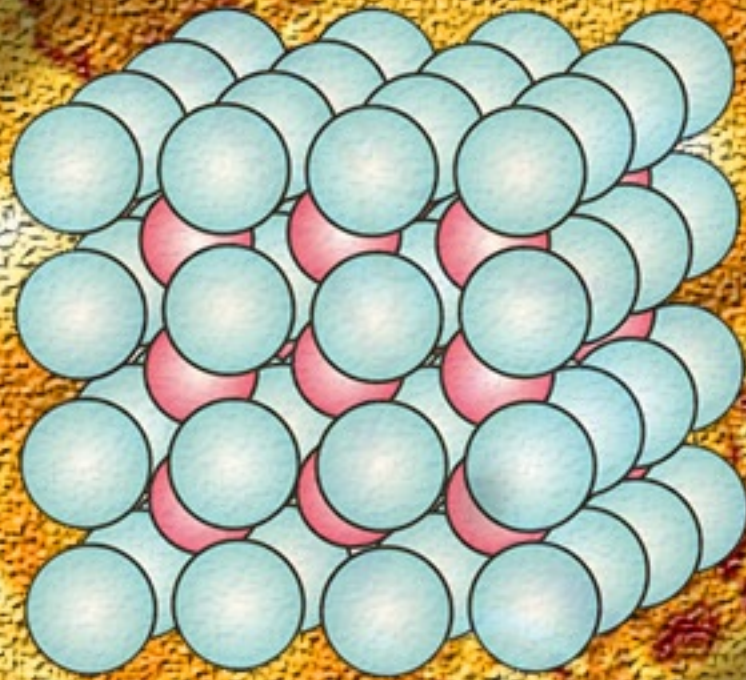


INTERNATIONAL SCIENTIFIC JOURNAL

"MATERIAL SCIENCE"



„NONEQUILIBRIUM PHASE TRANSFORMATIONS“

YEAR III, ISSUE 4/2017

ISSN PRINT 2367-749X

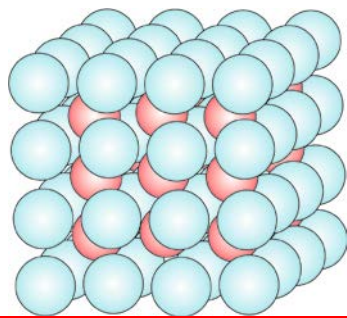
ISSN WEB 2534-8477

PUBLISHER: SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING
INDUSTRY 4.0

108 Rakovski str., 1000 Sofia, Bulgaria

tel./fax (+359 2) 986 22 40, tel. (+359 2) 987 72 90,

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INTERNATIONAL SCIENTIFIC JOURNAL MATERIALS SCIENCE. NON-EQUILIBRIUM PHASE TRANSFORMATIONS

PUBLISHER:

SCIENTIFIC TECHNICAL UNION OF MECHANICAL ENGINEERING

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ISSN PRINT 2367-749X, ISSN WEB 2534-8477
YEAR III, ISSUE 4/ 2017

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CONTENTS

TRANSFORMATION OF HETEROPHASE NON-METALLIC INCLUSIONS “HIGH-MELTING PHASE SURROUNDING WITH LOW-MELTING COVER” IN STEELS UNDER LASER ACTION Prof.. Dr. Sci. Gubenko S.	121
ANALYSIS OF THE GRAIN BOUNDARY MICROSTRUCTURE AND DEGRADATION IN A GAS TURBINE BLADE Davydov D.I., Kazantseva N.V., Vinogradova N.I., Ezhov I.V., Stepanova N. N.	126
THE IMPACT OF CURRENT SHAPE DURING THE CONSOLIDATION PROCESS ON PHYSICO-MECHANICAL PROPERTIES OF FUNCTIONAL Fe – Ti – C – B SYSTEM MATERIALS Sizonenko Olga Nikolaevna, DrSc Eng., Professor, Zaichenko Andrii Dmytrovych, PhD Eng., Kovalenko Aleksandr Aleksandrovich, Pristash Nikolay Sergeevich, Torpakov Andrey Sergeevich	130
EVOLUTION OF PHASES AT THE BIFURCATION POINT Prof .Aldabergenov M.K., Prof. Balakaeva G.T.	134
NONCONVENTIONAL METHODS OF HEAT TREATMENT OF ALUMINUM ALLOYS Prof. Dr. Eng. Afanasyev V., Prof. Dr. Eng. Popova M., Prof. Dr. Eng. Prudnikov A.	137
THE STRUCTURAL AND TOPOLOGICAL HEREDITARITY UPON CRYSTALLIZATION OF NEAR-EUTECTIC ALLOYS Ass. Prof. Ph.D. Degtyareva Antonina, Ass. Prof. Ph.D. Tundybayeva Elmira, master Imankulova Sar.....	141
MAGNETIC AND ELECTROCONDUCTIVE PROPERTIES OF THE PURE CARBON SOOT SYNTHESISED BY ARC DISCHARGE Zaikovskii A.V. PhD.	146
MODELING OF METAL CRYSTALLIZATION BY MEANS OF CELLULAR AUTOMATON Ass. Prof., Dr. Eng. Donii O.	150
STUDY OF PHASE TRANSFORMATIONS IN THE ROLLS OF ALLOY STEELS DURING QUENCHING BASED ON FINITE-ELEMENT MODEL Dr.Sc. Bobyr S.V., Dr. Krot P.V., eng. Loschkarev D.V., eng. Dedik M.O., eng. Sharfnadel S.A.	154
EFFECT OF INITIAL MOLD TEMPERATURE ON THE CRYSTALLIZATION KINETICS OF Cu47Ni8Ti34Zr11 ALLOY Associate prof. Kosynska O.L.	158
EFFECT OF HIGH PRESSURE TORSION ON THE STRUCTURE, MICROHARDNESS AND HEATING BEHAVIOUR OF THE MAGNESIUM ALLOY WE43 PhD Lukyanova E.A., PhD student Martynenko N.S., PhD Li E.V., PhD Serebryany V.N., Prof., Dr. Sci. Belyakov A.N., Prof. Dr. Sci. Rokhlin L.L., Prof. Dr. Sci. Dobatkin S.V., Prof. Estrin Yu.Z.	161
CORROSION PROPERTIES OF DIFFUSIONAL ZINC COATINGS OBTAINED BY NANOGALVANIZING Galin R. G., Biryukov A. I., Zakharyevich D. A., Batmanova T. V., Yankov E., Fiskuchev S.	165

TRANSFORMATION OF HETEROPHASE NON-METALLIC INCLUSIONS “HIGH-MELTING PHASE SURROUNDING WITH LOW-MELTING COVER” IN STEELS UNDER LASER ACTION

ТРАНСФОРМАЦІЯ ГЕТЕРОФАЗНИХ НЕМЕТАЛІЧЕСКИХ ВКЛЮЧЕНІЙ «ТУГОПЛАВКАЯ ФАЗА, ОКРУЖЕННАЯ ЛЕГКОПЛАВКОЙ ОБОЛОЧКОЙ» В СТАЛЯХ ПРИ ЛАЗЕРНОМ ВОЗДЕЙСТВИИ

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Abstract. Melting and crystallization of heterophase non-metallic inclusions “high-melting phase surrounding with low-melting cover” was investigated. It was shown that under laser action the initial structure of inclusion-steel matrix boundaries transits into unstable equilibrium high-energy condition that cause development of the dissipation processes connecting with aspiration of system inclusion-matrix to the state with minimum of free energy. In the result of the system heterophase inclusion-matrix transits to the state of unstable equilibrium which determines structure and properties of laser-quenched interphase boundary. Processes of melting, fusion and dissolution of non-metallic inclusions “high-melting phase surrounding with low-melting cover” and also of the melting of steel matrix play the great role in transformation of interphase inclusion-matrix boundaries under laser action.

KEYWORDS: HETEROPHASE NON-METALLIC INCLUSIONS “HIGH-MELTING PHASE SURROUNDING WITH LOW-MELTING COVER”, STEEL, STRENGTHENING, LASER TREATMENT

1. Introduction

Except homophase non-metallic inclusions of oxides, nitrides, sulphides, silicates there are different heterophase inclusions in steels having various nature and structure [1]. The first one are inclusions “high-melting phase (ph2) surrounding with low-melting cover (ph-c1)” with interphase boundary $ph-c1 \leftrightarrow ph2$. These inclusions influence on the character of strengthening during laser quenching. In the process of laser treatment different phases of these non-metallic inclusions are fully or partly melted down or are remained hard [1, 2]. Distribution of temperature on the surface of specimen influence on the process of interaction between inclusions and steel matrix [3]. In spite of short-term treatment the energy of laser radiation turns out sufficient for melting of the high-melting phase ph-2 and low-melting cover ph-c1, and also for the development of mass transfer processes which lead to enrichment of steel matrix with the elements of inclusions and also transfer of matrix elements to the surface zone of inclusions. Areas of steel matrix near non-metallic inclusions are the strongly oversaturated solid solution [1, 2]. In steel matrix near non-metallic inclusions the relaxation processes including speed local shear-rotational deformation and elements of return and recrystallization are occurred. The character of steels strengthening depends on the types of heterophase non-metallic inclusions and steel matrix, speed transformations which flow in steel matrix. The goal of this investigation was to research the processes of melting, dissolution, crystallization of heterophase non-metallic inclusions “high-melting phase surrounding with low-melting cover” in hyper-nonequilibrium conditions and the influence of non-metallic inclusions on the peculiarities of structural changes in steel matrix and its strengthening under laser treatment.

2. Materials and Procedures

Specimens made of steels R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3, 60G were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5kV and pulse energy of 10, 18, 25 and 30 J at heating rate of 10^5 °C/s and cooling rate of 10^6 °C/s with the action time of (1,0, 2,5, 3,6, 4,2 and 6,0) 10^{-3} s. Non-metallic inclusions were identified by metallographic, X-ray micro spectral and petrographic methods [1]. Distribution of elements, microhardness and nanohardness of steel matrix near non-metallic inclusions were determined.

3. Results and discussion.

Investigation of high-speed melting and crystallization of heterophase inclusions discovered variety of processes happening in inclusions and steel matrix near inclusions when in the moment of melting micro metallurgical bath is formed and melting of inclusion phases and steel matrix are interacted. Melting of inclusions and both interphase boundaries inclusion-matrix $ph-c1 \leftrightarrow m$ and inside inclusions $ph-c1 \leftrightarrow ph2$ connects with formation of heavy disordered areas on surface of inclusions (nucleus of melting) and abnormal mass transfer as the process of melting of homophase non-metallic inclusions.

Both phases of inclusions “high-melting phase surrounding with low-melting cover” in the moment of laser action are melted but the behavior of their phases is differ with degree of melting. Low-melting sulphide or silicate cover is melted fully, high-melting phase of oxide or nitride is melted partly or fully (Fig.. 1, a, b).

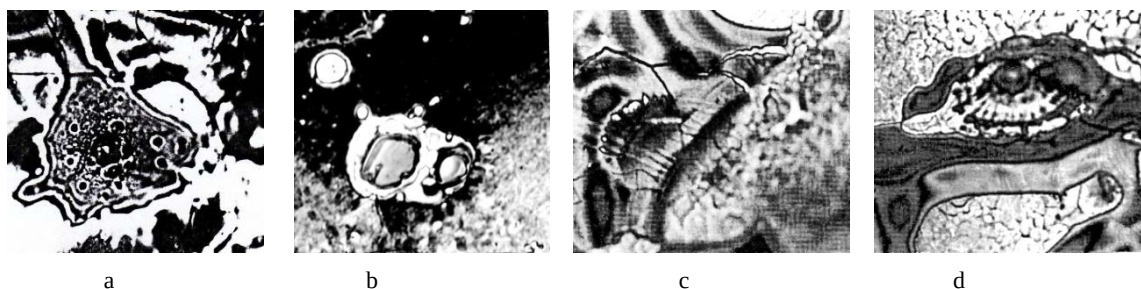


Figure 1. Dissolution and melting of heterophase non-metallic inclusions “high-melting phase surrounding with low-melting cover” under laser action; x500

On the surfaces of both phases mutual saturation was discovered and interphase boundaries inside inclusions are not legible. The interaction between interphase boundaries $ph-c1 \leftrightarrow m$ and steel matrix is similar to interaction for homophase inclusions. But low-melting cover of inclusion has interaction with both steel matrix and high-melting phase of inclusion, so it can to dissolve different atoms on the both sides and it can to accelerate process of dissolution or melting if solubility of elements in sulphide or silicate is sufficiently great. On surface of high-melting phase of oxide or nitride saturating with elements of low-melting cover the heavy disordered areas are formed which pass into liquid low-melting phase. Since in the conditions of laser action the relaxation processes in surface layers of both phases of inclusion “high-melting phase surrounding with low-melting cover” are not have time for happen the time for the achievement of quasiequilibrium conditions on both interphase inclusion-matrix boundaries $ph-c1 \leftrightarrow m$ and interphase boundaries inside inclusions $ph-c1 \leftrightarrow ph2$ is increased considerably. Inner stresses in surface layers of both phases of inclusion control the development of melting process which happens in limited volume owing to preservation of contact between phases of inclusion and also between low-melting cover and steel matrix. Elementary act of stresses relaxation causes activation and drawing in considerable number of atoms of both phases of inclusion to the process of disordered similar melting.

In the moment of laser melting of inclusions “high-melting phase surrounding with low-melting cover” origin the high degree of nonequilibrium of liquid phases (both phases of inclusion and steel matrix) and bifurcation instability of melt. This ensures gradient of vibration pressure on both interphase boundaries inclusion-matrix $ph-c1 \leftrightarrow m$ and inside inclusions $ph-c1 \leftrightarrow ph2$ (fully or partly liquid) which checks convective and abnormal flows of mass transfer. Considerable stresses appearing in thin surface layers of both phases of inclusion and steel matrix in the result of local heat flashes of laser radiation together with action of reactive forces of recoil by ejection from zone of treatment of liquid allows to high-temperature deformation of liquid interlayers continuing under crystallization during rapid cooling.

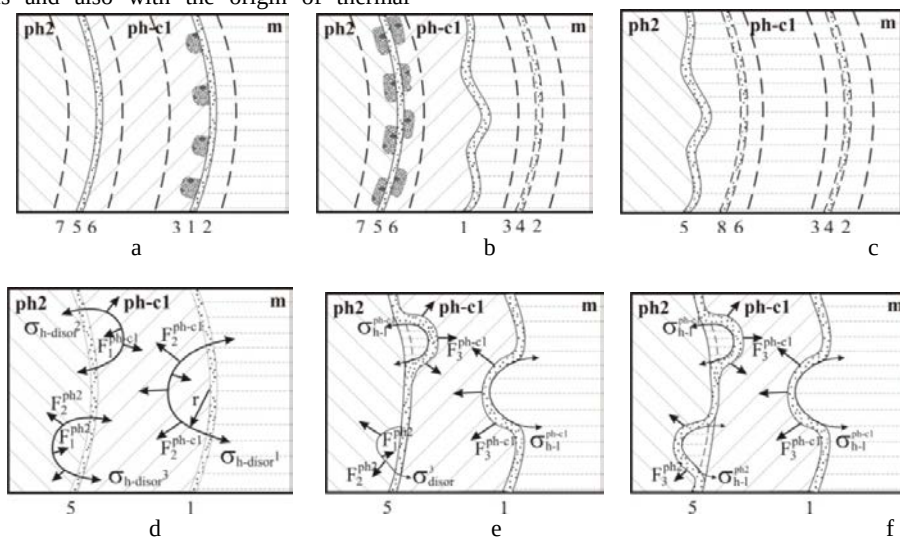
After high-speed melting of inclusions “high-melting phase surrounding with low-melting cover” happens the hyper-nonequilibrium crystallization connecting with formation of microphases, nanophases and sometimes of amorphous phases.

It was shown the formation of gradient and composite zones in steel matrix near non-metallic inclusions take place [1, 2]. Peculiarities of the structure of saturated zones in steel matrix near heterophase non-metallic inclusions depends on their type. All heterophase non-metallic inclusions promote the heterogeneous strengthening of steel matrix. That connects with its microalloying from inner sources – the different phases of non-metallic inclusions and also with the origin of thermal

Amorphous cover forms on the base of silicate or sulphide phase. Evidently silicate compositions have mostly display tendency for amorphization. After laser quenching from liquid state in low-melting cover zone with columnar shape of grains and liquation is formed (Fig. 1, c, d). Sequence of heavy distortion areas on the surfaces of phase-cover $ph-c1$ and phase $ph2$ and also of the movement of both interphase boundaries $ph-c1 \leftrightarrow m$ and $ph-c1 \leftrightarrow ph2$ under process of melting one can to present with next image (Fig. 2).

On the surface of phase-cover $ph-c1$ saturating with elements of steel matrix from one side and also saturating with elements of phase $ph2$ from other side the heavy disordered areas (the areas of melting) are formed (Fig. 2, a, b). Position of both interphase boundaries is changed owing to their melting (Fig. 2, b, c) in dependence on character of mass transfer between both phases of inclusion and phase-cover $ph-c1$ and steel matrix. Low-melting phase-cover $ph-c1$ is rapidly melted and it is become the liquid medium in which the high-melting phase $ph2$ is melted under transition of disordered areas into liquid phase-cover $ph-c1$. The phase-cover 1 is saturated with elements of phase $ph2$. Process of melting of the inclusions “high-melting phase surrounding with low-melting cover” is corresponded with the change of distribution of forces near heavy disordered areas in the surface layers in both phases of inclusion (fig. 2, d - f). Action of liquid steel matrix causes the change of surface tension of the phase-cover $ph-c1$ that breaks equilibrium shape of boundary $ph-c1 \leftrightarrow m$. Action of liquid phase-cover 1 causes the change of surface tension of the high-melting phase $ph2$ and that breaks equilibrium shape of the boundary $ph-c1 \leftrightarrow ph2$.

Evidently grain boundaries of the both phases of inclusion are melted more quickly than body of grains. That will cause the transition of complexes of former grains (micrograins, nanograins) into liquid state (Fig. 2, g, h). These complexes of phase-cover 1 are become the component of structure of liquid steel matrix and liquid layer on the boundary of phases of inclusion containing both complexes of phase of inclusion has complicated structure. Evidently more complicated processes happen in phase-cover 1 that causes with its contact with steel matrix and phase 2 having different chemical composition and structure. Complicated distribution of stresses in phase-cover 1 causes the moment stresses as in the moment of speed melting and both speed crystallization that causes convective mixing of layers of liquid phase. stresses, big density of crystalline defects and localization of relaxation processes having high-speed character. The interaction between phases of non-metallic inclusions and steel matrix promote the formation of complicated composite zones in the areas of saturating. Such zones consist of microstructural, nanostructural and amorphous elements.



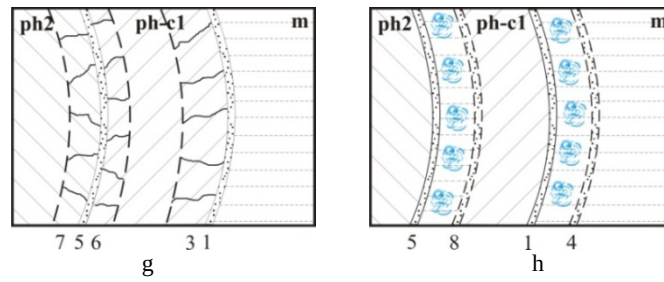


Figure 2. Schemes of laser melting of inclusions “high-melting phase surrounding with low-melting cover”: F_1^{ph-c1} , F_1^{ph2} , F_2^{ph-c1} , F_2^{ph2} , F_3^{ph-c1} , F_3^{ph2} – forces of surface tensions on the interphase boundaries, σ_{n-1} – stresses on boundary between hard heavy distortion area of inclusion and liquid steel matrix, $\sigma_{h-disor}$ – stresses on boundary between disordered area and hard inclusion, 1 – inclusion-matrix boundary, 2 – zone of steel matrix saturation with elements of inclusion, 3 – zone of saturation of phase-cover ph-c1 of inclusion with elements of steel matrix, 4 – initial position of inclusion-matrix boundary, 5 – interphase boundary inside inclusion, 6 – zone of saturation of phase-cover ph-c1 with elements of phase ph2, 7 – zone of saturation of phase ph2 with elements of phase-cover ph-c1, 8 – initial position of interphase boundary inside inclusion

Near inclusions “high-melting phase surrounding with low-melting cover” formation of saturated zones of steel matrix is controlled with the phase-cover ph-c1 which is the source of alloying of steel matrix (Fig. 3). Phase ph2 of inclusion do not takes part in the formation of saturated zones in steel matrix. In the results near these inclusions the composite liquation zones of a few types are formed: the cascade type that bears witness about formation of layers composite zones near such inclusions; “spot” type with heterogeneous distribution of elements of phase-cover ph-c1 and steel matrix; dispersed type that connects with formation of “satellite” particles; complicated layer-dispersed composite with cascade distribution of chemical elements. Characteristic sign of saturated zones is bond of their formation with behavior of the phase-cover ph-c1 in the moment of laser action and with ability of their elements for the speed mass transfer to steel matrix.

Analysis of oversaturated steel matrix areas near non-metallic inclusions “high-melting phase surrounding with low-melting cover” was shown that their structure is heterogeneous. There are a few versions of their structure revealing by heat etching under laser action. It may be one zone, or two zones, or three zones (Fig. 4). By that in non-metallic inclusions surface zone may be absebt or may be one zone or two zones.

Results of distribution of nanohardness of steel matrix were shown that its value (H_n^i) near non-metallic inclusions

“high-melting phase surrounding with low-melting cover” (one oversaturated zone or first zone) is more bigger then far from non-metallic inclusions (Table 1). Its value depends from chemical composition and structure of steel defining degree of strengthening by laser action. In the first (or sole) oversaturated zone values of (H_n^i) in 1,41...1,86 times bigger (coefficient K_i) then in steel matrix far from inclusion. These results are closed to results obtaining in [1, 2]. In the second and third oversaturated zones values of nanohardness lower then in the first zone but exceeds values of H_n far from non-metallic inclusions accordingly in 1,2...1,59 and 1,1...1,35 times. Thus cascade of nanohardness values by removal from non-metallic inclusions “high-melting phase surrounding with low-melting cover” was observed. Value of nanohardness of steel matrix in all oversaturated zones near non-metallic inclusions “high-melting phase surrounding with low-melting cover” and value of coefficient K_i depends from condition of non-metallic inclusion “high-melting phase surrounding with low-melting cover” and steel matrix in the moment of laser action. Values of H_n^i and K_i are maximum by fusion of non-metallic inclusions and steel matrix, they are decreased by fusion of steel matrix near hard non-metallic inclusion and they are minimum in the cases of hard condition of non-metallic inclusion and steel matrix.

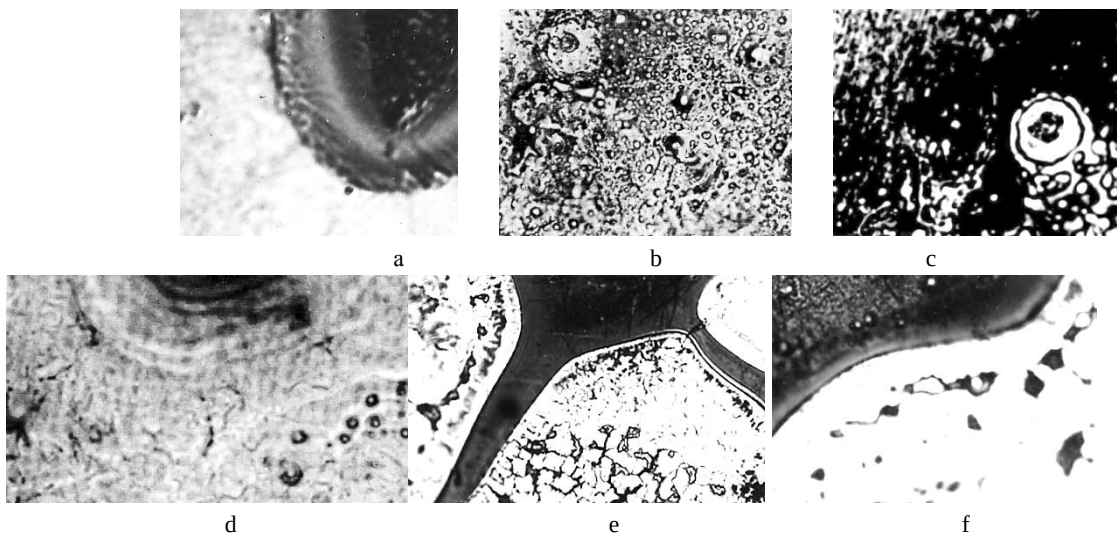


Figure 3. Zones of interaction between heterophase non-metallic inclusions and steel matrix under laser action: a – $FeS+MnO \cdot Al_2O_3$, b – $(Fe,Mn)S+Al_2O_3$, c – $MnO \cdot SiO_2+ MnO \cdot Al_2O_3$, d – $MnO \cdot SiO_2+Al_2O_3$, e – $MnO \cdot SiO_2+Al_2O_3$, f – «satellite» inclusions; x500x6

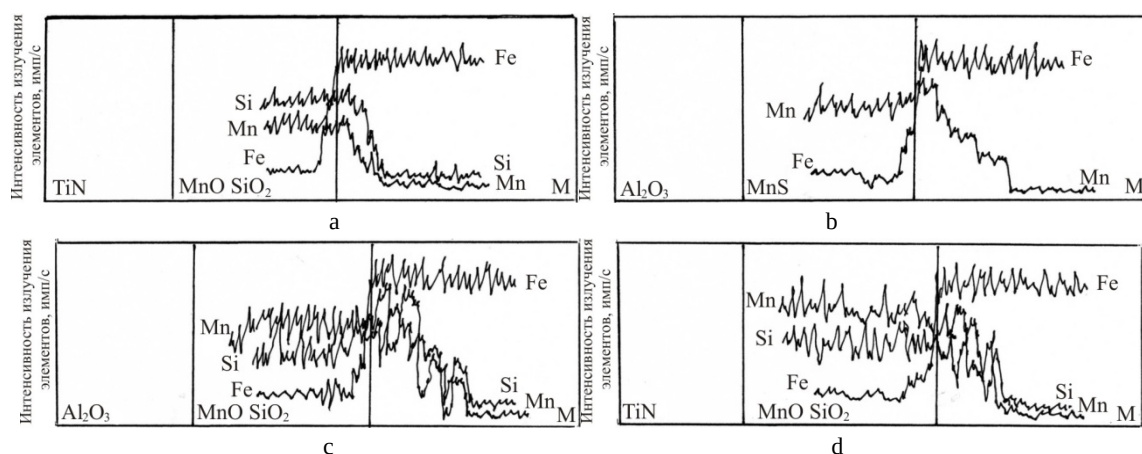


Figure 4. Distribution of chemical elements in inclusions “high-melting phase surrounding with low-melting cover” and oversaturated zones of steel matrix after laser treatment

This connects with phenomenon of maximum saturation of liquid steel matrix by fusion or full melting of non-metallic inclusions [1]. In cases of fusion of oxides, sulphides, silicates in the moment of laser action nanohardness of steel matrix near non-metallic inclusions bigger then near hard non-metallic inclusions and values of coefficient K_i in all oversaturated zones increase. Saturation of steel matrix by

elements of non-metallic inclusions and their fix in solid solution promotes increase of H_n^i and K_i values. Degree of steel matrix saturation in the second and third zones less then directly near non-metallic inclusions (in the first zone) that is confirmed by difference of H_n^i and K_i values.

Table 1.

Values of nanohardness of steel matrix near non-metallic inclusions “high-melting phase surrounding with low-melting cover” (H_n^i) and far from them H_n under impuls energy 25J and action time $3,6 \cdot 10^{-3}$ s

Inclusion ph-c1 – ph2, steel	Condition of inclusion in the time of laser action	Condition of steel matrix in the time of laser action	$H_n, \times 10, \text{ MPa}$	$H_n^i, \times 10, \text{ MPa}$ in zones		
				1	2	3
FeS+Al ₂ O ₃ , (Fe,Mn)S+ MnO·Al ₂ O ₃ , 08Yu	liquid	liquid	286	531 (1,86) 524 (1,83)	- (1,5)	- (1,3)
MnO·SiO ₂ + MnO·Al ₂ O ₃ , 60G	liquid	liquid hard	620	1054 (1,7) 868 (1,4)	776 (1,25) -	-
MnO·SiO ₂ + MnO·Al ₂ O ₃ , FeO·SiO ₂ + Al ₂ O ₃ , NB-57	liquid	liquid	748	1190 (1,59) 1346 (1,8)	890 (1,19) 980 (1,31)	- (1,1)
TiN+TiCN, 08T	hard, fusion	liquid	280	483 (1,73) 518 (1,85)	- (1,29) 361	-
FeO-TiO ₂ + TiCN, 08T	fusion	liquid, hard	280	470 (1,68) 423 (1,51)	346 (1,24) -	-
FeO-MnO+ SiO ₂ , 08kp	liquid / fusion	liquid hard	260	444 (1,7) 382 (1,47)	335 (1,29) -	-

Dependence of nanohardness of the first (or sole) oversaturated zone of steel matrix near non-metallic inclusions “high-melting phase surrounding with low-melting cover” has non-monotonic view for all laser action time (Table 2). This

evidence about existence of certain ranges of laser beam energy values that correspond to maximum strenghtening of local layers of steel matrix.

Table 2.

