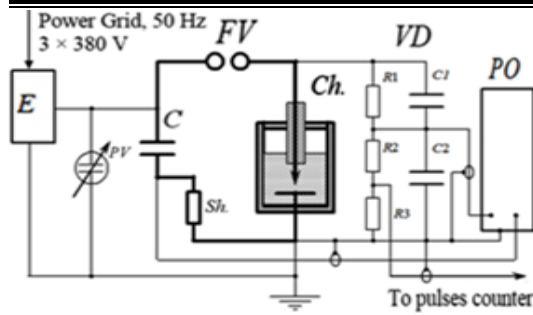


Fig. 1. Electrical scheme of HVED

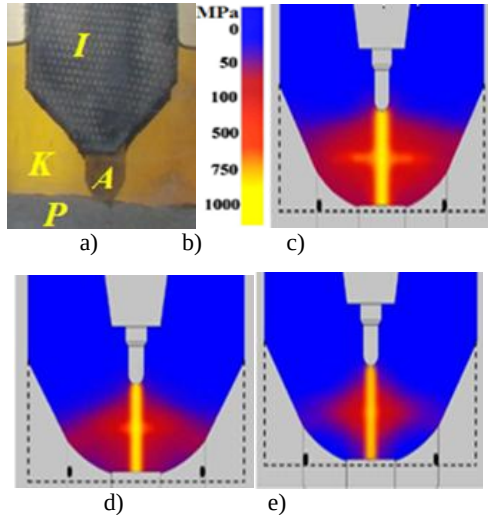


Fig. 2. a) - working chamber: I – isolator; F – anode; K – kerosene; P – research powder, b) - pressure scale, c, d, e) pressure wave peaks during HVED treatment with single discharge energy of 1, 0.5 and 0.25 kJ, respectively.

Since at the high voltage electric discharge (HVED) pressure in the discharge channel reaches 1GPa (Fig.2 a,b,c,d,e) the temperature in the discharge channel can reach 50 000K and at the interface between the plasma channel and environment it is down to 1000 K, the transition layer thickness is 2 mm, pyrolysis of kerosene, with the formation of solid carbon and atomic and molecular hydrogen gas, is possible^{24,25}.

For example, treatment of 75%Fe–25%Ti powder mixtures was performed with specific energy of $W_{s\Sigma} = 25$ MJ/kg, which ensures synthesis of necessary amount of carbon for formation of stoichiometric Ti carbide. Current rise rate varied from 13 up to 24 GA/s, which provided different intensity of pressure waves impact (see Fig.1d,e,f). Frequency of pulses passing was $f = 0,6$ Hz.

2.2. Distribution of particles by diameter values.

Mean diameter of powder particles after treatment in all studied modes decreased from 80 to ~3 μ m (see Fig. 3a).

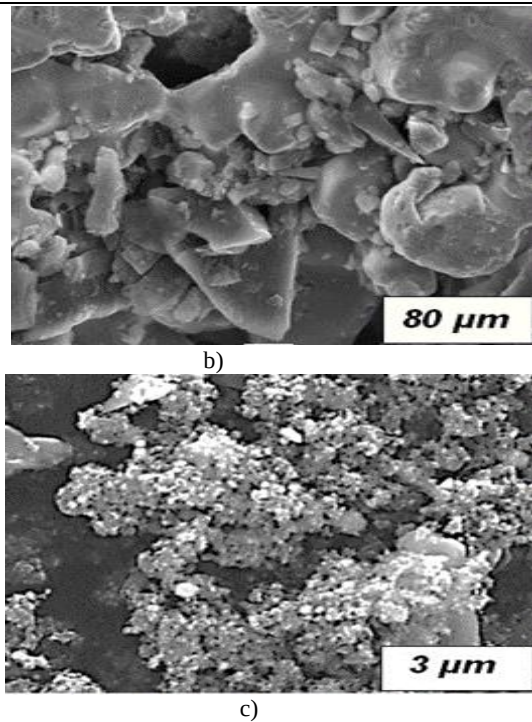
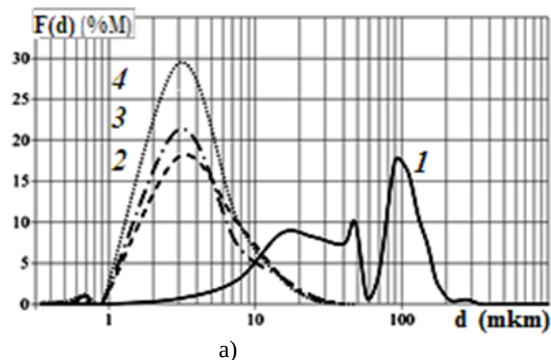


Fig. 3. The 75%Fe–25%Ti mixture. a) - Distribution of particles percentage $F(d)$ by diameter values (1– initial mixture; 2– after HVED treatment with $di/dt = 13$ GA/s; 3– $di/dt = 19$ GA/s; 4– $di/dt = 24$ GA/s), b)- Mixtures micro-photo-graphs: initial mixture, c)- after HVED treatment with $W_{s\Sigma} = 25$ MJ/kg and $di/dt = 24$ GA/s.

The high modulus (ceramic) TiC (with homogeneity area up to TiC_{0.92}) and FeC (with size varying from 10 up to 600 nm) phases are synthesized at this time. Worth noting that maximum amount of powder with ~ 3 μ m diameter (~ 30 %) was obtained after treatment with maximal considered current rise rate of $di/dt = 24$ GA/s (see Fig.3a, curve 4). Most of initial mixture particles had irregular fragmental shape (see Fig.3b), but after processing they have shape, close to spherical (see Fig.3c) – this shows, that they were synthesized due to impact of discharge channel current (ablation and electric erosion). Thus, due to the combined action of simultaneously mechanical (forced compaction during processing), spark plasma (electric discharge between particles), plasma (local heating after the breakdown of the oxide films on the surface of powder particles) it is possible to receive composite material with improved physical and performance properties at sufficiently low temperature compared to traditional approaches.

3. The Raman scattering results.

In order to control the chemical composition of components during SPS, the Raman spectroscopy analysis was applied using micro-Raman system based on Renishaw inVia spectrometer. In Fig.4, micro-Raman (with spatial resolution of 1 μ m) spectrum of individual grain (is shown in center in Fig. 3c) for the 75%Fe – 25%Ti mixture obtained by HVED treatment is presented. The sharp strong line at 1583 cm^{-1} , observed on the curve in Fig. 4, is attributed to C₇₀ molecules²⁶, undoubtedly while the line at 1355 cm^{-1} is close to the one related to the C₆₀ molecules. The deviation from the classic position will be explained later in Table 1.

