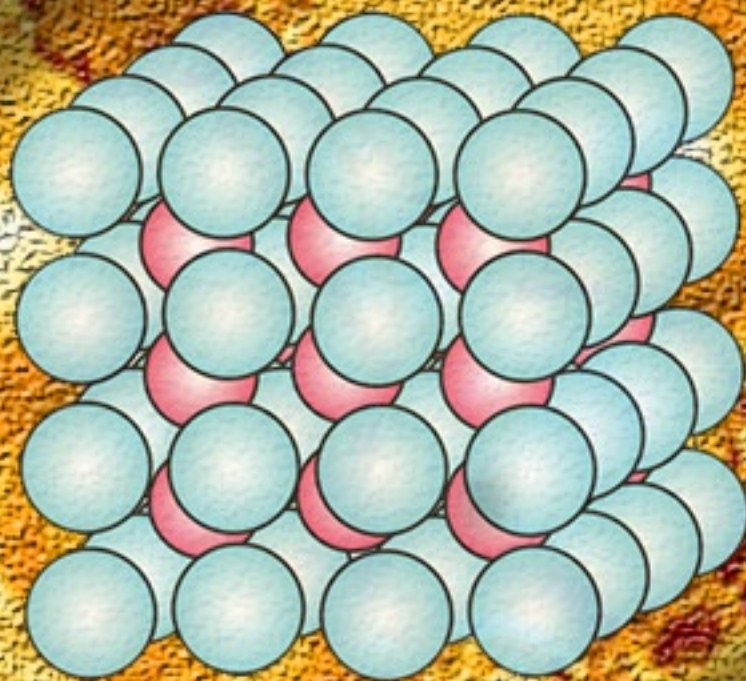


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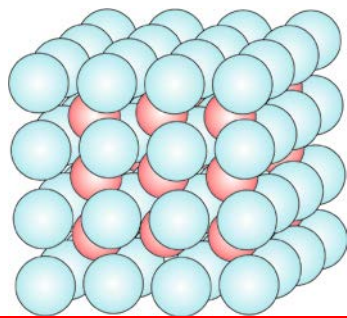
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DEVELOPMENT OF TECHNOLOGY FOR MANUFACTURING PRODUCTS WITH HIGH MECHANICAL STRENGTH BASED ON ALUMINUM OXIDE

РАЗРАБОТКА ТЕХНОЛОГИИ ИЗГОТОВЛЕНИЯ ИЗДЕЛИЙ С ВЫСОКОЙ МЕХАНИЧЕСКОЙ ПРОЧНОСТЬЮ НА ОСНОВЕ ОКСИДА АЛЮМИНИЯ

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Abstract: The results of development of the technology for manufacturing samples of insulators made of alumina ceramic with an aluminum oxide content of up to 95% are presented. The maximum tensile strength of the produced insulators has been investigated. The structures of the chip of the ceramic insulator surface have been obtained. It is shown that a change in the aluminum oxide content by 8-10% leads to an increase in the strength properties of the product by 1.5 times. The developed technology can be used to produce high-strength dielectric products, for example, antenna rod insulators, applied in the field of electrical engineering, radio engineering and other industries.

KEYWORDS: ALUMINA CERAMIC, TECHNOLOGY, CHARGE, PRESSING, SINTERING, PROPERTIES.

1. Introduction

Alumina ceramic with Al_2O_3 content up to 95% has wide application in various fields of engineering, electronics and other areas of the national economy. In particular, it is used for manufacturing various insulators [1-5]. In this regard, high requirements on such ceramics are imposed concerning the electrophysical properties: electrical strength, dielectric loss tangent, density and tensile strength.

The manufacturers of alumina ceramics are dealing with complex sintering processes. To obtain the highest mechanical strength of such materials, it is necessary to sinter them in a strictly defined temperature range, which depends on the characteristics of the initial material and the technique of producing (molding) the product [6].

Having regard to the above, the actual task is to develop a technology for manufacturing products made of ceramic material with increased dielectric and strength properties.

The purpose of this work was to develop a technology for manufacturing products based on aluminum oxide, which have high mechanical strength and high electrophysical parameters.

2. Method of procedure

To obtain a composite ceramic material, a wet mixing of the initial material containing more than 80% Al_2O_3 , SiO_2 , MgO and B_2O_3 was carried out for 12-14 hours. The powder then was dried and granulated.

To obtain structural elements, which are parts of a complex volumetric configuration, the isostatic pressing method was used [7].

The pressed samples were sintered at a temperature of 1400-1500 °C for 1-2 hours in air atmosphere. The insulators were then sealed in metal fastenings and transferred for testing to determine the minimum destructive force for tensile. Tests of ceramic rod samples for tensile were carried out in the Test Center of the State Scientific Institution "Powder Metallurgy Institute" in accordance with GOST 24409-80 [8] on the universal testing machine "Instron 1195" (England), and also at Gomel Radio Plant (Belarus).

Further studies were carried out on samples obtained from ceramic insulators that had undergone tensile strength tests.

The samples for water absorption were tested in accordance with GOST 26093-84 [9].

Investigation of surface morphology and determination of the grain sizes of the phases of the studied ceramic materials was performed using LEO 1455 VP scanning electron microscope of Karl Zeiss company.

Dielectric measurements of ceramic insulators based on alumina were carried out at a frequency of 1 MHz using E7-20 immittance device. Open porosity was investigated on polished samples using Olympus GX 41 optical microscope. Experimental data was processed using Autoscan 2500 Studio software.

3. Experimental

Ceramic insulators were made of powders with different alumina contents (more than 83% and more than 90%) for research and tests. Ceramic half-finished products were pressed in the State Scientific Institution "Powder Metallurgy Institute" using the isostatic pressing technique on ISPR.1 isostat with an elastic shell. The appearance of the unit is shown in Figure 1.



Fig. 1 The appearance of the unit of isostatic pressing of ISPR.1

In order to make the required shape of the insulator, a pressing tool was developed and manufactured. It was a structure consisting of a shape-generating steel rod and a polyurethane membrane in the form of a pipe. The assembly of the tool was fixed with flanges. The drawing of the shape-generating rod of the tool is shown in Figure 2 and the appearance of the tool for isostatic pressing is shown in Figure 3.

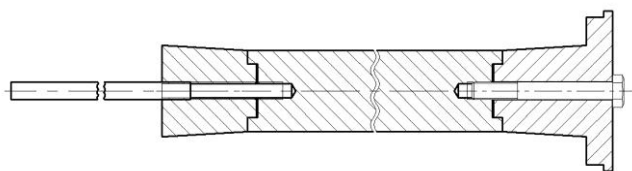


Fig. 2 The drawing of the shape-generating rod of the tool for pressing insulators



Fig. 3 The appearance of the tool for isostatic pressing

The prepared charge was poured into the cavity of the tool. The tool was then installed in the isostatic pressing unit and pressed at a pressure of 100 MPa. The appearance of the pressed insulators is shown in Figure 4.



Fig. 4 The appearance of the pressed ceramic insulator based on aluminum oxide

Ceramic insulators made of powder with an aluminum oxide content of more than 83% were tested at the Test Center of the State Scientific Institution "Powder Metallurgy Institute" on the universal testing machine "Instron 1195". The testing machine is shown in Figure 5. The maximum tensile strength of such samples was 4900-5880 kg.



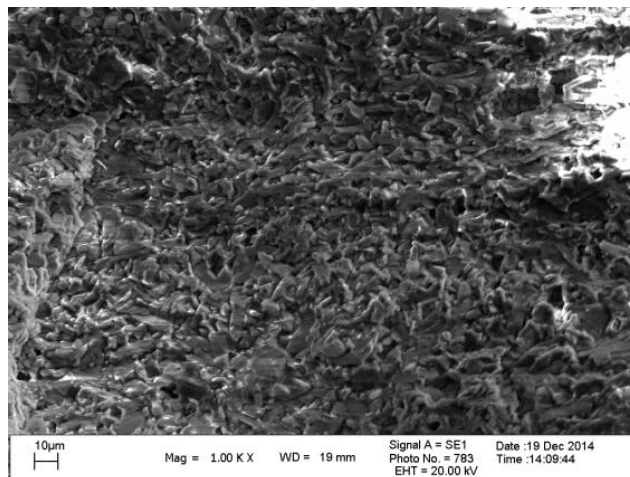
Fig. 5 Universal testing machine "Instron 1195"

Ceramic insulators made of powder with an aluminum oxide content of more than 90% were presented for testing at Gomel Radio Plant. The maximum tensile strength of these samples is in the range of 6200-10800 kgf.

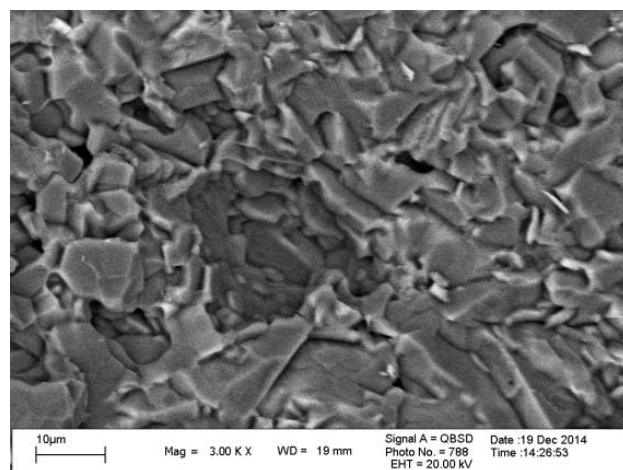
The test results showed that with increasing alumina content in the samples, the maximum breaking force is increased. It was found that a change in the content of aluminum oxide does not lead to an increase in the tensile strength.

A ceramic insulator with the highest strength properties (with a maximum tensile strength of 10800 kgf) was chosen for further investigations.

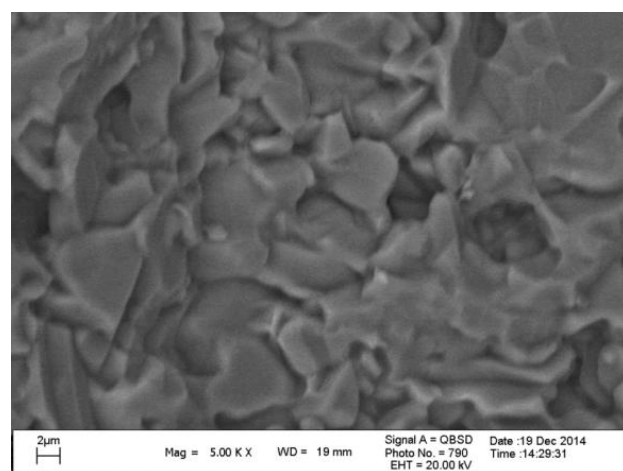
Investigation of the microstructure was carried out on the fracture of a ceramic sample produced after testing for an insulator rupture. The results of investigations of the microstructure are shown in Fig. 6.



a)



b)



c)

Fig. 6 The microstructure of the ceramic rod fracture formed after the tensile tests with a maximum tensile strength of 10800 kgf: a) $\times 1000$; b) $\times 3000$; c) $\times 5000$

In the presented photographs of the microstructure, it can be seen that the ceramics consist of dense-packed prismatic grains. The processing of the experimental data, carried out with the help of Autoscan 2500 Studio software, showed that the main grain size is 3-4 μm .