Influence of laser beam energy on nanohardness of steel matrix near inclusion (Fe,Mn)S+ MnO·Al₂O₃ in steel 08Uy under different time of action

$\tau_{\text{imp}}, \cdot 10^{-3}, \text{ s}$	$W_{\text{imp}}, \text{ J}$			
	10	18	25	30
1,0	432	495	520	464
3,6	465	520	524	486

Main factor of laser strengthening of local areas of steel matrix is its microalloying from inner sources - non-metallic inclusions “high-melting phase surrounding with low-melting cover”. Creation of cascade of oversaturated zones near these inclusions by formation of local liquational strengthened areas is formation of layers composite near non-metallic inclusions. Structure of these zones maybe single-phase (oversaturated solid solutions) but often dispersal microphases and nanophases – “satellite” particles are observed (see Fig. 3). Chemical composition of “satellite” particles connects with initial inclusion but slightly differs from it thanks to participation of elements of steel matrix in their formation [1, 2]. Process of “satellite” particles formation is connected with abnormal mass transfer in the moment of inclusions and steel matrix melting then in steel matrix areas enriching by elements of phase ph-c1 of inclusions and also containing of complexes (clusters) of former nano-graines of phase ph-c1 are formed. Local areas of the type of metallic emulsion smelts are formed. They are “freezed” by abrupt cooling and clusters of former nano-graines of phase ph-c1 of non-metallic inclusions are crystallized into “satellite” particles. And also process of “satellite” particles formation maybe connects with decrease of solubility of elements of phase

ph-c1 of non-metallic inclusions in areas of enrichment of liquid or hard steel matrix by abrupt cooling. In the result in steel matrix near initial inclusions composite structure with dispersal particles are formed. Appearance of “satellite” particles promotes formation of dispersal composite layers or by presence in steel matrix it promotes formation of zones with combine layers-dispersal structure near non-metallic inclusions “high-melting phase surrounding with low-melting cover”. Obviously variation of regime of laser action will allows to regulate structure of these composite systems.

4. Conclusions.

Peculiarities of formation of contact interaction zones in steel matrix in the conditions of abnormal mass transfer from inner sources (non-metallic inclusions “high-melting phase surrounding with low-melting cover”) by laser treatment are connected with origin of liquational strengthened zones representing different types of composite layers. Gradiental zones with cascade and “spot” distribution of elements and nanohardness, dispersal zones with different types of strengthening micro- and nanophases, “tunnel” zones, and also zones with combine structure were formed.

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ANALYSIS OF THE GRAIN BOUNDARY MICROSTRUCTURE AND DEGRADATION IN A GAS TURBINE BLADE

АНАЛИЗ МИКРОСТРУКТУРЫ ГРАНИЦ ЗЕРЕН И ДЕГРАДАЦИИ В ЛОПАТКЕ ГАЗОВОЙ ТУРБИНЫ

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Abstract: We studied the different parts (lock and feather) of Inconel 738C gas turbine blade, which were cut from the working turbine blade after long operation and recovery heat treatment. Undesired phases such as TCP phase (sigma phase) and some of continuous carbides such as $M_{23}C_6$ in the grain boundary are found. The presence of $M_{23}C_6$ carbides in studied samples testifies to the diffusion process of decomposition of MC carbide and the associated softening of the alloy. The appearance of sigma phase leads to embrittlement of the alloy. Generation of these specifications in the structure results in degradation of metallurgical and mechanical properties of the blade and eventually its destruction.

KEYWORDS: NICKEL SUPERALLOYS, MICROSTRUCTURE, DEGRADATION, PHASES, GAS TURBINE BLADE

1. Introduction

During the exploitation, the gas turbine blades and other components of turbine are subject to wear and damage. Operation aggressive environment, high mechanical and thermal stresses are the main factors, which influence lifetime of the main components of a gas turbine. After a prolonged service, moving blades undergo mechanical and structural degradation and show a decrease in the creep strength, fatigue, impact, and corrosion resistance. Microstructural degradation is considered as a major course for replacement or recovering of gas turbine blades [1]. Because of that the microstructural analysis of the degree of degradation and estimation of the residual lifetime of the blades are very important.

The nickel based super alloys mechanical properties depends on the volume fraction, size, form and composition of both the gamma prime phase (Ni_3Al) and grain-boundary MC carbides. Increase of heat resistance in the nickel super alloys is realized due to strengthening the grain boundaries with elements such as B and Zr, which reduce the probability of TCP phase formation and carbide transformation, which lead to reduce the strength of the alloy. Microstructural changes include the coarsening of the γ' -phase particles, change of the grain boundary morphology and the chemical composition of the carbide phase, as well as the precipitation of brittle intermetallic TCP phases, for example, σ phase [2]. Loss of long-term strength provides the growth of internal stresses, which leads to the grain boundary destruction of the alloy. Although most microstructure changes can be restored by special heat treatments, many structural defects can be persist after them [3, 4].

The Inconel 738C (IN738) super alloy, developed in 1968, is one of the important nickel based super alloys. This alloy shows the improved creep, hot corrosion, and oxidation resistance and is used in land-based gas turbines [5]. IN738 is used in manufacturing of gas turbine, jet engines, nuclear reactors, high-pressure vessels due to the high stability of its mechanical properties at elevated temperatures (up to 800 °C). The main phases of IN738 are nickel solid solution (gamma phase), a hardening intermetallic compound Ni_3Al (gamma prime phase), carbide and boride phases (MC and Cr_3B_2) [6].

The aim of work is to study the structure of the cast polycrystalline gas turbine blade made from Inconel 738C super alloy after long time exploitation and recovering heat treatments.

2. Experimental procedure

Chemical composition of Inconel 738C super alloy is presented in Table 1. We study the samples cut from the hottest and the most stressed part of the feather of gas turbine blade taken from the stationary gas turbine plant as well as the sample cut from the

lock part of the blade. Standard two steps recovering was done at 1100°C for 2 h following by aging at 840°C for 24 h. Air cooling was done after every step of heat treatments.

Table 1. Chemical composition of Inconel 738C, wt.% [5].

Ni	Cr	Co	Mo	W	Ta	Ti	Al	other
base	16	8.51	1.7	2.6	1.7	3.4	3.4	Nb, Zr, C, B

Structural studies were done with an optical microscope Micromed MET, a JEM-200CX transmission electron microscope and a scanning electron microscope JSM 6490 with the Oxford Inca energy dispersive and wave microanalysis. X-ray diffraction analysis was done with the X-ray diffractometer DRON-3 used the $CuK\alpha$ radiation.

3. Results and discussion

Optical study reveals the change in the microstructure of both feather and lock samples (Fig.1). The grain size in the samples changes from 100 up to 800 micrometers. Carbides are observed in both samples inside the grains and along their boundaries. Intergranular carbide precipitations have a well-defined globular shape which is typical for MC carbide. Grain-boundary carbides have the globular and elongated shapes. Elongated carbides are supposed to be the $M_{23}C_6$ carbides, which completely cover the grain boundaries.

It is known that the IN738 is an alloy with MC type carbide hardening based on Nb, Ti, W chemical elements. Doping with the boron is also used. To increase the heat resistance of the material, the grain-boundary carbide precipitations should be globular shape, have a size of 1 μm or less, and be evenly distributed along the grain boundaries without the formation of a continuous grid [6].

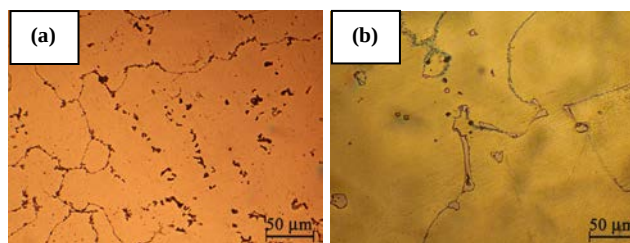


Fig.1. Microstructure of the studied gas turbine blade, optical microscopy: a- feather; b- lock

TEM study of the γ' -phase morphology in hottest and most stressed part of the feather can be seen in Figure 2. Bimodal distribution of the γ' -phase particles in cuboid-shaped particles with

size of about 350 nm and spherical-shaped particles with a diameter of about 50 nm is observed.

One can see that the recovering heat treatment eliminates the planar defects (stacking faults, dislocations) inside of the γ' -phase cuboids formed during long-term operation of the blade (Fig.2).

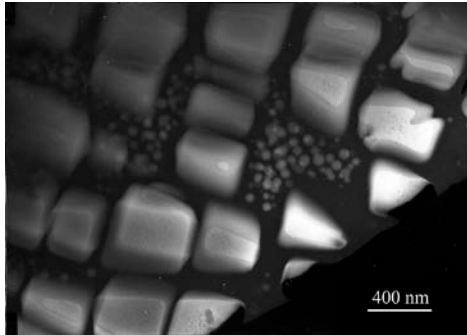


Fig.2 Structure of the feather, TEM, the dark-field image in γ' -phase reflex

Figure 3 shows the carbide transformation in the lock part of the gas turbine blade. It can be seen that partial dissolution of MC carbides and precipitation of a large number of $M_{23}C_6$ carbides occur during the exploitation. Recovering heat treatment according to the standard regime does not lead to the dissolution of $M_{23}C_6$ carbides. $M_{23}C_6$ carbides are mainly concentrated on the grain boundaries (Fig. 3b). Some of $M_{23}C_6$ carbides are observed on the structural defects in the grain (Fig. 3a).

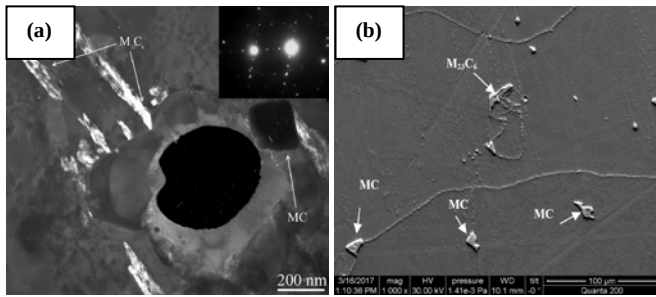


Fig.3. – Structure of carbide phases, lock,: a- TEM, the dark-field image in $M_{23}C_6$ reflex; b- SEM

The same carbide transformations one can see in the feather part of the blade (Fig.4). Intragrain MC carbide has a shape close to cubic one (Fig. 4a). $M_{23}C_6$ carbides are observed on the grain boundaries and have the elongated form (Fig.4b). Chemical composition of the carbides is shown in Tables 2-3 and in Figures 5-6. In the lock part of the blade, secondary $M_{23}C_6$ carbides, which are close to the MC carbide, have high content of nickel, chromium and cobalt. Intragrain MC carbides have high content of titanium, niobium and tantalum and practical absence of chromium (Table 2).

In contrast to the MC carbides of the locking part, the MC carbides in the sample cut from the feather of the blade contain in two times smaller amount of tantalum. $M_{23}C_6$ carbides located along the grain boundaries have approximately the same chemical composition as in the $M_{23}C_6$ carbides of the lock part (Table 3).

In addition to carbides in this part of the blade, precipitations of TCP σ -phase inside the grains are found (Fig.7). Chemical composition of this phase is close to MC carbide, however high nickel content is found in this phase (Table 2)

In comparison with the sample cut from the lock part of the blade, γ - (nickel solid solution) and γ' (Ni_3Al) -phases in the feather part of the blade have the less nickel content and higher percentage of tantalum and molybdenum (Tables 1-2).

The results of X-ray diffraction analysis support the structural studies (Fig. 8). X-ray diffractograms show the diffraction lines of the γ/γ' -phases and carbides in the lock part of the blade (Fig. 8a). In the structure of the sample cut from the feather part of the blade, in

addition to the γ/γ' -phase and carbide diffraction lines, the diffraction lines of the TCP σ -phase are observed (Fig. 8b).

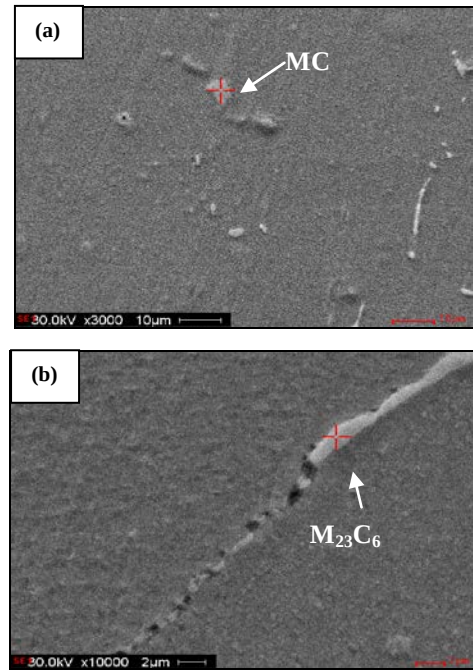


Fig.4 Structure of carbides (pointed by cross), feather: a- MC; b- $M_{23}C_6$



Fig. 7. Structure of σ -phase in the feather, SEM

During the operation time, gas turbine blades can be compressed, stretched, twisted or bended. This changes the aerodynamic characteristics and coordination of the turbine stages. Maximum tensile stresses are achieved in the surface layer of the feather of the gas turbine blade [7]. In differ from the feather of the gas turbine blade, the lock of the gas turbine blade undergoes only thermal influences [4]. In order to reduce the rate of diffusion processes in the solid solution and the exchange processes between the solid solution and the hardening γ' -phase, the high-temperature nickel alloys are especially alloyed with chromium, tungsten and molybdenum. Gorsky explained the main course of the concentration change in the stressed alloy. He call it the effect of ascending diffusion [8]. Change in the chemical composition of the feather part of the nickel gas turbine blade after the long exploitation was also found in [9]. It was observed the decreasing of the nickel content in the surface layer of the feather in compare with inner part of the feather or lock part of the gas turbine blade [9].

In this study, we researched the surface of the gas turbine blade. The change in the chemical composition of the hottest and stressed feather part of the blade indicates the degradation of both the solid solution and the strengthening phase.

The formation of TCP phases (σ , μ , Laves phases), as well as of M_6C or $M_{23}C_6$ carbides, leads to softening of the alloy and it is undesirable in high-temperature nickel alloys [4].

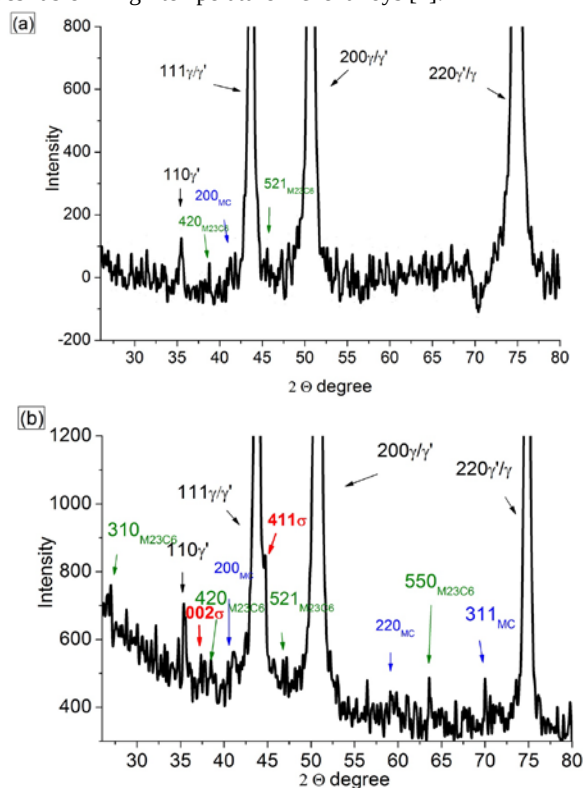


Fig.7. X-ray diffractograms of studied alloys: a- lock; b- feather

Usually carbides in high-temperature nickel alloys are resistant to high temperatures. Grain boundary $M_{23}C_6$ carbides have a solvus of about 1025 °C and dissolve at higher temperatures. MC carbides are resistant up to ~1235 °C [7]. Thermal stability and shape of the carbides also depends on the carbon content in the alloy. Redistribution of the alloying elements in primary MC carbides and in the surrounding carbide zones may occur under high temperature and stress. Precipitation of primary MC carbides during solidification is usual for Inconel 718 [10]. Serrated network of grain-boundary nano-scale $M_{23}C_6$ carbide and M_5B_3 boride precipitates were found in standard heat-treated commercial nickel base superalloy Inconel 738 [11]. Grain-boundary $M_{23}C_6$ carbides were observed in Inconel 738C after long time annealing at 850 °C for 100 hours [12].

Size and position of the $M_{23}C_6$ carbides in our case allow us to suggest its formation under exploitation time. Standard recovering heat treatment at 1100 °C should dissolve the $M_{23}C_6$ carbides. However, TEM studies (Fig 3) and high concentration of Cr in the grain-boundary carbides detected using X-ray microanalysis (Tables 1-2) give an experimental evidence that these carbides are secondary $M_{23}C_6$ carbides. It also means that our grain-boundary $M_{23}C_6$ carbides form under grain-boundary MC carbide transformation; to recover the chemical composition of the MC carbide phase, the alloy should be heated up to γ -phase melting temperature.

It is known that discrete grain-boundary $M_{23}C_6$ carbides improve creep life and ductility, but continuous network grain-boundary $M_{23}C_6$ carbide is the place for future destruction of the nickel heat temperature alloys because they promote crack blunting due to their effectiveness as dislocation sources [13]. In our case, the carbide network precipitated along the grain boundaries diverts the chromium from the solid solution that promotes the decrease of it oxidation and hot corrosion resistance and weakens the border regions.

Conclusion

Standard recovering heat treatment of the Inconel 718C gas turbine blade after long time operating does not lead to a complete restoration of the structure. Such kind of temperature treatments allows us to restore the structure of the hardening intermetallic γ' -phase. However, the presence in the structure the large number of continuous network of grain-boundary brittle $M_{23}C_6$ carbides and TCP σ -phase change the chemical composition of the γ/γ' -phases. This fact may testify about degradation process in the gas turbine blade; it leads to a significant decrease in the strength characteristics of the material at elevated temperatures and limits the service life of the blade.

Acknowledgments

The research supported by the grant from the Russian Science Foundation No 15-12-00001.

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Table 2 – Chemical content of different phases in the lock part of the blade, wt.%, SEM

Phases/Elements	Al	Nb	Mo	Ti	Cr	Fe	Co	Ni	Ta	W, Zr
MC	0,53	13,85	2,35	23,38	1,73	0,7	1	5,17	44,25	5,08
M ₂₃ C ₆	2,19	1,49	2,52	3,58	16,17	0,7	8,24	58,1	2,76	2,24
γ - phase	2,05	1,56	1,86	3,28	15,32	0,73	7,94	59,54	3,93	2,01
γ' - phase	2,15	2,16	2,40	4,09	14,63	0,99	7,21	56,85	4,86	3,31

Table 3 – Chemical content of different phases in the feather part of the blade, wt.%, SEM

Phases/Elements	Al	Nb	Mo	Ti	Cr	Fe	Co	Ni	Ta	W, Zr
MC	0,52	19,07	14,79	22,59	2,32	-	0,92	6,67	21,06	2,69
M ₂₃ C ₆	2,27	2,5	2,97	4,36	13,62	0,22	7,72	56,95	4,32	0,82
γ - phase	2,26	1,32	4,75	3,28	15,47	0,17	8,19	56,67	3,39	1,08
γ' - phase	2,01	1,27	3,16	3,4	14,4	0,62	7,93	54,27	5,14	0,81
σ-phase	0,67	15,78	11,64	19,83	4,27	0,19	1,72	12,37	21,94	1,49

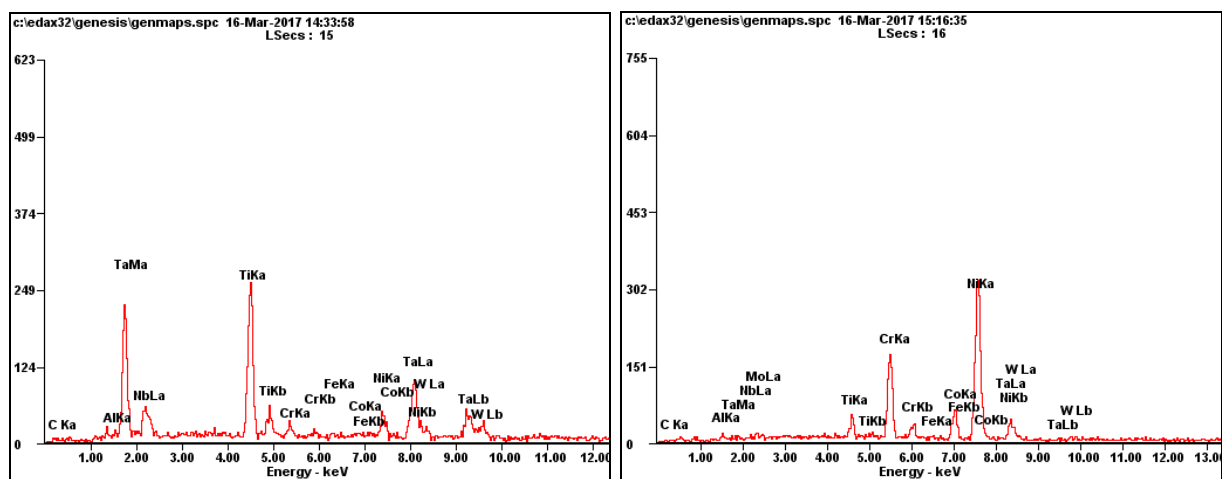


Fig.5. – EDX spectrum of carbide phases, lock part of the blade: a- MC; b- M₂₃C₆

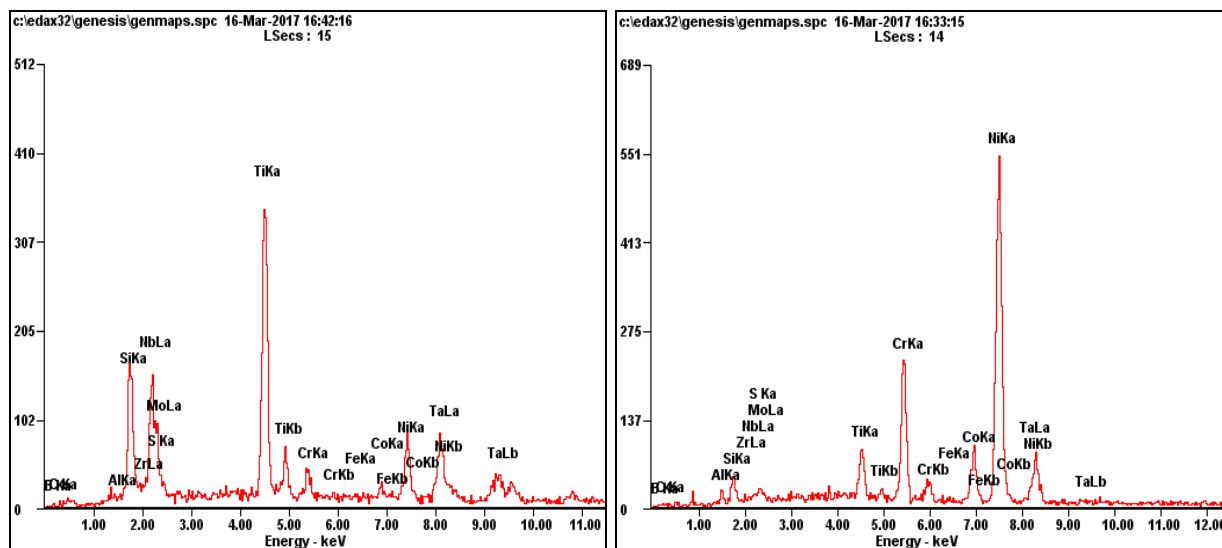


Fig.6. – EDX spectrum of carbide phases, feather part of the blade: a- MC; b- M₂₃C₆

THE IMPACT OF CURRENT SHAPE DURING THE CONSOLIDATION PROCESS ON PHYSICO-MECHANICAL PROPERTIES OF FUNCTIONAL Fe – Ti – C – B SYSTEM MATERIALS

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Abstract: The impact of current shape during consolidation of Fe – Ti – C – B system materials on the physio-mechanical properties of obtained specimens is studied in present paper. It is experimentally found that the use of method of decrease of voltage surge on output Schottky diodes of SPS device and the decrease of operation time of overcurrent protection in power circuit of SPS generator allowed changing current harmonic composition which lead to an increase of properties of consolidated Fe – Ti – C – B specimens – porosity decreased from 15.8 to 2.8 %, hardness increased from 50 to 55 HRC, loss of mass during abrasive wear decreased from 2 to 0.5 mass. %, and bending strength increased from 750 to 1500 MPa. It is found out that increase of input power during consolidation from 1.3 to 7.5 kJ/s by changing current harmonic composition leads to an increase of physico-mechanical characteristics of Fe – Ti – C – B system metal-matrix composites. Density of consolidated specimens increased from 75 to 95 %, their hardness increased from 35 to 50 HRC, loss of mass during abrasive wear decreased from 10 to 1 mass. % and their bending strength increased from 400 to 1100 MPa.

KEYWORDS: SPARK PLASMA SINTERING, ELECTRIC CURRENT, CONSOLIDATION, HARDNESS, WEAR RESISTANCE, POWDER, FUNCTIONAL MATERIALS

1. Introduction

Modern technologies, in which composite materials dispersion-hardened by ultrafine particles are used, allow significant increase of physico-mechanical properties of functional materials. Thus, analysis of literature sources shows that the use of metal matrix composite materials based on Ferrum with homogeneously distributed refractory particles of ultrafine size range allows obtainment of materials with high functional properties, prime cost of which is significantly lower than prime cost of materials based on high alloy steel [1-6].

Preservation of fine-grain structure (ultrafine size range of hardening particles) of material with density higher than 95 % is possible when consolidation is performed using methods with highly concentrated energy flows which feature higher heating rates and lower times of holding at maximal temperature if compared to conventional consolidation methods (hot pressing, sintering by ultrahigh pressure, hot isostatic pressing) [7-9]. Method of spark-plasma sintering (SPS) is one of such methods. It consists in passage of superposition of direct and pulsing currents through powder load in graphite matrix at constant mechanical load [10].

2. Problem discussion

It is known that physico-mechanical and functional properties of sintered powder materials are highly dependent on porosity, and SPS method ensures accelerated consolidation of powder materials due to quick and homogeneous distribution of spark plasma energy between powder particles during passage of electric current superposition through them [11, 12]. Therefore, studies of an impact of current shape during SPS consolidation on density and functional properties of consolidated Fe – Ti – C – B system materials is an urgent task.

The goal of present work is to study an impact of current shape during SPS consolidation of Fe – Ti – C – B system specimens on physico-mechanical and functional properties of obtained specimens.

3. Objective and research methodologies

Mixture of powders of 75 % Fe + 20 % Ti + 5% B₄C initial mass composition, which was treated by high voltage electric discharge (HVED) on kerosene with specific energy of 6.25 MJ/kg that ensured content of hardening refractory components up to 25 %, size of which lies in range between 100 and 600 nm while mean diameter of metal matrix particles was ~ 15 µm, was used as initial powder mixture for sintering [13, 14]. Phase composition (see Fig. 1) of obtained powder mixture is 75 % Fe + 5 % Ti + 5% B₄C + 14 % TiC + 6 % (Fe₃C, Fe₂Ti, TiH) according to RIR method (Rigaku Ultima IV (CuKα) diffraction meter) [15].

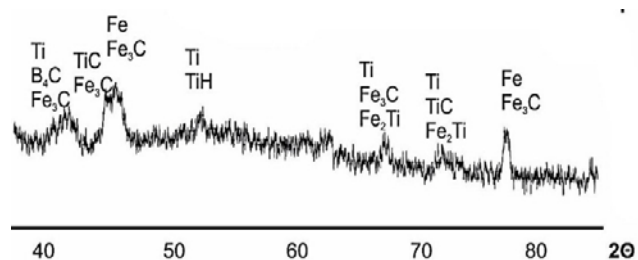


Fig. 1 – Phase composition of Fe – Ti – C – B system powder mixture

Consolidation of powder materials was performed in 10⁻⁴ MPa vacuum on “GEFEST” («ГЕФЕСТ») universal experimental complex [10], designed for usage of two electric current sources, both of which have maximum power of 10 kW. First electric current source is based on passage of superposition of direct and pulsing currents with frequency of 10 kHz at working voltage of $U = 2$ V, and second one is based on passage of alternating current of industrial frequency of 50 Hz at voltage of $U = 10$ V (method of Field Activated Pressure Assisted Synthesis (FAPAS)). Measurements of temperature, electric current intensity and voltage were performed using specially developed software. Thermal couple for measurement of temperature was introduced into matrix surface and calibrated by temperature in specimen inside matrix. Data on consolidation of selected powder mixtures on “Eran 2/1” («Эран 2/1») by direct current (conductive sintering (CS)) and “Impulse BM” («Импульс БМ») (by high voltage discharge (HVD)) was used for comparative analysis.

Recording of oscillograms of electric current and voltage during the use of electric current of different harmonic compositions was performed using Tektronix digital oscilloscope in order to determine energetic characteristics of consolidation process. Obtained oscillograms were processed in National Instruments Signal Express: Tektronix Edition software and imported to MathCAD software, which allowed obtainment of sintering electric power curve.

Experimental analysis of changes of consolidated materials structure was performed using computer metallography according to ISO 643:2009 using “Biolam-I” («Биолам-И») optic microscope and ImageJ software.