In Fig. 5 the detail results about micro-Raman spectra refer to individual grains of the 50% Al – 50% Ti powder are given.

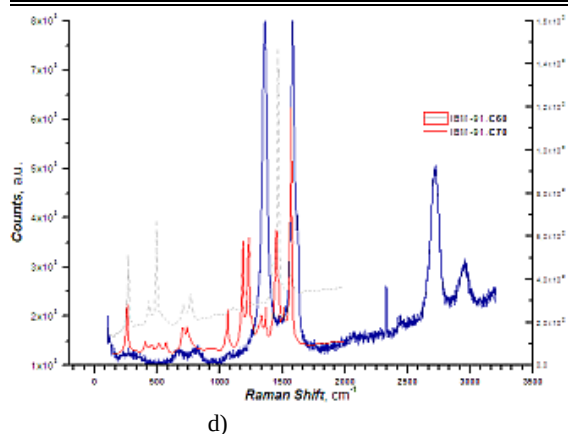


Fig. 4. Raman spectra: blue for above mixture; red for C_{60} and C_{70} mixture [26].

The shape of the spectra is changed with each step but two lines at 1355 cm^{-1} as well as at 1596 cm^{-1} are clearly shown on each presented in Fig. 5 spectra. A large variety of the C_n fullerene molecules could be attributed to the wide line at about 1360 cm^{-1} (see Table 1) while line at about 1590 cm^{-1} , is referred to C_{70} , and is the strongest one in the 24 point. The lines observed in the region from 2300 cm^{-1} to 3000 cm^{-1} refer, probably, to Ti–C alloy (with the exception of the line at 2720 cm^{-1} , which is certainly the overtone of the line at 1355 cm^{-1}) and the lines observed in the region from 500 cm^{-1} to 900 cm^{-1} – to Al – C alloy.

4. Conclusion.

Therefore, the new method of the metal matrix-carbon nanoparticles composite fabrication based on the HVED treatment of the initially prepared powder is proposed. Proposed method of preparation of powders for consolidation differs from known methods⁷⁻¹⁶ by the fact that hardening particles are not mechanically added to powder mixture, but are instead

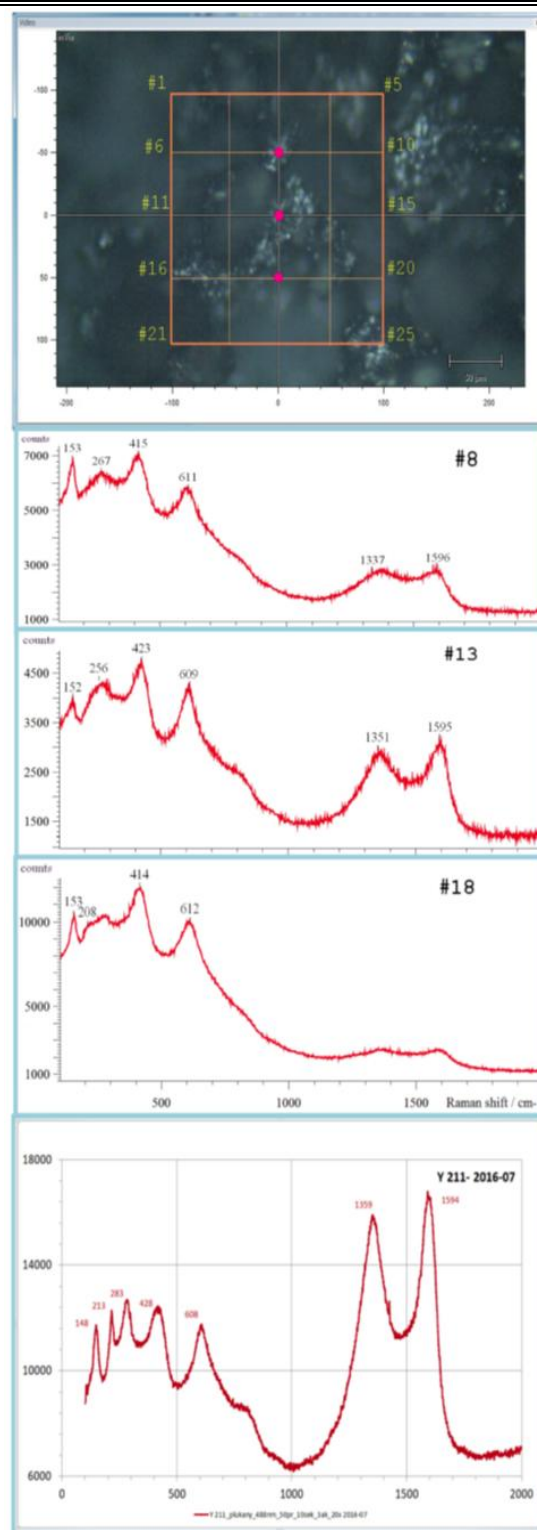


Fig. 5. Mapping of Raman spectra on researched grains of the 50% Al – 50% Ti nanoparticles composite. (a) – the map of the surface of powder; (b) – Raman spectra obtained for the points on map: 8, 13, 18 and 24.

Table 1. Identification of the lines observed in the Raman spectra (s-strong, m-medium, w-weak)

	Position of line or group of lines (cm^{-1})	Raman spectrum designation: point number on the map, line pattern (w - weak, m - medium, s – strong)	Identification	References
1	148 – 154	1s,2(w),8(w), 10(w),13(w),14(w), (18-22) (w)	Al – C alloy	12,14,15
2	208 – 213	5(w),6(w), (10-12)(w), (14-16)(w), (20-21) w	Al (Ti)– C alloy	12,14,15

3	256 – 267	1-3w, 8w, 13w, (16-18)w, 21w	Al (Ti)– C alloy	12,14,15
4	415 – 428	1-3, (5-7)m, 8(-10)s, 13s, 17s,18s, 21m, 23s, 24m, 25w	Al (Ti)– C alloy	12,14,15, 26
5	608 –613	1-3, 6s, 7m, 8s, 9, 10, 13s, 14, 17s,18s, 21, (23 – 25)m	Al (Ti)– C alloy	12,14,15, 27
6	820 – 840	4, (5-9)s, 10 – 14, 15s, 16, 19s, (20-22)m, 23s, 24s, 25m	Al ₄ C ₃	12
7	1355 – 1359	(1-8)m, (9-16)s, (19-22)s, 24sm, 25s	C ₆₀ including Fe or Al atoms and other allotropic C forms	15, 26, 27
8	1594 – 1596	(1-3)m, (4-6)s, 7m, 8m, (9-16)s, 17w 18w, (19-22)s, 24s, 25s	C ₇₀	26, 27
9	2700 – 2720	(3-7)w, (8 – 16)w, (19-25)w	overtone of line at 1355 cm ⁻¹	28, 29
10	2930 – 2950	3m, 4m, (5-7)w, (9 – 16)w, (19-25)w	Ti – C alloy	28, 29
11	2320	(1-4)w, (5-7)s, 8w, 9s, (10-16)m,	Ti – C alloy	28, 29

synthesized during HVED treatment of “kerosene – Fe (Al) – Ti powder mixture” disperse system with its simultaneous grinding, which can be used for creation of composite materials with increased mechanical and performance characteristics.