The grain size distribution is relatively uniform. This ensures a good packing density and, correspondingly, the density of the ceramic as a whole.

The electrophysical properties of ceramics samples based on aluminum oxide are presented in Table 1.

Table 1. *Electrophysical properties of ceramics based on Al_2O_3*

Property	Value
Relative dielectric permittivity, ϵ	9,4 $\pm$ 0,5
Dielectric loss tangent, $\text{tg } \delta$	Max. 0,0005
Porosity, %	5,5
Water absorption, %	0,015

The developed technology can be used to produce high-strength dielectric products used in the field of electrical engineering (for example, for the production of antenna rod insulators (Figure 7)), radio engineering and other industries.

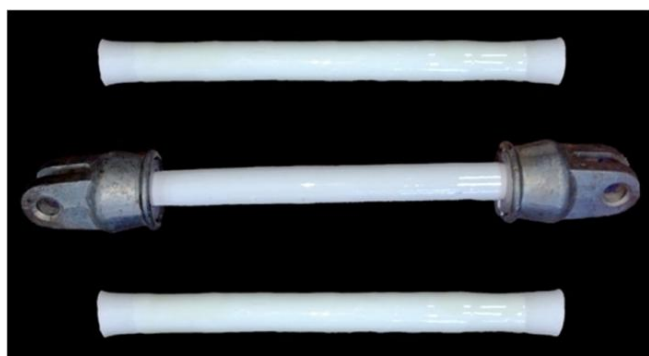


Fig. 7 *Antenna rod insulator with a minimum breaking strength of more than 5000 kg*

4. Conclusion

As a result of the work carried out, it was found that the strength properties of the products are affected by the amount of aluminum oxide in the content of ceramic material. The change in the content of aluminum oxide by 8-10% leads to an increase in the strength properties of the product by 1.5.

Based on the obtained results, a technology was developed for the manufacture of products made of alumina ceramic, which has high dielectric and strength characteristics.

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ELASTIC PROPERTIES OF Fe UNDER HIGH PRESSURES

УПРУГИЕ СВОЙСТВА Fe ПРИ ВЫСОКИХ ДАВЛЕНИЯХ

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Abstract. The definition of the n -order ($n \geq 2$) elastic constants of a loaded crystal and the calculation method of the second and third order elastic constants of hcp crystal under hydrostatic pressure from the energy-deformation relation are given. The energy at the various pressures and deformations of hcp iron is obtained in framework of DFT. The calculations of the second and third order elastic constants of hcp Fe at 20-340 GPa ($T=0K$) are performed. The Gruneisen parameters for long wave acoustic modes in hcp iron are defined. The obtained results are used for the stability analyses of the hcp phase of iron at high pressures.

Keywords: HIGH PRESSURES, NONLINEAR ELASTICITY, PHASE STABILITY, METALS

1. Introduction

According to the experimental data, at the pressures 10-15 GPa (the room temperature) BCC Fe experiences the phase transition in HCP structure (ϵ -Fe). The HCP phase at the pressures above 50 GPa is nonmagnetic and is stable till the pressures 300-400 GPa. The elastic properties of ϵ -Fe were investigated in many experimental and theoretical works. This is connected mainly with the problems of geophysics (the pressures in the internal part of Earth core are nearly 330-360 GPa, and it consists mainly from ϵ -Fe). Accordingly, the elastic properties are important for the interpretation of the seismic observations.

The experiments were performed on the polycrystalline samples of ϵ -Fe at the different pressures using diffraction (RXD) [1], the inelastic X-ray scattering (IXS) [2], and the Raman spectroscopy [3]. On this base the second order elastic constants (SOEC) of single crystal were found. In the theoretical papers the SOEC of HCP-Fe in the pressure interval were calculated by the first principles DFT method [4-7].

The SOEC define the linear response of a material. The third order elastic constants (TOEC) define the lowest order of the nonlinear response. TOEC are important for understanding the physical effects connected with the lattice anharmonism, such as the heat expansion, the temperature and the pressure dependences of the elastic response. Besides TOEC define the waveform distortion of the ultrasound waves with the finite amplitude in solid, and the second harmonic amplitude. The data on TOEC are absent in the literature.

In the present paper the definition of the n -order ($n \geq 2$) elastic constants of a loaded crystal is given. The calculation method of SOEC and TOEC from the energy-finite deformations for the crystals with the hexagonal symmetry at the hydrostatic pressure is given. The SOEC and TOEC of HCP Fe were calculated by this method in the pressure interval 20–340 GPa ($T=0K$). The energy of a crystal at the different pressures and deformations was defined by the DFT method. The expression was obtained for the calculation of Gruneisen parameters of the longwave acoustic modes in the HCP crystal via the second and the third order elastic constants. The calculations of these parameters for the longitudinal and the transverse acoustic modes in the high symmetry directions were performed in the investigated pressure interval. The obtained results were used for the investigation of Iron HCP phase stability at the high pressures.

2. Definition of high order elastic constants of a loaded crystals

The n -order ($n \geq 2$) elastic constants of a loaded crystal characterize the elastic response on an arbitrary finite deformation of a material under hydrostatic pressure. The different order isothermal elastic constants (EC) at the given pressure can be defined as [8]

$$\tilde{C}_{ijkl\dots} = (1/V_0)(\partial^n G / \partial \eta_{ij} \partial \eta_{kl} \dots)_T \quad (1)$$

Here G is the Gibbs potential, η_{ij} are of the Lagrange finite deformations tensor components, V_0 is the volume of a crystal in the undeformed state at the given P . The change of G under additional deformation η_{ij} (pressure P , temperature T) on the unite volume in the undeformed state is equal

$$\Delta G / V_0 = \Delta F / V_0 + P \Delta V / V_0, \quad (2)$$

where ΔF is the change of the free energy, $\Delta V = V - V_0$ is the volume change due to the deformation η_{ij} . So, the elastic constants (1) take in to account not only the change of the free energy under deformation, but also the work against the external load done by the forces due to the additional small deformation η_{ij} . In this is the main difference between the elastic constants

of a loaded and unloaded crystals. So, $\tilde{C}_{ijkl\dots}$ are defined not only by the interatomic forces, but also by the applied load. They fully characterize the elastic properties of a loaded material. Under the hydrostatic pressure $\tilde{C}_{ijkl\dots}$ have the full Voigt symmetry relative to the indexes permutation. For the definition of EC according to (1), the elasticity theory relations have the same form as at the hydrostatic pressure, and as at the $P = 0$.

3. Calculation details

Now, we express EC (1) via the derivatives of the free energy and pressure by decomposition $\Delta G / V_0$ и $\Delta F / V_0$, and also $\Delta V / V_0$ in the series over η_{ij} , including the third order contributions [9]. HCP lattice has the 5 independent SOEC $\tilde{C}_{\alpha\beta}$, and 10 third order elastic constants $\tilde{C}_{\alpha\beta\gamma}$ (EC are given in Voigt notations). The initial loaded state defined by atomic volume V_0 . For such each state the different deformations of the unite cell were considered. The full energy of HCP Fe ($T = 0K$) at the different values of V_0 and deformation η_{ij} was calculated by DFT method using VASP [10]. The all initial configurations of the loaded crystal in the interval $V_0 / V(0) = 1 \div 0.7$ have been relaxed. The exchange-correlation contribution was taken in to account in the generalized gradient approximation with the PW91 parametrization. The APW method was used to take in to account the ion-electron interaction. The integration

over the BZ was done by the tetrahedron method with the point massive 28x28x18 using the Monkhorst-Pack method. The limited energy of the plane waves was 700 eV. The big values of the calculation parameters defined by the smallness of the third order contributions over η_{ij} . The pressure and the different order EC defined by the mean square method (30 points with the step

0.003 in the interval $\eta = \pm 0.045$) from the polynomial dependences $\Delta F(\eta)/V_0$ [9].

4. Results and discussion

The calculation results of the equation of state and SOEC are given in Table 1. The equation of states is in a good agreement with the experimental and theoretical results [4,11].

Table 1. The equation of state and SOEC of HCP-Fe at the different pressures ($T=0K$). The pressure and EC are given in GPa, B is the bulk modulus.

$V_0 A^3$	P	B	$\tilde{C}_{11}$	$\tilde{C}_{12}$	$\tilde{C}_{13}$	$\tilde{C}_{33}$	$\tilde{C}_{44}$
9,668	17,10	365,6	667,9	220,5	195,9	732,4	199,8
8,886	54,30	521,1	912,5 576 * 599(33)''	336,5 307* 403(20)''	300,6 324* 318(22)''	991,6 539* 650(45)''	253,7 237* 187(40)''
8,354	90,70	664,1	1134	444,5	399,4	1224	300,7
7,954	126,6	799,4	1341	547,6	493,9	1444	343,7
7,639	162,1	929,5	1538	647,2	585,8	1654	384,3
7,366	197,4	1055	1727	744,6	675,8	1855	422,3
7,138	232,4	1178	1910	840,2	763,5	2049	458,1
6,939	267,3	1297	2088	934,4	849,6	2237	492,3
6,764	302,1	1415	2260	1027	935,3	2421	525
6,683	319,4	1473	2345	1073	977,6	2511	540,9
6,607	336,6	1530	2429	1118	1020	2601	556,7

*) experiment[11], (RXD), $P=52 \text{ ГПа}$, $T = 300K$

“)) experiment [11]. (IXS), $P=52 \text{ ГПа}$, $T = 300K$

The stability conditions for the HCP lattice are following

$$\tilde{C}_{11} \geq |\tilde{C}_{12}|, \quad \tilde{C}_{33}(\tilde{C}_{11} + \tilde{C}_{12}) \geq 2(\tilde{C}_{13})^2, \quad \tilde{C}_{11}\tilde{C}_{33} \geq 2(\tilde{C}_{13})^2, \quad \tilde{C}_{44} \geq 0$$

For the HCP Fe they are fulfilled in the all investigated pressure interval. Our SOEC data are in a good agreement with the first principles calculation results at the different pressures [4-7]. For some SOEC there is the big difference between the experimental and theoretical data (see Table 1, line 2). This may be due to the fact that the X-ray scattering and the diffraction experiments were carried out on the polycrystalline samples under non-hydrostatic conditions. The elastic constants of single crystals were defined from these data by the inversion, what is the difficult task. The difference between the experimental data, obtained by the different methods ,also points on it (see Table.1).