Hardness of specimens was measured according to ISO 6508-1:2013. Resistance to abrasive wear was studied on SMC-2 (CMI-2) friction machine using roller-block scheme. 1A1 diamond circle with AC4 80/63 grain was used as counter-body. Obtained results were compared with results of tests of HSS M2 steel.

Oscillograms of current and voltage with corresponding microphotograph of material (see Fig. 2) were obtained during SPS consolidation of specimens with diameter of 10 mm. Amplitude of voltage was not higher than 30 V, frequency of pulses passage was not higher than 54 kHz, applied pressure was 60 MPa and time of isothermal holding was not higher than 180 s. Current amplitude in load during sintering in such regime was 1025 A (see Fig. 2, a) while DC component was 815 A and AC component was 210 A. Therefore, modulation depth of output current was 20 %. Microphotograph of consolidated Fe – Ti – C – B system specimen is shown on Fig. 2, b. This specimen has following properties: porosity – 15.8 %, hardness – 50 HRC, bending strength – 750 MPa, loss of mass during abrasive wear – 2 %.

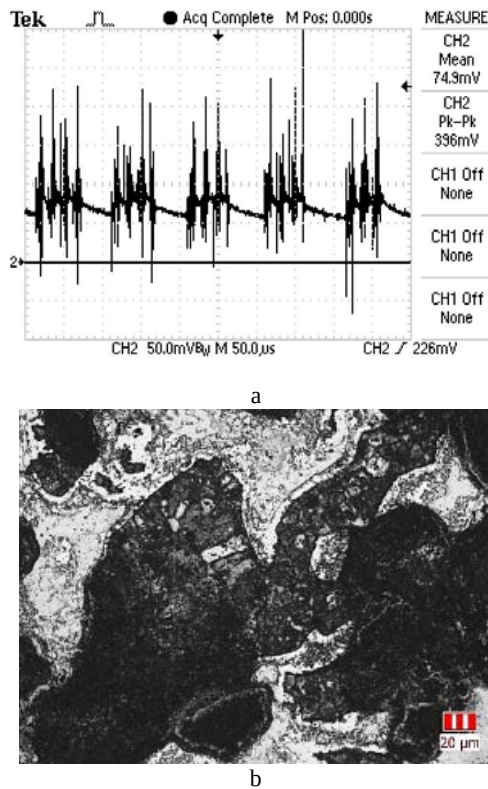


Fig. 2 – Oscillogram of SPS generator output current shape (a) and microphotograph of consolidated specimen of Fe–Ti–C–B system, $\times 200$ (white phase – Ferrum, dark phase – carbides)

Porosity of obtained specimens was more than 15 %, which indicates insufficient power release in sintered specimen. Alter “Method for decrease of voltage surge on output Schottky diodes of device for spark plasma sintering of disperse compositions” [16] was applied and operation time of protection from overcurrent in power module of SPS generator was decreased, specimens with enhanced characteristics were obtained. Their porosity was 2.8 %, hardness – 55 HRC, bending strength – 1500 MPa, loss of mass during abrasive wear – 0,5 %. In this case, current amplitude in load during sintering was 2500 A, DC component was 1024 A, AC component was 1476 A, so modulation depth of output current was 144 % (see Fig. 3).

Thus, decrease of voltage surge on output Schottky diodes of SPS device and decrease of operation time of protection from overcurrent in power module of SPS generator leads to an increase of obtained Fe–Ti–C–B system specimen properties.

However, as it was mentioned earlier, SPS method is just one of many methods of powders consolidation by highly concentrated energy flows. Obtained data allowed comparison of SPS method after decrease of voltage surge and such consolidation methods as HVD, FAPAS and CS as well as

study of peculiarities of impact of current of different harmonic composition on density and physico-mechanical properties of consolidated Fe–Ti–C–B system specimens.

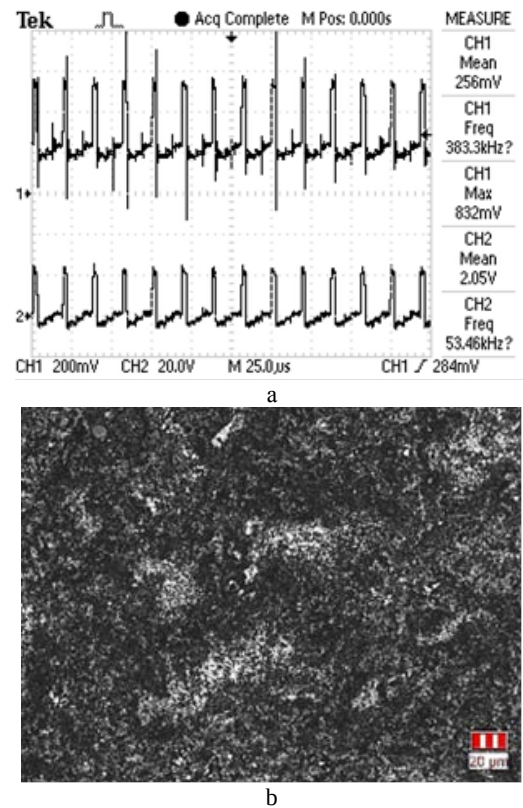


Fig. 3 – Oscillogram of SPS generator output current shape (a) and microphotograph of consolidated specimen of Fe–Ti–C–B system after application of method of voltage surge decrease, $\times 200$ (white phase – Ferrum, dark phase – carbides)

Consolidation by CS, SPS and FAPAS methods was performed at temperature of 1100 °C during 180 s under the impact of 60 MPa pressure with heating rate of 10 °C/s. Compaction by HVD method was performed during 30 μs at temperature of 1100 °C and impact of pressure up to 600 MPa. As a result, dependences of porosity, hardness, loss of mass during abrasive wear and bending strength on input sintering power during 1 s, which is numerically and physically equal to electric power of sintering process for given method (see Fig. 4). For method of HVD it was 1.3 kJ/s, for FAPAS – 1.65 kJ/s, for CS – 3 kJ/s and for SPS method it was 7.5 kJ/s.

It was found out that an increase of input power from 1.3 kJ/s to 7.5 kJ/s by changing electric current harmonic composition allows decreasing porosity of consolidated Fe – Ti – C – B system specimens from 25 % to 5 % due to processes of liquid metal transfer between powder mixture particles.

Increase of density of specimens, consolidated by SPS method, leads to significant increase of their hardness from ~ 35 HRC to 50 HRC, decrease of loss of mass during abrasive wear from 10 % to 1% and increase of bending strength from ~ 400 MPa to ~ 1100 MPa (see Fig. 5).

Obtained data experimentally confirm prospects of using SPS method after voltage surge decrease for obtainment of metal-matrix composites based on Ferrum, dispersion hardened by refractory components, with high values of hardness and abrasive wear resistance.

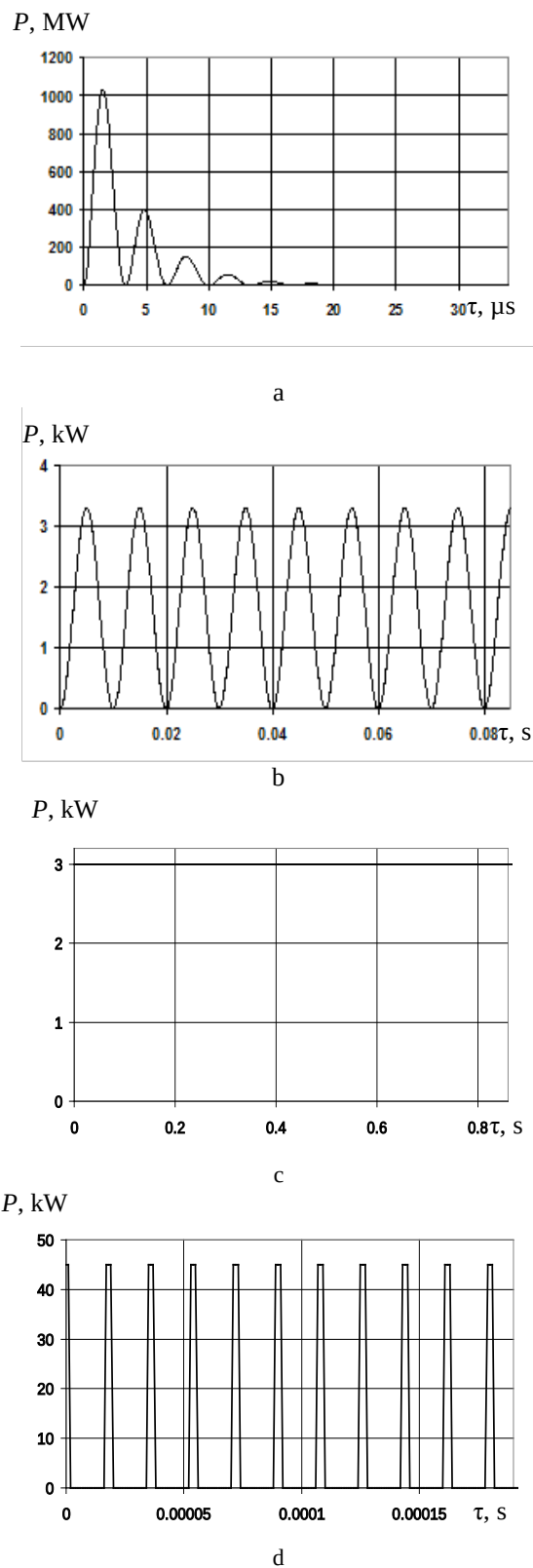


Fig. 4 – Values of sintering process electric power

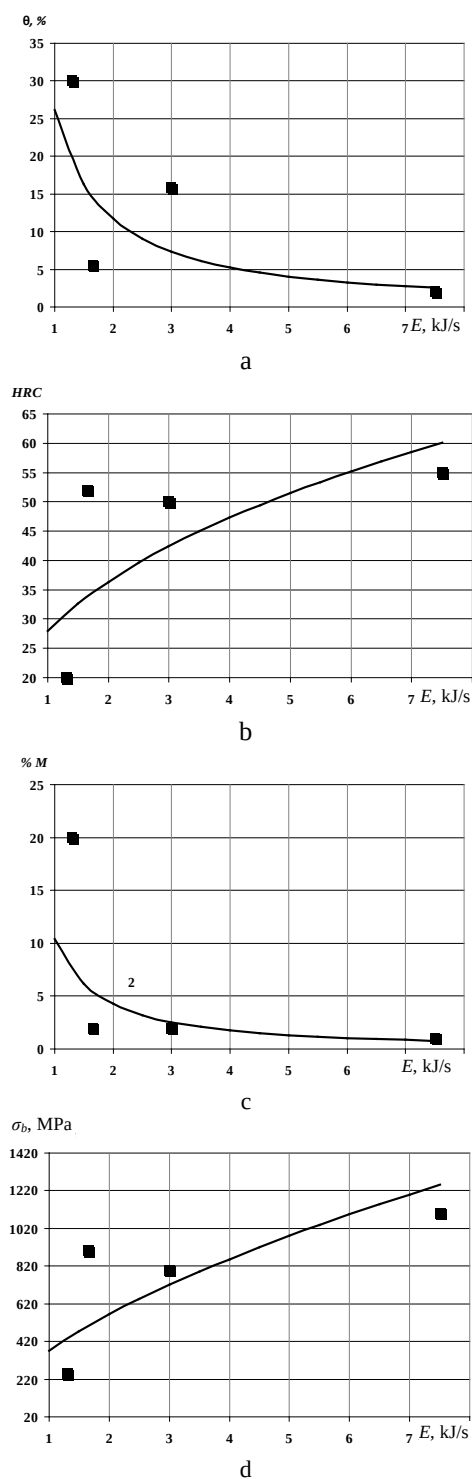


Fig. 5 – Dependences of porosity (a), hardness (b), loss of mass (c) and bending strength (d) of consolidated materials of Fe–Ti–C–B system on sintering process input energy

4. Conclusions

1. It is experimentally found out, that application of method of decrease of voltage surge on output Schottky diodes of SPS device and decrease of operation time of protection from overcurrent in power module for SPS generator allows changing electric current harmonic composition, namely increasing electric current amplitude in load during sintering from 1025 A to 2500 A, DC component from 815 A to 1024 A and AC component from 210 A to 1476 A, which leads to an increase of consolidated Fe–Ti–C–B system specimens properties (porosity decreases from 15.8 % to 2.8 %, hardness increases from 50 HRC to 55 HRC, loss of mass during abrasive wear decreases from 2 % to 0.5 % and bending strength increases from 750 MPa to 1500 MPa).

2. It is found out, that an increase of input electric power during consolidation from 1.3 kJ/s up to 7.5 kJ/s by changing sintering electric current harmonic composition leads to an increase of physico-mechanical properties of Fe – Ti – C – B system sintered metal matrix composites (density of consolidated specimens increases from 75 % to 95 %, hardness increases from ~ 35 HRC to ~ 50 HRC, loss of mass during abrasive wear decreases from 10 % to 1 % and bending strength increases from ~ 400 MPa to ~ 1100 MPa).

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EVOLUTION OF PHASES AT THE BIFURCATION POINT

ЭВОЛЮЦИЯ ФАЗ В ТОЧКЕ БИФУРКАЦИИ

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Abstract In chemical reactions, the bifurcation points are determined through the triangulation of the system. In the interaction of the components, bifurcation sequence formed and the system evolves along one of them to form a stable compound. The transformations of the components at the bifurcation point are determined basis on the "The Gibbs function normalized to the total number of electrons". All transformations are described through chemical potential, affinity, thermodynamics force. Calculated the production of entropy, the entropy flux and the reaction rate constant, which allowing the system to choose a certain path of evolutionary transformations.

KEYWORDS: NONEQUILIBRIUM THERMODYNAMICS, TRIANGULATION, THE GIBBS FUNCTION NORMALIZED TO THE TOTAL NUMBER OF ELECTRONS.

1. Introduction

In a chemical reaction at the bifurcation point, the system loses its stability and passes into a nonequilibrium state in which it is possible to acquire a new quality of the evolution of the dynamic system. There is a restructuring of the nature of the movement and structure of the system. When the system moves to the bifurcation point, the chemical potential and the affinity of the system play a significant role. At the bifurcation point, the system begins to produce entropy, the passage of the reaction is characterized by a certain rate constant. It is from these factors that the evolutionary branch depends on the system, passing through the point of bifurcation. In the interaction of chemical reagents in a real system, it is possible to determine all the ways of evolution of the system. Evolutionary processes between two points of bifurcations obey deterministic regularities [1-3].

The processes of evolution in chemical reactions can be described basis on the transformation of the phase composition of the system's compounds as a cause-effect relationship between the phases. This problem can be solve by the teachings of Kurnakov through the triangulation of systems [4]. The composition-property diagram is an exact geometric model of complex function, which reflects the relationship between temperature, volume, concentration and other physical and chemical factors, which can determine the state of the open system. The composition-property diagram linked into one matter of indissoluble chemical transformations and geometric transformations of space.

2. Method of research

For example, considered the system CaO-SiO₂-H₂O. In this system was established the formation of 86 compounds (table), and the system was triangulated basis on the Kurnakov's teaching [4] (figure) and using the "The Gibbs function normalized to the total number of electrons". The principle of triangulation of systems is given in [5]. Thermodynamic indices of compounds are calculated basis on the method of ion increments and increments of Aldabergenov [5]. The calculations show good consistency with the literature data, the relative error does not exceed 0.87%. The thermodynamic parameters of many compounds were calculated for the first time.

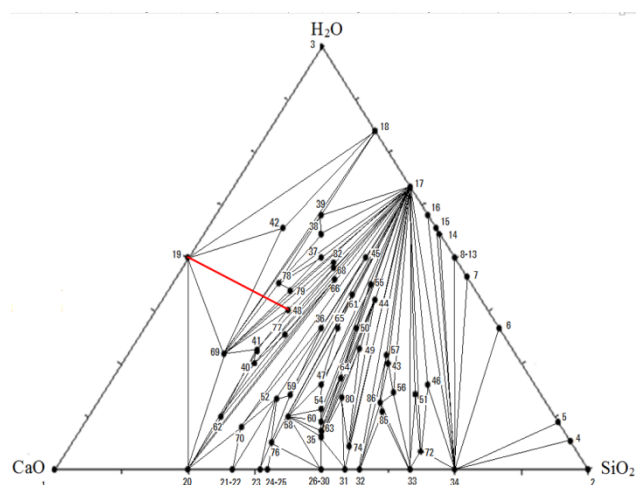


Figure1 - Triangulation system CaO-SiO₂-H₂O

Table - The values of the Gibbs energy of formation ($-\Delta_f G_{298}$) and "The Gibbs function normalized to the total number of electrons" ($-\Delta \bar{G}_{298}^0$) compounds of CaO-SiO₂-H₂O system

Compounds	$-\Delta_f G_{298}$, kJ/mol		% av.	$-\Delta \bar{G}_{298}^0$, kJ/mol.el
	by increments	[6]		
1	2	3	4	5
1. CaO		603.5		21.55
2. SiO ₂		892.6		29.75
3. H ₂ O		237.2		23.72
4. H ₂ Si ₁₄ O ₂₉	12437.23			28.92
5. H ₂ Si ₈ O ₁₇	7274.17			29.10
6. H ₂ Si ₂ O ₅	2111.11			30.16
7. H ₁₀ Si ₆ O ₁₇	7113.49			30.93
8. H ₂ SiO ₃	1250.60			31.26
9. H ₄ Si ₂ O ₆	2501.19			31.26
10. H ₆ Si ₃ O ₉	3751.79			31.26
11. H ₈ Si ₄ O ₁₂	5002.38			31.26

1	2	3	4	5
12. $\text{H}_{10}\text{Si}_5\text{O}_{15}$	6252.98			31.26
13. $\text{H}_{12}\text{Si}_6\text{O}_{18}$	7503.58			31.26
14. $\text{H}_{10}\text{Si}_4\text{O}_{13}$	5392.47			31.72
15. $\text{H}_8\text{Si}_3\text{O}_{10}$	4141.87			31.86
16. $\text{H}_6\text{Si}_2\text{O}_7$	2891.28			32.13
17. H_4SiO_4	1640.68			32.81
18. H_8SiO_6	2099.28			29.99
19. $\text{Ca}(\text{OH})_2$		897.5		23.62
20. Ca_3SiO_5	2788.84	2785.1	0.13	24.46
21. Ca_2SiO_4	2185.34	2191.3	0.27	25.41
22. $\text{Ca}_6\text{Si}_3\text{O}_{12}$	6460.24			25.04
23. $\text{Ca}_8\text{Si}_5\text{O}_{18}$	9548.14			25.53
24. $\text{Ca}_3\text{Si}_2\text{O}_7$	3724.29	3756.7	0.87	25.86
25. $\text{Ca}_6\text{Si}_4\text{O}_{14}$	7362.80			25.57
26. CaSiO_3	1538.95	1543.9	0.32	26.53
27. $\text{Ca}_2\text{Si}_2\text{O}_6$	3077.90			26.53
28. $\text{Ca}_3\text{Si}_3\text{O}_9$	4616.85			26.53
29. $\text{Ca}_6\text{Si}_6\text{O}_{18}$	9233.70			26.53
30. $\text{Ca}_7\text{Si}_7\text{O}_{21}$	10772.65			26.53
31. $\text{Ca}_5\text{Si}_6\text{O}_{17}$	8587.31			26.84
32. $\text{Ca}_3\text{Si}_4\text{O}_{11}$	5509.41			27.01
33. CaSi_2O_5	2431.51			27.63
34. CaSi_3O_7	3324.07			28.17
35. $\text{CaSiO}_3 \cdot 0,16\text{H}_2\text{O}$	1574.15			26.41
36. $\text{CaSiO}_3 \cdot \text{H}_2\text{O}$	1758.95			25.87
37. $\text{CaSiO}_3 \cdot 2\text{H}_2\text{O}$	1978.95			25.37
38. $\text{CaSiO}_3 \cdot 2,5\text{H}_2\text{O}$	2088.95			25.17
39. $\text{CaSiO}_3 \cdot 3\text{H}_2\text{O}$	2198.95			24.99
40. $\text{Ca}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$	2405.34			25.06
41. $\text{Ca}_2\text{SiO}_4 \cdot 1,17\text{H}_2\text{O}$	2442.74			25.00
42. $\text{Ca}_2\text{SiO}_4 \cdot 4\text{H}_2\text{O}$	3065.34			24.33
43. $\text{CaSi}_2\text{O}_5 \cdot \text{H}_2\text{O}$	2651.51			27.06
44. $\text{CaSi}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$	2871.51			26.59
45. $\text{CaSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$	3091.51			26.20
46. $\text{CaSi}_3\text{O}_6(\text{OH})_2$	3553.37			27.76
47. $\text{Ca}_2\text{Si}_2\text{O}_6 \cdot \text{H}_2\text{O}$	3297.90			26.17
48. $\text{Ca}_3\text{Si}_2\text{O}_6(\text{OH})_2 \cdot 2\text{H}_2\text{O}$	4393.59			25.25
49. $\text{Ca}_2\text{Si}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$	4367.57			26.31
50. $\text{Ca}_2\text{Si}_3\text{O}_8 \cdot 2,5\text{H}_2\text{O}$	4477.57			26.18
51. $\text{Ca}_2\text{Si}_5\text{O}_{12} \cdot 1,5\text{H}_2\text{O}$	6085.58			27.54

1	2	3	4	5
52. $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot \text{H}_2\text{O}$	3944.29			25.61
53. $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	4384.29			25.20
54. $\text{Ca}_3\text{Si}_3\text{O}_9 \cdot \text{H}_2\text{O}$	4836.85			26.29
55. $\text{Ca}_3\text{Si}_6\text{O}_{15} \cdot 7\text{H}_2\text{O}$	8834.53			26.45
56. $\text{Ca}_3\text{Si}_6\text{O}_{13}(\text{OH})_4$	7753.13			27.30
57. $3[\text{Ca}_3\text{Si}_6\text{O}_{13}(\text{OH})_4] \cdot 4\text{H}_2\text{O}$	24139.39			27.06
58. $\text{Ca}_4\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$	5473.24			25.82
59. $\text{Ca}_4\text{Si}_3\text{O}_{10} \cdot 1,5\text{H}_2\text{O}$	5583.24			25.73
60. $\text{Ca}_4\text{Si}_4\text{O}_{12} \cdot \text{H}_2\text{O}$	6375.80			26.35
61. $\text{Ca}_4\text{Si}_6\text{O}_{13}(\text{OH})_6 \cdot 4\text{H}_2\text{O}$	9508.82			26.27
62. $\text{Ca}_5\text{Si}_2\text{O}_9 \cdot \text{H}_2\text{O}$	5108.40			24.33
63. $\text{Ca}_5\text{Si}_5\text{O}_{15} \cdot \text{H}_2\text{O}$	7914.75			26.38
64. $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 3\text{H}_2\text{O}$	9247.31			26.42
65. $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 5,5\text{H}_2\text{O}$	9797.31			26.13
66. $\text{Ca}_5(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot 8\text{H}_2\text{O}$	10576.61			25.80
67. $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 9\text{H}_2\text{O}$	10567.31			25.77
68. $\text{Ca}_5\text{Si}_6\text{O}_{17} \cdot 10\text{H}_2\text{O}$	10787.31			25.68
69. $\text{Ca}_6[\text{Si}_2\text{O}_7] \cdot (\text{OH})_6$	6222.69			24.12
70. $\text{Ca}_6\text{Si}_3\text{O}_{12} \cdot \text{H}_2\text{O}$	6680.24			24.93
71. $\text{Ca}_6\text{Si}_6\text{O}_{18} \cdot \text{H}_2\text{O}$	9453.70			26.41
72. $\text{Ca}_7\text{Si}_{16}\text{O}_{39} \cdot \text{H}_2\text{O}$	18768.35			27.36
73. $\text{Ca}_8\text{Si}_6\text{O}_{17}(\text{OH})_6$	11085.71			25.54
74. $\text{Ca}_8\text{Si}_{10}\text{O}_{28} \cdot \text{H}_2\text{O}$	14316.72			26.81
75. $\text{Ca}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4 \cdot 6\text{H}_2\text{O}$	17960.44			27.05
76. $\text{Ca}_9\text{Si}_6\text{O}_{21} \cdot \text{H}_2\text{O}$	11221.31			25.39
77. $\text{Ca}_9\text{Si}_6\text{O}_{21} \cdot 7\text{H}_2\text{O}$	12541.31			24.98
78. $\text{Ca}_9(\text{Si}_3\text{O}_9\text{H})(\text{Si}_2\text{O}_7\text{H})(\text{OH})_8 \cdot 6\text{H}_2\text{O}$	12651.03			24.71
79. $\text{Ca}_9(\text{Si}_6\text{O}_{18}\text{H}_2) \cdot (\text{OH})_8 \cdot 6\text{H}_2\text{O}$	13467.81			24.85
80. $2[\text{Ca}_{10}\text{Si}_{12}\text{O}_{31}(\text{OH})_6] \cdot 3\text{H}_2\text{O}$	36385.04			26.56
81. $\text{Ca}_{10}\text{Si}_{12}\text{O}_{31}(\text{OH})_6 \cdot 8\text{H}_2\text{O}$	19622.52			26.16
82. $\text{Ca}_{10}\text{Si}_{12}\text{O}_{31}(\text{OH})_6 \cdot 18\text{H}_2\text{O}$	21822.52			25.67
83. $\text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$	9463.00			26.43
84. $\text{Ca}_{12}(\text{Si}_6\text{O}_{17})_2(\text{OH})_4 \cdot 12\text{Ca}(\text{OH})_2$	29696.00			25.34
85. $\text{Ca}_{14}\text{Si}_{24}\text{O}_{58}(\text{OH})_8 \cdot 2\text{H}_2\text{O}$	31828.10			27.16

86. Ca ₁₄ Si ₂₄ O ₆₁ (OH) ₂ · 6H ₂ O	32020.20			27.09
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In the CaO-SiO₂-H₂O system, the most active and reactive is Ca(OH)₂. Therefore, considered the interaction of Ca(OH)₂ (compound # 19) with Ca₃Si₂O₆ (OH)₂·2H₂O (compound # 48) in the exchange reactions. For this purpose, a straight line 19-48 runs between the poles of these compounds, which intersects the stable sections: 42-69; 18-69; 39-69; 69-78; 69-79; 69-17; 69-82 (Figure). The intersection points of the lines are bifurcation points. At this point the system loses stability and new solutions to evolution arise due to branching (bifurcation). The line Ca(OH)₂-Ca₃Si₂O₆ (OH)₂·2H₂O (19-48) shows that in the presence of a small displacement of the original components, the system is capable of jumping between stable states.

3. Results and discussion

To determine the ways of evolution of the system in chemical reactions are used two concepts:

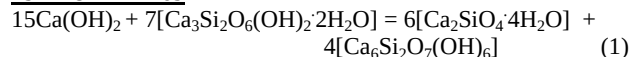
- "The Gibbs function normalized to the total number of electrons" [5,7];

- triangulation of a multicomponent system [4].

The physical meaning of the "The Gibbs function normalized to the total number of electrons" ($\Delta\bar{G}_{298}^0$) is to define the chemical bond as a collective effect of electron-nuclear interaction. It is calculated by dividing the Gibbs energy of formation of a compound by the total number of electrons in a given compound, i.e. determines the energy density of the formation of a compound per electron. This function characterizes the accumulation of the Gibbs energy density on molecular bonds. The "The Gibbs function normalized to the total number of electrons" in the formation of bonds adequately reacts to all changes in the structure of the compound. This property allows us to describe many characteristics, like the reactivity of the compound, its stability [7], determine the chemical potential and affinity, calculate the production and flux of entropy, thermodynamic force and flow, the thermodynamic "probability" of interaction, the degree of conversion of components in the course of a chemical reaction, describe the processes of "self-organization" [8], triangulate multicomponent systems and establish mechanisms of reactions. The "The Gibbs function normalized to the total number of electrons" interpreted as the chemical potential of the substance, i.e. $\bar{G}_{298}^0 = \mu$.

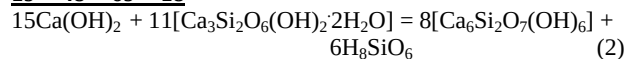
Described the chemical reactions of the interaction of Ca(OH)₂ with Ca₃Si₂O₆ (OH)₂·2H₂O at the points of bifurcations

19 + 48 = 42 + 69



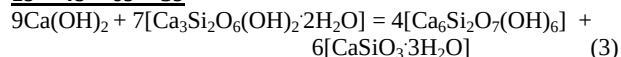
$$A = -0.42 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 18



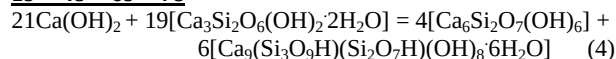
$$A = 5.24 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 39



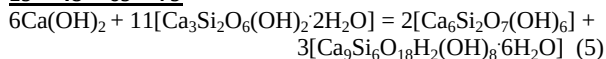
$$A = 0.24 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 78



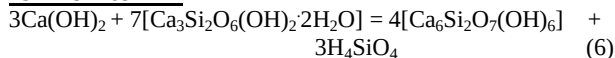
$$A = -0.04 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 79



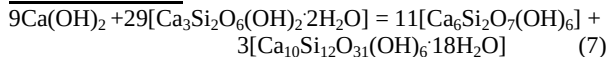
$$A = 0.1 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 17



$$A = 8.06 \text{ kJ/mol} \cdot \text{el.}$$

19 + 48 = 69 + 82



$$A = 0.92 \text{ kJ/mol} \cdot \text{el.}$$

The affinity (A) (according to T. de Donder [9]) defined for elementary collision acts. If the affinity is positive, then the reaction rate is also positive, i.e. the reaction goes from left to the right. The negative value of the affinity of the reaction indicates the impossibility of the spontaneous flow of this reaction. As can be seen from the reactions (1), (4) spontaneously do not flow, but (2), (3), (5-7) - flow. It is determine that the chemical affinity is the driving force of chemical reactions.