Raman spectra of obtained composites have shown presence of fullerenes C₇₀, as well as other allotropic forms of fullerenes, which allows us to predict strong thermo-stability in the wide temperature region, strength and wear resistance while maintaining ductility also.

5. References

- ¹ T. Tokunaga, K. Kaneko, K. Sato, Z. Horita. Scripta Materialia, **58** 735 (2008).
- ² F. A. Khalid, O. Befort, U. E. Klotz, B. A. Keller, P. Gasser, S. Vaucher, Acta Materialia, **51**, 4575 (2003).
- ³ S. R. Bakshi, V. Singh, S. Seal, A. Agarwal, Surface and Coatings Technology, **203**, 1544 (2009).
- ⁴ S. R. Bakshi, V. Singh, K. Balani, D. G. McCartney, S. Seal, A. Agarwal, Surface and Coatings Technology, **202**, 5162 (2008).
- ⁵ A. K. Keshri, K. Balani, S. R. Bakshi, V. Singh, T. Laha, S. Seal, A. Agarwal, Surface and Coatings Technology, **203**, (2009).
- ⁶ H. Uozumi, K. Kobayashi, K. Nakanishi, T. Matsunaga, K. Shinozaki, H. Sakamoto, T. Tsukuda, C. Masuda, M. Yoshida, Materials Science and Engineering A, **495**, 282 (2008).
- ⁷ C. S. Gon, J. Wei, L. C. Lee, M. Gupta, Composites Science and Technology, **68**, 1432 (2008).
- ⁸ M. Paramsothy, S. F. Hassan, N. Srikanth, M. Gupta, Applied Science and Manufacturing, **40**, 1490 (2009).
- ⁹ D. K. Lim, T. Shibayanagi, A. P. Gerlich, Materials Science and Engineering A, **507**, 194 (2009).
- ¹⁰ A. M. K. Esawi, M. A. El Borady, Composites Science and Technology, **68**, 486 (2008).
- ¹¹ H. J. Choi, G. Kwon, G. Lee, D. Bae, Scripta Materialia, **59**, 360 (2008).
- ¹² L. A. Yolshina, R.V. Muradymov, I. V. Korsun, G. A. Yakovlev, S. V. Smirnov, J. Alloys and Compounds, **663**, 449 (2016).
- ¹³ A. M. K. Esawi, K. Morsi, A. Sayed, A. A. Gaward, P. Borah, Materials Science and Engineering A, **508**, 167 (2009).
- ¹⁴ H. J. Choi, J. H. Shin, D. H. Bae, Composites Part A: Applied Science and Manufacturing, **43**, 106 (2012).
- ¹⁵ K. Choi, J. Seo, D. Bae, H. Choi, Trans. Nonferrous Met. Soc. China, **24**, 47 (2014).
- ¹⁶ R. Pérez-Bustamante, C. D. Gómez-Esparza, I. Estrada-Guel, M. Miki-Yoshida, L. Licea-Jiménez, S. A. Pérez-García, R. Martínez-Sánchez, Materials Science and Engineering A, **508**, 159 (2009).
- ¹⁷ M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, Science of Fullerenes and Carbon Nanotubes, Academic Press, NewYork, NY/San Diego, CA, 1996.
- ¹⁸ R. Deves, D. Aspimvall, J. Simao, H.G.Lee. Electric Al, Materials Word, **11** 16 (2003).
- ¹⁹ D. Golberg, Y. Bando, O. Stéphan, and K. Kurashima, Appl. Phys. Lett. **73**, 2441 (1998).
- ²⁰ O. N. Sizonenko, A. I. Vovchenko, International virtual journal for science, technics and innovations for the industry, **8**, 41 (2014).
- ²¹ Z. A. Munir, U. Anselmi-Tamburini, M. Ohyanagi, Journal of Materials Science, **41**, 763 (2006).
- ²² E. Osawa, Perspectives of Fullerene Nanotechnology, Springer Science & Business Media, 2002, 375 p.
- ²³ R. Saito, M. Hofmann, G. Dresselhaus, A. Jorito and M. S. Dresselhaus, Advances in Physics, **60**, 413 (2011)
- ²⁴ O. N. Sizonenko, E. G. Grigoryev, A. D. Zaichenko, N. S. Pristash, A. S. Torpakov, Y. V. Lypian, V. A. Tregub, A. G. Zholnin, A. V. Yudin, and A. A. Kovalenko, High Temp. Mater. Proc. **36**, 891 (2017).
- ²⁵ O. N. Sizonenko, G. A. Baglyuk, E. I. Taftai, A. D. Zaichenko, E. V. Lipyman, A. S. Torpakov, A. A. Zhdanov, N. S. Pristash, Powder Metall. Met. Ceram. **52**, 247 (2013).
- ²⁶ D. S. Bethune, G. Meijer *, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, M. S. de Vries, Chemical Physics Letters, **179**, 175 (1991)
- ²⁷ O. Chernogorova, I. Potapova, E. Drozdova, V. Sirotinkin, A. V. Soldatov, A. Vasiliev, and E. Ekimov, Appl. Phys. Lett., **104**, 043110 (2014)
- ²⁸ K.J. Cai, Y. Zheng, P. Shen, S. Y. Chen, CrystEngComm, **24** (2014).
- ²⁹ K. J Cai, Y. Zheng, P. Shen and S. Y. Chen. CrystEngComm, **16**, 5466 (2014)

ELECTROPLATING WITH TUNGSTEN AND TUNGSTEN-MOLYBDENUM ALLOYS FROM METAPHOSPHATE-CONTAINING HALIDE-OXIDE AND OXIDE MELTS

Prof., D.Sc. Malyshev V.¹, Prof., D.Sc. Kushchevska N.¹, Prof., D.Sc. Bagliuk G.², Ph.Dr. Shakhnin D.B.¹, Prof., Ph.Dr. Paprotskaya O.¹, Ph.Dr. Zaliubovskiy M.¹

Institute for Engineering & Technology – University "Ukraine", Ukraine¹

I.M. Frantsevich's Institute for Problems in Materials Science of the National Academy of Sciences of Ukraine, Ukraine²
gbag@ukr.net

Abstract: The electrochemical behavior of dimeric tungsten complexes in metaphosphate-containing melts is studied potentiometrically and voltammetrically. The electrodeposition of tungsten and tungsten coatings from halide-oxide and oxide melts and the correlation between the properties of deposits and the conditions of electrolysis are investigated.