In the Table 2 the results of TOEC calculations are given. It is seen, that the all TOEC are negative and are increased by modulus with the pressure increasing. The results given in the Table 2 have a practical meaning, because these data are absent in the literature. In particular, they may be used for the interpretation of the experimental data on X-ray diffraction in the non-hydrostatic conditions.

Using SOEC and TOEC, we have calculated for HCP Fe the Gruneisen parameters γ_j of the long wave acoustic modes

in the high symmetry directions.

$\gamma_j = -(V_0 / \omega_j)(d\omega_j / dV)_P$ defines the change of the normal mode frequency ω_j with the volume changes and

characterize anharmonicity of the lattice vibrations The calculations results are given on Fig 1.

It is seen that in HCP-Fe the Gruneisen parameters for the longitudinal modes are larger than for the transverse modes. The frequencies of the lattice vibrations are increased with the pressure increasing, what points on the dynamical stability in the investigated pressure interval. But this increasing is diminished with the pressure increasing, so, possibly, at the higher pressures in the beginning the frequencies of the transverse modes become to soften.

The work is executed at financial support of the Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005) and the Russian Foundation for Basic Research (Grant 16-02-00699 and Grant 16-02-01027).

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Table 2. TOEC of HCP-Fe at the different pressures ($T=0K$). $\tilde{C}_{\alpha\beta\gamma}$ are given in 10^{-1} GPa.

P	$-\tilde{C}_{111}$	$-\tilde{C}_{222}$	$-\tilde{C}_{333}$	$-\tilde{C}_{112}$	$-\tilde{C}_{113}$	$-\tilde{C}_{123}$	$-\tilde{C}_{133}$	$-\tilde{C}_{144}$	$-\tilde{C}_{155}$	$-\tilde{C}_{344}$
17,10	784,7	707,8	713,3	87,97	72,05	17,45	151,3	34,89	105,4	168,0
54,30	1021	918,5	919,6	118,1	99,71	18,95	201,2	47,01	135,2	220,1
90,70	1231	1105	1103	144,2	124,4	19,69	245,8	57,73	161,6	266,3
126,6	1424	1277	1280	169,2	145,9	19,73	286,8	67,46	186,0	308,3
162,1	1603	1436	1440	193,0	167,7	20,05	326,1	76,70	209,0	348,0
197,4	1772	1586	1590	215,9	188,8	21,39	363,8	85,45	231,0	385,9
232,4	1934	1728	1733	237,1	209,5	22,43	399,0	93,81	252,3	423,0
267,3	2089	1865	1872	256,7	229,8	23,47	433,3	102,0	273,1	460,0
302,1	2243	2001	2012	274,8	249,4	24,56	466,9	110,0	293,3	497,2
319,4	2318	2066	2082	284,0	259,4	25,27	483,8	114,0	303,3	516,0
336,6	2392	2130	2152	293,0	269,2	25,68	501,2	118,0	313,4	535,0

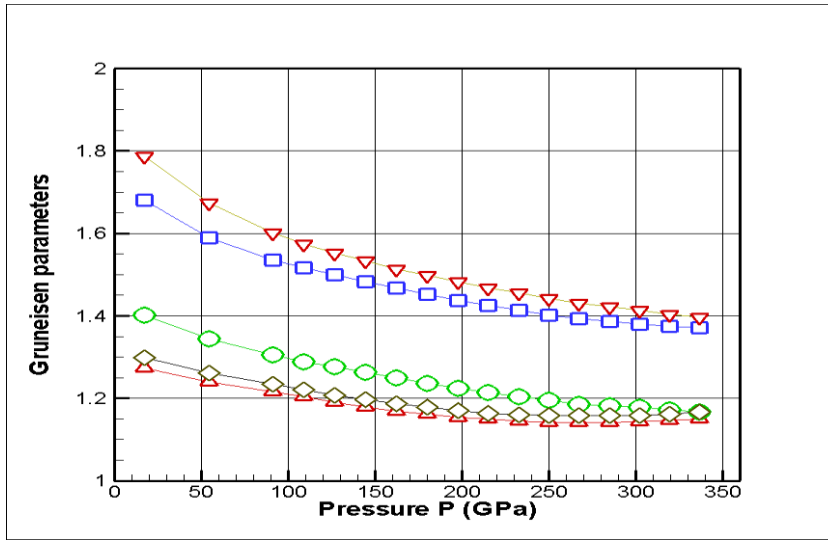


Fig. 1. HCP-Fe; the pressure dependence of the Gruneisen parameters for the long wave acoustic modes . Δ , $\diamond$ and O are the transverse modes $[001]/[100]$, $[100]/[001]$ and $[100]/[010]$ accordingly; $\square$ and ∇ are the longitude $[001]$, $[100]$ modes.

INFLUENCE OF THE EXTERNAL MAGNETIC FIELD ON THE STRUCTURE AND PROPERTIES OF THE HYPEREUTECTIC ALUMINUM-SILICON ALLOY

ВЛИЯНИЕ ВНЕШНЕГО МАГНИТНОГО ПОЛЯ НА СТРУКТУРУ И СВОЙСТВА ЗАЭВТИЧЕСКОГО АЛЮМИНИЕВО-КРЕМНИЕВОГО СПЛАВА

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Abstract: The effect of a constant magnetic field during the crystallization of a hypereutectic aluminum alloy on its structure in the solid state investigated. It is shown that the superposition of the magnetic field positively affects the structure of the alloy. A uniform distribution of the doped phases and eutectic in the volume of the alloy is observed. The phase of primary silicon significantly changes the size and the shape. It is established that the influence of an external magnetic field reduces the dimensions of the shrinkage defects. In general, the effect of an external magnetic field on the structure of the alloy leads to an improvement in the operational properties. The obtained measurement results showed more stable hardness values over the cross section of the sample in comparison with the alloy that was not processed.

KEYWORDS: CRYSTALLIZATION, STRUCTURE OF ALLOYS, HYPEREUTECTIC ALUMINUM-SILICON ALLOYS, EXTERNAL MAGNETIC FIELD

1. Introduction

Aluminum casting hypereutectic alloys are used in engineering for the manufacturing of critical parts. Pistons are produced from these alloys for internal combustion engines. These parts should have high operational properties. Without further processing, the structure of the alloy in the bulk of the metal is distributed unevenly. The primary silicon phase is predominantly large in size and is in the form of clusters. It has sharp angles that act as stress concentrators. The primary silicon is strong and brittle at the same time. Its uneven distribution in the structure contributes to the formation of various defects during operation, which lead to the destruction of parts.

2. Preconditions and means for resolving the problem

To improve the operational properties of hypereutectic silumin, doping, modification, physical or physicochemical treatment are used [1-10]. In the first two cases chemical elements are added to the melt; they, as a rule, are expensive, improvement of metal's characteristics is not always achieved. Hypereutectic alloy in any country has a normalized chemical composition, which must be adhered to and therefore the possibility of entering chemical elements is limited. The use of melt processing by energy fields of different physical nature also makes it possible to obtain the necessary properties of the material. Such techniques are easier to implement in practice, but they are not yet perfect. Therefore, in this paper we give results of our investigations of the effect of an external magnetic field during crystallization process on formation of the structure of the hypereutectic silumin and on some of its properties in the solid state.

The aim of the work was to study the effect of a constant magnetic field during the crystallization of a hypereutectic alloy on its structure and properties in the solid state.

The alloy was melted at 700° C and poured into a metal mold. A permanent magnet was placed beneath the bottom of the metal mold, which interacted with the material to create a magnetic field in the middle of the alloy.

3. Results and discussion

3.1. Results of metallographic analysis

Figure 1 shows the macrostructures of the original hypereutectic alloy and of alloy after exposure to it of a constant magnetic field

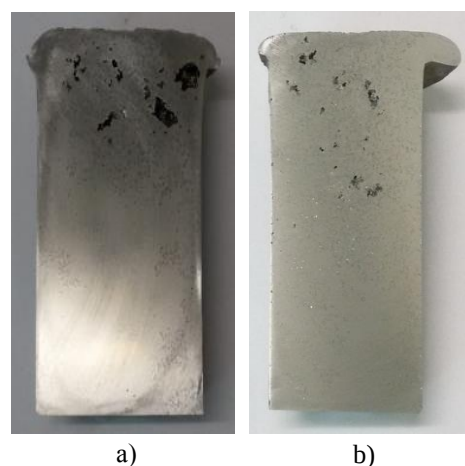
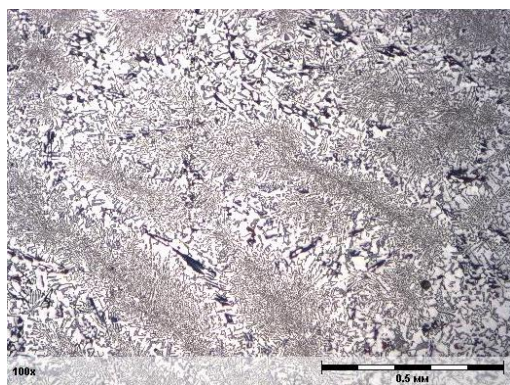


Fig. 1. Section of hypereutectic alloy:
a) without processing; b) overlapping the magnetic field.

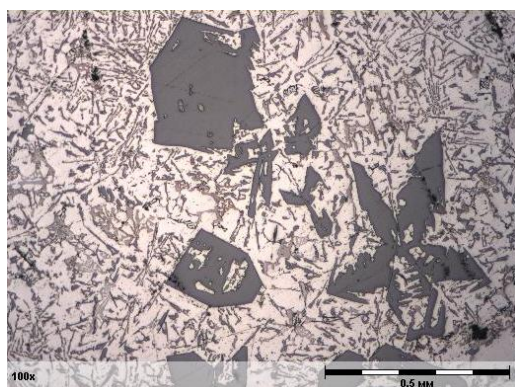
during the crystallization. It can be seen from the figure that in the alloy that was being processed, shrinkage defects are much smaller in size than shrinkage defects in the alloy without treatment. On the macrosection of the alloy the phase components are distributed, which are probably phases with alloying elements. In Silumin, which was exposed to a magnetic field, the distribution of such phases is uniform in comparison with the alloy without treatment. With the help of light metallography, the microstructure of the alloy was analyzed. The size of the structural components and their distribution were estimated. The main attention was paid to the shape, size, distribution in the volume of the investigated samples of primary silicon crystals and phases with iron. Images of the microstructures of the alloy without and after the action of the magnetic field are shown in Figures 2 - 3.

The microstructure of the untreated alloy is characterized by a nonuniform distribution of the eutectic and inclusions of the needle phases observed in the form of colonies. In some places in the structure of the alloy, the available silicon phases are large in size, from 180 μm to 300 μm with sharp angles. Also, phases with a star-shaped structure, whose size is from 350 μm to 500 μm , are observed.