Calculated the temperature of the process of transformation of the initial component into a stable compound, the thermodynamic force, entropy production, the entropy flux, and the conversion rate constant.

4. Conclusion.

The "The Gibbs function normalized to the total number of electrons".and the triangulation of the system make it possible to determine the bifurcation points in the interaction of the components. Appears the bifurcation sequence, the further transition of the system to the evolutionary path with the formation of a stable compound depends on the production of entropy, the entropy flux, and the reaction rate constant.

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NONCONVENTIONAL METHODS OF HEAT TREATMENT OF ALUMINUM ALLOYS

НЕТРАДИЦИОННЫЕ СПОСОБЫ ТЕРМИЧЕСКОЙ ОБРАБОТКИ АЛЮМИНИЕВЫХ СПЛАВОВ

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Abstract: *This paper presents new methods of thermal processing of the aluminum alloys. It analyses the effects of boiling treatment of alloys Al–Cu and Al–Si in an oxidizing atmosphere on their microstructure, hydrogen content and the coefficient of linear thermal expansion (CLE). An increase of boiling time from 15 to 75 hours results in an initial increase in the hydrogen content in alloys later followed by a decline in the hydrogen content. These changes in the hydrogen content correlate with the dynamics of alloys' microstructure and their CLE. This study shows that atmosphere with a high oxygen content induces an acceleration of diffusion processes in aluminum alloys. If boiling time does not exceed 30 hours, the hydrogen content in a solid solution and etchability of grain boundaries of α -solid solution decrease and intermediate phases get partially dissolved. We demonstrate that boiling treatment of aluminum alloys in an oxidizing atmosphere leads to a decline of the CLE measured under the temperature 50-450°C which is especially strong when measured under the temperature 250-350°C.*

KEYWORDS: ALUMINUM, ALLOYS, ATMOSPHERE, BOILING TREATMENT, HYDROGEN, MICROSTRUCTURE, COEFFICIENT OF LINEAR EXPANSION

1. Introduction

Alloys with a low specific weight and a small coefficient of linear expansion (CLE) play a significant role in industry. Such alloys are especially important for aerotechnics and spacecraft engineering [1, 2]. In particular, aluminum alloys with a low coefficient of linear expansion (CLE) are required for the construction of special instruments, obtaining vacuum-tight junctions with different materials as well as for providing dimensional consistency of details. In most cases reduction of the coefficient of linear expansion is achieved by means of alloying. An important task for the current research is to explore and analyze other ways of reducing the coefficient of linear expansion of these materials.

In our previous studies we showed that if the content of alloying elements is kept constant technological factors such as fusion treatment, melt treatment and crystallization conditions can have considerable influence on microstructure, hydrogen content and coefficient of linear expansion of aluminum alloys [3, 4]. Furthermore, we showed that the composition of atmosphere significantly affects the structure formation and physic-mechanical properties of aluminum alloys [5-7]. Particularly, we demonstrated that heating treatment in atmosphere with higher hydrogen and nitrogen contents accelerates the process of phase transformations in aluminum alloys [7]. This happens because heating treatment stimulates hydrogen diffusion in aluminum alloys. In addition, there are a lot of other studies that also support the thesis that hydrogen plays an important role in the process of structure formation of aluminum alloys and has significant impact on their properties [8-12].

U.R. Evans proposed a mechanism of oxide spallation from the metal surface according to which oxygen on the metal surface induces acceleration of hydrogen inside of the metal [13, 14]. Hence, atmosphere with a high oxygen content should also affect the hydrogen diffusion inside of a metal in the course of heating treatment. Boiling treatment in water solutions could be considered as an example of such heating treatment. Hydrogen exhibits the highest degree of diffusive mobility in the temperature range of 80-100°C. Consequently, by means of boiling treatment of alloys in strong oxidizing atmospheres one could achieve acceleration of hydrogen diffusion inside of a metal. Water solutions of KMnO_4 , NaNO_3 , KOH could serve as examples of such oxidizing atmospheres that force hydrogen to move from intermetallics to solid solution. This, in turn, leads to the change of the structure and properties of aluminum alloys, in particular, it affects their coefficient of linear expansion [15].

2. Materials and Experiment

We analyzed how boiling treatment of alloys in water solutions of strong oxidizers affects microstructure and the coefficient of linear expansion of these alloys. For our analysis we used aluminum alloys Al – 5% Si, Al – 10% Si, Al – 5% Cu and Al – 10% Cu. Alloys were melted out of pure metals: aluminum A7, silicon Kp0, copper M1. Alloys were melted in the laboratory electric resistance furnace in aluminum melting pot. First aluminum was melted, and then alloying elements were added. Alloys Al – 5% Cu and Al – 10% Cu were poured starting at the temperature 850-870°C into metal mold without hot-conditioning. Alloys Al – 5% Si, Al – 10% Si were poured at the temperature 730°C into cooling mold with further quenching into water being undertaken.

From the resulting ingots bars were cut out which then were used for further metallographic analysis and dilatometer investigation. These bars were treated using boiling water solutions KMnO_4 и KOH . Three metal bars were exposed to each treatment regime. Alloys Al – 5% Cu and Al – 10% Cu were boiled in 0.05–0.1% water solution KMnO_4 during 5-45 hours, alloys Al – 5% Si, Al – 10% Si were boiled in 0.1% water solution KOH during 15-75 hours.

After boiling treatment we implemented dilatometer investigation, metallographic analysis and measured hydrogen content. Coefficient of thermal linear expansion was measured using the Chevenard photodilatometer. Metallographic analysis was implemented using optical light microscope OLYMPUS GX51. The content of atomic hydrogen was measured using vacuum hot extraction method implemented on the installation B-1 according to the State Standard GOST 21132.1-98 «Aluminum and aluminum alloys. Methods for determination of hydrogen in solid metal by vacuum hot extraction». The method is based on the extraction of hydrogen from the metal heated to the temperature lower than its melting temperature – in the range of 500-600°C – under vacuum and residual pressure of $(6.65\text{--}9.31) \cdot 10^{-5}$ Pa.

3. Results and discussion

We implemented comparative analysis of the properties of alloy Al – 5% Cu after boiling treatment during 15, 30 and 45 hours respectively. In the course of our empirical study we established that during the first 30 hours of boiling the hydrogen content in the alloy decreases from 3.3 to 1.9 $\text{cm}^3 / 100 \text{ g Me}$, grain boundaries of α -solid solution get thinner and less exposed to etching (their etchability decreases) than they were under initial conditions, the continuity of grain boundaries is also affected (Fig. 1, a, b). Grain boundaries of α -solid solution exhibit different degrees of etchability, particularly, there are no breakdown products in the core of grains whereas considerable amount of these breakdown

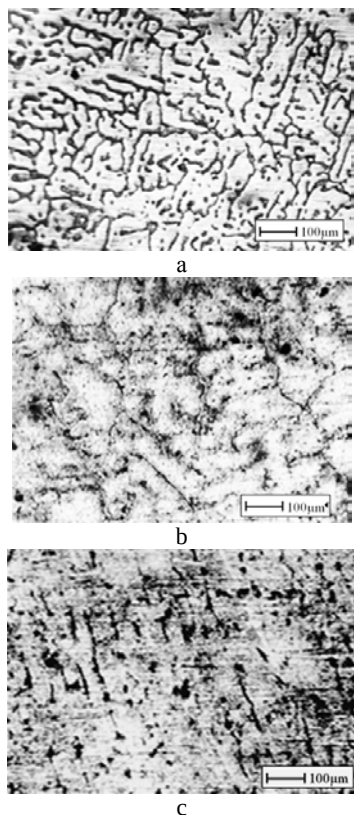


Fig. 1. Microstructure of alloy Al – 5% Cu: a – no treatment, $[H] = 3.3 \text{ cm}^3 / 100 \text{ g Me}$; b – after boiling treatment in 0.1% water solution of KMnO_4 during 30 hours $[H]=1.9 \text{ cm}^3 / 100 \text{ g Me}$; c – after boiling treatment in 0.1% water solution of KMnO_4 during 45 hours, $[H]=4.5 \text{ cm}^3 / 100 \text{ g Me}$

products was identified at the periphery of grains. This shows that the solid solution is characterized by a high hydrogen content in areas near grain boundaries due to breaking-up of the phase CuAl_2 .

When boiling time is increased to 45 hours the hydrogen content again increases up to $4.5 \text{ cm}^3 / 100 \text{ g Me}$ (Fig. 1, c) and etchability of all structural components weakens. So, particles of the phase CuAl_2 almost cannot be etched and grain boundaries of α -solid solution partially cannot be revealed, too.

After boiling treatment in 0.1% water solution of KMnO_4

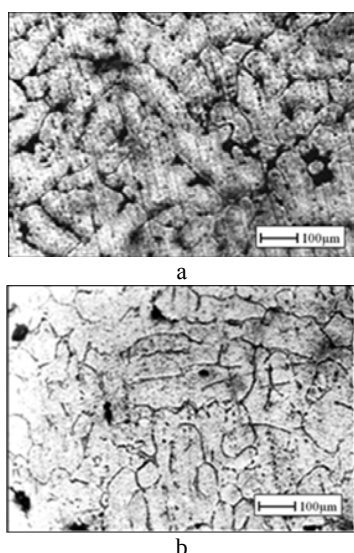
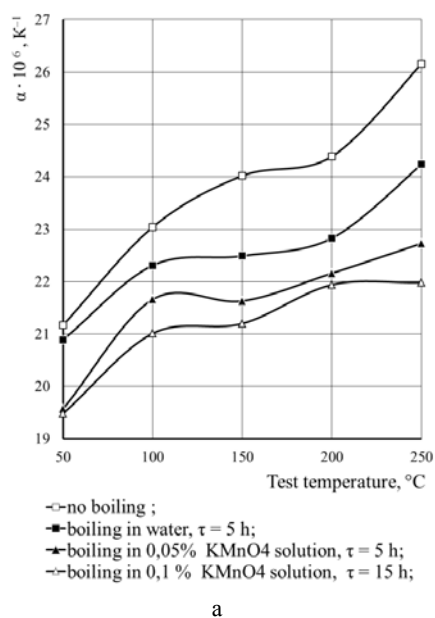


Fig.2. Microstructure of alloy Al–10% Cu: a – after boiling treatment in 0.1% water solution of KMnO_4 during 45 hours $[H]=12.2 \text{ cm}^3 / 100 \text{ g Me}$; b – after boiling treatment in 0.1% water solution of KMnO_4 during 75 hours, $[H]=3.5 \text{ cm}^3 / 100 \text{ g Me}$

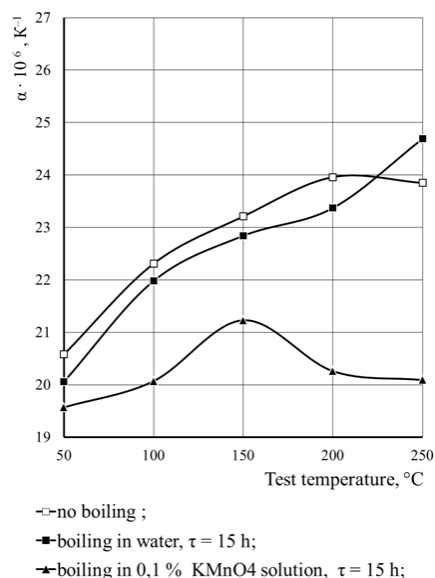
during 45 hours the hydrogen content in alloy Al–10% Cu increases from 4.3 to $12.2 \text{ cm}^3 / 100 \text{ g Me}$. This happens because under the influence of oxidizing atmosphere hydrogen segregated at the interphase boundaries as well as hydrogen dissolved in the phase CuAl_2 migrate to the α -solid solution. At the same time etchability of the phase CuAl_2 and of α -solid solution increases (Fig. 2, a).

When boiling time is increased to 75 hours the hydrogen content in alloy Al–10% Cu again decreases to $[H] = 3.5 \text{ cm}^3 / 100 \text{ g Me}$. We believe that this happens due to further progressing diffusion processes and hydrogen moving out of an alloy into the atmosphere. This corresponds to the empirical finding that the overall etchability of metallographic spicement goes down, grain boundaries get much thinner and there are fewer particles of intermediate phase of CuAl_2 (Fig. 2, b).

In the course of comparative dilatometric analysis it was established that following boiling treatment in potassium permanganate solution the CLE of alloys Al–(5÷10) % Cu decreases to a larger extent than it does after boiling in water. Moreover, the more concentrated the KMnO_4 solution is, the more pronounced is the reduction of the CLE (Fig. 3).



a



b

Fig. 3. Effects of atmosphere composition and boiling time on the coefficient of linear expansion of aluminum alloys with copper: a - Al–5% Cu; b - Al–10% Cu

The average inaccuracy of the computed coefficient of linear expansion is $\pm 0.1 \cdot 10^{-6} \text{ K}^{-1}$. As an illustration, the average CLE of alloy Al-5% Cu after five hours of boiling in water measured in the temperature range of 50–250°C is $23.0 \cdot 10^{-6} \text{ K}^{-1}$, after boiling in 0.05% KMnO_4 solution during five hours this alloy's CLE is $21.5 \cdot 10^{-6} \text{ K}^{-1}$ and, finally, after boiling in 0.1% KMnO_4 solution during 15 hours the alloy's CLE is $21.1 \cdot 10^{-6} \text{ K}^{-1}$. Hence, in comparison to CLE of as-cast alloys boiling treatment in 0.1% KMnO_4 causes a decrease of the CLE of alloys Al-5% Cu measured in the range of test temperatures 50–250°C by 10–12%.

Generally, alloys Al-Si can only hardly be affected by atmosphere. However, a long boiling treatment with a hold of up to 75 hours in a 0.1% KOH water solution causes gradual breaking-up of eutectic silicon. This results in an increased measurable hydrogen content from 0.7 to $3.8 \text{ cm}^3 / 100 \text{ g Me}$. Metallographic analysis also confirms this finding: the etchability of dendrites of α -solid solution increases and there are plenty of breakdown products on grain bodies (Fig. 4).

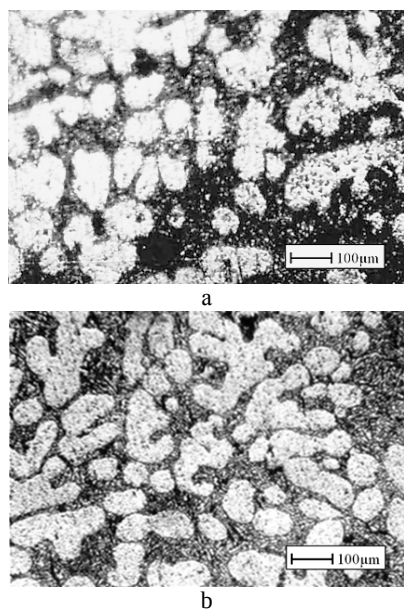


Fig. 4. Microstructure of alloy Al-10% Si: a – without treatment, $[\text{H}] = 0.7 \text{ cm}^3 / 100 \text{ g Me}$; b – after boiling treatment in 0.1% water solution of KOH during 75 hours, $[\text{H}] = 3.8 \text{ cm}^3 / 100 \text{ g Me}$

Empirical measurement of the coefficient of linear expansion of aluminum alloys with 5 and 10% of silicon provides evidence that boiling treatment in oxidizing environment leads to a reduction of the CLE over the whole range of test temperatures (Fig. 5). The maximum reduction of the CLE of alloy Al-5% Si is observed in the course of the first 30 hours of boiling whereas for alloy Al-10% Si the same result is achieved already after the first 15 hours of boiling. A further increase of boiling time leads only to a minor reduction in the coefficient of linear expansion. We believe that this phenomenon can be explained by the fact that hydrogen moves in and out of the solid solution.

The decrease of CLE is particularly strong in the temperature range of 250–350°C when casted alloys feature anomalous linear expansion. This effect is more pronounced for the alloy with 10% Si. As an illustration, after boiling treatment during 15 hours the CLE of alloy Al-10% Si decreases from $\alpha = 31.0 \cdot 10^{-6} \text{ K}^{-1}$ to $\alpha = 22.4 \cdot 10^{-6} \text{ K}^{-1}$ in the temperature range 250–300°C – i.e. the CLE decreases by 28%. The maximum reduction of the CLE of alloy Al-5% Si in the temperature range of 300–350°C is achieved only after boiling during 60 hours – the CLE decreases from $\alpha = 31.1 \cdot 10^{-6} \text{ K}^{-1}$ to $\alpha = 23.8 \cdot 10^{-6} \text{ K}^{-1}$, i.e. by 24%.

The reduction of the CLE can be explained in the following way. The role of hydrogen in the process of alloy's expansion is determined by the overall hydrogen content that is made by the hydrogen in a solid solution and by the hydrogen that gets dissolved

during the precipitation of intermetalloid phases. Under low temperatures the CLE is equally determined by the hydrogen in a solid solution and the hydrogen in the phase. Under higher temperatures, however, the speed of diffusion process significantly increases and the hydrogen contained in a solid solution contributes more to the expansion than the hydrogen in the phase. When the share of the hydrogen in a solid solution is high the CLE takes on its maximum values whereas when it is low the CLE goes down. The reduction of CLE is caused by an overall decline of the hydrogen concentration in an alloy as well as by the partial dissolution of intermetalloid phases and an alloying element moving into the solid solution.

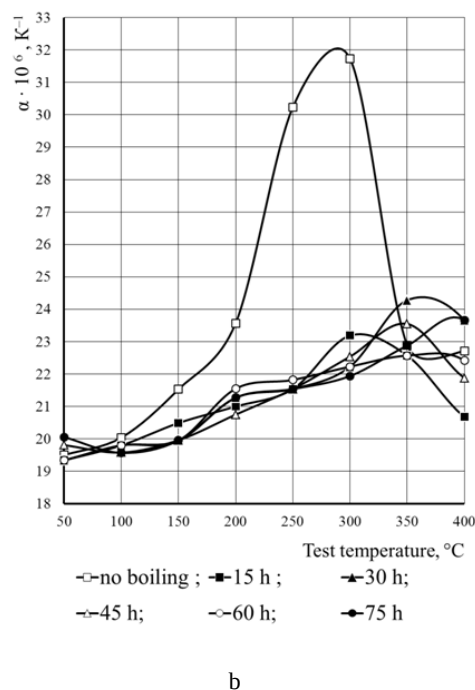
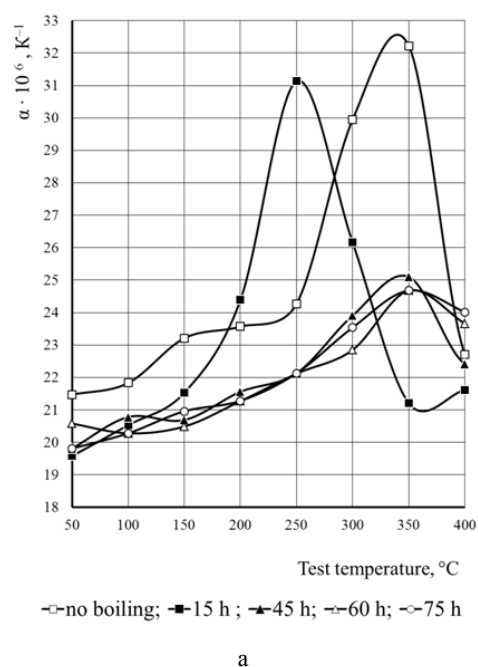


Fig 5. Effects of boiling time on the coefficient of linear expansion of aluminum alloys with silicon: a- Al-5% Si; b – Al-10% Si

4. Conclusions

In this paper we empirically demonstrated that in the course of boiling treatment atmosphere composition has a considerable impact on microstructure, hydrogen content and coefficient of linear expansion of alloys Al-(5-10)% Cu and Al-(5-10)% Si. Atmosphere with high hydrogen content is conducive to acceleration of diffusion processes inside of alloys, particularly, to the acceleration of atomic hydrogen diffusion. If boiling time does not exceed 30 hours hydrogen content in solid solution goes down, etchability of grain boundaries of α -solid solution decreases and intermediate phases get partially dissolved.

In the course of our study we established that boiling treatment in an oxidizing atmosphere causes a reduction of the CLE of alloys Al-(5-10)% Cu by 10-12% measured in the range of test temperatures of 50 - 250°C. For alloys Al-(5-10)% Si this effect is more pronounced, i.e. the CLE goes down in the range of test temperatures 50-400°C. In the temperature range 250-350°C the CLE reduction is particularly large – i.e. by 24-28%.

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THE STRUCTURAL AND TOPOLOGICAL HEREDITARY UPON CRYSTALLIZATION OF NEAR-EUTECTIC ALLOYS

СТРУКТУРНО-ТОПОЛОГИЧЕСКАЯ НАСЛЕДСТВЕННОСТЬ ПРИ КРИСТАЛЛИЗАЦИИ БЛИЗЭВТЕКТИЧЕСКИХ СПЛАВОВ

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Abstract. A new representation of a heterogeneous long-range ordered structure of metal melts consisting of "liquid" and "solid" component atoms mixture has been formulated. The elements of a super-high level structure that are directly associated with a quasicrystalline liquid phase structure have been revealed. Like any solid, they are caused by distortion of long-range order in its "quasilattice" made up by "liquid" component atoms at the temperatures exceeding their melting point. Upon crystallization, these structural elements convert excess phases dendrites into macroscopic spherical formations that reflect a "polygrain" melt structure, its topology, and unique "genetic code" acquired during the transfer of layout topological hereditary information from a melt to a solid.

KEYWORDS: SPATIAL ARRANGEMENT, EUTECTIC CRYSTALLIZATION, A LONG-DISTANCE ORDER, LONG-RANGE ORDER, "LIQUID" AND "SOLID" ATOMS, "QUASILATTICE", SPHERICAL CONFIGURATION ELEMENTS, TOPOLOGY, AND HEREDITARY.

1. Introduction

The basic property of liquids (melts) recognized by most experts, is the absence of a long-range order. In a solid, the long-distance order depends on (i.e. genetically fixed by) the type of a crystal lattice and is caused by the periodicity of the lattice. At the same time, the available information about an abnormal temperature dependence of the structure-sensitive metal melts properties proves the contrary [1-11, etc.]. The values of the observed property anomalies are comparable to similar effects in a long-range ordered solid at polymorphic and martensitic transformations [8] that indicates the structural similarity of the liquid and solid states of matter. Moreover, such abnormalities are manifested not only in melts of pure metals, but also in their alloys approximately at the same temperatures [12]. This fact demonstrates that there is a specific type of heredity, when hereditary information is transferred from the main component to its alloys.

In our opinion, the reference publications cited [1-12, etc.] indicate the global character of the processes that occur in the liquid phase, and contradict the standard concept of a short-range order and microheterogeneous nature of a liquid phase. This research provides a new approach to the analysis of a metal melt structure and study of interrelation of a substance liquid and solid states. The theoretical basis of the approach is a concept of heterogeneous nature of liquids with long-range ordered structural elements outlined by its authors [13, 14]. According to the authors, the dimensional parameters of the order in liquids considerably exceed the crystallographic proportions in the solid. For this reason, conditions of X-ray diffraction and, accordingly, conditions for obtaining a distinct characteristic radiation spectrum are not satisfied.

The key provisions of the concept of long-range ordered state of melts and the interrelations of a substance liquid and solid states are as follows:

1. Atoms found in a liquid phase and in a solid phase radically differ from each other, as they refer to different states of aggregation of matter. Their transformation during a "melt→solid" phase change causes the decomposition and heterogeneous structure of eutectic melts at temperatures below the melting points of the eutectic components.

2. Liquid-phase transformations of a different nature, such as "liquid-peritectic", "liquid-eutectic" and dystectic, develop between the "liquid" and "solid" atoms of the components in the melt, causing the generation of intermediate metastable phases and a nonmonotonic change in the structure-sensitive properties.

3. Structural (metallurgical) heredity in the "melt → casting" phase transition is possible only in case of long-range order, since only a long-range order has sufficient information capacity for encoding and transmission of information about the structure and properties of the liquid to a solid.

This research paper is devoted to the development, promotion and discussion of the concept; and the subject matter of this paper is the substantiation of the long-ordered structure of molten metals.

2. Materials and Methods of Research

Near-eutectic alloys are the most appropriate object for such studies as they have the most extended area of simultaneously coexisting liquid and solid phases. This fact provides for a retracing the development of the "liquid → solid" phase transition during the precipitation from the liquid (melt) of a proeutectoid constituent, "hardening" the liquid structure and fixing (*encoding*) this information. In pure eutectics, the "liquid → solid" phase transition and subsequent crystallization often develop at high rates, causing the "erasure" of all or the major part of information on the structure of the liquid phase.

For this study, the near-eutectic alloys of the following systems are chosen: Al-97%Zn, Al-30%Cu

and Al-16%Si. And, aluminum grade A99, copper grade M0, zinc grade TS and silicon grade Kr00 were used as metal charge. The melting was carried out in a laboratory shaft furnace under a flux layer consisting of equal amounts of sodium chloride and potassium chloride. After complete melting of the components, the melt was soaked in the furnace for 30 minutes. Prior to casting, the scum had been skimmed off, and the melt was actively mixed up and cast into cylindrical metal molds, with a massive polished steel plate served as the bottom. To increase the heat dissipation in the vertical direction, the side walls of the mold are covered with heat-insulating ceramics. The superheating temperature above the liquidus line was 200 °C in all cases.

The obtained samples had a cylindrical shape with a diameter of 15 mm and a height of 20 mm. The end layer contacting the steel plate, was removed to a depth of 0.5 mm, and then a metallographic specimen was prepared. Three samples had the same temperature point. The etching reagent consisted of equal amounts of nitric acid, hydrofluoric acid and glycerol. The metallographic analysis was carried out using Neophot 21 optical microscope at a magnification of 200, 500 and 2000.

3. Outcomes of the Experiment

The microstructure of metals and alloys in terms of its content (origin) is a geometric image of structural and phase transformations of various types, and characterizes their patterns of development and determines the structure dependent properties. The microstructure of near-eutectic alloys of aluminum-zinc (a-d), aluminum-copper (e, f), and aluminum-silicon (g, h) systems is given in Figure 1. It consists of a eutectic mixture and primary dendrites of zinc (Al-Zn system) and aluminum (Al-Cu system) phases, as well as excess silicon crystals (Al-Si system). For all cases, the microstructure has a non-regular configuration element represented by the spatial arrangement of primary phase precipitates. They are distributed not chaotically, as is in a homogeneous or microheterogeneous liquid, but are arranged along circles or arcs of different diameters. According to the author [15], a stereological reconstruction of microvolumes of high-strength cast iron shows that the distribution of graphite is also not random and irregular, but corresponds to quasi-spherical spatial configurations of various sizes in the matrix. However, the author does not associate their origin with the long-range order in melts, preaching the classical theory of colloid-disperse systems and the electrochemical theory of metallic liquids.

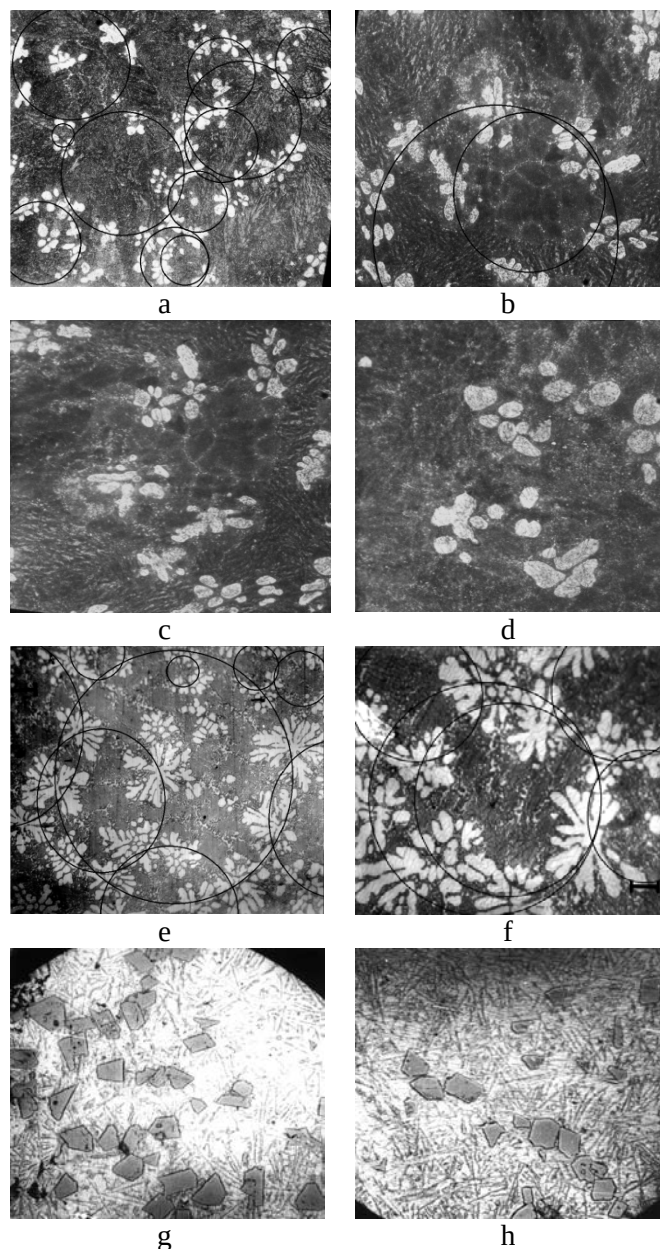


Figure 1. The microstructure of near-eutectic alloys of Al-Zn (a-d), Al-Cu (e, f), Al-Si (g, h) systems. $\times 200$ (a), 500 (b-e, g, h), 2000 (f).