Keywords: ELECTROPLATING, TUNGSTEN, TUNGSTEN-MOLYBDENUM ALLOYS, METAPGOSPHAT, HALIDE AND HALIDE-OXIDE MELTS

1. Introduction

For the purposes of applied electrochemistry, it is convenient to use cheap, nonaggressive, and non-hygroscopic solvents, such as an equimolar KCl-NaCl composition. The concentration of stable oxygen-containing complex tungsten anions in this melt is sufficient, and the losses due to sublimation are insubstantial. The advantages of such baths are their stability in air and compatibility with aluminum oxide (alundum or corundum), which allows one to work with open electrolyzers with a soluble tungsten anode. Because of its binding in stable complexes, tungsten becomes less noble and, without contact deposition, can be cathodically applied not only to the metals of platinum family (as in purely halide solutions), but also to graphite, copper, and nickel. However, nonadherent coatings of complex composition are electroplated from these melts to steel specimens [1-3]. The melts based on tungstates and molybdates are typical ionic liquids: they are thermally stable, have comparatively low viscosity and melting point and relatively high electroconductivity and decomposition voltage [4, 5].

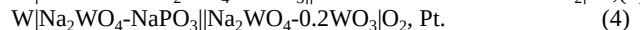
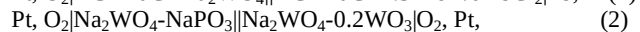
2. Experimental

The details of preparing electrolytes, the design of electrodes and cells, and the techniques of the investigation of coatings were considered in detail in [6].

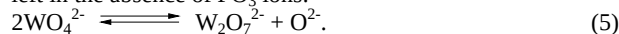
3. Result and discussion

3.1 Ionic composition of metaphosphate-containing melts

Electromotive forces (EMFs) of the following electrochemical circuits were measured:



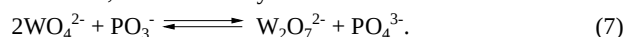
According to the conventional hypothesis on the acid-base equilibria, the equilibrium in the melts in question is shifted to the left in the absence of PO_3^- ions:



The introduction of metaphosphate leads to the binding of oxygen ions:



that is, to the summary reaction



The decrease in the activity of O^{2-} ions upon the introduction of PO_3^- ions in a chloride-tungstate melt is confirmed by the increase in the equilibrium potential of the oxygen electrode $E(\text{O}_2)$ with an increase in the concentration of PO_3^- (see Fig. 1), which, by Eq. (6), decreases the activity of the reduced oxygen form in the melt. The

derivation of an equation for $E(\text{O}_2)$ is awkward in this case because of the complex composition of the melt.

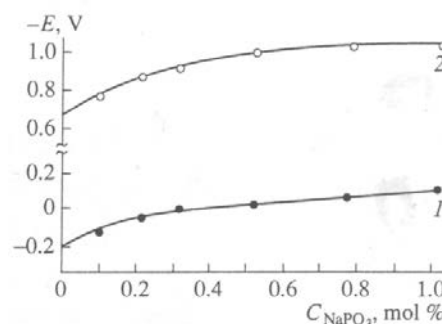
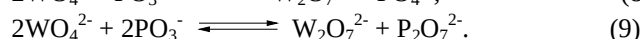
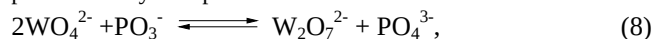


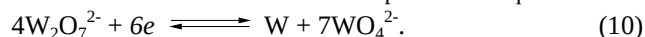
Fig. 1: The dependence of the potential of a platinum-oxygen electrode on the concentration of NaPO_3 in a $\text{NaCl-KCl-0.35 mol/dm}^3 \text{Na}_2\text{WO}_4$ melt vs. the reference electrodes (1) $\text{Pt, O}_2 / \text{KCl - NaCl - 0.3 mol/dm}^3 \text{Na}_2\text{WO}_4$ and (2) Pb/Pb^{2+} .

In the presence of PO_3^- ions in a Na_2WO_4 melt, the following processes may take place:



Using the same mathematical approach, as we applied in [7] for deriving an equation for $E(\text{O}_2)$, we come to a conclusion that in the concentration range studied, reaction (9) actually proceeds with the formation of $\text{W}_2\text{O}_7^{2-}$ and $\text{P}_2\text{O}_7^{2-}$ ions.

In $\text{KCl-NaCl-Na}_2\text{WO}_4\text{-NaPO}_3$ melts, a noticeable corrosion of tungsten is observed. At Na_2WO_4 and NaPO_3 concentrations of 0.175 and 0.06 mol/l, respectively, and a temperature of 1023 K, it is about 12.0 to 15.3 g/(m²h). The number of electrons formally calculated from the value of the pre-logarithmic factor in the $dE/d\log C$ dependence is 0.5 to 0.8, which is substantially smaller than the value of 1.5 that should correspond to the equation



The EMF of a circuit (4) was measured in a NaPO_3 concentration range from 1.0 to 10.0 mol %. At a metaphosphate concentration lower than 1.0 mol %, tungsten insubstantially corrodes (at a corrosion rate of 3 to 5 x 10⁻⁷ g/(m²h)). At a NaPO_3 concentration higher than 1.0 mol %, the corrosion is not practically observed. An equation for the attained steady-state potential of a tungsten electrode can be written in the form of Eq. (10).

Taking into account reaction (9), from the $dE/d\log 2C_{\text{NaPO}_3}$ dependence (see Fig. 2), we can estimate the number of electrons per one electrochemically active particle as 1.5. In the concentration range studied, $n = 1.44$ to 1.51. This value corresponds to electrode reaction (10).