It can be seen that silicon, which is unevenly distributed in the alloy structure, is mainly in the form of clusters. The sharp corners of the silicon phase can be stress concentrators, this significantly reduces the mechanical properties of the material. Such a distribution of crystals of primary silicon leads to a rapid destruction of a part of

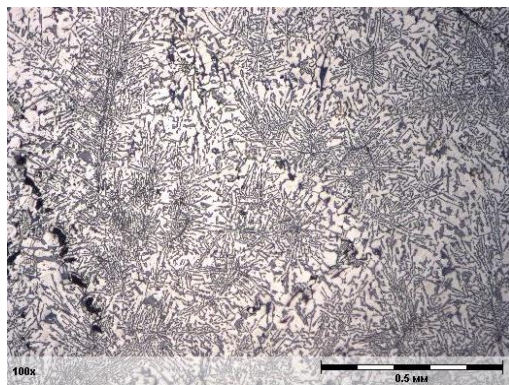


a)

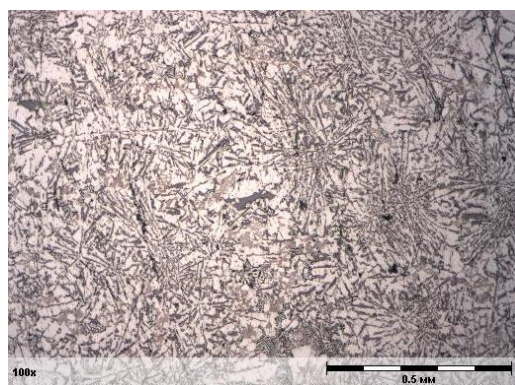


b)

Fig. 2. Microstructure of hypereutectic alloy without processing (a, b - different fields of view), $\times 100$



a)



b)

Fig. 3. Microstructure of the magnetic field after treatment of the hypereutectic alloy (a, b - different fields of view), $\times 100$.

such an alloy during operation. It is known [11] that the presence of primary silicon in the structure of large crystals leads to large intervals of α -solid solution between them, which are easily scratched by abrasive particles, which leads to a decrease in the wear resistance of the piston and to formation of such operational defects as scuffs.

The microstructure of the hypereutectic alloy treated with a constant external magnetic field compared with the previous case has a more evenly distributed eutectic, and the dimensions of the inclusions of primary silicon are much smaller. The distribution of primary silicon in the volume of the alloy is uniform, and this helps to reduce the interstitial spaces of the α -solid solution between the primary silicon crystals and increases the wear resistance of silumin with an increased silicon concentration [11]. According to the metallographic analysis in the hypereutectic alloy after the action of the magnetic field, the sizes of the primary silicon particles were in the range 20-60 μm .

To obtain a more contrast image of the distribution of different phases and determine their chemical composition, raster electron microscopy was used. The obtained images of microstructures with the help of REM for an alloy without and after exposure to it a magnetic field are shown in Figures 4 - 5.

Analyzing the structure of the alloy in the initial state, it is worth noting that it has an inhomogeneity in the distribution of both the main phases and the alloying elements at the grain boundaries. This is evidenced by the uneven location of light areas on the image.

A local chemical analysis of the phases and structural constituents for the alloy without treatment was also determined. Analysis of the image and local chemical composition shows the formation of the $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ phase, which has no classical needle shape, that is due to the action of nickel (point 2). The eutectic $\text{Al} + \text{Si}$ (point 1) and the solid solution based on aluminum (point 3) were also found. The presence of a primary silicon phase was determined (point 4, figure 4 b).

The data of the local chemical phase analysis for the hypereutectic alloy, which crystallized without the influence of external magnetic action, are given in Table 1.

Table 1 - Chemical analysis of the phases of a hypoutectic alloy without processing by a magnetic field

№	Chemical composition of the phase, % mas					Phase
	Al	Si	Mn	Ni	Fe	
1	76,83	23,17	—	—	—	(Al+ Si) eutectic
2	40,43	0,46	0,59	52,90	5,61	$\text{Al}_{15}(\text{FeMn})_3\text{Si}_2 + \text{Ni}$
3	96,88	2,68	0,10	0,13	0,21	(Al)
4	1,06	98,80	0,02	0,016	0,047	(Si)

According to the data of the local chemical phase analysis (Figure 5), in the structure of the alloy after the action of the magnetic field the following things are observed: the $\text{Al} + \text{Si}$ eutectic (point 1), the $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ phase containing nickel (point 2), the solid solution point on the basis of aluminum (point 3) and the primary phase of silicon (point 4). Local chemical phase analysis data for the alloy after the action of the magnetic field are given in Table 2.

Table 2 - Chemical analysis of the phases of a hypoutectic alloy after its treatment by a magnetic field

№	Chemical composition of the phase, % mas					Phase
	Al	Si	Mn	Ni	Fe	
1	43,17	3,41	—	33,60	19,81	$\text{Al}_{15}(\text{FeMn})_3\text{Si}_2 + \text{Ni}$
2	6,30	93,43	0,11	0,16	—	(Si)
3	98,76	0,89	0,02	0,30	0,02	(Al)
4	68,81	30,91	0,07	0,17	0,04	(Al+ Si) eutectic

At point 2 (Figure 4) and 1 (Figure 5) there are phases whose chemical composition and stoichiometry indicate that Ni interacts with iron. Due to the presence of Ni, the stoichiometry of the $\text{Al}_{15}(\text{FeMn})_3\text{Si}_2$ phase changes, as well as its appearance. Instead of extended inclusions of a needle-like shape, compact inclusions are observed.

3.2. Analysis of microhardness and Brinell hardness

Measurements of the microhardness were performed to determine the influence of the magnetic field on the properties of the hypereutectic alloy. The study was conducted in an area that was guaranteed to be subjected to an external magnetic field, from the

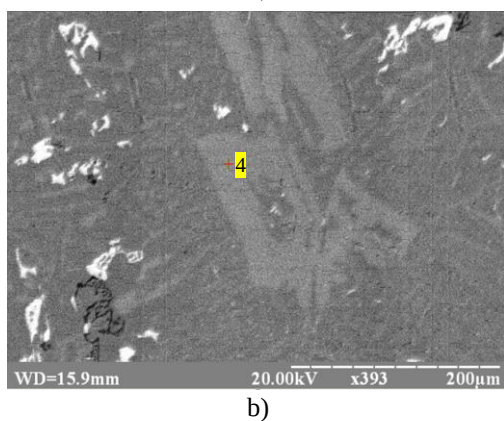
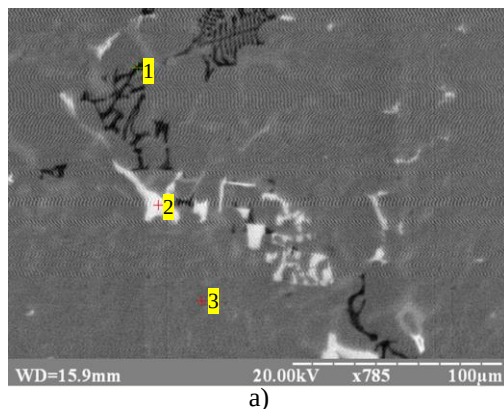


Fig. 4. Microstructure of hypereutectic alloy, which wasn't influenced by a magnetic field, with different magnitudes: a) $\times 785$; b) $\times 393$

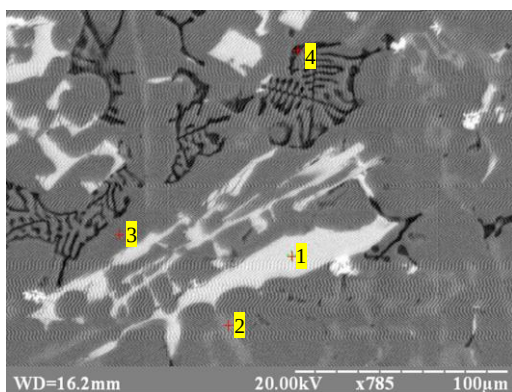


Fig. 5. Microstructure of hypereutectic alloy, which was influenced by a magnetic field, with different magnitudes, $\times 785$.

lower edge of the sample to the depth of the metal. The load on the diamond pyramid was 50 g, the holding time was 10 s. The results were compared with measurements in a similar region in the original alloy. The results obtained are presented in the form of graphs of microhardness's change in Figure 6.

From the obtained results it can be seen that the superposition of the magnetic field positively influences the structure of the hypereutectic alloy. An increase of the microhardness is observed. The graph shows the changes in the microhardness of the alloy after the action of an external magnetic field (Figure 6, b). Stable results

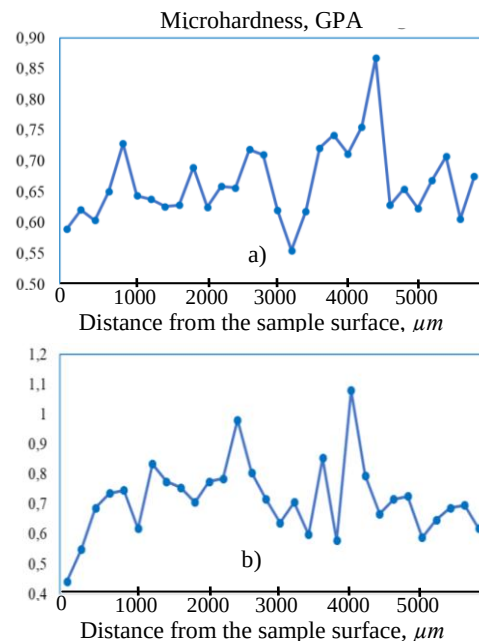


Fig. 6. Microhardness alloy: a) in the initial state; b) after external magnetic influence.

are obtained in comparison with the untreated alloy (Figure 6, a). This may indicate a uniform distribution of alloying elements in the alloy structure.

In Brinell hardness measurements, the mean change in the HB of the samples from the bottom to the top of the cast was estimated. When carrying out the measurements, a steel ball with a diameter of 5 mm was used, the load F was 2452 N (or 250 kgf), and the holding time was 10 s. Graphs of the average values of the change in hardness for hypereutectic silumin are shown in Figure 7 a, b.

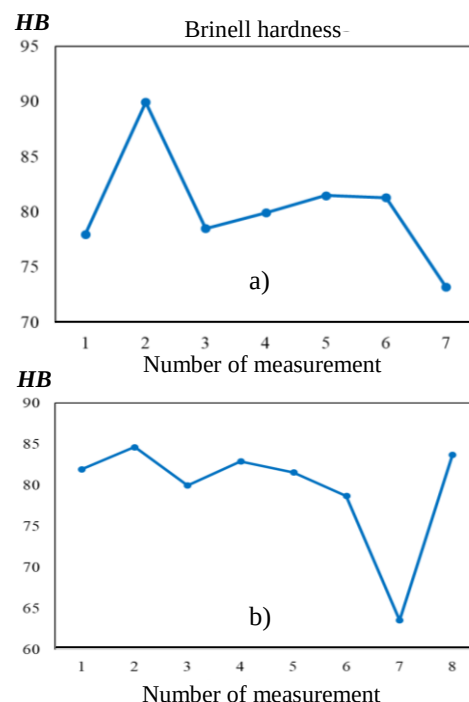


Fig. 7. Hardness of the alloy according to Brinell: a) in the initial state; b) after external magnetic influence.