The provided reconstruction of the primary phase arrangement in the obtained microstructures (Fig. 1 a, b, c, d) shows that the spherical shape of the surfaces remains the same upon contact. They are independent and "transparent" to each other. It is impossible for solid-phase transformations and, most likely, is associated with a heterogeneous macroscopic structure of melts, as compared to a solid. The dimensions of these structural formations exceed an order of magnitude both the dimensions of eutectic phases, as well as the dimensions of eutectic colonies. One might assume that they reflect some "virtual" reality, which is not directly related to the solid eutectic and represents the structural elements similar to the "grain" boundaries of the liquid. A primary phase precipitation thereon shows that before the beginning of crystallization, these surfaces were in a quite different state than the rest of

the melt. Information on the liquid eutectic topology is encoded precisely therein – in the "grain" structure and long-range order, the carriers of which are the "liquid" component atoms.

4. Discussion of the Findings

There are many photos with elements of a spherical configuration in the early papers on the metallography of cast irons, [16, 17], which did not attract the attention. Microstructures given in Figures 2 and 3 were taken from classical papers on the structure and properties of high-strength and malleable cast irons with options for reconstruction of the arrangement of graphite inclusions.

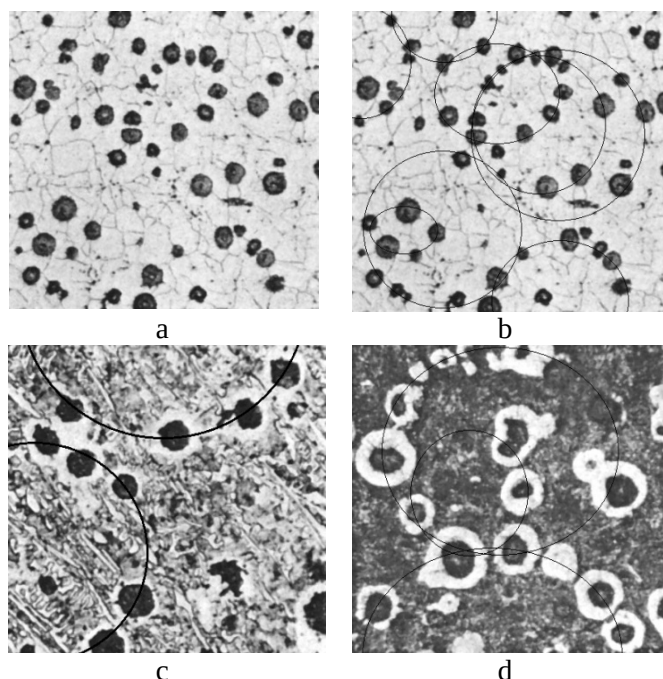


Figure 2. Microstructure of high-strength cast iron and distribution of graphite precipitates (reconstruction): (a, b) – ferrite, (c) – pearlite-cement carbide-ferrite, (d) - pearlite-ferrite matrices [16].

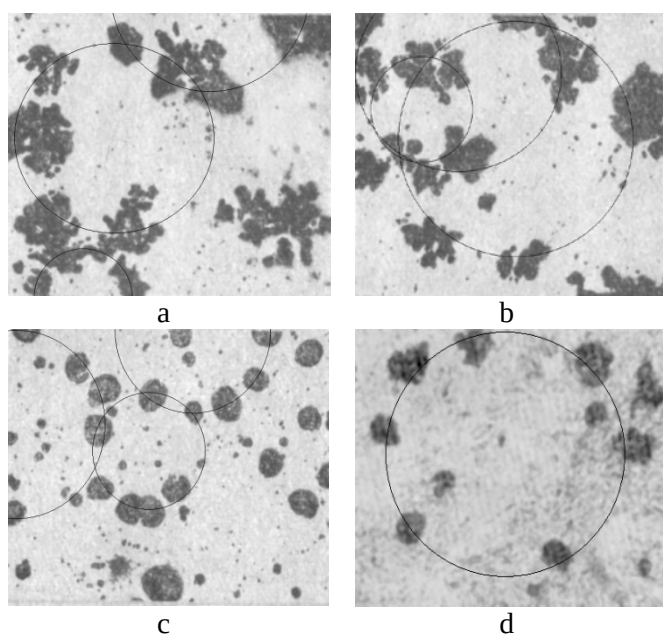


Figure 3. Microstructure and distribution of graphite precipitates (reconstruction) in malleable cast iron (a, b) and high-strength cast iron (c, d) [17].

The following model of the structure formation processes during crystallization is proposed in the study in terms of near-eutectic alloys. It is known that phase transformations in the solid state, for example, in eutectoid and martensitic states, are mainly developed from grain boundaries of high-temperature phases. A similar situation should occur during the crystallization (a "melt $\rightarrow$ solid" phase transformation) in case of long-range order in the melts. Carriers of long-range order, similar to a solid, are the "liquid" component atoms, which form a specific "quasilattices" of macroscopic dimensions. The disturbance of order in such "quasi-lattice" leads to the formation of a "poly-structure" structure of metallic liquids in the form of structural elements of a spherical configuration. Primary crystals of both before-eutectic and after-eutectic phases only decorate the "grain" structure of the long-ordered liquid phase (metallic melt) similar to boundaries of former austenite grains in the pearlite and martensitic transformations.

In this regard, it is necessary to note one more class of spherical formations in the liquid phase – the Rayleigh–Bénard convection. According to [18, 19], it represents the areas of "long-range" ordering recorded in the form of convection cells on the surface of the heated liquid layer. As a rule, the convective Bénard cells have a form of cylindrical shafts and regular right hexagonal prisms in section. The issue of their three-dimensional configuration remains open for discussion. It is not inconceivable that in fact the cells represent thermally detectable (etched) "grains" of liquid; and convection only allows the information about the structure of the liquid phase embedded (coded) therein to appear.

The following ideas on the structure of metallic melts arising from this study, are proposed to be discussed:

- metal melts are long-range ordered heterogeneous systems, consisting of a "liquid" and "solid" component atoms mixture at temperatures above their melting points;

- "liquid" atoms are carriers of long-range order in the melts and form "quasilattices" with dimensional parameters much larger than interplanar spacing in the crystalline lattice of a solid;

- in the event of distortion of long-range order in the "quasilattice," a "poly-grained" structure of the melt occurs in the form of giant formations – the "grains" of a spherical configuration that carry hereditary information about the structure and natural topology of the liquid phase;

- during the crystallization of near-eutectic alloys, the "genetic code" or "genetic memory" of the liquid is manifested in the form of structural topological

heredity in the structure of a solid;

- the spherical shape of the "grains" of the liquid and the "transparency" of their boundaries provide it with high mobility (flowability) and the ability to conform to the shape of the containing vessel.

Thus, the "super-macroscopic" elements of the spherical configuration found in the near-eutectic alloys are directly related to the liquid phase of the substance matter and determine its spatial arrangement. They decorate the proeutectoid constituent during the grain crystallization and reflect the long-ordered "grain" structure of the melt, and its specific genetic code. The "genetic memory" of liquids on their natural topology manifests itself in these structural elements, which is fixed in the structure of the crystallized alloy by the transfer of hereditary information.

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MAGNETIC AND ELECTROCONDUCTIVE PROPERTIES OF THE PURE CARBON SOOT SYNTHESISED BY ARC DISCHARGE

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Abstract: The electroconductive and magnetic properties of nanomaterials containing carbon nanoforms synthesised for electrocatalytic, electrochromic, and ferrofluid applications, etc., are of interest to researchers. This article aims to understand the physical effects influencing the electroconductive and magnetic properties of materials synthesised by arc discharge. The nanomaterial formation processes leading to the formation of magnetic and electroconductive structures are also discussed. Arc discharge between graphitic electrodes results in the emergence of a fan-shaped jet of helium and carbon. The gasdynamic and temperature parameters of the jet depend on the parameters of the arc discharge and the buffer gas. Variations in the parameters of the carbon vapour flow change the kinetics of carbon condensation, leading to variations in the morphology and structure of the carbon material. The main external parameter of the synthesis (buffer gas pressure) was varied in the study, and correlations between the intensity ratio of the D to G peaks on the Raman spectrum and the electrical conductivity and magnetic susceptibility values were found. During the synthesis, nanographite structures were formed. However, the formation of an amorphous carbon structure on the free 'zig-zag' edges of the graphite fragments reduced the magnetic susceptibility, the electrical conductivity and the ID/IG ratio.

Keywords: ARC-DISCHARGE, CARBON NANOMATERIALS, ELECTRICAL CONDUCTIVITY, MAGNETIC SUSCEPTIBILITY

1. Introduction

The current interest in nanostructured materials is due to their unique properties and potential applications. One of the bottom-up physical methods for nanomaterial synthesis is arc discharge which results in sputtering of the electrode materials and a condensation process that leads to nanoparticle formation.

Arc discharge between coaxial graphite electrodes results in the formation of a fan-shaped jet emerging from the interelectrode gap. This jet consists of buffer gas and the products of graphite sputtering [1, 2]. Variation in the external discharge conditions leads to changing parameters in the discharge plasma and the fan-shaped jet.

The arc discharge method allows synthesis metallic [3, 4] and composite [5, 6] nanoparticles stabilised by a carbon matrix. This method prevents the coagulation of the nanoparticles and, correspondingly, the increase in size and loss of reactivity of the nanoparticles. Many parameters of the synthesised materials depend on the properties of the carbon matrix.

Electroconductivity influences the electrocatalytic [6] and electrochromic [7] applications of synthesised nanomaterials. Electrical conductivity, in turn, depends on the consistency and structure of the carbon. For wide-gap semiconductors in the case of diamond structures consisting of sp^3 -hybridised carbon atoms, this value is $\sim 10^{-13}$ S/m. On the other hand, the metallic conductivity value for the parallel orientation of graphitic layers consisting of sp^2 -hybridised carbon atoms is $\sim 10^5$ S/m.

The magnetic properties of the carbon matrix are of interest for applications relating to ferrofluid creation [8], bio-inert magnetic materials and others. Magnetic properties and electroconductive properties depend on the internal structure of the carbon material [9]. Both the core of the carbon atom [10] and bulk forms such as graphite [11, 12] and diamond [13] have diamagnetic properties. The same is true for nanoscale carbon forms such as nanotubes [14] and fullerenes [15]. Paramagnetism and even ferromagnetism at room temperature have been predicted and discovered in such forms as nanotubes in a closed torus [16] and nanofragments of graphite [17]. In the case of nanographite, paramagnetism is determined by the presence of free 'zig-zag' edges that lead to the formation of unusually high Fermi level density states [18, 19], which in turn leads to increases in Pauli paramagnetism [20].

Various parameters of arc discharge synthesis determine the structural features of the carbon material such as fullerenes [21], graphene [22, 23], carbon nanotubes [24], etc. The most common product of arc discharge sputtering of the graphite electrodes is

carbon soot, which consists of sp^2 -, sp^3 -hybridised carbon atoms [25]. The main effects on the structure of the material are caused by the buffer gas pressure in the reactor chamber. The present study examines the effects of buffer gas pressure on the electroconductive and magnetic properties of synthesised carbon materials.

The aim of this study is to investigate the electroconductive and magnetic properties of carbon materials synthesised at the discharge parameters used for nanoparticle synthesis.

2. Materials and methods

The carbon materials were synthesised using a plasma-chemical reactor presented on Fig. 1. The reactor consists of a sealed chamber (1). A movable graphite cathode (2) is mounted in the chamber. Solid graphite rod used as sprayed anode (3) is mounted coaxial with the cathode. The amount of impurities of used graphite was less than 1 ppm, and the amount of Fe less than 0.1 ppm. Helium was used as the buffer gas. The reactor chamber was first purged by helium then filled with helium at a certain pressure. The experiments were carried out with a consistent direct current of 120 A supplied by DC source (4), and the buffer gas pressure ranged from 3 to 200 Torr. Arc discharge is ignited between the electrodes, which results in spraying of the anode. The arc discharge voltage is stabilised with help of a voltmeter (5) and screw assembly (6). Spraying of the anode results on the evaporation of graphite and emergence of the carbon atoms and clusters in the discharge area. Flows of the sputtered graphite products and helium from electrode gap to the reactor chamber result in carbon condensation and nanoparticle formation. Synthesised carbon material is collected on water cooled screen (7). The experiments were carried out on various buffer gas pressure ranged from 3 to 200 Torr. The buffer gas pressures are controlled with help of digital pressure sensor (8) and solenoid valve (9) controlled by a control board (10).

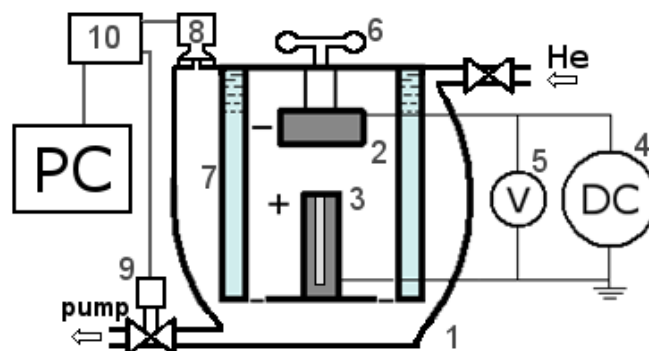


Fig.1. Set-up of plasma-chemical reactor

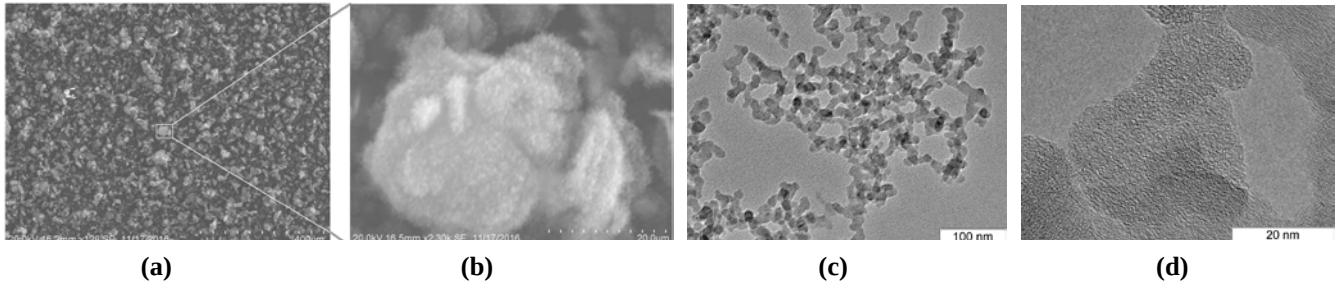


Fig. 2. (a) SEM image of the deposited carbon layer, (b) SEM image of the single agglomerate, (c) TEM image of the chains carbon globules, (d) HRTEM image of the single carbon globule.

Synthesised carbon nanomaterials were labelled C3, C6, C12, C25, C50, C100 and C200, with these numbers corresponding to the pressure in Torr.

The magnetic properties of the synthesised nanomaterials were studied at room temperature using a SM-150L magnetic susceptibility meter (ZH instruments, Czech Republic) with a working frequency of 16 kHz and a stretch field of 320 A/m.

The electrical conductivity of the synthesised materials was studied using resistivity analysis while compressing the materials between parallel flat copper contacts. The density was determined by dividing the mass of the tested material by the filled volume.

Scanning electron microscopy (SEM) was carried out using a S-3400N microscope (Hitachi Science Systems Ltd., Japan) in secondary electron detection mode. The size distributions were plotted according to the sizes of the carbon agglomerates measured from the SEM images.

Transmission electron microscopy (TEM) was carried out using a JEM-2010 microscope (JEOL Ltd., Japan). The size distributions were plotted according to the sizes of the nanoparticles measured from the TEM images.

Raman spectroscopy was carried out using a Spex Triplemate Raman spectrometer (Princeton Instruments, USA) equipped with an LN-1340 PB multi-channel detector.

3. Results and discussion

After synthesis the materials that were produced were deposited on the product-gathering screen forming a low-density carbon layer. The layer consisted of agglomerates (Fig. 2(a)), of a characteristic size of around 10 μm . Single agglomerates had a rarefied hairy structure (Fig. 2(b)) consisting of chains of solid carbon globules. Ultrasonic treatment of the material resulted in the destruction of the agglomerates into separate chains (Fig. 2(c)) consisted of carbon globules (Fig. 2(d)).

Mechanical compressing of the synthesised materials between the parallel flat contacts resulted in a disturbance of the agglomerate structure that decreased the content of voids, increased the number of globules per unit volume, and caused the emergence of new contacts between the globules and the emergence new percolation skeletons. This in turn led to an increase in the electrical

conductivity of the synthesised materials (Fig. 3(c)).

According to Fig. 3(c), the resistivity of the synthesised materials decreases as the density increases. This dependence is approximated using the following power law for a system near a percolation threshold: $(\rho - \rho_0) \sim (p - p_c)^{-7}$. The value ρ_0 is used to calculate the electroconductivity of the materials.

Raman spectroscopy is a robust analysis method for carbon structures. Fig. 3(b) shows the characteristic spectrum of the synthesised materials. The presence of peaks at 1350 cm^{-1} and 1584 cm^{-1} is evidence of the presence of a graphite structure. Peak G (1584 cm^{-1}) corresponds to oscillations of the bonds between the sp^2 -hybridised carbon atoms, although this does not constitute firm evidence of the presence of carbon rings. However, peak D (1350 cm^{-1}) corresponds to breathing oscillations in the six-membered rings of the carbon atoms and appears on the free edges and defects of the graphene planes [26]. D' (1510 cm^{-1}) is associated with the presence of amorphous carbon [27].

Fig. 3(a) shows the pressure dependencies of electrical conductivity, magnetic susceptibility and the intensity ratio of peaks D and G (ID/IG) on the Raman spectrums. As indicated by the diagram, these parameters have complex pressure dependencies, which nevertheless correlate with each other. These correlations are due to the structure of the carbon globules that are formed during nanomaterial synthesis.

The sputtering of the graphite electrodes results in a fan-shaped jet emerging from the interelectrode gap. The jet itself contains both the product of this sputtering and buffer gas atoms [2-1, 3-2]. Fig. 4 shows a simplified outline of the sections of the fan-shaped jet. The temperature of the jet's axis decreases in line with the distance from the electrodes. However, condensation of the carbon vapour leads to the formation of chains, rings and clusters of carbon atoms [1]. Further coagulation leads to the formation of nanoparticles whose stable graphite-like structure forms in sufficiently hot areas of the jet (areas 1 and 2). In instances where the particle does not reach a size sufficient for the formation of the graphite-like structure, the further coagulation of such particles in area 3 leads to the formation of the amorphous soot globule structure.

The jet is unstable, leading to turbulent mixing with the buffer gas. This buffer gas already contains carbon nanoparticles, and

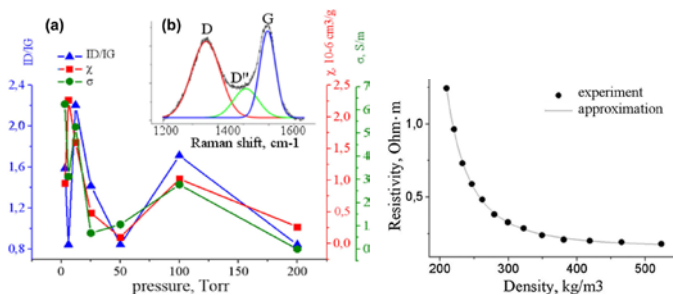


Fig.3. (a) pressure dependence of the ID/IG ratio, the magnetic susceptibility and the electroconductivity of the synthesized materials, (b) Raman spectrum of C100, (c) density dependence of the resistivity of C12.

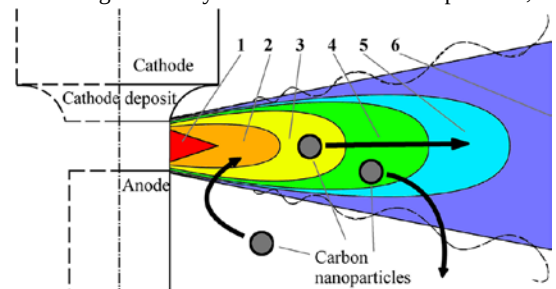


Fig.4. Simplified outline of the jet sections: 1-jet core; 2-area of graphitisation of nanoparticles from the buffer gas; 3-area of formation of graphite-like structure; 4-area of formation of the amorphous carbon layer on the nanoparticles; 5-area of formation of globule chains; 6-area of micro-agglomerate formation.

should one of these enter the hot areas of the jet (area 2 on Fig. 4) the effect of the heat treatment leads either to the formation of the graphite-like structure (in the case of the graphitising structure) or an amorphous structure (Fig. 5 (a)) (in the case of the non-graphitising structure) [28]. Further movement of the nanoparticles within colder areas of the jet (area 4 on Fig. 4) may result in surface carbon deposits in the form of amorphous layers (Fig. 5(b)). Collisions of the carbon nanoparticles in even colder areas (area 5 on Fig. 4) result in the formation of chains of carbon globules (Fig. 2(c)). The formation of micro-agglomerates (Fig. 2(b)) takes place

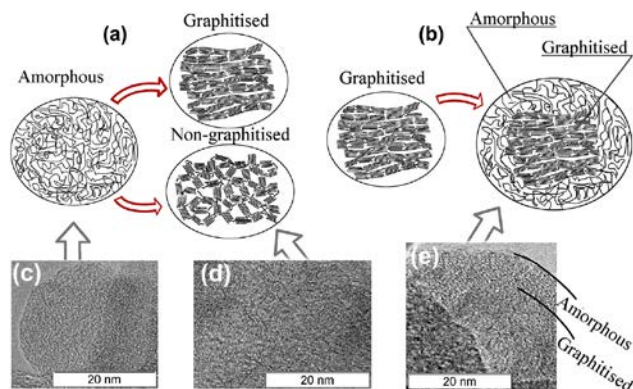


Fig. 5. (a) transformation of amorphous nanoparticle to graphitized and non-graphitized structures (Franklin) [39]; (b) deposition of amorphous carbon layer on graphitized nanoparticle; (c) HRTEM image of amorphous carbon nanoparticle in C100; (d) HRTEM image of non-graphitized carbon structure in C100; (e) HRTEM image of amorphous carbon layer on graphitized structure in C100.

in distant areas of the jet (area 6 on Fig. 4) and in the buffer gas.

The formation of an amorphous carbon layer on the surface of the nanoparticles with a graphite-like structure creates bonds with the atoms of the rings on the edges of the graphitic structure, reducing the intensity of peak D on the Raman spectrum. The dependence of the ID/IG ratio on the buffer gas pressure used for material synthesis also correlates with the pressure dependences of electrical conductivity and magnetic susceptibility (Fig. 3(a)).

A positive paramagnetic contribution in magnetic susceptibility is given by the structure of the free ‘zig-zag’ edges of the graphitic nanofragments (Fig 7(a)). The deposition of the amorphous carbon layer leads to the emergence of bonds between these ‘zig-zag’ edges and the amorphous layers (Fig. 7(b)), which in turn leads to a decrease in electron state density at the Fermi level. The amorphous layer on the graphitic nanofragments hence reduces the Pauli paramagnetism component for the magnetic susceptibility of the carbon nanoparticle.

The graphite-like structure has good electroconductivity due to the presence of delocalised electrons. An amorphous carbon structure with random σ - and π - bonds has a significantly weaker electrical conductivity value than a graphitic structure. The amorphous layer on the particle surface hence contributes significantly to the electrical resistivity by creating additional contact resistance between the particles with graphite-like structures.

Thus, the amorphous carbon layer on the surface of the particles with a graphite-like structure has an identical effect on the electroconductive, paramagnetic properties and ID/IG ratio of the synthesised materials, which explains the correlation of these properties (Fig. 4(a)).

In the pressure range used in the work (3–200 Torr), the jet flowing from the interelectrode gap can take various characteristics, such as composition (C/He), speed, flow regimes, etc. The saturated vapour pressure of the carbon is 7.5 Torr at 3800K temperature, which is close to the evaporation temperature of carbon. The composition of the jet in the initial area varies from pure carbon ($x(C) \sim 100\%$), to the prevailing helium ($x(He) > 97\%$). The mass speeds of the anode sputtering and the cathode deposit

formation were measured in the experiments. The difference in these speeds determines the speed of production of the carbon nanomaterial, which together with helium form the jet and allow determination of the speed of the jet, and the Knudsen and Reynolds numbers at the initial area of the jet. The Kn and Re exhibit values across a wide range depending on the buffer gas pressure values (Fig. 8). These jet parameters have non-monotonic dependencies on the buffer gas pressure. Thus, the pressure of the buffer gas in the reactor chamber affects the temperature and gas-kinetic parameters of the jet. Variation in the buffer gas pressure leads to the change in the size of the areas of nanoparticle formation marked in Fig. 5 and the duration of the residence of the nanoparticles in these areas.

A larger Kn for carbon atoms, which is characteristic of lower buffer gas pressures, taking into account the composition of the C-He mixture, characterises the smaller number of collisions of the carbon particles with each other and correspondingly the smaller probability of formation of carbon particles large enough for the graphite structure in the hot areas of the jet, on the one hand, and the smaller probability of precipitation of the amorphous layer on the already formed graphite-like particles in colder regions, on the other hand. A larger Re, which is characteristic of higher pressures, characterises the more intensive mixing of the jet with the buffer gas, which leads to more intensive cooling of the jet and to decreases in the size of the particle formation areas, which affects both the formation of primary particles and the deposition of the amorphous layer on the already formed graphite-like particles. In addition, the more intensive mixing of the jet with the buffer gas leads to a larger probability of the carbon particle entering from the buffer gas into the jet and therefore to heat treatment and graphitisation of the structure, when it enters into the hot areas, and to deposition of the amorphous carbon layer, when the carbon particle enters into the colder areas of the jet.

As can be seen from the complex dependencies of the electrical conductivity and magnetic susceptibility on the buffer gas pressure, gasdynamic processes have different effects on the formation of the nanomaterial structure at various pressures.

4. Conclusion

A plasma-arc synthesis of carbon nanomaterials was carried out at various buffer gas pressures. The synthesised materials are soot agglomerates at micron sizes, which consist of chains of carbon globules of nanometre sizes. Increasing the pressure of the buffer gas leads to the formation of globules of larger sizes. Nevertheless, the effect of buffer gas pressure on the internal structure is complex, which affects the electrical conductivity, the magnetic susceptibility, and the ID/IG ratio on the Raman spectrum of the synthesised materials.

At various buffer gas pressures, the helium-carbon jet flows from the interelectrode gap, with different thermal and gasdynamic characteristics, which lead to various conditions for the formation of the amorphous carbon layer on the nanoparticle surface. Nevertheless, the correlation of the dependencies of the electrical conductivity, the magnetic susceptibility and the ID/IG ratio of the synthesised materials on the buffer gas pressure indicates an affinity in the effects of the internal structure of the carbon globules on these parameters.

It was found that the values of the electrical conductivity, the magnetic susceptibility and the ID/IG ratio are affected by the amorphous carbon layer formed on the carbon nanoparticle surface with a graphite-like structure. The amorphous carbon layer forms bonds with free graphite edges, thereby reducing the value of the ID/IG ratio, including forming bonds with zig-zag edges, which reduces the paramagnetic contribution to the magnetic susceptibility, and also creates an additional contact resistance upon contact of nanoparticles, which leads to a decrease in the electrical conductivity of the synthesised carbon nanomaterials.

Acknowledgements The work was supported by grant RFBR 16-38-00322.

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MODELING OF METAL CRYSTALLIZATION BY MEANS OF CELLULAR AUTOMATON

МОДЕЛИРОВАНИЕ КРИСТАЛЛИЗАЦИИ МЕТАЛЛОВ С ПОМОЩЬЮ КЛЕТОЧНОГО АВТОМАТА

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Abstract: Simulation model of crystallization, which is based on combination of mathematical modeling methods and a probabilistic cellular automaton, is presented here. Such combination makes it possible to predict process of metals and alloys structure formation whiles crystallization under various cooling conditions, and also to study this process both in the course of homogeneous and heterogeneous nucleation.

KEYWORDS: CRYSTALLIZATION, STRUCTURE OF METALS AND ALLOYS, COMPUTER MODELING, CELLULAR AUTOMATON

1. Introduction

Traditional approach to the theoretical description of metals crystallization is based on the usage of classical thermodynamics or mathematical physics methods, which use the solution of heat equation (Stefan's problem) [1]. However, such description of the processes of solid phase's nucleuses formation and of their subsequent growth has a number of significant drawbacks. Thus, nonequilibrium conditions for the processes are not considered in equilibrium thermodynamics, while they take place in the overwhelming majority of real production technologies. Besides this, calculations, which are based on the well known formula for the critical radius of the solid phase's nucleus, that was obtained with the help of Gibbs's free energy, show that the embryo consists of a finite number of atoms (3 - 600) [2]. It means that such physical object should be described with the help of quantum mechanics. Stefan's problem is not suited for describing of crystallization of melt's volume, which was supercooled at the initial moment of time (that is typical for real, as a rule - non-equilibrium, technological processes), although its development led to creation of theory of quasi-equilibrium two-phased zone, which is based on the simultaneous solution of heat conduction and diffusion equations and satisfactorily describes processes of binary melts' mass crystallization, and is rather widely used to describe various processes of obtaining ingots and castings. However, usage of heat conduction and diffusion equations to study crystallization can not provide solutions, which describe the process of solidifying metal's structure formation, but it is namely this process of structure formation during crystallization of metals and alloys, which is of the most interest for the practitioners. Therefore, theoretical studies of the crystallization process under various cooling conditions are of current interest.