3.2 Electroreduction of oxide tungsten (VI) forms in metaphosphate-containing melts

Tungstate ions WO_4^{2-} are not electrochemically active particles in a chloride melt. Upon the introduction of PO_3^- ions in the melt, two waves appear on the voltammograms (see Fig. 3, curve 3) at potentials of -0.1 to -0.2 V and -0.3 to 0.5 V vs. a Pb/Pb^{2+} reference electrode. At a concentration of PO_3^- in the range $0.01 < [\text{PO}_3^-]/[\text{WO}_4^{2-}] < 0.18$, the product of potentiostatic electrolysis at the above potentials is metallic tungsten. An increase in the NaPO_3 concentration to $[\text{PO}_3^-]/[\text{WO}_4^{2-}] \gg 0.18$ results in the appearance of tungsten phosphides in the products of electrolysis.

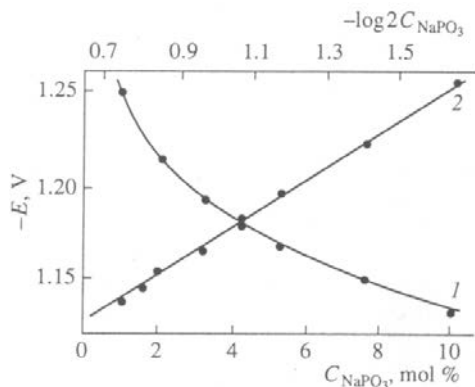


Fig. 2: (1) The dependence of the potential of a tungsten electrode on the concentration of NaPO_3 in a sodium tungstate melt and (2) its representation in logarithmic coordinates.

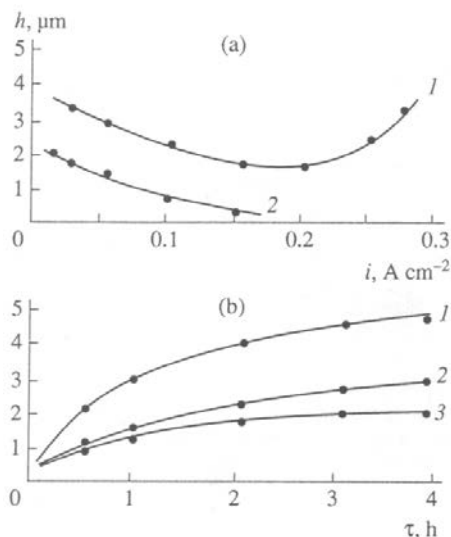
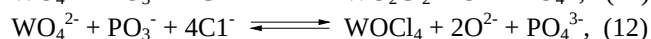
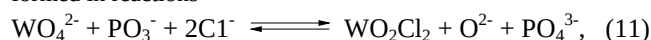


Fig. 3: The roughness amplitude of tungsten coatings on specimens of (a, curve 2; b, curves 2 and 3) St3 steel and (a, b, curves 7) copper vs. (a) the current density ($\tau = 1.5 \text{ h}$) and (b) the duration of electrolysis (1, 2) at a direct current i_c of (7) 10 and (2) 15 A/dm^2 and (3) under reversal conditions of plating ($i_c = 15 \text{ A/dm}^2$, $t_c = 25 \text{ s}$, $i_d = 30 \text{ A/dm}^2$, and $t_d = 0.5 \text{ s}$): (1) $\text{KCl-NaCl} - 2.5 \text{ mol \% Na}_2\text{WO}_4 - 0.35 \text{ mol \% NaPO}_3$ and (2, 3) $\text{Na}_2\text{WO}_4 - 5 \text{ mol \% NaPO}_3$.

Cyclic voltammograms ($E^{c-a} = (0.550 \dots 0.630) > 0.047 \text{ V} = 3.2RT/2F$) and the dependence of the half-peak potentials of the waves on the polarization rate of the electrode indicate the irreversible character of the electrode process. Modeling electrode processes [7] allows us to believe that the first wave ion the voltammogram of a $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4 - \text{NaPO}_3$ system corresponds to the discharge of tungsten oxychlorides, which are formed in reactions



while the second wave appears due to the discharge of ditungstate ions, which are formed in reaction (7). On the voltammograms of $\text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melts, a wave corresponding to the reduction was observed at a potential of -1.1 to -1.2 V. The limiting currents were proportional to the concentration of metaphosphate added rather than to the summary concentration of tungsten in the melt. The

reduction proceeds in one stage, and the product of potentiostatic electrolysis of the melt at a potential of -1.2 V is metallic tungsten.

The proportionality of the limiting current to the concentration of sodium metaphosphate, the constancy of the $i_d/V^{1/2}$ ratio (where i_d is the limiting current and V is the polarization rate), and the value of the kinetic constant i_d/nFc , which is 8.3 to $9.5 \times 10^{-5} \text{ cm/s}$ for the steady-state waves, indicate the fact that the electrode process is limited by the diffusion of electrochemically active particles to the electrode. Ditungstate ions, which are formed in reaction (8), become electrochemically active in the summary electrode process (10). Under the steady-state conditions, the slope of the $E - \log(i_d - i)$ dependence varies from 38 to 42 mV at different NaPO_3 concentrations, while the number n of electrons, which are transferred in the electrode process, is 5.8 ± 0.3 . This means that the charge transfer stage of Eq. (10) is reversible. The number of electrons, which is determined from the half-widths of the peaks in non-steady-state voltammograms according to Matsuda-Ayabe criterion for the NaPO_3 concentrations lower than 10 mol % and the polarization rates from 0.04 to 0.2 V/s, equals 5.9 to 6.1.

3.3 Electroplating with tungsten and tungsten-molybdenum alloys from metaphosphate-containing melts

3.3.1. The effect of the electrolysis conditions on the structure of tungsten coatings

The tungsten coatings were electroplated from $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4$ or Na_2WO_4 baths with NaPO_3 admixtures. The effect of the change in Na_2WO_4 and NaPO_3 concentrations, in temperature, cathodic current density, and the duration of electrolysis on the composition and structure of the deposits was investigated, and the optimal conditions with current reversal were found for plating.

3.3.2. The effect of sodium tungstate and metaphosphate concentrations

The tungsten coatings from the $\text{KCl} - \text{NaCl} - \text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melts are fit when the aforementioned concentration condition is met: $0.02 < [\text{PO}_3^-]/[\text{WO}_4^{2-}] < 0.18$. At a Na_2WO_4 concentration lower than 1 mol %, the deposit is not adherent, and no phosphide can be found in it. At a concentration higher than 10 mol %, the diffraction patterns show the presence of tungsten oxides. At a metaphosphate concentration $[\text{PO}_3^-]/[\text{WO}_4^{2-}] > 0.18$, tungsten again is deposited with phosphides, and no adherent coating is formed.