Figure 7 (a) shows a different distribution of hardness values. This can be explained by a nonequilibrium structure. The stable values at the beginning of the graph (Figure 7, b) for the alloy after the action of the magnetic field can be explained by a more even distribution of the alloying elements in the alloy structure, and the decrease in

hardness observed at the end of the graph is due to the fact that the upper part was less exposed to the magnetic field.

Thus, the effect of a constant magnetic field in the process of crystallization of the hypereutectic silumin has a noticeable effect on its structure and properties.

4. Conclusions

1. The application of an external constant magnetic field for 10-15 seconds during crystallization positively influences the formation of the structure of the hypereutectic alloy of the Al-Si system.
2. It has been established that treatment with a magnetic field leads to a reduction in shrinkage defects, and the gas porosity of the treated alloy does not exceed 1 point in accordance with [12].
3. In the microstructure after treatment, a uniform distribution of the doped phases in the bulk of the material and the grinding of the primary silicon phase is observed. In an alloy without a block, the size of silicon inclusions is 150 μm - 300 μm , and after processing 30 μm - 60 μm , this indicates its uniformity, which leads to the improvement of the operating properties of the alloy.
4. It is established that the superposition of the magnetic field positively affects the microhardness of the hypereutectic silumin. An average microhardness increase by 7.5% is observed. Its minimum indicator increased by 2%, and the maximum by 72.6%.
5. An increase of the values from 3% to 15% for 66% of the Brinell hardness measurements after the action of the magnetic field on the hypereutectic silumin has been shown.
6. The developed technique can be recommended for controlling the structure formation and pulverization of the phases of primary silicon of hypereutectic silumins.

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COVALENCE OF THE Fe-C INTERATOMIC BOND AND THE HARDNESS OF MARTENSITE OF CARBON AND ALLOYED STEELS

КОВАЛЕНТНОСТЬ МЕЖАТОМНОЙ СВЯЗИ Fe-C И ТВЕРДОСТЬ МАРТЕНСИТА УГЛЕРОДИСТЫХ И ЛЕГИРОВАННЫХ СТАЛЕЙ

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Abstract: A technique for determining the generalized degree of covalence of the interatomic Fe – C bond is proposed by the addition rule taking into account the fractions of Fe₂C, Fe₄C and Fe₆C clusters and cementite in steel. The correlation dependence of the generalized degree of covalence of the interatomic Fe – C bond with the hardness of microstructures observed in eutectoid carbon steel, as well as the hardness of ferrite and cementite, is revealed. A functional relationship between the generalized degree of covalence of the Fe-C interatomic bond and the martensite hardness at different mass content of carbon is established, which ensures the correspondence of the calculated and experimental data.

KEYWORDS: COVALENCE; INTERATOMIC BOND, MARTENSITE, CARBON STEEL, ALLOYED STEEL, MARTENSITE HARDNESS

1. Introduction

The fundamental problem of modern material's science is the search for new theoretical approaches to the task of developing the foundations of the synthesis of steels and alloys with a given set of physical and chemical properties of the metal in the finished product. This problem has a huge amount difficult factors to take into account, including the limits of the melt production and processing, technological redistribution between the liquid metal and the finished product, which makes it difficult to solve it. To simplify the tasks necessary to transition to a single system of reference for the evaluation of the effects of these factors. This may be a consideration of their influence on the structure of the atomic hierarchical level of the metal structure.

The atomic level is the initial in the hierarchical row of the metal structure: atomic → nanostructural → microstructural → mesostructural → macro-structural level.

The atomic level is usually characterized by the belonging of atoms to specific chemical elements, the spatial arrangement of atoms and vacancies in the crystal lattice and interatomic interaction. At the same time, the structure of the set of interatomic bonds in the alloy, characterized by generalized degrees of metallicity C_m^g , covalence C_k^g and ionicity C_i^g , ($C_m^g + C_k^g + C_i^g = 1$), is potentially able to reflect the chemical and phase composition, structure and mechanical properties of the metal. But the corresponding equations have not yet been obtained. This problem will be theoretically investigated and the results compared with experimental data on the example of carbon steel.

The problem can be formulated as: Development of a method for determining the generalized degree of covalence C_k^{gFe-C} , characterizing in general all interatomic bonds between iron and carbon atoms in all structural components of carbon steel and establishing a connection C_k^{gFe-C} with the type of microstructure, as well as with the hardness of martensite.

2. Results and Discussion

In the crystal lattice α -Fe the most energy-efficient placement of the carbon atom in the octahedral pore, located in the plane A, (Figure 1A). The Fe 1 and 2 atoms are shifted in the direction with a lower packing density of atoms. As a result, the atom C is placed at an equal distance from the nearest six Fe atoms. This configuration of 6 iron atoms and a carbon atom can be considered as a cluster Fe₆C. In the crystal lattice. As is known, there are Fe₂C clusters in ferrite [1, 2], and in martensite there are Fe₄C clusters along with Fe₂C clusters [2, 3]. One of the possible variants of the spatial arrangement of Fe₂C and Fe₄C clusters in the

formation of tetragonal distortion of the martensite crystal lattice is shown on the figure 1B.

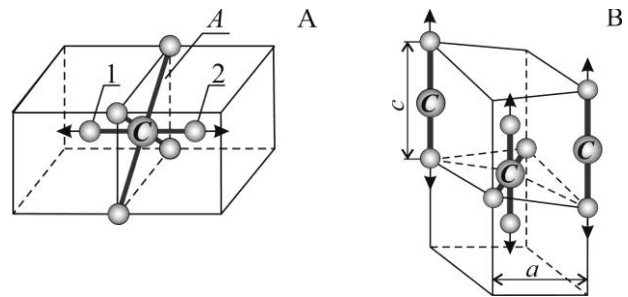


Fig. 1. Cluster Fe₆C (A) in the BCC lattice and clusters Fe₂C and Fe₄C (B) in the formation of tetragonal distortion of the martensite crystal lattice; 1, 2 – displaced Fe atoms

Table 1 shows the calculation data of the degree of covalence of Fe–C bonds in the Fe₂C, Fe₄C, Fe₆C and cementite Fe₃C clusters, where i corresponds to the number of Fe atoms forming a bond with the C atom.

Table 1

Degree of Covalence of Fe–C bond at different for i [4]				
i	2	3	4	6
$C_{k_i}^{Fe-C}$	0,3141	0,2654	0,2438	0,224

For ferrite, including ferrite, which is a part of pearlite, sorbitol, troostite and bainite, the generalized value of the degree of covalency of Fe–C bond, related to the solid solution is determined by the dependence:

$$C_k^F = \sum_i n_i C_{k_i}^{Fe-C} \quad (1)$$

where n_i is the fraction of C atoms in octahedral pores in ferrite; $i = 2, 6$.

For perlite, sorbitol, troostite, and bainite, the generalized value of the degree of covalence of the Fe–C bond with respect to the mechanical mixture as a whole is given by the equation:

$$C_k^{gFe-C} = m_F C_k^F + m_{cem} C_{k_3}^{Fe-C} \quad (2)$$

where m_F , m_{cem} are the mass fraction of ferrite and cementite in the phase mixture, respectively; $C_{k_3}^{Fe-C}$ – degree of covalence of Fe–C bond in cementite (table 1). In the table 2 shows the m_F and m_{cem} values of the various mixtures formed

in eutectoid carbon steel calculated on the basis of the mass conservation law.

Table 2

m_F and m_{cem} values for various microstructural components of eutectoid steel

Type of structural component	Carbon content of ferrite, %	m_F	m_{cem}
Perlite, sorbite, troostite	0,022	0,883	0,117
Bainite upper	0,1 [5]	0,894	0,106
Bainite lower	0,16 [5]	0,902	0,098

Table 3 summarizes the Fe–C bond covalency for ferrite, cementite, and various possible types of microstructural components of eutectoid steel, their respective hardness, and estimates of the fraction of carbon atoms Q_{Fe_iC} , where $i = 2, 4, 6$, octahedral pores in the formation of clusters, respectively, Fe_2C , Fe_4C and Fe_6C . The values Q_{Fe_2C} on table 3 obtained based on assumptions about the defining and the proportional contribution of Fe_2C clusters in the hardening of the ferrite included in the mechanical mixture.

Table 3

Generalized degrees of Fe–C bond covalency $C_k^{g_{Fe-C}}$ for ferrite, cementite and various possible types of structural components of eutectoid steel, their hardness and Q_{Fe_iC} [6]

Structural component	HB, MPa (HB in kg/mm ² or HRC)	$C_k^{g_{Fe-C}}$	Estimation of the possible fraction of carbon atoms in octahedral pores for Fe_iC clusters at $i = 2, 4, 6$
Ferrite	588 (HB≈60)	0,224 (Table 1)	$Q_{Fe_2C} = 0$; $Q_{Fe_6C} = 1$
Perlite	2000 (HRC≈15)	0,23156 (2)	$Q_{Fe_2C} = 0,034$; $Q_{Fe_6C} = 0,966$
Sorbite	2800 (HRC≈30)	0,23564 (2)	$Q_{Fe_2C} = 0,085$; $Q_{Fe_6C} = 0,915$
Troostite	3640 (HRC≈40)	0,24045 (2)	$Q_{Fe_2C} = 0,146$; $Q_{Fe_6C} = 0,854$
Bainite upper	4125 (HRC≈45)	0,2429 (2)	$Q_{Fe_2C} = 0,18$; $Q_{Fe_6C} = 0,82$
Bainite lower	5075 (HRC≈55)	0,24821 (2)	$Q_{Fe_2C} = 0,248$; $Q_{Fe_6C} = 0,752$
Martensite	7350	0,26 (8)	Q_{Fe_2C} for (4); Q_{Fe_4C} for (5); Q_{Fe_6C} for (6) to $C = 0,8\%$
Cementite	8330 (HB≈850)	0,2654 (Table 1)	-

Note: conversion between different hardness units was performed according to ISO 18265.

The data on table 3 are presented in figure 2.