2. Preconditions and means for resolving the problem

Computer modeling is a method, which combines theory and experiment. In this work a simulation model of crystallization and investigation of homogeneous crystallization of aluminum, which were carried out with its help, are presented. The basis of the model is combination of mathematical modeling methods and of idea of a probabilistic cellular automaton, that allows to avoid significant mathematical difficulties and predict the process of metal structure formation during crystallization under various cooling conditions, and investigate the process in the course of homogeneous and heterogeneous formation of embryos.

A cellular automaton in the model is a network of elements, which can change their state (liquid or solid) at discrete moments of time. Change of element's state occurs according to a certain law, depending on external conditions, as well as on the state of its nearest network neighbors at the previous discrete moment of time. In this model, functioning of the cellular automaton is the subject to the external cooling conditions of the investigated system and is managed by numerical solutions of the heat conduction and diffusion equations.

3. Structure and capabilities of the model

The algorithm of the model is constructed with the usage of basic techniques of system analysis by decomposing of the investigated system into separate blocks (subsystems) and determining the connections between them. In the process of investigation of a pure metal or binary alloys crystallization, we can distinguish the basic physical processes that determine course of crystallization. First of all, it is transferring of heat, which occurs in the melt's volume under the influence of external factors. It is this process, which is crucial, since the temperature gradient is one of the most important parameters in the formation of crystal's structure. Therefore, the main unit, which determines the dynamics of the model's work, is the block, which determines the temperature field during the whole process. It is based on the Fourier's equation of thermal conductivity with boundary conditions of the third kind. Processes associated with redistribution of the second component of the alloy in the liquid due to different solubilities in the metal's liquid and solid states are the second the most significant physical phenomenon in this case. To calculate these processes, the characteristic points of the corresponding double alloy's phase diagram are introduced into the model, and liquidus and solidus lines are approximated. Fick's equation is used for description of the second component's diffusion in the liquid.

The boundary conditions in this case assume absence of exchange by substances at the boundaries of the system. Taking into account the big difference of diffusion's coefficients in liquid and solid states, the redistribution of elements along the grain (dendrites), is not considered. Temperature and concentration at each melt's point determine the size of the local supercooling at this point, which is calculated as difference between the liquidus temperature for this point and its temperature at a given moment of time.

It should be noted that calculation of the second component's concentration in the liquid is not performed in the model, when crystallization of pure metal is modeled. Local supercooling in this case is defined as the difference between the metal's temperature of crystallization and given point's temperature at a given time.

In case of supercooling, conditions for crystal's formation or for growth of an already existing embryo appear in the liquid state of the melt. It is known [3] that growth of the crystal occurs under smaller supercoolings, that is, these processes differ from each other in terms of energy. Taking into account the fluctuating nature of solid-state's nuclei formation and growth of crystals in accordance with normal mechanism, which is characteristic for metals [4], in model these processes are separated and an element of randomness is built into them. For the element in which transition from liquid to a solid state is possible, the states of the nearest cells are checked. If there is at least one cell in the solid state, then it is considered that the growth of the already existing embryo is possible, otherwise the emergence of a new center is possible. To emphasize the energetical differences of the processes of crystals' formation and growth, conditional "barriers" are introduced, the size of which is determined by subcooling at a given point and is set at the level between 0 and 1.

The cellular automaton, which implements the above mentioned scheme, is part of the general algorithm of the simulation model. Its flowchart is shown in Figure 1. The operation of the cellular automaton begins with examination of the nearest neighbors of the cell, in which supercooling exists and phase transformation is possible (block 1). After this, a decision is taken: either a new crystallization center appears, or an already existing crystal grows, (block 2).

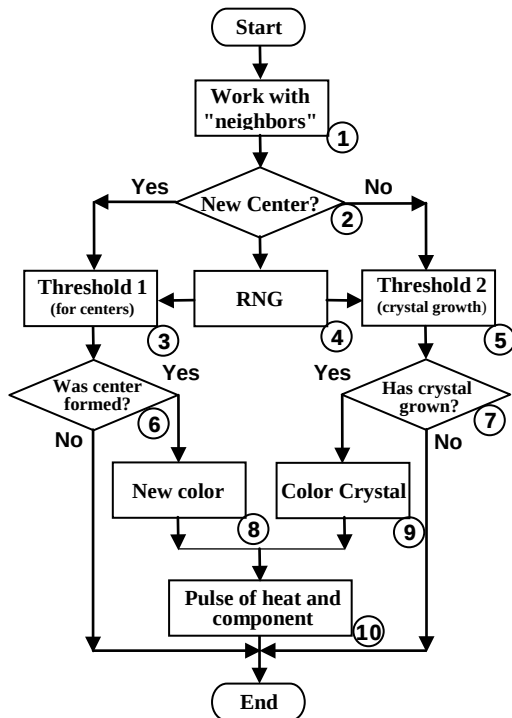


Fig.1. Fragment of algorithm of the probabilistic cellular automaton of the simulation model of crystallization.

or nothing happens (block 2). In blocks 3 and 4 conditional thresholds of transformation for a new center or for an existing crystal are determined, the values of which depend on the supercooling. After the appropriate threshold is calculated, a random number from the random number generator (RNG, block 5) enters blocks 3 or 4, and if it exceeds this threshold, a phase transformation occurs, that is, the transition of this point from liquid to solid state. Usage of RNG (Block 5) is a characteristic feature of the simulation model and allows to emphasize the random nature of the process [4].

Differentiation of colors is used to display the emerging structure of solid phase's growing grains on the computer screen. If a new embryo is formed, it is colored with a new randomly selected color. The growth of the existing crystal is supported by the color of the "solid neighbor". Black-and-white version of the image also exists, here grains' boundaries are digitally fixed according to a specially designed algorithm. Phase transition is accompanied by release of crystallization's heat and, for melts, also by second component's change in concentration at given point's region. Formation of the corresponding "impulses" is taken into account when calculating the thermal field and concentration of the second component of the alloy.

Results of simulation are as following:

- files in which the following data are recorded during the program's work: temperature in the central point at each step of the calculation, the number of centers of crystallization which have appeared and speed of their formation, the amount of solid phase and its growth rate, magnitude of temperatures' gradient along the system's cross section;
- picture, which is modeled by a cellular automaton, is an output window that eventually is filled with colored dots, at that color indicates belonging to a certain generation of transformed cells;
- quantitative evaluation of grain's size;

- presence of supercooling in the system and distribution of the second element's concentration along system's cross section when modeling the crystallization of the alloy.

Adequacy of the simulation model of crystallization is proved by comparing the data obtained in real and in computer experiments. Figure 2 shows results of modeling of the process of formation of structure of aluminum during crystallization. In this case, coefficients of thermal transfer are set equal on three sides and one

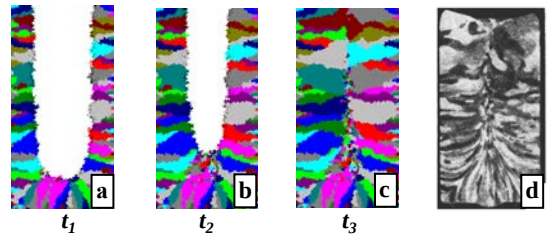


Fig. 2. Structure (a, b, c), which has been modeled in crystallization of aluminum at the moments of time ($t_1 < t_2 < t_3$) and real structure of pure aluminum (d) [5].

coefficient from the top is absent.

It can be seen that front of crystallization has not flat, but diffusion character, which is typical for the normal type of crystallization. At the beginning of the process, relatively small grains appear in the corners and on the walls, and during further growth they begin to interact with each other, and some of them stop growing, while others turn into long grains directed toward the center. At the end of crystallization, small disoriented grains appear in the center of the casting. The real structure of pure aluminum is shown for comparison (Fig. 2 d).

4. Results and discussion

Before computational experiment with the simulation model of crystallization is carried out, the model has to be adjusted for modelling of the particular metal's crystallization. To do this, at first experiment with the real metal is performed, and as a result one can obtain macro structure of the metal and recorded cooling curve of the thermal analysis. Then the model's parameters are selected in such a way that the calculated results of modeling of the structure and of cooling curve coincide with the experimental ones. This is achieved by adjusting of the model's parameters, which are the following: initial temperature and temperature of calculation's end; environment's temperature (left, right, bottom, top); coefficients of heat transfer from all sides (left, right, bottom, top); specific thermal capacity; specific latent heat of crystallization; coefficient of thermal conductivity; density; geometric dimensions of the system and time interval of calculations; temperature of pure metal's crystallization and parameters of the alloy state's diagram; amount (or absence) of the modifier. There are also heuristic parameters: metastability's interval for crystallization centers' formation; maximum supercooling for crystallization centers' formation; metastability's interval for crystals' rate of growth; maximum supercooling for crystals' rate of growth. The paper presents studies of cooling rate's (V_c) influence on the process of formation of structure of pure aluminium during its homogeneous crystallization. It should be noted that in this case an ideal system is being studied, in which there are no impurities at all. During the experiments, coefficients of heat transfer were chosen to be the same from all directions: 5; 10; 20; 50; 100; 150 and 200 W/(m²·s·K). At that, for the system with geometric parameters 0.03×0.03 m², the cooling rate, which was calculated from the simulated cooling curve, acquired the following values: 0.17; 0.33; 0.67; 1.67; 3.33; 5.00 and 6.67 degrees/s. The modifier in the form of already solid particles was absent. Metastability interval for crystallization centers' formation in this case was chosen to be 5 degrees, and metastability interval for growth of crystallization was 1 degree. As it can be seen from Figure 3, shape of the cooling curve begins to change as the cooling rate increases. For V_{ox} in the range from 0.17 to 1.67 deg/s (Fig. 3 a, b, c), thermograms differ very slightly from one another and have a classical shape. With a stronger cooling ($V_c = 3.33, 5.00$ and 6.67 deg/s), the shapes of curves are changed significantly. Initially, a peak appears at the end of crystallization (Fig. 3 d), and

then the recalcence of the temperature disappears at the beginning of the process and curves take on a shape with the region of almost constant temperature, which is below the temperature of crystallization (Fig. 3 e, f).

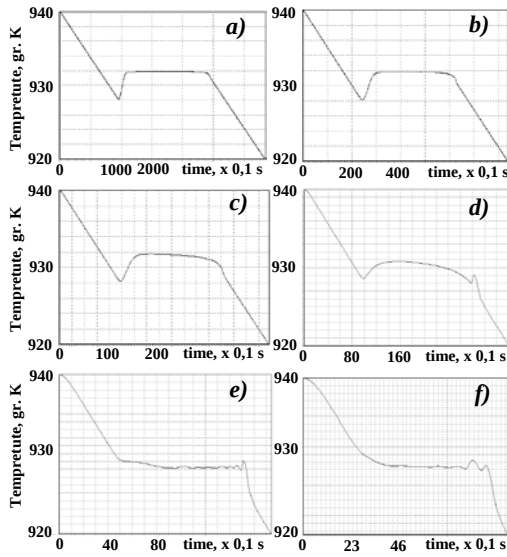


Fig. 3. Cooling curves of pure aluminum, simulated at different cooling rates : a) - 0.17 deg./s; b) - 0.67 deg./s; c) - 1,67 deg./s; d) - 3,33 deg./s; e) - 5,00 deg./s; f) - 6,67 deg./s

Temperatures' fluctuations, which are observed in thermograms (Fig. 3 d, e, f), occur also in real experiments, but in much smaller ranges. This can be explained by inertia of a real thermocouple, which has protection elements. Explanations of cooling curves shapes' changes could be done by analyzing dependence of the number of crystallization centers (Fig. 4) and the rate of their formation (Fig. 5) on time in the process of crystallization.

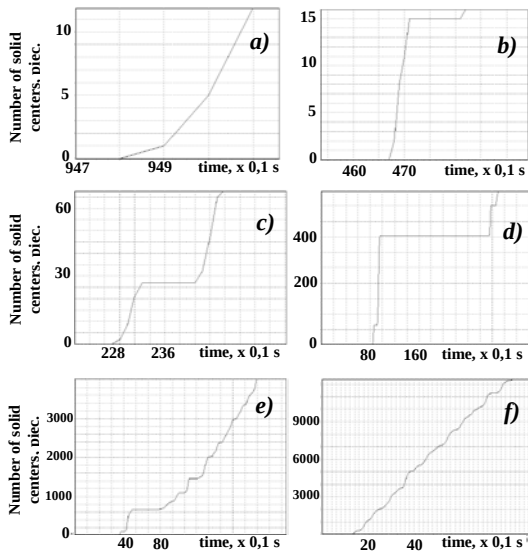


Fig. 4. Number of solids in the solid formed by homogeneous crystallization of aluminum at different cooling rates: a) - 0.17 deg./s; b) - 0.67 deg./s; c) - 1,67 deg./s; d) - 3,33 deg./s; e) - 5,00 deg./s; f) - 6,67 deg./s

At a low cooling rate of the liquid metal $V_{ox} = 0.17$ deg/s, the curve of the dependence of the formed crystallization centers on the time $N = f(t)$ is smoothly increasing (Fig. 4 a), the rate of their formation has one extremum (Fig. 5 a). All embryos appeared during a short interval of time (0.3 s). After centers' appearance, supercooling disappears, recalcence appears in the thermogram and then a gradual growth of crystals takes place, to which rectilinear portion of the cooling curve is corresponding ("a shelf"). The structure of a

solid metal in this case consists of large almost non-oriented grains (Fig. 6 a).

Increase of the cooling rate ($V_c = 0.67$ deg/s) leads to appearance of a "stair" in the curve $N = f(t)$ (Fig. 4 b), and the rate of their

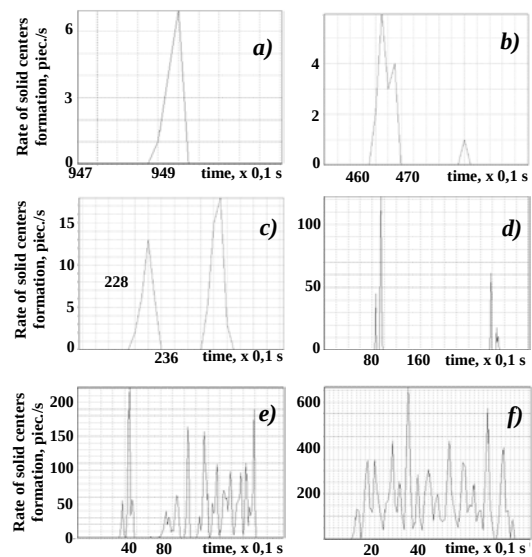


Fig. 5. Rate of homogeneous formation of solids in crystallization of aluminum at different cooling rates: a) - 0.17 deg./s; b) - 0.67 deg./s; c) - 1,67 deg./s; d) - 3,33 deg./s; e) - 5,00 deg./s; f) - 6,67 deg./s

formation has already two peaks (Fig. 5 b). That is, centers of crystallization arise in two stages: at the beginning of the process as well as its end. At that, changes in the cooling curve are insignificant. The temperature of the "shelf" decreases slightly (by a tenth of a degree) and, before the end of crystallization, temperature decreases in a slightly slower rate (Fig. 3 b). The structure of the solid metal remains practically unchanged (Fig. 6 b), although there are almost invisible small undirected grains in the center.

With a subsequent increase of V_c up to 1.67 deg/s, the total number of formed centers solid phase increases, and the "stair" on the curve of their time dependence becomes well noticed (Fig. 4 c). The rate

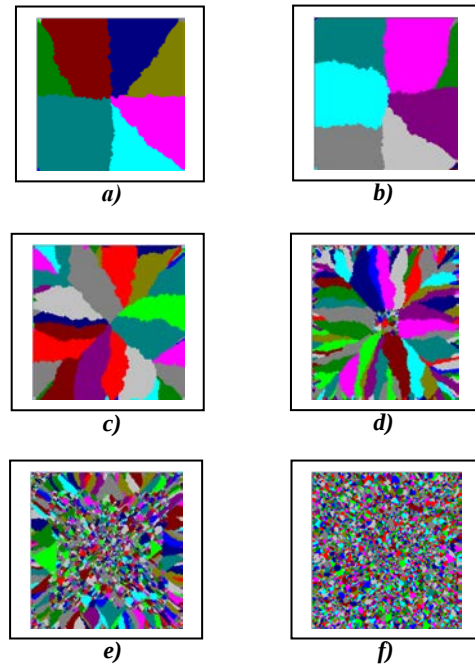


Fig. 6. Macrostructures of pure aluminum, modeled at different cooling rates: a)- 0.16 deg./s; b) - 0.67 deg./s; c) - 1,67 deg./s; d) - 3,33 deg./s; e) - 5,00 deg./s; f) - 6,667 deg./s

of centers' formation has two brightly visible peaks (Fig. 5 c). Changes in the cooling curve become more noticeable. Thus, the temperature of the "shelf" decreases before the end of crystallization (Fig. 3 c). The structure of the solid metal is substantially crushed (Fig. 6 c) and the grains become more elongated toward the center of the system.

Further growth of the cooling rate ($V_c = 3,33$ deg/s) leads to the appearance of several "stairs" on the curve $N = f(t)$ (Fig. 4 d). Two peaks that were observed in the previous case on the curve of dependence of rate of embryos' formation begin to split up, and we can see already four extrema (Fig. 5 d). Thus, the process of formation of crystallization centers becomes multistage. Significant changes are observed in the cooling curve: the value of recalcence decreases, the temperature's "shelf" practically disappears, the temperature before the end of crystallization decreases even faster. The structure of the solid metal becomes three- zoned (Fig. 6 d). Small grains are observed on the form's conditional walls (at the edges of the system), some of them are suppressed by other crystallites. Then a zone of crystals, which are elongated and oriented to the center, is formed. There is a small zone of non-oriented grains in the center.

A significant increase of the cooling rate ($V_c = 5.00$ deg/s) leads to the appearance of many "stairs" in the curve $N = f(t)$ (Fig. 4 e). Actually this dependence becomes "wavy" by nature. This is clearly seen also in the curve of dependence of nuclei rate's formation (Fig. 5e). There are a lot of formed peaks and the process of crystallization centers' formation becomes almost periodic. Although at the beginning of crystallization, formation of centers has, as before, an explosive character. The shape of the cooling curve changes in principle: recalcence disappears, the temperature's "shelf" appears again, but its temperature decreases and is actually equal to the temperature of crystallization minus the interval of metastability for embryos' formation (Fig. 3 e). The structure of the solid metal becomes grained differently (Fig. 6 e). Larger grains are observed near to the mold's conditional walls, and there are smaller ones in the center of the casting.

The next increase of the cooling rate V_c to 6.67 deg/s emphasizes the effects observed in the previous case. Dependence $N = f(t)$ has a "wavy" character (Fig. 4 f). The process of crystallization centers' formation becomes quasi-periodic and continuous in time (Fig. 5 f). The shape of the thermogram has an almost straight lane corresponding to the crystallization of the liquid metal. But at the beginning of crystallization the form of the cooling curve becomes smoother, which is explained by the effect of the temperature gradient across the cross section of the system at already sufficiently high cooling rate (Fig. 3 f). The structure of the solid metal becomes finely granular (Fig. 6 f).

The obtained results of the changes in the cooling curves, dependences of the number of crystallization centers and of their formation's rate on time, and the structure of the solid metal, which are observed in the computational experiment, can be explained as follows. In the case of slow cooling, nucleus of the solid phase appear after the metal's temperature becomes lower than the temperature of crystallization by (T_0) by value of interval of metastability (ΔT). At that, the heat of crystallization is released. The rate at which this heat is released significantly exceeds the rate of heat transfer, that results in system's temperature increase almost to a temperature, which is below T_0 by the value of metastability's interval for crystals' growth ΔT , which is close to zero (i.e., the supercooling value is about ~ 0.1 degrees). With this supercooling new crystallization centers do not appear and only already formed crystals grow. After the end of the phase transformation, the metal is simply cooled and its temperature decreases gradually.

In the case of faster cooling, temperature in the whole system or in its parts decreases after appearance of the first formations of the solid phase, in spite of the released heat of crystallization, due to sufficiently rapid cooling. After a certain time, supercooling occurs and conditions appear for the formation of new nuclei of the solid phase. Their appearance and corresponding releasing of crystallization's heat reduces the supercooling and growth of already existing crystals continues. Such processes can occur either

one or several times, after that crystallization ends and the metal simply is cooled. Formation of the classic three-zoned casting's structure can be explained by formation of the nucleation of the solid phase in several stages (Fig. 6 d). Centers of crystallization appear at two stages: at the beginning of crystallization and at the stage which corresponds to formation of the central zone of equilibrium crystals.

When the system is cooled at high speed, the rapid heat removal does not give the metal's temperature to rise despite release of crystallization's heat. Conditions are created for the simultaneous formation of crystallization's centers and for the growth of already existing crystals, as Figures 4 f and 5 f demonstrate.

5. Conclusion

1. The simulation model of crystallization is presented, which is based on the combination of cellular automaton with the classical problems of heat conduction and diffusion. This model allows us to investigate the process of the metal structure formation during crystallization and the dynamics of this process under various cooling conditions.

2. Computer experiments which were carried out on modeling of homogeneous crystallization of aluminum showed:

- formation of all the centers of the solid phase at a cooling rate of 0.17 degrees/s occurs in a short time interval (about 1 s) and then centers' further growth occurs;
- with an increase of the cooling rate, the centers of the solid phase are formed in two stages - at the beginning of crystallization and in the second half of the process; this leads to the formation of three-zoned structure;
- at a cooling rate of 5 degrees/s and higher, the solid phase's centers are formed over a long period of time, their growth proceeds in parallel, and the structure of the solid metal becomes finely granular.

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STUDY OF PHASE TRANSFORMATIONS IN THE ROLLS OF ALLOY STEELS DURING QUENCHING BASED ON FINITE-ELEMENT MODEL

ИССЛЕДОВАНИЕ ФАЗОВЫХ ПРЕВРАЩЕНИЙ В ВАЛКАХ ИЗ ЛЕГИРОВАННЫХ СТАЛЕЙ ПРИ ЗАКАЛКЕ НА ОСНОВЕ КОНЕЧНО-ЭЛЕМЕНТНОЙ МОДЕЛИ

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Abstract/Резюме: The studies are represented of phase and structure transformations during the process of multi-stage heat treatment of large-scale rolls. Adapted analytical models are introduced and applied to the calculation of phase transformations together with the finite-element models of rolls. The results show phase components distribution over the hardened layer of rolls of the special alloy steels 50CrMnMoV and 45Cr3MnNiMoV at different stages of the manufacturing process.

KEYWORDS: HEAT TREATMENT, PHASE TRANSFORMATION, FINITE-ELEMENT MODEL, ROLLS, ALLOY STEEL

1. Introduction / Введение

Improvement of heat treatment process is efficient, if a complete picture is known of the main features and characteristics of processed alloys. Important information is about the kinetics of supercooled austenite transformation, on which the basis issues are addressed of hardenability, heat treatment schedules and the mechanical properties (YTS, UTS, E% and HB).

Experimental study of microstructure components in the heat treatment of alloy steels consists of the building of time-temperature (TTT) and continuous cooling (CCT) transformation diagrams, as well as in the study of steels hardenability. At the same time, the use of numerous experimental tests to study the phase transformations are limited especially for large-scale parts. Isothermal TTT diagrams are used only for qualitative assessment of the effect of chemical composition on the process of austenite decomposition. The CCT diagrams cannot provide reliable information on the steel microstructure, if the industrial cooling schedule differs from the cooling conditions in the experiments. For this reason, CCT diagrams are only used to quantify the stability of the austenite under continuous cooling. Hardenability makes it possible to predict the structure of steel after heat treatment based on its chemical composition, which is characteristic of only a particular grade of steel. Limitations associated with the method of experimental data presentation can be eliminated by creating analytical and finite element mathematical models whose parameters are determined from the abovementioned experimental methods.

The most fundamental results in the modelling of phase transformation kinetics were obtained in works of A.N. Kolmogorov, M. Avrami, W.A. Johnson and R.F. Mehl [1-3]. The basic model known as JMAK (Johnson-Mehl-Avrami-Kolmogorov) is still widely used with various modifications where the volume of the newly formed phase is supposed dependent on the probability of nucleation centres, the linear speed of growth and the elapsed time.

Fundamental review of mathematical modelling of phase transformation process was performed by J.W. Christian [4]. In this book, it is indicated that the analytical models do not take into account the clearly non-stationary nucleation process, which is contrary to the real conditions.

Any variations of microstructure cause change of mechanical properties of the materials, therefore models were used of grains growth and refinement [5] during dynamic and static recrystallization based on C.M. Sellars equation [6] that can significantly improve metal flow patterns under plastic deformations.

Modern researches are implemented in the special purpose software packages like JMatPro or ESI Group products for steels

modelling. User is able to calculate phase changes for an assigned chemical composition of steel and different modes of treatment, e.g. continuous heating and tempering. That makes it possible to predict the details of the structure after heat treatment [7-9] including large-scale rolls [10-12]. However, the possibility of universal FEM software in nonlinear thermo-mechanical models calculation with properties changing at each time step is limited to the analysis of special alloy steels used for rolls manufacturing. User needs to integrate own routines for calculating diagrams of phase transformations, for example, when heat treatment is combined with cryogenic processing [13]. This opportunity can provide only advanced special purpose software products like QForm, DEFORM or MSC.Marc due to embedded interface for external user modules inclusion. Anyway, the ability to calculate a real topology of microstructure is remaining the challenge.

The aim of this work is to simulate the phase transformations during the heat treatment of large-scale rolls of special alloy steels. Simulations of multi-stage heat treatment is conducted in accordance with technological schedules of the rolls manufacturer [14], namely, stages of spray quenching and differential heat treatment (DHT). It was necessary for customer to determine the ratio of phase components in the hardened layer of rolls (50-100 mm) for various grades of new alloy steels. Additionally, the efficiency of DCT application for wear resistance of rolls is estimated by the samples of special alloy steels, 50CrMnMoV and 45Cr3MnNiMoV.

2. Theoretical models / Теоретические модели

Analytical model of austenite transformation was applied for the steel structure modelling based on the results obtained in [13, 15, 16]. The M. Avrami equation was used of the phase transformation kinetics, written in the following form:

$$P_{\alpha} = 1 - \exp(-(V\tau)^n), \quad (1)$$

where P_{α} – result of the phase transformation (amount of formed pearlite or bainite); V – relative rate of transformation; n – degree of equation; τ – time of transformation (below critical point Ac_1 for the pearlite and Ac_0 – for bainite).

The relative rate of conversion is given by [15, 16]:

$$V = K \cdot \Delta T \exp(-Q/2RT), \quad (2)$$

where $\Delta T = T_c - T$, T – current temperature; T_c – temperature critical points of transformation Ac_1 or Ac_0 ; Q – the activation energy of carbon diffusion in the alloy steel; K – constant coefficient; R – universal gas constant, $1.987 \text{ [cal K}^{-1} \text{ mol}^{-1}]$.

Temperature A_{c0} for roll steels is calculated from the condition that the maximum of the bainite growth rate coincides according to temperature, calculated from equation (2) and its experimental value on an isothermal diagram. This value is 500°C for steel 50CrMnMoV and 380°C for steel 45Cr3MnNiMoV.

Equation (2) describes the temperature dependence of the growth rate of transformation products in cooling steel with a maximum at certain supercooling temperature ΔT determined on the charts of isothermal transformation of austenite. This relation gives the experimental value of the diffusion activation energy Q . The steel used for model verification is 65Cr2Si3MoV with known diagrams of austenite transformation and the structure after treatment.

The exponent of the kinetic equation for the bainite transformation is given by the formula [17]:

$$n = \frac{1,7665}{\lg(\tau_{95\%}) - \lg(\tau_{5\%})}, \quad (3)$$

where $\tau_{5\%}$ – the least time of 5% phase formation; $\tau_{95\%}$ – the least time of 95% phase formation. These times are determined from TTT and CCT diagrams of austenite transformation for each phase (pearlite or bainite). The maximum transformation rate was calculated using the formula:

$$V_{\max} = \sqrt[3]{0,0513 / \tau_{5\%}} \quad (4)$$

Based on this value $V_{\max}$, the coefficient K is determined in formula (2). The amount of martensite formed in the steel can be calculated from the following equation:

$$P_{\alpha} = A_m (1 - \exp \left(-K_{\alpha} \frac{M_s - T}{T - M_f} \right)), \quad (5)$$

where A_m – the amount of austenite retained to M_s temperature; M_s – temperature of the start of martensite transformation; M_f – temperature of the end of martensite transformation, K_{α} – coefficient of martensite formation rate at the temperature M_s .

The improved model explicitly contains the rate of phase and structure transformation (ferrite, pearlite, bainite) that allows more clearly to interpret physical coefficients. To describe the process of martensite formation, the model includes both the start and end temperature of transformation.