Tungsten coatings in a $\text{Na}_2\text{WO}_4 - \text{NaPO}_3$ melt form at a metaphosphate concentration from 0.5 to 15.0 mol %. Above this limit, along with tungsten, its bronzes form, and the deposit soon begins to grow as dendrites.

3.3.3. The effect of the temperature of electrolysis

Continuous tungsten coatings from a halide-oxide electrolyte were obtained at a temperature from 973 to 1073 K and a current density of up to 25 A/dm^2 . At a higher temperature, the system loses its stability, and its volatility increases. At a temperature below 973 K, only thin (up to 5 μm) tungsten layers can be obtained, and the deposit quickly transforms into a powder. At a current density higher than 25 A/dm^2 , dispersed tungsten powders are formed.

Continuous tungsten coatings from an oxide electrolyte were obtained at a temperature from 1023 to 1123 K and a current density of up to 40 A/dm^2 . At a temperature below 1023 K, only thin (up to 15 or 20 μm) tungsten layers are formed. At a current density higher than 40 A/dm^2 , highly dispersed tungsten powders with a specific surface area of 40 to 50 m^2/g form.

3.3.4. The effect of the cathodic current density and the duration of electrolysis

The effect of the cathodic current density, as well as the duration of electrolysis and the reversal conditions of plating, was

studied in KCl-NaCl — 2.5 mol % Na_2WO_4 — 0.35 mol % NaPO_3 and Na_2WO_4 — 5 mol % NaPO_3 electrolytes. Adherent, continuous, and nonporous coatings were obtained from the above electrolytes at temperatures of 923 and 1173 K and current densities of 1 to 15 and 3 to 25 A/dm^2 , respectively.

The grains size in the deposit has a minimum depending on the current density, and above 25 A/dm^2 , the crystallites become substantially larger, while the surface grows rougher. Finally, the deposit transforms into dendrites. At a current density lower than 2.5 A/dm^2 , the corrosion rate of a substrate is too large, and no adherent coating is formed.

The deposition rate of tungsten in the studied range of current densities is 5 to 15 $\mu\text{m/h}$ in a halide-oxide electrolyte and 20 to 45 $\mu\text{m/h}$ in an oxide electrolyte. The current efficiency of a tungsten coating is up to 60 and 95%, respectively. The time dependences of the thickness of a coating and its current efficiency are shown in Fig. 5. As the duration of electrolysis increases, the current efficiency drops.

From halide-oxide electrolytes, we obtained adherent continuous tungsten coatings on nickel, copper, graphite, tungsten, and molybdenum. In oxide melts, the coatings were obtained also on different instrumental steels, hard alloys and nitric-, copper-, or nickel-plated titanium.

3.3.5. The controlling of the structure of coatings by reversal conditions of plating

Profilometric investigation shows that, as the deposit thickens, its single-phase fine-crystalline structure transforms into a coarser one. We tried to prevent the formation of a coarse-grain structure by applying reversal conditions of electrolysis. The duration ratio of the cathodic to anodic period was varied from 15 to 50 at a duration of the anodic period from 0.5 to 3.0 s, and the anodic current density was changed from 20 to 50 A/dm^2 . The following conditions are optimal for a Na_2WO_4 - 5 mol % NaPO_3 electrolyte at 1173 K: ($i_c = 15 \text{ A/dm}^2$, $i_a = 30 \text{ A/dm}^2$, $\tau_c = 25 \text{ s}$, and $\tau_a = 1.5 \text{ s}$). In this case, relatively smooth coatings of a thickness of up to 0.5 mm were obtained at the cathode.

3.4. Physicochemical properties and performance of tungsten coatings

The coatings are light-gray microgranular continuous deposits. By the data of x-ray spectral microanalysis, alien metallic admixtures are contained in an amount of up to 0.02 wt % and do not noticeably affect the structure of coatings. According to standard estimates [8], the pores area in coatings is 0.0 to 0.2%, which is considered as an indication of a practically nonporous coating.

The microhardness does not change across the coating and equals 460 to 485 kgf/mm^2 . The diffusional area of 5 to 20 μm , revealed with the x-ray spectral microanalysis of the cross sections of a specimen, indicates that there is a mutual diffusion of the elements of the coating and the substrate, which provides the proper adherence of the coating. The continuity of the transition from the coating to the substrate was confirmed by stereoscanograms of spallings of the specimens, which concurrently showed a pronounced columnar structure of the deposit.

The specimens of steel 45 with a tungsten coating were thoroughly tested in a friction pair with a quenched steel 45 counterbody. As a result of the plating, the wear resistance increased by a factor of 4.5 to 5.7.

The specimens of steel 45 with tungsten coatings were tested for abrasive resistance in an electrocorundum 100- μm fraction at a load of $52 \pm 0.25 \text{ N}$. Due to the coating, the abrasive resistance increased 2.5 to 4.3 times.

4. Conclusion

Thus, we studied the electrochemical behavior of tungsten-metaphosphate melts, the electroplating with tungsten from them, and the properties of the coatings.

5. Literature

- [1] Wilkes J.S., A short history of ionic liquids – from molten salts to neoteric solvents, *Green Chem.*, 4, 2002, 73-80.
- [2] Nishikata A., Numata H., Tsuru T., Electrochemistry of molten salt corrosion, *Materials Science and Engineering: A*, 146, 1991, 15-31.
- [3] Malyshev V.V., Gab A.I., Uskova N.N., Soloviev V.V., Chemistry and Electrochemistry of Tungsten-Containing Ionic Melts, *Molten Salts Bulletin*, 2, 2004, 1-10.
- [4] Malyshev V., Shakhin D., Influence of temperature and the composition of tungstate-molybdate alloys on the morphology of their electrolytic deposits, *Materials Science*, 48, 2012, 375-383.
- [5] Gua Y., Liu J., Qu S., Deng Y., Han X., Hua W., Zhong C., Electrodeposition of alloys and compounds from high-temperature molten salts, *Journal of Alloys and Compounds*, 690, 2017, 228-238.
- [6] Malyshev V.V., Soloviev V.V., Chernenko L.A., Rozhko V.N., Management of composition cathodic products in the electrolysis of molybdenum-, tungsten- and carbon-bearing halogenide-oxide and oxide melts, *Materialwissenschaft und Werkstofftechnik (Materials Science and Engineering Technology)*, 45, 2015, 67-72.
- [7] Malyshev V.V., Kushkhov H.B., Electrochemical behavior of platinum-oxygen and tungsten electrodes in the melt of sodium tungstate-sodium metaphosphate, *Ukr. Khim. Zhurn.*, 63, 1997, 115-118.
- [8] Damaskin B.B., Petrij O.A., Cirlina G.A., *Electrochemistry*, Koloss, Moscow, 2006.