Equation 1 on figure 4 is determined by the dependence of $HB = -41301,08 + 187004,83C_k^{g_{Fe-C}}$ with $R = 0,999$, which in terms of hardness HRC at $HRC \geq 12$ with $R = 0,997$ takes the form:

$$HRC = -17040,87 + 193296,32C_k^{g_{Fe-C}} - 730579,208(C_k^{g_{Fe-C}})^2 + 923819,288(C_k^{g_{Fe-C}})^3. \quad (3)$$

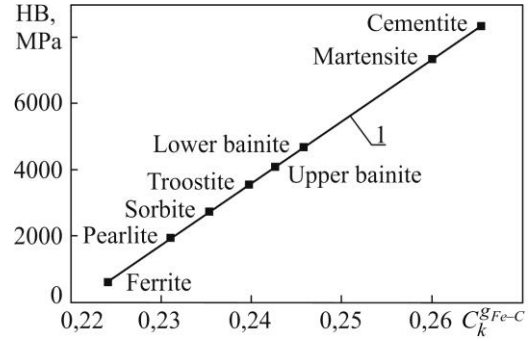


Fig. 2. Hardness of ferrite, cementite and different types of possible structural components of eutectoid steel (table 3), depending on the generalized degree of covalence of Fe–C structural component: 1 – regression equation

Martensitic transformation hasn't diffusion character and is carried out by the corporate movement of atoms. The proportion of carbon atoms in octahedral voids $Q_{Fe_2C}(C)$ on the edges with the formation of clusters Fe_2C (Figure 1B) can be considered proportional to the known angular coefficient of the concentration dependence of the lattice period martensite, in which the processes of redistribution of carbon atoms between the internodes, $\alpha = 0,118$ [5, 7]. That is:

$$Q_{Fe_2C}(C) = a_l + 0,118C \quad (4)$$

where C is mass concentration of carbon in steel; a_l – coefficient; $l = 1, 2$.

In low-carbon steel at the initial stage of formation of tetragonal lattice distortion α -Fe can be considered that:

– the probability of placing an atom C in any of the 18 octahedral pores of the elementary lattice α -Fe is $P_{p.o.} = 1/18$;

– the probability of the joint occurrence of two independent events of the placement of atoms of C in 12 octahedral pores on the edges with the formation of the Fe_2C cluster is $P_{pair} = 1/(12 \cdot 12)$.

In the joint appearance of these cases $a_1 = P_{p.o.} + P_{pair} - P_{p.o.}P_{pair} = 0,0621$. At $C \geq 0,16\%$

$Q_{Fe_2C}(C)$ in the equation (4) corresponds to the probability of placing one of the two atoms on the edges of C with the formation of the cluster Fe_2C as joint events and the coefficient a_2 in the equation (4) corresponds to the probability of co-location of pairs of atoms on the edges and is 0,1597 (table 4).

The placement of carbon atoms in octahedral voids with the formation of a cluster Fe_4C is a random process and for its description the most suitable logarithmically normal distribution. The proportion of carbon atoms in octahedral voids forming Fe_4C clusters is the same:

$$Q_{Fe_4C}(C) = \frac{1}{C\sigma_l\sqrt{2\pi}} \exp\left[-\frac{(\ln C)^2}{2\sigma_l^2}\right] \quad (5)$$

where σ_l is the standard deviation. The values of σ_l in (5), providing the closest correspondence of the calculated martensite hardness values to the experimental data, are given in table 4.

Table 4

The coefficients a_j and σ_l with different contents of carbon in the martensite

Coefficient	$C < 0,16\%$	$C \geq 0,16\%$
a	$a_1 = \frac{1}{18} + \frac{1}{12 \cdot 12} - \frac{1}{18 \cdot 12 \cdot 12} = 0.0621$	$a_2 = \frac{1}{12} + \frac{1}{12} - \frac{1}{12 \cdot 12} = 0.1597$
σ	$\sigma_1 = \ln 2,96$	$\sigma_2 = \ln 2$

The fraction of carbon atoms forming Fe_6C clusters is:

$$Q_{Fe_6C}(C) = 1 - [Q_{Fe_2C}(C) + Q_{Fe_4C}(C)]. \quad (6)$$

Generalized value of the degree of covalency of $Fe-C$ coupling in martensite:

$$C_k^{gFe-C}(C) = C_{k_6} Q_{Fe_6C}(C) + C_{k_2} Q_{Fe_2C}(C) + C_{k_4} Q_{Fe_4C}(C) \quad (7)$$

where C_{k_2} , C_{k_4} , C_{k_6} – is the degree of covalency of the $Fe-C$ bond at i , equal, respectively, 2, 4 and 6 (table 1).

The solution of equations (3) – (7) with respect to the concentration of C is given on figure 3.

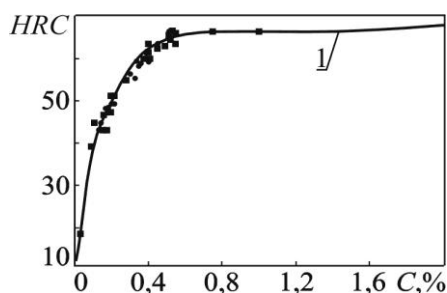


Fig. 3. Martensite hardness depending on the mass content of carbon: 1– solution of equations (3) – (7); experimental data [8]: ■ – carbon steel, ● – alloy steel

3. Conclusion

It is shown that the generalized degree of covalently describing in general all inter-atomic bonding between atoms of iron and carbon in all the structural components of carbon steel, reflects the chemical and phase composition of the steel, the structure and functionally determines the hardness of martensite.

This shows the fruitfulness of the proposed path to the creation of a new approach to the synthesis of steels and alloys with the given physical and chemical properties of the metal in the finished product, in which the entire set of factors, including the parameters of the production and processing of the melt, technological redistribution between the liquid metal and the finished product, will be considered in a single reference system, taking into account their influence on the structure of the atomic hierarchical level of the metal structure, that is the influence on the generalized degree of metallicity and covalency, characterizing the whole

set of all interatomic bonds in all structural components of the alloy.

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SWELLING, MECHANICAL AND THERMAL PROPERTIES OF MICROWAVE – SYNTHESIZED INTELLIGENT SOFT MATERIALS

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Abstract: Advances in technology since the second half of the 20th century are followed as well as induced by the development of intelligent materials. These materials are able to respond to external stimuli by measurable changes in structure and intrinsic properties. Stimuli-responsive hydrogels are soft smart materials as they exhibit significant changes in physicochemical properties in response to small external stimuli. Acrylate hydrogels are widely used in applications where their smart and soft nature comes to the fore. Synthesis of those materials by conventional heating is time-consuming and unsuitable from the point of energy and sources saving. Microwave-assisted synthesis is promising method that provides polymerization under the more favourable conditions, reducing the reaction time. The focus of present work was to investigate the swelling behaviour, mechanical and thermal properties of acrylate hydrogels synthesized by microwave heating.

Keywords: INTELLIGENT SOFT MATERIALS, POLY (ACRYLAMIDE-CO-ACRYLIC ACID), MICROWAVE SYNTHESIS, SWELLING DEGREE, MECHANICAL PROPERTIES

1. Introduction

Functional materials play an important role in modern society and technologies. Development of IT, safeguarding, packaging technologies, trafficking, medicine, agriculture and other fields of contemporary life is strongly influenced by development of functional materials. This term refer to a material which possess special native properties and, based on it, perform, distinct functions. They cover all type of materials including organic, inorganic, hybrid, soft, hard, etc., with functions which make them stimuli-responsive, electroconductive, optically active, or able for storage of energy. Hydrogels as polymer soft materials have excellent properties which make them suitable for many applications [1]. They are defined as polymer networks consisting of crosslinked hydrophilic polymer chains which swell, but do not dissolve in the water [2,3]. Using the appropriate monomers and constituent particles, it is possible to obtain hydrogels which change their properties as response to environmental stimuli such as temperature, pH, ionic strength, pressure, electrical and magnetic field [4,5,6] which classified them as intelligent soft materials [7]. Stimulation implies activation of chemical mechanism which leads to the changes in volume, colour or viscosity of hydrogel [8]. Different types of hydrogels have been developed in the last years and they have become materials of choice for many applications. Hydrogels swell in contact with thermodynamically compatible solvent such as water. Molecules of water first hydrate the hydrogel surface and diffuse into the polymer network causing the segmental mobility that manifests as transition from glassy to rubbery phase. Consequently, the meshes in the rubbery phase expand permitting the penetration of solvent molecules [9]. Great swelling capacity of hydrogels is due to the osmotic pressure, capillary forces and presence of hydrophilic groups in their structure [10].

pH-sensitive swelling is attributed to the hydrogels having ionisable anionic and/or cationic pendant groups. It depends upon the environment pH relative to the pK_a of anionic and pK_b value of cationic pendant groups. Anionic or acidic groups on polymer chains realise proton when the environment pH value is higher than their pK_a value, leading to the production of negative fixed charges in polymer network. Electrostatic repulsion between negatively charged groups enables penetration of water molecules in hydrogel matrix causing the swelling. Cationic polymer networks, on the other hand, possess alkaline pendant groups which develop positive fixed charges in the conditions when the pH of surrounding medium is below their pK_b value. Electrostatic repulsion between polymer chains as well as increased number of fixed positive charges results

in increase water uptake. One of the most studied synthetic intelligent hydrogels having both, acidic (-COOH) and alkaline (-NH₂) functional groups are poly (acrylamide-co-acrylic acid) or poly (Aam-co-Aac) hydrogels. This type of intelligent material responds to the changes in environmental pH value, by swelling or deswelling, which consequently causes changes in its volume, shape and rheological properties. It is possible to project the poly(Aam-co-Aac) hydrogels with desired properties by the variation of synthesis parameters such as monomers ratio, crosslinking agent content and synthesis method. The conventional heating is widely applied in preparation of those hydrogels, but this process takes a significant energy and time consumption [11,12]. In order to make process more economical and environmentally friendly, principles of microwave chemistry are implemented in preparation of hydrogels. Synthesis in microwave reactor has some advantages over the conventional ovens: reduction of synthesis time, lower energy consumption, performing the reaction in ambient conditions obtaining a high yield of reaction product [13]. Due to their intelligent nature, this kind of soft materials have potential applications as sensors [14], flocculants [15], drug delivery vehicles [16]. In order to consider the possibilities of microwave synthesis for preparation of intelligent hydrogels based on acrylic acid and acrylamide for different applications, the properties of microwave synthesized hydrogels should be investigated. This work aims to provide information about swelling, mechanical and thermal properties of microwave synthesized poly (Aam-co-Aac) hydrogels.

2. Experimental part

2.1. Materials

Acrylic acid (Aac), acrylamide (Aam) and N,N'-Methylenebisacrylamide (MBAM) were procured from Sigma-Aldrich, Co. St. Louis, MO USA. N,N,N',N'-Tetramethylethylenediamine (TEMED) and ammonium persulfate (PPS) were supplied from Fisher Scientific and used without further purification. Distilled water was used as reaction medium. Swelling measurements were carried out in citric (pH 3) and borate (pH 10) buffer solution (Alfapanon, Bački Petrovac, Serbia).

2.2 Methods

2.2.1 Synthesis of hydrogels

Hydrogels were prepared by free-radical polymerization in microwave reactor, using redox initiator-accelerator system.