3. Studies of alloy steels on models / Исследование легированных сталей на моделях

The large-scale backup rolls for modern hot and cold rolling mills are up to 2000 mm in diameter and of 50 t weight. The main mechanical properties of rolls include the following parameters: required microstructure (tempered troostite with uniformly distributed carbides) through the whole depth of hardened layer (70-80 mm), hardness 55-65 HSD with variation 2-3 HSD, tensile strength 1200-1400 MPa. Special alloy steels 50CrMnMoV, 45Cr3MnNiMoV are used for the work rolls and backup rolls production respectively. The chemical composition of roll steels are given in Table. 1.

Table 1. The chemical composition of rolls steels.

Steels	Chemical composition, %						
	C	Mn	Si	Cr	Ni	Mo	V
50CrMnMoV	0.59	1.42	0.41	0.85	0.1	0.16	0.10
45Cr3MnNiMoV	0.45	0.9	0.45	2.75	0.5	0.61	0.11

Strict requirements to rolls quality are mainly satisfied due to multistage heat treatment process, which lasts up to several days. Sampling of rolls barrels for microstructure testing is almost unavailable. Therefore, mathematical model is implemented to

calculate temperature and stresses. Actually, FEM modelling (Fig. 1) is practically the only way to get additional information inside the rolls for the quenching control of newly developed steels and schedules including deep cryogenic treatment for high-chromium steels. However, such models should account phase transformations to be adequate to reality that have certain issues.

Based on the changes in the yield limit of the roll material, it can be argued that the maximum voltage does not exceed 1120 MPa yield strength at the end of 2nd stage, however, are close to the value of inelastic deformation. Therefore, they should not increase the intensity of the roll cooling and reduced, but at the same time increase the quenching on the 1st or the 2nd stage.

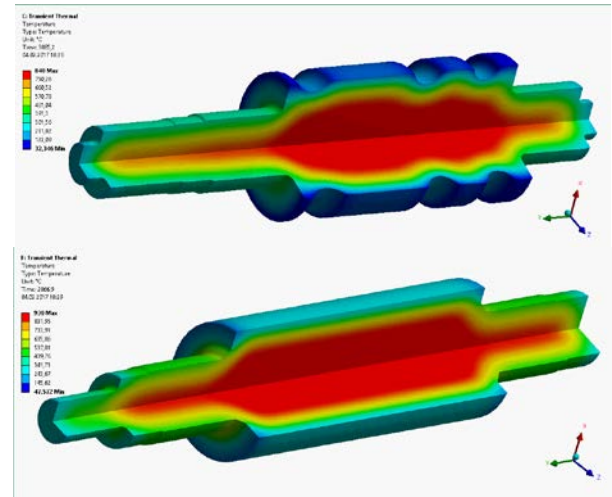


Fig. 1. FEM models of work roll (steel 50CrMnMoV) and backup roll (steel 45Cr3MnNiMoV)

The analytical equation of phase transformations was adopted to be applicable in the FEM modelling. The developed analytical model along with the TTT and CCT diagrams of austenite decomposition is used to analyse the structure of alloy steels 50CrMnMoV and 45Cr3MnNiMoV.

The algorithm for modeling phase transformations in rolls of alloy steels is as follows.

- 1) Developing the FEM model from the rolls drawings.
- 2) Modeling of temperature and stresses over the roll volume.
- 3) Calculation of critical points of phase transformations according to the regression model developed for certain range of chemical compositions of alloy steels.
- 4) Building of TTT for the calculated critical points.
- 5) Construction of a CCT by the proposed calculation method.
- 6) Matching the temperature curves over the roll barrel depth with the CCT diagram.
- 7) Calculation the boundaries of phase transformations from the cooling curves at different depths of roll and their comparison with the points of the CCT.
- 8) Calculation the number and fractions of microstructure components in the steel at a given depth after the end of cooling.

The analytical TTT and CCT diagrams are currently determined for a given range of chemical composition of rolls by the statistical processing of the highly alloyed steel grades. That is resulted in a possibility to take into account the complete list of alloying elements and enough wide range of their mass fraction. This is the advantage of the developed analytical models in contrast to the experimental methods of the TTT and CCT determination by the dilatometric measurements.

In steel 50CrMnMoV (Fig. 2a) there is practically no temperature range of austenite stability between the areas of pearlite and bainite, which formation begins earlier than in 45Cr3MnNiMoV steel.

Under isothermal conditions, alloy steel 45Cr3MnNiMoV undergoes two transformations: pearlitic and bainitic (Fig. 2b) between which an area exists of increased stability of austenite in the temperature range 350-450°C. The region of pearlite

transformation is shifted to the right side, which indicates an increased stability of austenite due to alloying elements.

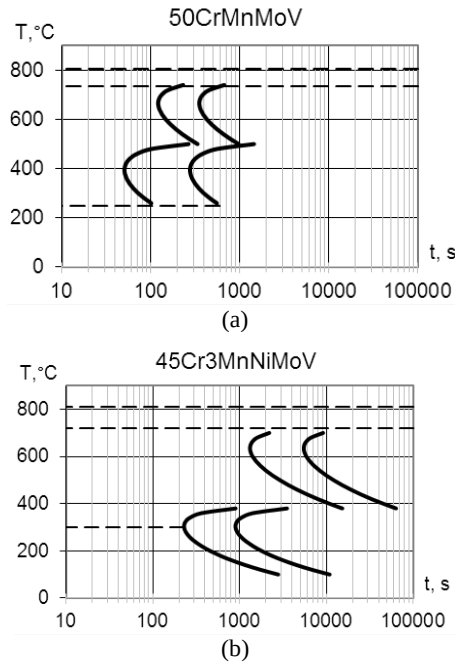


Fig. 2. TTT diagrams of alloy steels:
(a) 50CrMnMoV ($Ac_3=810^\circ\text{C}$, $Ac_1=757^\circ\text{C}$, $M_s=250^\circ\text{C}$);
(b) 45Cr3MnNiMoV ($Ac_3=815^\circ\text{C}$, $Ac_1=720^\circ\text{C}$, $M_s=300^\circ\text{C}$)

Differences in alloy elements of these steels determine the type of diagrams (Fig. 3). The steel structure 50CrMnMoV cooled at a rate 0.24°C/s (corresponds to roll depth 80 mm) has at 20°C pearlite (93%) and bainite (7 %). Steel 45Cr3MnNiMoV cooled at a rate 0.24°C/s includes at room temperature bainite (48%), martensite (47%) and retained austenite (5%).

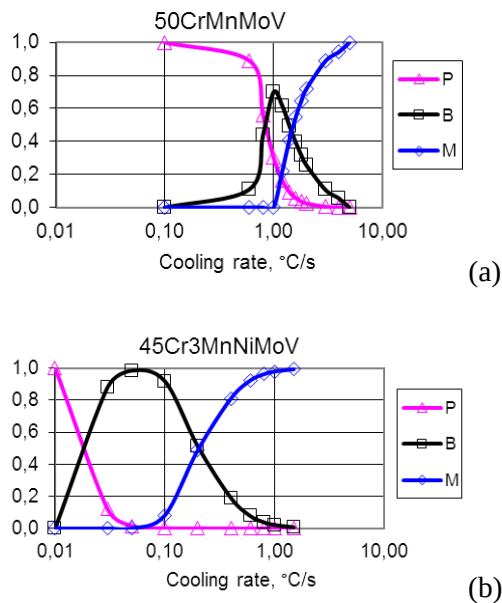


Fig. 3. Diagrams of structure components in steels 50CrMnMoV (a) and 45Cr3MnNiMoV (b) depending on the cooling rate (P – pearlite; B – bainite; M – martensite).

The calculated CCT of steel 50CrMnMoV has an intersection of bainite and pearlite regions at the temperature at 400°C , where these microstructure components are formed simultaneously (Fig. 3a). The areas of pearlitic and bainitic transformations for 45Cr3MnNiMoV steel (Fig. 3b) are shifted to the region of lower cooling rates compared to steel 50CrMnMoV.

Thus, the working layer of the roll at a depth of 80 mm has quenching microstructure components that provide high hardness of rolls at this depth (more than 50 HRC). The depth of rolls

hardenability is assumed as the distance from the roll surface where not less than 50% of bainite and martensite are formed for this cooling rate.

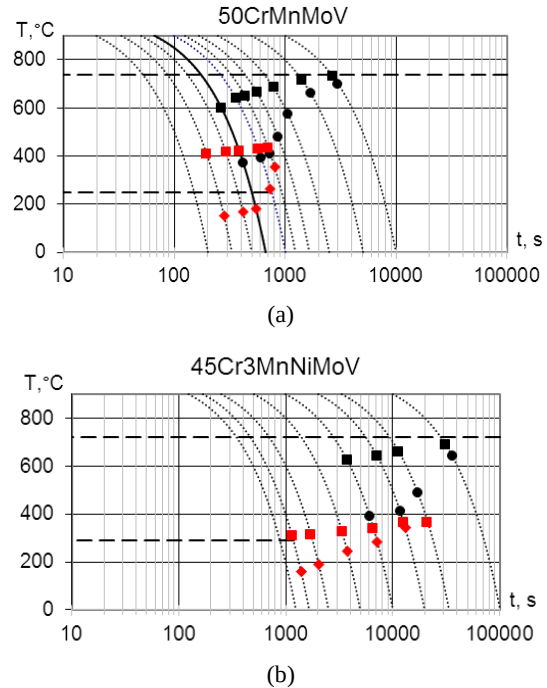


Fig. 4. CCT diagrams of alloy steels 50CrMnMoV (a) and 45Cr3MnNiMoV (b)

Thus, the working layer of the roll at a depth of 80 mm has quenching components of microstructure that provide high hardness of rolls at this depth (more than 50 HRC). The depth of rolls hardenability is assumed as the distance from the roll surface where not less than 50% of bainite and martensite are formed for this cooling rate.

The calculations for the 50CrMnMoV and 45Cr3MnNiMoV steels are given in Fig. 5 and 6 with roll temperatures at a depth of 0...200 mm (with increment of 20 mm). Results are obtained by the finite element model for the applicable modes of spray quenching. These graphs also contain the Ac_3 , Ac_1 , M_s calculated points bainite (B1, B2) transformations and regions of pearlite (P1, P2) and bainite (B1, B2) transformations from the building CCT diagrams.

3.1. Analysis of steel 50CrMnMoV

During spray quenching (I stage 0...600 s; II stage 600...1200 s) the formation of bainite is only on the surface of the roll, and perhaps to a depth of 10 mm. At a depth of 20...200 mm, the temperature is the pearlite (P1, P2) region. After termination of the cooling (2400 s) and subsequent self-heating from internal layers, roll temperature converges to an average value of about 600°C , thus bypassing the bainite region up to a depth of 120 mm and providing pearlite structure at that depth.

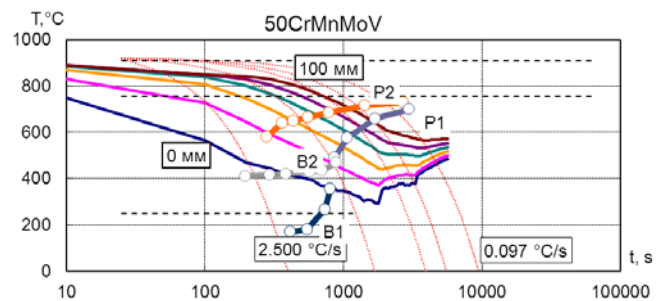


Fig. 5. Calculations of spray quenching for work rolls of 50CrMnMoV steel

3.2. Analysis of steel 45Cr3MnNiMoV

In the process of spray quenching (I stage 0...600 s; II stage 600...1200 s) martensite region (below M_s line) is not captured even on the roll surface. Within the whole depth of 200 mm the temperature is in the regions bainite (B1, B2) transformations. After termination of the cooling (2400 s) and subsequent self-heating from internal layers, roll temperature converges to an average value of about 600°C, slightly higher than the desired tempering temperature (500°C), thus bypassing the bainite region. Subsequent heating of the roll takes place entering the pearlite region at a depth of 20...200 mm.

The modelling of phase transformation is based on calculated CCT and TTT diagrams of 50Cr5NiMoV and 70Cr3MnNiMoV steels. Results of modelling showed their conformity by final phase composition with the experimental data. The real trajectories of cooling and rates at different points do not provide quenching structure (bainite, martensite) in the whole depth of backup rolls barrel (70 mm). For steel 50Cr5NiMoV, bainite structure is only possible in a thin surface layer (10 mm) due to self-heating from internal layers. It was recommended to increase the cooling time of the rolls at the spray-hardening machine for achieving lower temperatures at the desired depth of the roll.

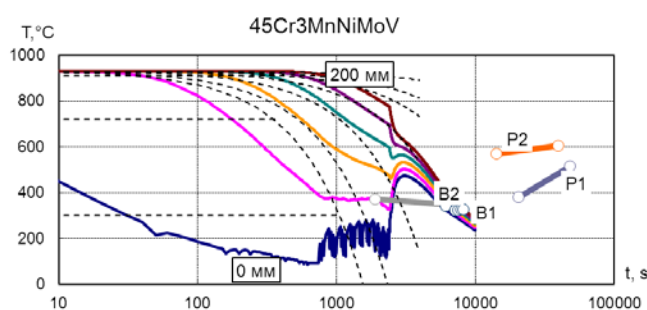


Fig. 6. Calculations of spray quenching for backup rolls of 45Cr3MnNiMoV steel

4. Conclusions / Заключение

The technique is improved for determining the phase composition of steels in the quenching process, allowing the calculation of the number of structural components in the steel at any time along the actual cooling trajectory at any point of the roll obtained by the finite element model.

Based on the developed regression model, isothermal and structural diagrams for 50CrMnMoV and 45Cr3MnNiMoV steels have been constructed; their correspondence to experimental data has been established. The analysis is performed of the spray quenching of rolls of alloy steels 50CrMnMoV and 45Cr3MnNiMoV, according to the existing heat treatment schedules in the rolls production.

For work roll of steel 50CrMnMoV, it is possible to obtain a bainitic structure only in a thin (up to 10 mm) near-surface layer. Corrections of schedule was proposed. While for the backup rolls of steel 45Cr3MnNiMoV, the quenching hardness and bainite with martensite microstructure is achieved through the whole depth of the working layer (up to 200 mm).

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EFFECT OF INITIAL MOLD TEMPERATURE ON THE CRYSTALLIZATION KINETICS OF $\text{Cu}_{47}\text{Ni}_8\text{Ti}_{34}\text{Zr}_{11}$ ALLOY

ВЛИЯНИЕ НАЧАЛЬНОЙ ТЕМПЕРАТУРЫ ИЗЛОЖНИЦЫ НА КИНЕТИКУ КРИСТАЛЛИЗАЦИИ
СПЛАВА $\text{Cu}_{47}\text{Ni}_8\text{Ti}_{34}\text{Zr}_{11}$

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Abstract: Using the method of mathematical modeling, the effect of the initial temperature of the mold T_2^0 on the thermal conditions and kinetics of crystallization of chill castings of $\text{Cu}_{47}\text{Ni}_8\text{Ti}_{34}\text{Zr}_{11}$ alloy was investigated. According to the results, established that the value T_2^0 can have a significant effect on the final structure of the ingots. Depending on the value of T_2^0 , it is possible to provide thermal conditions under which formation of amorphous, amorphous-crystalline and fully crystalline states is possible. It is shown that the changes in the initial temperature of the mold are reflected in the final parameters of the microstructure of the resulting ingots, the average crystal size can vary from tens of nanometers to several micrometers.

KEYWORDS: MELT CASTING INTO THE MOLD, THERMAL COOLING MODE, CRYSTALLIZATION KINETICS, MICROSTRUCTURE PARAMETERS

1. Introduction

Advantages of materials with amorphous and nanocrystalline structures, in comparison with traditional crystalline analogs, today is not in doubt. Therefore, the study of the conditions for obtaining such materials is a priority of modern science. The success of development in this area is due to an understanding of the relationship between the chemical composition of alloys and technological parameters that allow controlling the nucleation and growth of crystals during cooling of a metallic melt. In the study of these relationships is most convenient to use methods of mathematical modeling. With their help, it is possible to study the joint development of thermal and kinetic processes under melt cooling conditions and, accordingly, to determine the influence of thermal regimes on the formation of the final structure of the casting.

In connection with the foregoing, the paper presents the results of a joint solution of the thermal and kinetic problems applied to the conditions of chill casting melt. The bulk amorphizing alloy $\text{Cu}_{47}\text{Ni}_8\text{Ti}_{34}\text{Zr}_{11}$ (Vit101) was selected as the test material, which was cooled in a copper mold with a wall thickness of 15 mm.

2. Method of calculation

The mathematical basis of the model was based on the one-dimensional Fourier thermal equation for melt (containing a source of latent heat release due to crystallization) and for a copper mold with boundary conditions that take into account the features of casting the melt into the mold [1]. And also on the kinetic equation, which describes the change in the crystallized volume fraction with time [2]:

$$x(t) = \frac{4}{3} \pi \int_{t_m}^{t_e} (1 - x(t')) I(t') \left[R_c(t') + \int_{t'}^{t_e} (1 - x(t'')) u(t'') dt'' \right]^3 dt',$$

where I – frequency of formation of crystal nuclei with a critical radius R_c ; u – crystal growth rate; t_m – the time to reach the melting temperature by the melt T_m ; t, t', t'' – current times: $t_m \leq t' \leq t'' \leq t_e$, t_e – the time of ingot solidification processes end, or due to achieve them the glass transition temperature T_g , or due to complete crystallization processes ($x(t_e) \approx 9,9 \cdot 10^{-1}$).

The system of equations described above mathematical model was performed finite difference method using an implicit finite difference scheme [3]. A detailed mathematical model and algorithm for the solution are presented in the paper [4].

To study the effect of the initial mold temperature on the thermal regime and the crystallization kinetics of the investigated alloy, the primary results of the simulation were obtained in the form of the time dependences of the melt temperature $T_1(t)$ and the crystallized volume fraction $x(t)$. Besides calculating the temperature field and the kinetic depending developed computer program enabled to calculate the parameters of the alloy microstructure: the number of crystals per unit volume of N_5 and the average radius of crystals $\bar{R}$.

The dependences $T_1(t)$ and $x(t)$ were plotted for the central melt zone. Calculations were performed for the half-thickness castings $l_1 = 550 \mu\text{m}$, which is critical for this alloy for casting into a mold at room temperature [5]. The initial temperature of the mold T_2^0 was varied from 293K to 793K. The values of heat transfer coefficient at the boundary of the melt-mold is determined from the relations presented in [6] to $l_1 = 550 \mu\text{m}$ it was $3,2 \cdot 10^3 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$, and on the boundary of the mold-air environment, according to the [7], was assumed to be $5 \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$.

3. Results and analysis

Figure 1 shows examples of the obtained dependences $T_1(t)$ and $x(t)$. It can be seen that by changing the initial temperature of the mold it is possible to obtain three types of ingot cooling regimes. The first mode (at $T_2^0 = 273\text{K}$) characterized by a smoothly falling cooling curve (fig.1a), under such conditions, the processes of nucleation and growth of crystals are suppressed. The melt under this regime solidifies to form an insignificant amount of the crystalline component ($x \approx 4 \cdot 10^{-6}$), those an amorphous structure with "frozen" nuclei of the crystalline phase is formed, the average dimensions $\bar{R}$ of which are 17 nm, $N_5 = 2,4 \cdot 10^{17} \text{ m}^{-3}$. The realization of such a cooling regime is possible at $273\text{K} \leq T_2^0 \leq 643\text{K}$, the volume of the crystalline phase formed in this case is $4 \cdot 10^{-6} \leq x \leq 4 \cdot 10^{-4}$, and N_5 and $\bar{R}$ with an increase in T_2^0 varies from $2,4 \cdot 10^{17} \text{ m}^{-3}$ to $1,1 \cdot 10^{18} \text{ m}^{-3}$ and from 17 nm to 44 nm, respectively.

In the second cooling mode (fig. 1b) the curve $T_1(t)$ is also characterized by reduction in temperature during the cooling process. However, the cooling of the melt is carried out in two stages. At the first stage at the initial moments of time, there is an intense decrease in temperature, and in the second stage, starting from a certain time t_{eq} , the slope of the cooling curve changes and a significant slowdown of the cooling process occurs. Such a course of the temperature curve can be explained by the fact that before the t_{eq} mold temperature is much lower than the temperature of the melt and the ingot cooling occurs due heat transfer to the metal mold. From the moment t_{eq} , in the region of deep supercoolings, the

temperature of the melt and molds are compared with each other, and cooling occurs due to heat exchange with the surrounding air environment. Such a cooling regime is observed at $643\text{K} < T_2^0 < 723\text{K}$ with the formation of a volume fraction of the crystalline phase of $4 \cdot 10^{-4} < x < 9,9 \cdot 10^{-1}$. The crystalline component is formed by rapid nucleation ($I \sim 10^{18} \text{ m}^{-3} \cdot \text{s}^{-1}$) at very low crystal growth rates ($u \sim 10^{-11} \text{ m} \cdot \text{s}^{-1}$), i.e. increase a crystallized volume fraction is mainly due to increasing the volume density of crystals to values 10^{20} m^{-3} , and their average size in this case is increased to 132 nm.

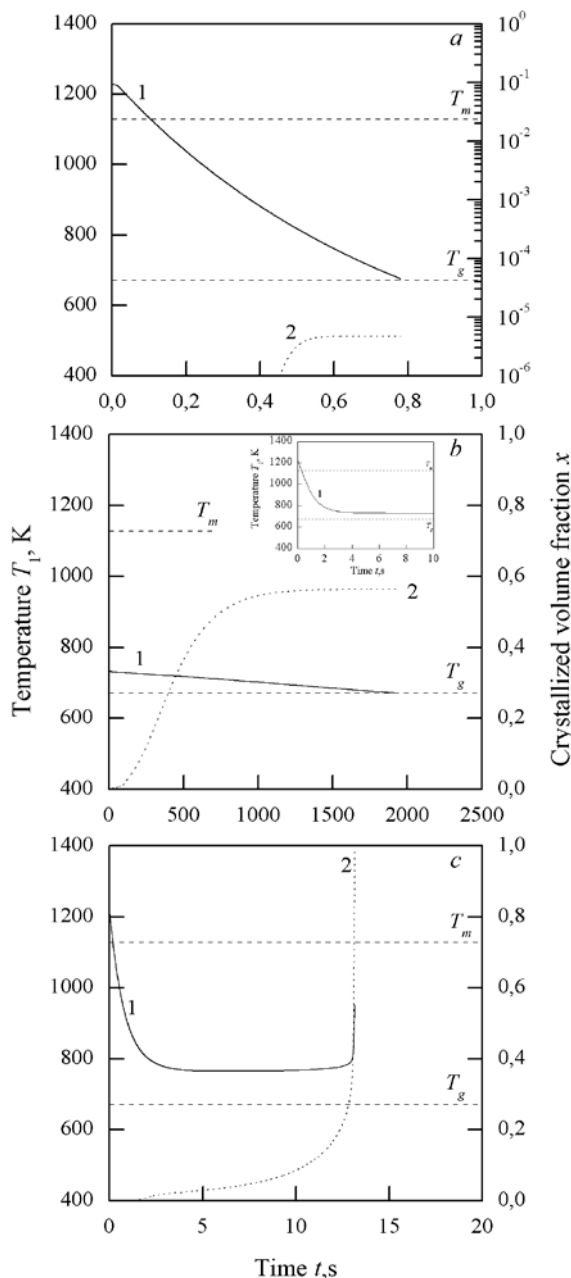


Figure 1 – The curves of the changes with time of the melt temperature (1) and the crystallized volume fraction (2) for the Vit 101 alloy castings by the half-thickness $l_1=550 \mu\text{m}$, obtained by casting in a copper mold at different initial temperatures of the mold T_2^0 : a – $T_2^0=293\text{K}$; b – $T_2^0=710\text{K}$; c – $T_2^0=743\text{K}$.

Finally, the third cooling mode (fig.1c) ensures the formation of completely crystalline structures ($x \approx 9,9 \cdot 10^{-1}$), and the recalcence areas appear on the $T_1(t)$ dependences. Such cooling mode is observed for melt casting in a mold with initial temperature $T_2^0 \geq 723\text{K}$. In these temperature conditions, an increase in the contribution of the crystallization processes of crystal growth processes is observed, crystal growth rate is increased by 3 orders of

magnitude ($u \sim 10^{-9} \text{ m} \cdot \text{s}^{-1}$) at maintaining a high nucleation rate ($I \sim 10^{18} \text{ m}^{-3} \cdot \text{s}^{-1}$). As a result in castings, complete completion of the crystallization processes and relative coarsening of the final microstructure, with an average crystal size of $0,2-2,3 \mu\text{m}$ and a volume density of crystals $2 \cdot 10^{19}-2 \cdot 10^{16} \text{ m}^{-3}$ is observed at $T_2^0 = 743 - 793 \text{K}$.

In a generalized form, the obtained modeling results, for the entire range of values of T_2^0 , are shown in figure 2 as a function of the basic kinetic characteristic x vs. the initial temperature of the mold T_2^0 . As can be seen in the range of values of T_2^0 from 293K to 693K, a smooth increase in x from $4 \cdot 10^{-6}$ to $2,5 \cdot 10^{-3}$ is observed.

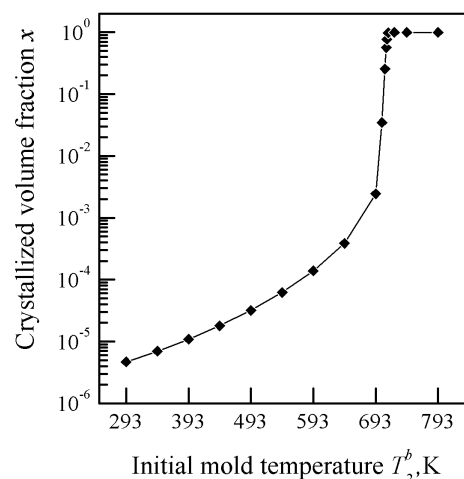


Figure 2 – Dependence of the crystallized volume fraction vs. the initial temperature of the ingot mold for castings with a half-thickness of $550 \mu\text{m}$.

With a further increase in T_2^0 , the rate of increase in the crystallized volume fraction increases sharply in a relatively narrow interval of values of T_2^0 (692–723K) and a transition from an amorphous-crystal structure to a completely crystalline structure is observed. Thus, using mathematical modeling, it is shown that by setting the initial temperature of the mold, it is possible to affect on the final structure of the resulting castings of a given thickness.

4. Conclusions

1. Using the methods of mathematical modeling, thermal regimes and crystallization kinetics of $\text{Cu}_{47}\text{Ni}_8\text{Ti}_{34}\text{Zr}_{11}$ alloy under conditions of melt casting in a preheated copper mold have been studied.
2. It is shown, that depending on the initial temperature of the mold, ingots can be obtained in different structural states: amorphous, amorphous-crystalline and completely crystalline.
3. It is established that, by initial heating of the mold, it is possible to control the final parameters of the ingot microstructure. Depending on the value of $T_2^0 = (293 - 793)\text{K}$, the average crystal sizes can vary from 14 nm to $2.3 \mu\text{m}$.

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EFFECT OF HIGH PRESSURE TORSION ON THE STRUCTURE, MICROHARDNESS AND HEATING BEHAVIOUR OF THE MAGNESIUM ALLOY WE43

ВЛИЯНИЕ КРУЧЕНИЯ ПОД ВЫСОКИМ ДАВЛЕНИЕМ НА СТРУКТУРУ, МИКРОТВЕРДОСТЬ И ПОВЕДЕНИЕ ПРИ НАГРЕВЕ МАГНИЕВОГО СПЛАВА WE43

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Abstract: In the present work, the magnesium alloy WE43 (Mg-Y-Nd-Zr) after high pressure torsion (HPT) was investigated. HPT was conducted at room temperature, 200 °C or 300 °C. As a result of HPT processing, a large number of twins with the twin size of 0.4 – 8.1 μm were formed. Furthermore, the HPT process led to the formation of a very fine grain structure with the average grain size of 30 - 100 nm. The deformation by HPT caused the formation of a displaced basal texture, which sharpens with an increase in the deformation temperature. The refinement of the microstructure brought about an improvement of the microhardness of the alloy over the as-received condition. The microhardness after HPT at the room temperature increased up to $1189 \pm 33 \text{ MPa}$ compared with $774 \pm 50 \text{ MPa}$ in the initial state. A subsequent aging after HPT led to an additional strengthening to a level of $1411 \pm 40 \text{ MPa}$. It was noted that thermal stability of strengthening caused by HPT did not depend on the deformation temperature and sustained up to 250 °C.

KEYWORDS: MAGNESIUM ALLOYS, HIGH PRESSURE TORSION, NANOCRYSTALLINE MATERIALS, MICROHARDNESS, AGE HARDENING, STRUCTURE, TEXTURE

1. Introduction

Nowadays, magnesium alloys are becoming more attractive as materials for biodegradable implant applications owing to their good mechanical properties and biocompatibility [1-3]. Magnesium alloy WE43 is one of the most popular Mg alloys for medical applications. This alloy has a good corrosion resistance, but it is necessary to improve its mechanical properties. It is well known that severe plastic deformation (SPD) can enable the formation of a very fine structure, which gives an increase in strength. There are several methods of SPD. Among the methods of SPD, equal channel angular pressing (ECAP) [4-6] and friction stir processing [7-9] were tested on the WE43 alloy. High pressure torsion (HPT) is one the most popular of SPD methods, which allows to investigate the microstructure evolution in case of high degrees of deformation and simulate hardening processes [10]. It is well known that HPT allows to obtain a grain structure in the submicron or nanoscale range. Analysis of the literature showed that HPT treatment is successfully used for refinement of the structure of pure magnesium and its alloys [11-14] to obtain structures with an average grain size of about 100 nm. HPT was also used for the WE43 alloy [15, 16], but, in general, only the structure after deformation and the subsequent aging process were studied. The purpose of this work is to study the effect of HPT on the structure, distribution of microhardness, texture and behavior during heating of the alloy WE43.