EFFECT OF DYNAMICAL AGING IN SLM Ti-6Al-4V ALLOYS

ЭФФЕКТ ДИНАМИЧЕСКОГО СТАРЕНИЯ В СЛС Ti-6Al-4V СПЛАВАХ

Davidov D. PhD.¹, Prof. Kazantseva N. Dr. of Sci.¹, Ezhov I. PhD Student 1, Fefelov A. PhD.², Merkushev A.², Afanasyev S. PhD.¹
Institute of Metal Physics, Ekaterinburg, Russia¹

Regional Engineering Center of laser and additive technology, Ekaterinburg, Russia²

kazantseva-11@mail.ru

Abstract: The application of the selective laser melting (SLM) method requires knowledge of not only the properties of the material after manufacturing, but also after mechanical loading. The aim of this work is to investigate the strain-rate dependence and microstructure of Ti6Al4V samples manufactured by SLM method with different angles to the building platform. SLM Ti-6Al-4V samples were manufactured using the EOSINT M280 (EOS GmbH) at angles of 0°, 30°, 45°, 90° to the building platform. A medicine Ti6Al4V (ASTM grade 23) powder was used for the study. Tensile tests were performed with an Instron test machine using two strain rates 0.5 mm/min and 2 mm/min at room temperature. It was found the strain-rate dependence in the studied samples. The features of the mechanisms of hardening and softening in an investigated SLM Ti-6Al-V alloy are discussed.

KEYWORDS: TITANIUM ALLOY, SLM, 3D PRINTING, MICROSTRUCTURE, STRAIN RATE DEPENDENCE

1. Introduction

Deformation process of metallic materials at high-temperature conditions is competing with non-equilibrium processes associated with their hardening and softening. An increase in the metal density of dislocations is considered as the main contribution to metal hardening [1]. The experimentally obtained curve of dependence of the deformation resistance σ on the degree of deformation ε may show two different variants of hardening of the deformed materials. In the first case, a wave curve may be observed. The appearance of the waves is associated with the Portwein-Le Châtelier (PLC) effect, which is explained by the occurrence of propagative localized bands [2]. In the second case, the curve shows the repeated hardening of the alloy after past appreciable weakening [1].

In the absence of phase transitions, softening of the alloy occurs by dynamic return, polygonization and recrystallization [1]. Under certain temperature-velocity conditions of deformation, the dynamic deformation aging (DDA) may be occur. DDA effect associated with the increasing of the ductility of the material with increasing of the strain rate in defined range of the temperatures and rates [1]. Increasing in the strain rate usually decreases the mechanical properties of the materials. However, in some cases the effect of dynamical deformation aging was observed in conventional titanium alloys and steels [3-4].

The main purpose of this work is to study the effect of dynamic deformation aging the Ti-6Al-4V alloys manufactured by the selective laser melting.

2. Experimental

Spherical argon-atomized Ti6Al4V (ELI) (45 μ m) powder from TLS Technik was used for study. The chemical composition complies with the ASTM B348 (Grade 23) for surgical implant applications. Ti-6Al-4V samples were manufactured by 3D printing using the selective laser melting (SLM) with the EOSINT M280 (EOS GmbH) 3D printing machine equipped with an Ytterbium fiber laser, and operating at 1075 nm wavelength (IPG Photonics Corp.). Standard EOS regime for manufacturing of the titanium alloys was used. SLM Ti-6Al-4V samples were manufactured at angles of 0°, 30°, 45°, 90° to the building platform. Structural studies were done with the QUANTA-200 scanning electron microscope equipped with a Pegasus system for the structural and texture analyses and with an EDAX energy-dispersive spectrometer for the elemental analysis. Tensile tests were performed at room temperature with an Instron test machine using two strain rates: 0.0013 s⁻¹ and 0.0004 s⁻¹. Samples were manufactured in the form of cylinders with a diameter of 12 mm and a length of 55 mm. Samples for mechanical testing were cut from the cylinders in accordance with GOST RF 1497-84. Density of the manufactured samples was defined as 99,7 %.

3. Results and Discussion

Figure 1 shows the schema of orientation of the sample to the building platform.

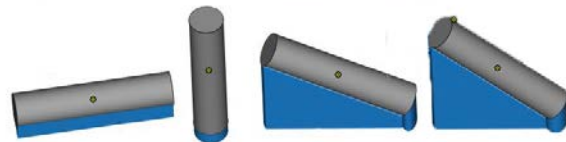


Fig.1 Schema of the orientation studied samples to the building platform in EOSINT 280M printer.

At the initial (as-build) state, all of the samples had the martensitic HCP α' -structure. Figure 2 presents the structure of the 45° sample. Such structure was found in all of studied samples.

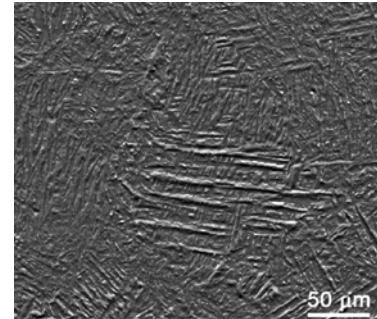


Fig.2 Structure of 45° sample, scanning electron microscopy.

In the structure of the as-build samples, we found the pores. Spherical pores are characteristic of materials obtained by selective laser melting. Small pores with dimensions of about 4-10 microns and pores with sizes up to 30 microns may be observed in the structure of the samples (Fig. 3).

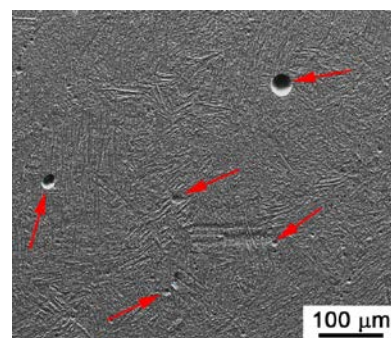


Fig.3 Pores in the as-build 45° sample, scanning electron microscopy.

Results of the mechanical testing are presented in the Table 1.