Monomers, Aam and Aac, in different mass feed ratios (100/0, 80/20, 50/50, 10/90) were added in glass vessels together with crosslinking agent MBAM (1% per monomers mass). After addition of aqueous solution of initiator and accelerator and homogenization of all components, simultaneous polymerization and crosslinking were carried out in microwave field, at frequency of 2.45 GHz, in duration of 2 minutes.

2.2.2 Characterization of hydrogels

The spectroscopy analysis of dry hydrogels were performed using the Fourier transform infrared spectroscopy (FTIR spectrophotometer Bomem Hartmann & Braun MB-series). The FTIR spectra were recorded in the range of 4000–400 cm^{-1} , using KBr pellets for the samples preparation.

Swelling measurements were performed in buffer solutions, at pH 3 and pH 10 at ambient temperature. Completely dried pre-weighed hydrogel samples were immersed in appropriate buffer. The swollen gels were taken out in regular time intervals (after 15 min., 30 min., 1h, 2h, 3 h, 6 h, 12 h, 24 h), gently blotted, weighed, and then placed in the same bath. The swelling degree was determined using the following expression:

$$\text{Swelling degree (\%)} = \frac{\text{Mass in different time intervals} - \text{Initial mass}}{\text{Initial mass}} \times 100 \quad (1)$$

Dynamic mechanical properties of microwave synthesized hydrogels were studied using a Haake Mars rheometer. Hydrogels were equilibrated in distilled water before were subjected to the rheological measurements. Stress sweeping test was conducted at 23 ± 0.1 °C, using the plate-plate geometry ($d = 35$ mm). The values of storage (G') and loss modulus (G'') were measured in function of applied oscillatory stress, at constant frequency.

Thermal behaviour of obtained xerogels were investigated using a differential scanning calorimetry (DSC). Thermograms were recorded by heating of samples from 25 to 250 °C, at rate of 10 °C/min, under constant purging of nitrogen.

3. Results and discussion

As results of microwave synthesis, xerogels with expanded structure were obtained. Expanded structure originates from water evaporation.

Fig. 1 shows the FTIR spectra of pure poly (Aam) and copolymer poly (Aam-co-Aac) hydrogels with monomers ratio 80/20, 50/50, 10/90. Absorption peak at 3445-3450 and 3220-3227 cm^{-1} are attributed to asymmetrical and symmetrical stretching vibration of $-\text{NH}_2$ group and $-\text{OH}$ group in copolymer hydrogels. Asymmetrical and symmetrical stretchings of C-H are appeared as absorption bands at 2937-2865 cm^{-1} . Carbonyl group ($\text{C}=\text{O}$) as part of carboxyl group give an absorption peak at 1733-1700 cm^{-1} and $\text{C}=\text{O}$ group as part of amide bond gives a peak at 1683-1662 cm^{-1} . Peak at 1601-1560 cm^{-1} corresponds to the stretching of COO^- group in copolymer hydrogels.

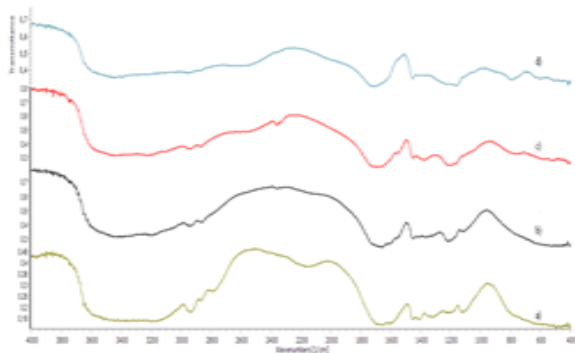


Fig. 1. FTIR spectra of the poly (Aam) hydrogel (a) and poly (Aam-co-Aac) hydrogels, respectively, 80/20 (b), 50/50 (c) and 10/90 (d).

The investigation of swelling properties in mediums with different pH values should have demonstrated the intelligent nature of these materials, regulated by their chemical composition, i.e. environmental pH relative to the pK_a of carboxylic and pK_b of amino groups. In acidic medium (pH 3), water uptake increases with increase in acrylamide amount in hydrogel composition (Fig. 2). The greater amount of Aam units in hydrogel composition signifies a higher concentration of amine groups those are in protonated form below their pK_b value (around 8.65). Positive charged groups repel each other, contributing to the greater swelling capacity. Therefore, the greatest value of equilibrium swelling degree is observed for pure poly (Aam) hydrogel (606 %).

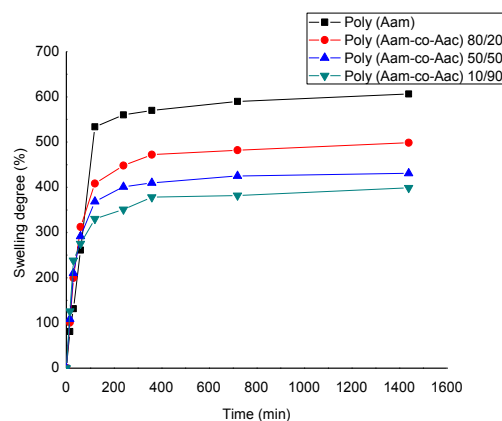


Fig. 2. Swelling behavior of poly (Aam-co-Aac) hydrogels in acidic medium (pH 3).

In alkaline medium (pH 10), hydrogels demonstrate inverse swelling pattern (Fig. 3). Water uptake increases with increasing in acrylic acid content in hydrogel composition. Carboxylic group, originated from Aac units, are in anionic form above pK_a value (around 4.5). Electrostatic repulsion between negatively charged ions leads to the greater water uptake. In opposite of swelling behaviour in acidic medium, in alkaline medium the greatest value of equilibrium swelling degree is observed for poly (Aam-co-Aac) hydrogel 10/90 (3811 %).

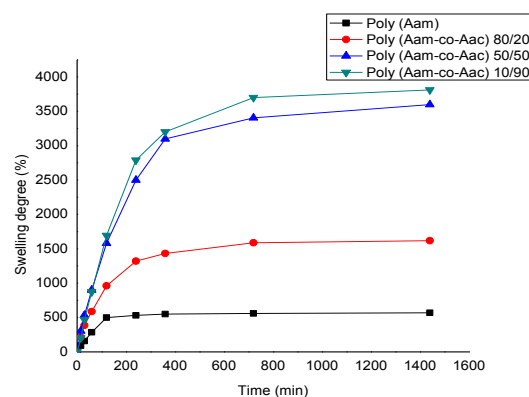


Fig. 3. Swelling behavior of poly (Aam-co-Aac) hydrogels in alkaline medium (pH 10).

In order to obtain information about the mechanical properties of synthesized soft materials, the same were subjected to a shear stress. The results of oscillation shear stress measurements are shown in Fig.4. Hydrogel 50/50 has the highest G' values and maintains linearity of viscoelastic behaviour up to applied stress value of 8.6 kPa. That implies its greater strength in comparison to the other samples. The other three hydrogel samples demonstrate non-linearity at lower stress values. Hydrogel retains the structural integrity while the storage modulus is higher than the loss modulus. When the loss modulus becomes greater than storage modulus, microstructure of hydrogel collapses. For hydrogel 50/50, it was achieved at applied stress of 8.6 kPa. Hydrogel 10/90 was broken

down at 6.2 kPa, and the hydrogels with higher Aam content (80/20 and 100/0) were desintegrated under the 3.3 kPa.

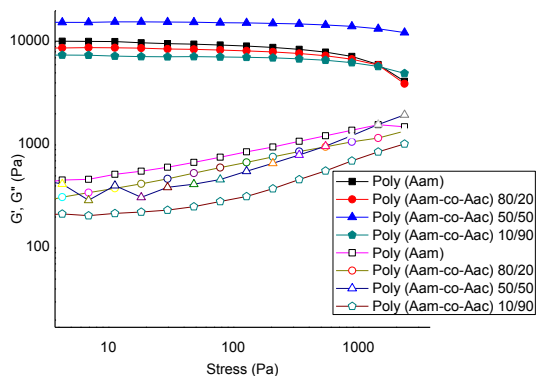


Fig. 4. Dynamic rheological spectra of poly (Aam-co-Aac) hydrogels.

DSC measurements were used to characterize the glass transition temperature values (T_g) of prepared hydrogels. Heating scans are shown in Fig. 5. Poly (Aam) hydrogel has the highest T_g value. Addition of Aac in hydrogel composition leads to the decrease in hydrogel rigidity, and consequently, decreasing in T_g value. Further increasing in Aac amount in hydrogel composition (above 50 wt%) leads to the decreasing in T_g value, due to the higher mobility of polymer chains.

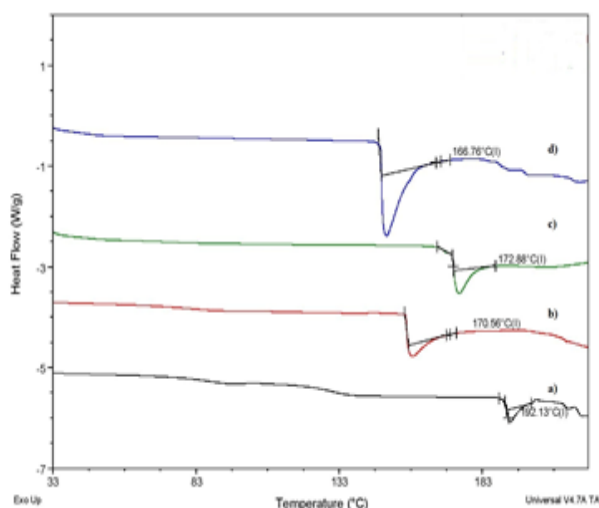


Fig. 5. DSC thermograms of poly (Aam-co-Aac) hydrogels.

4. Conclusion

Poly (Aam-co-Aac) hydrogels were synthesized in microwave reactor for 2 minutes, achieving the energy and time saving. The correlation between hydrogels composition and their “smart” nature were determined by performing of swelling, rheological and DSC measurements. Results of swelling measurements have confirmed the ability of projecting of hydrogels behaviour in different pH mediums by variation of synthesis parameters. Rheological and DSC study have confirmed mostly unpredictable nature of processes in microwave field.

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MODEL DESCRIPTION OF GRAIN BOUNDARY DIFFUSION PROCESSES IN MICROCRYSTALLINE SOLID SYSTEMS

МОДЕЛЬНОЕ ОПИСАНИЕ ПРОЦЕССОВ ЗЕРНОГРАНИЧНОЙ ДИФФУЗИИ В МИКРОКРИСТАЛЛИЧЕСКИХ ТВЕРДОФАЗНЫХ СИСТЕМАХ

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Abstract: The simple model of grain and phase boundaries diffusion into polycrystalline solid system with micro grain dimensions is proposed. There are considered different types of diffusion regimes which are realized by definite correlations between volume and grain boundary diffusion lengths and average grain sizes.