2. Materials and Methods

In this paper, the homogenized at a temperature of 525 °C for 8 hours WE43 alloy (Mg-3.56%Y-2.20%Nd-0.47%Zr) was obtained by HPT at room temperature, 200 °C and 300 °C. For this purpose, samples with a diameter of 20 mm and a thickness of 1.5 mm were deformed with 1 rpm rotation speed under 6 GPa pressure for 10 revolutions (a true strain on the half-radius of the disk was $\epsilon=5.7$). To study the thermal stability the alloy after deformation was heated in the temperature range 100-400°C with a step of temperature change 50 °C. A study of the kinetics of aging was carried out during heating of the alloy samples at 200 °C with a gradually increasing heating time. The microhardness was measured on a 402 MVD Instron Wolpert Wilson Instruments tester with a load of 50 g and 10 s holding time. The resistivity was measured using a BSZ-010-2 microhmmeter on the flat samples of 18×6×0.9 mm in size. The microstructures were observed using an optical microscope

Reichert MeF and transmission electron microscope (TEM) Jeol JEM 2100 operating at 200 kV.

Texture analysis was carried out using X-ray diffraction in a DRON-7 goniometer with the CuK α radiation in the reflection mode. Five incomplete pole figures, {00.4}, {21.1}, {10.2}, {10.3}, {11.0} were obtained with a step of 5° in the radial angle α and the azimuth angle β (0-360°) on a pole figure (α and β – radial and azimuth angles on the pole figure, maximum inclination angle $\alpha_{\text{max}}=70^\circ$).

3. Results and Discussion

Fig. 1 shows the microhardness distribution maps with an area of 13×13 mm² inscribed in a sample with a diameter of 20 mm for samples after HPT at 200 °C (Fig. 1a) and after the same treatment, but with subsequent aging at 200 °C for 2 hours (Fig.1b). It can be seen that the microhardness has the maximum values at the edges of the sample and gradually decreases approaching the center. Such a distribution of the microhardness along the diameter of the sample correlates with the dependence of the shear strain on the radius (rate of strain linearly increases along the radius of the specimen from the center to the edge). It can be seen that aging at 200 °C leads to an additional increase in microhardness, which is distributed as a function of the radius qualitatively similar way. So, according to Fig. 1 the microhardness values have the minimum at the center of the sample and the maximum at the edge of the sample, but on the middle of the radius the values of HV are close to the values at the edge. Thereby, all subsequent measurements of the microhardness were performed at the middle of the radius of the sample.

The results of measuring the microhardness of the WE43 alloy in the middle of the sample radius showed that HPT at all deformation temperatures leads to its significant hardening compared with the initial homogenized state. The average microhardness of the alloy samples were as follows: after homogenization – $774 \pm 50 \text{ MPa}$, after HPT at room temperature – $1189 \pm 33 \text{ MPa}$, after HPT at 200°C and 300°C – $1144 \pm 23 \text{ MPa}$ and $1118 \pm 21 \text{ MPa}$, respectively.

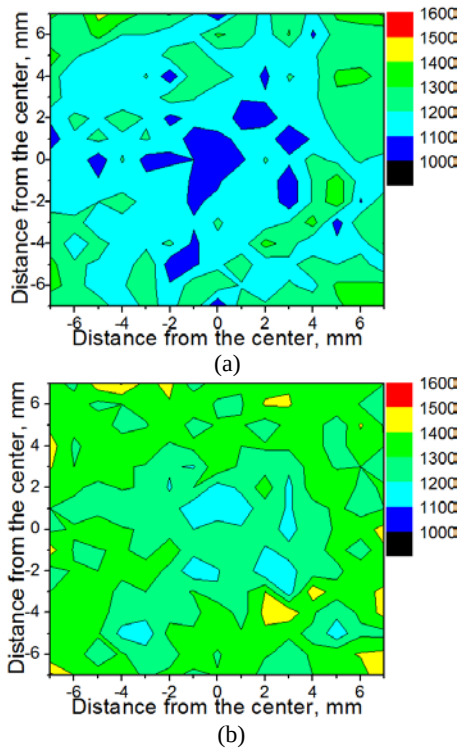


Fig. 1. Maps of microhardness distribution over the surface of samples of WE43 alloy after HPT at 200 °C (a) and after HPT at 200 °C + aging at 200 °C for 2 hours (b).

The change of microhardness and electrical resistivity of alloy samples after both homogenization and HPT at different deformation temperatures as a function of the heating temperature is shown in Fig. 2.

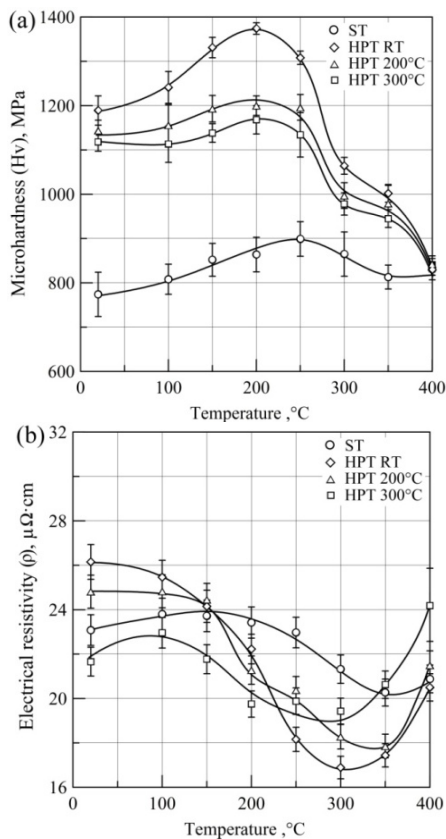


Fig. 2. Microhardness (a) and electrical resistivity (b) of the WE43 alloy as function of annealing temperature.

The microhardness of the WE43 alloy after the HPT at all deformation temperatures is much higher than in the initial state. At the same time, the highest values of microhardness are achieved after HPT at room temperature (Fig. 2a). It can be seen that the curves of microhardness changing have a maximum at 200 °C for alloy after HPT and at 250 °C for alloy in initial state. Herewith, the microhardness growth is greatest for the sample after the HPT at

room temperature. Apparently, precipitation of hardening metastable phases at given temperatures caused by the growth of microhardness [17]. This can be confirmed by a decrease in the electrical resistivity in this temperature range, which indicates a depletion of the magnesium solid solution (Fig. 2b). With a further increase in the temperature, the microhardness decreases, until the initial microhardness level of the homogenized state is reached. The solidification of the alloy with an increase in the heating temperature can be caused by the growth of grains and the dissolution of phase, which are rich in rare earth metals and formed in the previous stage of heating. This is also confirmed by the growth of the electrical resistivity at elevated temperatures. The change of microhardness and electrical resistivity of alloy samples as a function of the duration of isothermal aging at 200 °C is shown in Fig. 3 a,b.

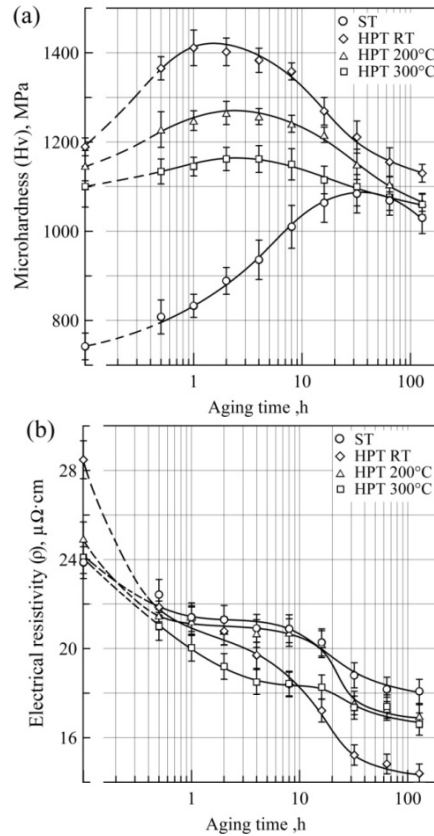


Fig. 3. Microhardness (a) and electrical resistivity (b) of the WE43 alloy as a function of aging time during isothermal aging at 200 °C.

With an increase in the heating time, the microhardness increases for all four alloy states of the alloy, but the greatest increase is observed for HPT at room temperature (Fig. 3a). Moreover, it was noted that the maximum of microhardness of the alloy after HPT is achieved much faster than for the undeformed state. The maximum of microhardness for the sample after HPT at room temperature (1411 ± 40 MPa) is already reached after aging for 1 h, after HPT at 200 °C (1265 ± 26 MPa) – for 2 hours, after HPT at 300 °C (1162 ± 30 MPa) – for 2-4 hours and, finally, for undeformed sample (1084 ± 43 MPa) – for 32 hours. Hardening during aging is probably caused by the precipitation of hardening metastable phases, as indicated by a decrease in the electrical resistivity (Fig. 3b). From the fact that the electrical resistivity decreases more acutely for the sample after the HPT at room temperature and less for the homogenized state, it can be concluded that the deformation induced by the HPT promotes an increase in the rate of decomposition of the supersaturated solid solution, which causes a reduction in the aging time to reach the maximum microhardness. The acceleration of the decomposition of a supersaturated solid solution based on magnesium in an alloy produced by HPT can be associated with the rapid nucleation and growth of phase particles because of the high density of dislocations and the branching of grain and subgrains boundaries, which are the nucleation centers for precipitates of rare-earth metals rich phases.

Fig. 4 shows the microstructures of the WE43 alloy after homogenization and after HPT at room temperature, 200 °C and 300 °C. The alloy structure after homogenization consists of equiaxed grains of magnesium solid solution with an average size of 65 µm (Fig. 4a). HPT leads to intensive twinning within initial grains (Fig. 4b). The greatest twinning density is observed in case of HPT at room temperature. In this case, the width of deformation twins is 0.4 - 3.7 µm. After HPT at 200 °C it is 0.6 - 2.9 µm and 0.8 - 8.1 µm – after HPT at 300 °C.

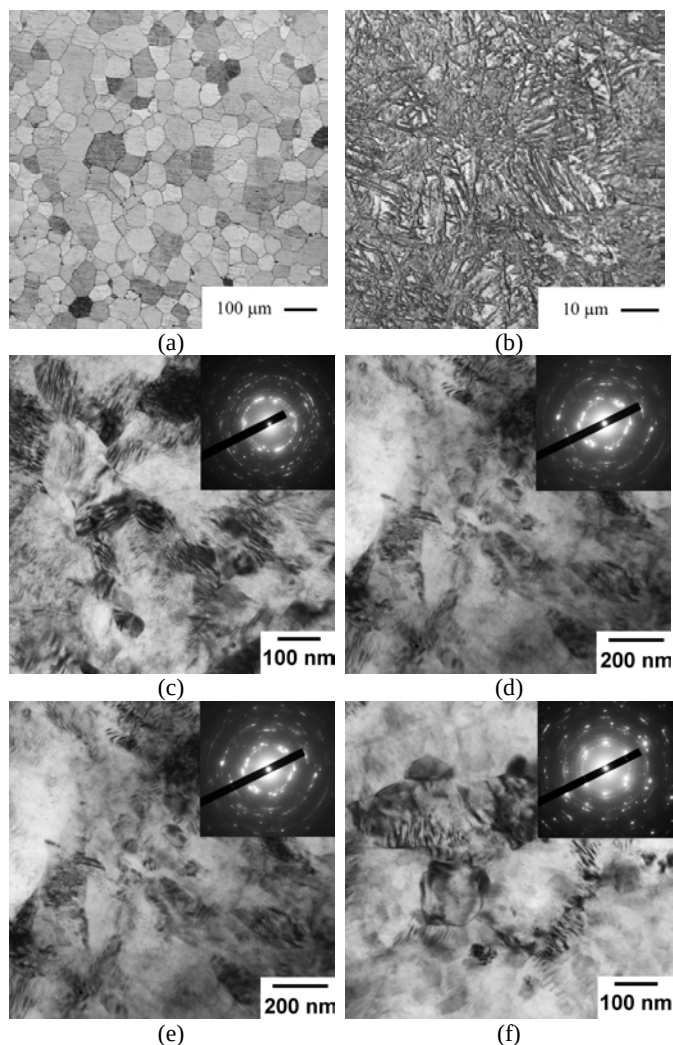


Fig. 4. Structure of WE43 alloy after homogenization (a), after HPT at room temperature (b, c), HPT at 200 °C and aging at 200 °C (2 hrs) (d), HPT at 300 °C (e) and HPT at 300 °C and aging at 200 °C (4 hrs) (f).

TEM examination showed that nanoscale grains are formed inside the twins (Fig. 4 c-f). The occurrence of high-angle boundaries is confirmed by ring-like electron diffraction patterns with a number of point reflexes. It should be noted that an increase in the deformation temperature led to an increase in the average grain size from 30 - 50 nm at room temperature to 80 - 100 nm at a temperature of 300 °C. Probably, hardening during HPT process is achieved, in a greater degree, due to grain refinement, since the maximum of hardening after HPT at room temperature corresponds to the minimum in grain size for this treatment. After subsequent aging, the grain size slightly increased to 60 - 80 nm after HPT at 200 °C and to 100 - 130 nm after HPT at a temperature of 300 °C. The strengthening precipitates are not visible in the structure after HPT and subsequent aging because of their small size, but their presence is suggested by the weak superstructure reflexes observed in the electron diffraction patterns.

Fig. 5 demonstrates the texture of the alloy before and after deformation. The texture of WE43 alloy after HPT at various deformation temperatures is sufficiently dissipated. The texture

obtained after HPT is characterized by a shift of the basal poles in the radial and azimuth angles, respectively, on 20 - 30° and 45 - 50° from the center of the pole figure {00.4} (Fig. 5). The basic orientations (02-27)[3-522], (01-14)[2-1-10], (02-27)[3-522], (02-27)[5-612], (01-14)[-14.591] provide this displacement of the basal poles. The deformation temperature has a minor effect on the type of obtained texture, but the texture becomes more acute as the temperature of the HPT increases. Subsequent aging of the alloy after HPT at room temperature provides a change in the type of texture. So the basal pole on the pole figure {00.4} after aging is shifted to its center, and the orientations (02-27) [3-522] go to the orientations (0001) [10-10].

The change in texture provides a change in the activity of the basic deformation systems in the magnesium WE43 alloy: basal {0001} and prismatic {1010} slip dislocation systems in the direction <1120>, pyramidal {1122} system – in the direction <1123> and twinning {1012} – in the direction <1011>. The formed after deformation and aging texture activates the basal and pyramidal slip as well as twinning, however, it makes dislocation sliding difficult for prismatic planes. This is confirmed by orientation factors calculated for different states of the alloy (Table 1).

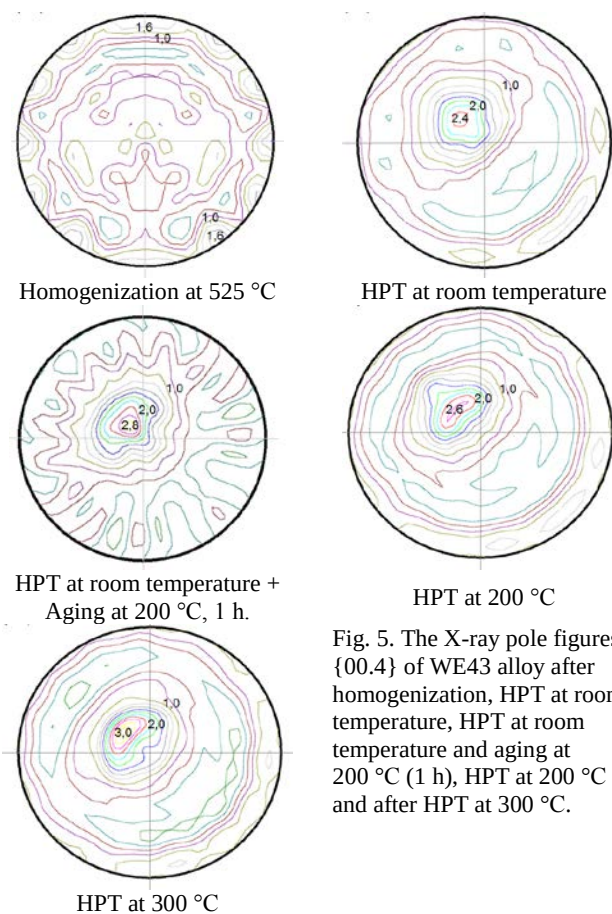


Fig. 5. The X-ray pole figures {00.4} of WE43 alloy after homogenization, HPT at room temperature, HPT at room temperature and aging at 200 °C (1 h), HPT at 200 °C and after HPT at 300 °C.

Table 1. The orientation factors for the different deformation systems of WE43 alloy

Treatment	Basal	Prismatic	Pyramidal	Twinning
HPT at 20 °C	4.800	6.031	5.210	5.540
HPT at 20 °C + Aging at 200 °C for 1 hour	4.864	6.183	4.936	5.129
HPT at 200 °C	4.749	5.920	5.131	5.407
HPT at 300 °C	4.735	6.296	4.898	5.061

Presumably the texture change after aging can be caused by the release of disperse metastable phases rich in rare earth metals, which, being coherent with the matrix of magnesium solid solution,

are released in certain planes, orienting the new ones formed as a result of the recrystallization of the grain.

4. Conclusions

1. The refinement of the structure of the WE43 alloy after the HPT occurs predominantly by deformation twinning. However, a partially nanocrystalline structure with a grain size of 30 - 100 nm is formed inside the deformation twins. Aging after HPT leads to grain growth up to 130 nm.
2. As a result of HPT at all deformation temperatures, a displaced basal texture is formed, which becomes more acute with an increase in the deformation temperature. The subsequent aging of the alloy after HPT at room temperature leads to a change in the type of texture
3. It was shown that HPT promotes significant hardening of WE43 alloy. The greatest hardening by the results of measuring the microhardness is achieved after torsion at room temperature, but with increasing deformation temperature, the microhardness gain decreases. Aging increases the strength according to the microhardness values.
4. The possibility of aging of the WE43 alloy after the HPT due to the decomposition of the magnesium solid solution is shown by the measurement of the electrical resistivity and microhardness. The maximum of hardening during the aging process is achieved by HPT at room temperature. It was shown that HPT significantly accelerates the decomposition of magnesium solid solution.

Acknowledgments

Part of this work relating to carrying out of high pressure torsion was funded by the Ministry of Education and Science of the Russian Federation (grant #14.A12.31.0001). Funding support of investigations of microstructure, texture and microhardness was provided by the Russian Science Foundation (project #17-13-01488).

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CORROSION PROPERTIES OF DIFFUSIONAL ZINC COATINGS OBTAINED BY NANOGALVANIZING

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Abstract: Corrosion properties of diffusional zinc coatings with various surface compositions, obtained by nanogalvanizing technology, are studied in model oilfield and aggressive chloride-containing media. A complex of physical and chemical methods for studying corrosion behavior, including polarization measurements, X-ray diffraction analysis and SEM, was used in the work. Corrosion resistance of diffusional zinc coatings obtained by nanogalvanizing is determined by the composition, texture and thickness of the coating.

KEYWORDS: CORROSION, DIFFUSIONAL ZINC COATING, NANOGALVANIZING, SIMONKOLLEITE

1. Introduction

The technology of diffusional galvanizing (DG, also known as sherardizing) is currently gaining popularity as a method of protecting steel products from corrosion damage. DG coatings have both high corrosion resistance and good mechanical properties (microhardness, ductility, etc.). With the help of thermal diffusion galvanizing, coatings of different phase composition are obtained, providing protection of products under conditions that were previously considered too aggressive for zinc. The author developed the technology of DG in zinc powders with a nanocrystallized particle surface [1], so-called nanogalvanizing. The technology of DG with nanocrystallized zinc powders allows galvanizing in a wide range of temperatures (400-700°C) and adjusting the distribution profile of zinc concentration across the thickness of the coating. In Fig. 1 shows the distribution of zinc in the thickness of the coating for a DG coating sample with a thickness of 45 µm consisting primarily of δ-phase FeZn₇₋₁₀.

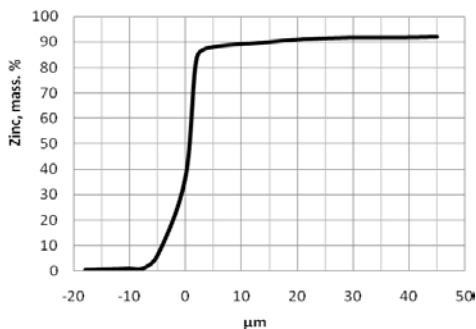


Fig.1. Distribution of zinc by coating thickness

The resulting coatings, depending on the composition, can provide high corrosion resistance of the products to be protected in media containing chloride ions and hydrogen sulfide [2]. The researchers from Chelyabinsk state university, "VIKA-GAL" and "Termo serviz" companies have been conducting joint research to optimize the composition and structure of DG coatings for various conditions of operation of galvanized products since 2006.

2. Experimental

To optimize the distribution profile of the zinc concentration and the structural state of the coating, studies carried out on the effect of the composition and structural state of the coating layers on their corrosive behavior were. In the work, diffusion-galvanized carbon steel samples galvanized by the

procedure [1] at a temperature of 450°C for 3 hours were investigated.

The gravimetry and various electrochemical methods were used as methods for investigating the corrosion behavior. Polarization curves of the coatings under investigation were obtained with the help of the potentiostat-galvanostat P-30J (Elins). The corrosion products formed on the surface of the DG coatings, were studied by X-ray diffraction and scanning electron microscopy. X-ray diffraction analysis was performed on a DRON-3 diffractometer, Cu K α -radiation, in the range $20^\circ \leq 2\theta \leq 60^\circ$ at scanning rate of 1-2 °/min. A scanning electron microscope "JEOL" JSM-6460 LV with an energy dispersive spectrometer "Oxford Instruments" was used to study the morphology of corrosion products and chemical microanalysis.

Investigation of corrosion behavior was carried out in model oilfield and aggressive chloride-containing media. As model oilfields media the highly mineralized solutions containing chloride, sulfate ions and metal ions, saturated with carbon dioxide or hydrogen sulfide were used. A solution of 3% sodium chloride was also used as the model corrosive medium.

To study the effect of the layer-by-layer distribution of zinc and the structural features of the DG coating layers on their corrosion behavior, the initial coating was etched in a 6% solution of nitric acid during time various intervals to obtain a series of samples with successively decreasing coating thickness in steps of 5 µm. The thickness of the removed layer for each etching was determined from the difference in mass before and after etching. After etching, photometric determination of iron (III) content in etching solutions at $\lambda = 400$ nm and $l = 0.5$ cm with salicylic acid was carried out. According to the obtained data, the percentage of iron (III) in the layers of iron-zinc coating was calculated. After etching, the samples were washed with distilled water and degreased with acetone.

Data on corrosion behavior, structural features are given depending on the depth of the layers (thickness) calculated from the surface of the coating.

X-ray diagrams of all samples contain the maxima of the δ-phase FeZn₇₋₁₀ only. However, the diffraction pattern changes with thickness. As was shown earlier [3], this is due to the lack of a δ-phase texture, typical for hot-dip zinc coatings, in diffusional coatings with thicknesses more than 30 µm. On the X-ray diagram of the original coating (without etching) there are maxima with a high third Miller index: (1.4.14) and (3.0.22). After the third and fourth etching, these maxima almost disappear, while the relative intensity of the maxima with the zero third index, for example, (330) and (500), increases. Subsequent etching of the coating leads to a further increase in the relative intensity of the maxima with a zero third index.

Thus, on the surface of the initial coating δ -phase crystals of different orientations are present, whereas in coating layers below 15 μm crystals with a 6th-order axis c directed parallel to the coating surface prevail.

The results of the studies show that the corrosion resistance of the DG coating is high enough both in solutions of 3% sodium chloride and in model oilfield environments.

Based on the results of gravimetric tests, it is established that the corrosion rate of the DG samples of coatings represented by the δ -phase in the 3% NaCl medium is 0.02 g/(m²·hour), while the corrosion rate of zinc and hot-dip zinc coatings is 0.04 and 0.05 g/(m²·hour), respectively.

X-ray diffraction analysis of corrosion products after prolonged exposure (30 days) in chloride-containing media shows that zinc hydroxochloride - simonkolleite is present on the surface of both zinc and zinc coatings obtained by various methods. However, the rate of its formation on the DG coatings is twice higher than on zinc or zinc coatings obtained from the melt [4].

Simonkolleite as a corrosion product of DG coatings is also detected after the samples are held in the NACE model oilfield (5% NaCl + 0.5% CH₃COOH + 0.3% H₂S + CO₂). During 720 hours the DG coating was preserved only on samples whose surface after galvanizing was formed by a δ phase with a Zn content of more than 90%. When studying the surface of samples that were tested in NACE medium using scanning electron microscopy, the morphology characteristic of simonkolleite was described by the authors in [5].

In the study of samples subjected to layer-by-layer etching, the following results were obtained. It is noted that the concentration of iron increases with the thickness of the layers, i.e. as they approach the substrate, but this growth occurs exponentially. A peculiar inflection point is 25-30 μm , at this depth there is a sharp increase in the concentration of iron. Minima of etching rate are observed at depths of 15 and 30 microns.

The steady-state potential of the DG coating samples in a 3% NaCl medium becomes more positive when approaching the substrate material. The steady-state potential of the substrate – carbon steel is equal to -0.38 V (according to the standard hydrogen electrode). However, even at a depth of 45 μm , the potential is more negative than the potential of the steel.

The dependence of the corrosion current on the thickness of the coating is not linear. Two characteristic points, at 15 and 30-40 μm can be seen. At the first point, the corrosion current is reduced by a factor of two compared to the value characteristic for neighboring regions. In the region of 30-40 μm , a sharp jump occurs, followed by a strong decrease in the corrosion current compared to the substrate material. In addition, at a thickness of 40 μm , the stationary potential shifts to a more positive region, the shape of the cathode curve changes, which may indicate a change in the depolarizer in the corrosion process.

For long-term corrosion study, the samples were immersed in a solution of 3% NaCl for certain time intervals (5, 10 and 30 days) and the effect of the resulting corrosion products on the polarization curves and the value of the corrosion current was studied. Based on the change of the corrosion current as function of the test time, the following regions can be distinguished: 5-10 μm : the corrosion current decreases linearly with time; 20 - 25 μm : corrosion current decreases for 10 days, and then it starts to increase. For a thickness of 15 μm there is an increase in current at small test times. For a thickness of 30 μm , the corrosion current decreases sharply on the fifth day.

Thus, the dependencies of the corrosion current on the test time gives two characteristic points - 15 and 30 μm , where the properties of the coating vary nonlinearly. These points also correspond to extrema on the dependence of the etching rate on the thickness of the coating.

Reduction of the corrosion current from the surface of the coating to a thickness of 15 μm is probably due to an increase in the concentration of iron in the layers, as well as to the non-textured state of the δ phase. Then, along with the enhancement of the

texture of the coating layers, despite the high iron content, the corrosion current is increased till a thickness of 30 μm . A sharp decrease in the corrosion current and a change in the shape of the polarization curve at a thickness greater than 30 μm , despite the increase in texture, can be related to the transition state of the coating at a given point.

After 30 days of test, according to X-ray diffraction analysis, simonkolleite is formed on all layers of the coating. According to the scanning electron microscopy, the surface is covered with a uniform film of corrosion products (Fig. 2). The iron content on the surface of all the samples is in the range from 0.7 to 1.3 at. %, The maximum content also corresponds to a thickness of 30 μm . The zinc content is actually at the same level and is about 40 at. %.

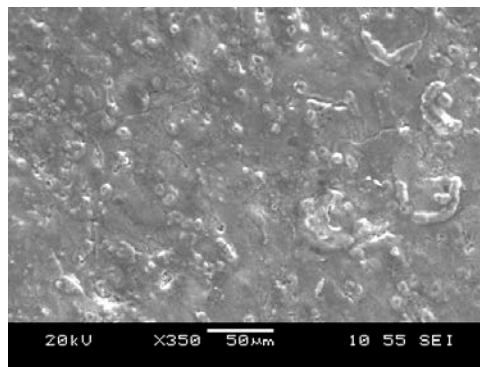


Fig.2. SEM image of the sample surface with a layer depth of 30 μm after 30 days in a 3% NaCl solution

3. Conclusion

Diffusional zinc coatings, whose phase composition is represented by the δ -phase, exhibit higher corrosion resistance than pure zinc (galvanic zinc coatings) and zinc coatings obtained from the melt.

In a 3% solution of sodium chloride, the DG coating layers have different corrosion behavior. Increased corrosion resistance of the upper layers is due to an increased content of zinc, and absence of a texture of the δ -phase.

The formation of simonkolleite as the main product of corrosion along the entire thickness of the coating provides increased corrosion resistance of DG coatings.

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