Table 1: Tensile properties of as-built Ti6Al4V samples

Building angle (grad)	UTS, (MPa)	YS, (MPa)	Elongation at break (%)	Strain rate, s ⁻¹
45	990	880	6.4	0.0004
45	1020	940	18.6	0.0013
0	1000	940	14.3	0.0013
30	1010	930	16.4	0.0013
90	980	890	13	0.0013

Figure 4 presents the strain-stress curves for 45° sample deformed at different rates. The dependence of the ductility on the strain rate was found in the 45° samples.

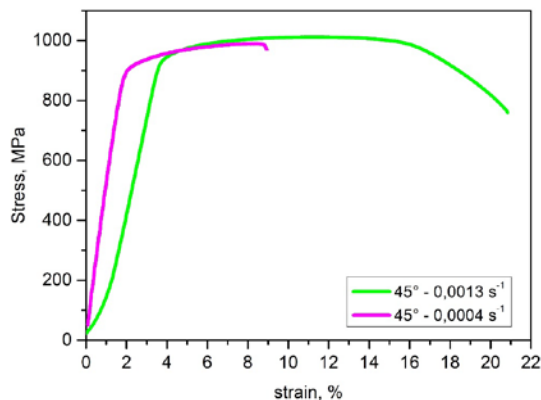


Fig.4 Strain-stress curves of 45° sample after deformation at different rates.

It is known that, the mechanical properties of the Ti6Al4V alloy strongly depend on the structure, heat treatment and the method of obtaining the samples [5]. As can be seen from the Table 1, the SLM samples grown at an angle of 45° to the building platform show the greatest plasticity. Increasing in strain rate up to 0.0004 s⁻¹ (this strain rate is a standard one for deformation of the small samples) leads to a significant decrease in plasticity of the 45° sample. The results of the mechanical testing at standard strain rate are in good correlation with the literature data for SLM Ti-6Al-4V alloys [5-7]. Usually, the mechanical properties of Ti6Al4V obtained by the SLM method are characterized by high yield strength (YS), high tensile resistance (UTS) and low ductility. High strength properties and low plasticity are associated with the formation of a martensitic structure at a high rate of crystallization [7].

Structure studies found the different distribution of the pores in the sample after deformation at different rates (Fig. 5).

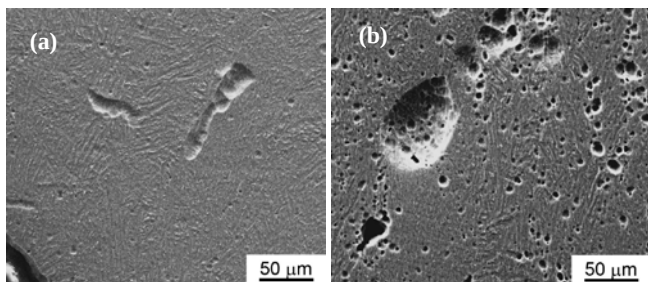


Fig.5 SEM structure of the pores in the 45° sample after deformation at different rates: (a) - 0.0004 s⁻¹; (b) - 0.0013 s⁻¹.

The sample deformed at standard strain rate (0.0004 s⁻¹) shows the weak neck formation, which is associated with coarsening and coalescence of the pores (Fig. 5a). In the case of the rapid strain rate (0.0013 s⁻¹), deformation occurs by formation of the deep necking region, which is associated with new pore formation and its coalescence (Fig. 5b). The pore behavior under standard rate of deformation was studied in [8]. Authors found the same behavior of the pores in the neck of the sample, which was associated with

coarsening and coalescence of the pores in the SLM Ti-6Al-4V sample under deformation.

4. Conclusion

1. Structure and deformation process of the SLM Ti6Al4V (grade 23) samples with a density 99.7% were studied. Microstructure of the SLM samples showed the presence of pores with the size from 4 to 30 μm.
2. Deformation process in the sample under different strain rates showed rate dependence of the plasticity of the sample. The elongation at the break was also found depending on the orientation of the sample to the building platform. The most elongation was found in the 45° sample.
3. The ductile fracture mechanism of the samples deformed at rapid strain rate (0.0013 s⁻¹) under tension is associated with formation of the deep necking region, which is associated with new pore formation and its coalescence.
4. The sample deformed at standard strain rate (0.0004 s⁻¹) shows the weak neck formation, which is associated with coarsening and coalescence of the pores.

Acknowledgments

This work was supported by the Russian Fund of Basic Research No 17-03-00084, State programs "Diagnostics" AAAA-A18-118020690196-3 and "Pressure" No. AAAA-A18-118020190104-3.

References

1. Zh.P. Pastukhova, A.G. Rakhshadt, Yu.A. Kaplun, *Dynamic aging of alloys*. Moscow: Metallurgy. (1985).
2. A. Yilmaz, The Portevin–Le Chatelier effect: a review of experimental findings, *Sci Technol Adv Mater*. 12(6) (2011) 063001.
3. Sang-hyun Cho, Yeon-chuL Yoo, J. J. Jonas. Static and dynamic strain aging in 304 austenitic stainless steel at elevated temperatures, *Journal of materials science letters*. 19 (2000) 2019–2022.
4. L. Ladani1, J. Razmi and S. Farhan, Choudhury Mechanical Anisotropy and Strain Rate Dependency Behavior of Ti6Al4V Produced Using E-Beam Additive Fabrication. *J. Eng. Mater. Technol*. 136(3), (2014) 031006.
5. T.H. Becker, M. Beck, and C. Scheffer, Microstructure and mechanical properties of direct metal laser sintered Ti-6Al-4V. *South African Journal of Industrial Engineering*. 26(1) (2015) 1-10.
6. A. Mertens, S. Reginster, H. Paydas, Q. Contrepolis, T. Dormal, O. Lemaire, and J. Lecomte-Beckers, Mechanical properties of alloy Ti-6Al-4V and of stainless steel 316L processed by selective laser melting: Influence of out-of-equilibrium microstructures. *Powder Metallurgy*, 57(3) (2014) 184-189.
7. P. Krakhmalev, G. Fredricsson, I.Yadroitseva, N. Kazantseva, A. Du Plessis, I.Yadroitsev, Deformation Behavior and Microstructure of Ti6Al4V Manufactured by SLM, *Physics Procedia*, 83 (2016) 778 – 788.
8. M.G. Moletsane, P. Krakhmalev, N. Kazantseva, A. Du Plessis, I. Yadroitsava & I. Yadroitsev Tensile properties and microstructure of direct metal laser-sintered Ti6Al4V (ELI) alloy, *South African Journal of Industrial Engineering*, 27(3) Special Edition (2016) 110-121.