Keywords: DIFFUSION COEFFICIENT, MODEL, FISHER MODEL/

1. Introduction

Let us consider the process of propagation of diffusing atoms in a solid polycrystalline metal system. The diffusion at relatively low temperatures is of particular interest under the circumstances where the bulk diffusion coefficient is small, and most of the diffusion flow is carried along interfaces (grain boundaries) and linear lattice defects. If we are dealing with a microcrystalline system, i.e. if the average grain size d is not more than one micrometer, then the grain boundaries (and also the interphase boundaries in a multiphase metal system) and the triple junctions must be considered as accelerated paths of low-temperature diffusion. It has been well-established that at temperatures below $0.7T_m$ (T_m stands for the melting temperature of the system being studied) the grain boundary self-diffusion [1] and hetero-diffusion [2] coefficients are 10^3 – 10^5 times bigger than the bulk diffusion coefficients. It is shown in [3] that at even lower temperatures ($T \approx 0.55 \div 0.6T_m$) the diffusion penetration rate through triple junctions is over a thousand times higher than the diffusion rate along grain boundaries.

Let us choose the following conditions for description of a low-temperature diffusion process in a polycrystalline solid. Suppose the temperature (and the observation time) corresponds to the diffusion path of bulk diffusion $L_V = 2 (D_V t)^{1/2}$ (D_V is the bulk diffusion coefficient) which does not exceed the width of the grain boundaries – δ . This equates to the C mode of the grain boundary diffusion according to the Harrison classification [4], which means that bulk diffusion can be disregarded in the total balance of diffusion flows. Additionally, let us consider that at the given external conditions $D_T \gg D_B$, D_B – diffusion coefficient along the grain boundaries (its value is the same for all grain boundaries), D_T – diffusion coefficient along triple boundary junctions (its value is also the same for all triple junctions). In such a way, the advance diffusion of diffusing atoms occurs along triple junctions with substance outflow to the grain boundaries; the diffusion from grain boundaries to the grain bulk is not considered. Fig. 1 shows a simple scheme of a network of triple junctions which are parallel to each other in two orthogonal directions – along the y and x axes.

2. Problem discussion

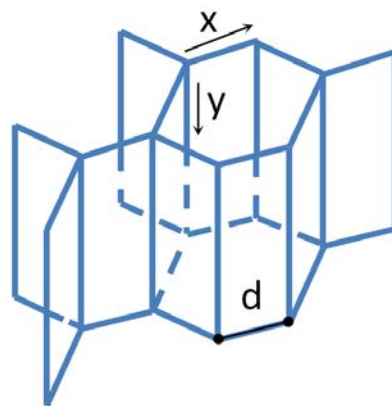


Figure 1 - Triple junctions network in the polycrystalline solid-state system;

axes x - directions of grain boundaries that spreading from each triple junction (y axes) in a perpendicular plane

The distances between the lines of triple junctions parallel to the y axis are equal to d ; let us use the value of d as an estimation of the average grain size in the sample. The source of the diffusing substance is located on the sample's surface ($y = 0$) and has a constant concentration c_0 . The diffusion flow along triple junctions is directed along the y axis. The high transfer rate along triple junctions and the ratio of grain size d to the sample size l ($d \ll l$), allows us to ignore redistribution of the diffusing substance between triple junctions that are directed from the diffusion source into the sample depth (along the y axis) in transverse directions perpendicular to the y axis. It can be assumed that a single diffusion front exists along triple junctions whose distance from the source surface is determined by the diffusion path along triple junctions – L_T . The triple junction inside each grain layer along which the diffusing substance spreads is the diffusion source for the three grain boundaries "belonging" to this junction. Meanwhile, the sources of the diffusing substance for each of these three boundaries are two adjacent triple junctions (Fig. 2).

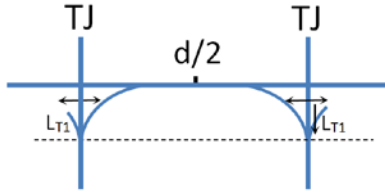


Figure 2 – The spread of diffusing atoms in nearby triple junctions and grain boundaries

According to the proposed scheme, the model of the diffusion process can be represented as follows:

$$\frac{\partial c_T}{\partial t} = D_T \frac{\partial^2 c_T}{\partial y^2} + \frac{3}{\delta} D_B \frac{\partial c_B}{\partial x} \Big|_{x=\pm \frac{\delta}{2}} \quad (1)$$

$$\frac{\partial c_B}{\partial t} = D_B \frac{\partial^2 c_B}{\partial x^2} \quad (2)$$

where C_T and C_B – the concentration of the diffusing substance in the triple junction (TJ) and the grain boundary (GB) respectively. This model is appropriate for describing self-diffusion. It can however be used for heterodiffusion as well, assuming that the diffusing substance distribution coefficient between TJ and GB is equal to 1.

This model is an extension of the Fisher model [5] for grain boundary diffusion. Depending on the ratio of two parameters (the grain boundary diffusion path L_B and the average grain size d) different variants of considering this diffusions problem are possible.

3. Objective and research methodologies

Variant 1.

$L_B/d \ll 1$ – a diffusion model along individual independent TJ with substance outflow to GB.

It can be assumed in this variant that the grain boundary diffusion path is so much less than the grain size that the concentration in GB in the middle of the distance between TJs falls to zero – $c_B(x = d/2, y, t) = 0$. The initial and boundary conditions will then be as follows: $c_B(x, y, t = 0) = 0$, $c_B(x = \pm \delta/2, y, t) = c_T$. If, following Fisher, we assume that $\pm \delta/2 \rightarrow 0$, then the concentration in GB is determined by the equation (2)

$$c_B(x, y, t) = c_T(y, t) \operatorname{erfc}(x/2(D_B t)^{1/2}) \quad (3)$$

The expression for concentration in each TJ can be obtained from the equation (1); in a quasi-stationary case, it will take the form

$$c_T(y, t) = c_0 \exp\left[-\frac{y}{L_{T_1}}\right]. \quad (4)$$

where the diffusion path along the triple junction, or, equivalently, the average position of the diffusion front depth along individual TJs, is described by the expression

$$L_{T_1} = \left(\frac{D_T \delta \sqrt{\pi t}}{3\sqrt{D_B}}\right)^{1/2}. \quad (5)$$

Variant 2

$L_B/d > 1/2$ – a diffusion model in a single system of connected triple junctions and grain boundaries.

The diffusion flows in this option from the adjacent TJs to GB collide and overlap. The solution of equation (2) for the diffusion in GB corresponds to the solution of the problem of diffusion in a plate, and has the form

$$c_B(x, y, t) = c_T(y, t) \left(1 - \frac{4}{\pi} \exp(-\lambda) \sin \frac{\pi x}{d}\right) \quad (6)$$

$$\text{where } \lambda = \frac{\pi^2 D_B t}{d^2}$$

The solution of equation (1) in a quasi-stationary approximation gives an expression similar to the equation (4)

$$c_T(y, t) = c_0 \exp\left[-\frac{y}{L_{T_2}}\right], \quad (7)$$

however, the diffusion path (the diffusion front position in the system of connected TJs) L_{T_2} is different from L_{T_1}

$$L_{T_2} = \left(\frac{D_T \delta d}{12 D_B} e^\lambda\right)^{1/2} \quad (8)$$

The depth to which the diffusing substance penetrates along the system of connected TJs depends not only on TJ diffusive permeability (D_T) and GB diffusive permeability (D_B), but on the average grain size d in the sample. According to the equation (8), the distance of the diffusion front in the connected TJ system from the outer surface which is the diffusion process source in a polycrystalline sample increases with decreasing d .

This variant has another peculiarity. Isoconcentration lines in each GB fall from TJs to the middle distance between TJs, i.e. at $x = d/2$ (see Fig. 3).

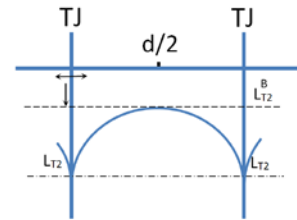


Figure 3 – The position of the diffusion fronts in triple junctions and grain boundaries in the related triple junctions model;

- - diffusion front along the grain boundaries;
- .-.- - diffusion front along the triple junctions.

When $x = d/2$, the concentration in GB is minimal. Using the equations (6, 7) it is possible to find the distance from the outer surface to the concentration minimum in GB, provided that the isoconcentration line corresponds to the concentration equal to the concentration in TJ at the depth L_{T_2} (i.e. it corresponds to the concentration in the diffusion front in the connected TJ system). Let us denote this distance $L_{T_2}^B$, which means that this is the diffusion path in GB (the superscript), formed due to advance diffusion along TJ (the subscript), which are the sources of filling GB with the diffusing substance. Its value can be determined by the formula

$$L_{T_2}^B = L_{T_2} \left[1 + \ln \left(1 - \frac{4}{\pi} e^{-\lambda} \right) \right] \quad (9)$$

The diffusion path $L_{T_2}^B$, which has the same value for the considered external conditions in all GB of the sample, means the diffusion front along GB. With decreasing average grain size, the distance between the diffusion front along TJ and the diffusion front along GB diminishes (see Fig. 4).

In order to demonstrate the dependence of the penetration depth of the substance diffusing into a polycrystalline solid on grain size, let us consider an example of low-temperature diffusion in a real binary system. Let us choose the Al-Zn system for this purpose, for which the bulk and grain boundary diffusion coefficients of zinc in aluminum are well known over a broad temperature range; and the value of the coefficient of zinc diffusion along the triple grain junction in a polycrystalline aluminum sample has been experimentally determined [3].

4. Conclusion

For calculation of zinc penetration depth along triple junctions L_{T_2} and along grain boundaries $L_{T_2}^B$, a temperature should be chosen that corresponds to an almost total absence of bulk diffusion, i.e. to the C mode of grain boundary diffusion according to Harrison. According to the diffusion data in the literature, an estimation of the bulk diffusion path of zinc in aluminum at 50 °C during 10 minutes gives $L_V = 4 \cdot 10^{-11} \text{ m}$ (0.04 nm), which corresponds to the C mode. The grain boundary diffusion coefficient at this temperature is $D_V = 1.66 \cdot 10^{-14} \text{ m}^2/\text{s}$, and the grain boundary diffusion path is $L_B = 6.3 \cdot 10^{-6} \text{ m}$ (6.3 μm). Let us assume that the D_T/D_B ratio in this case is not less than 10^4 according to [6]. The GB thickness and transverse TJ size are taken to be $5 \cdot 10^{-10} \text{ m}$. On the basis of these numerical data and using the formulas (8, 9), let us calculate L_{T_2} and $L_{T_2}^B$ for the average grain size from 10 to 2 μm. The calculation data are presented in the table and in the chart (Fig. 4).

Table 1. Zinc penetration depth along TJ and GB in polycrystalline aluminum depending on the grain size

d, μm	10	8	6	5	4	3	2
L_{T_2} , μm	5.48	6.28	8.21	10.42	15.29	30.22	128.4
$L_{T_2}^B$, μm	1.96	4.26	7.49	10.15	15.25	30.22	128.4

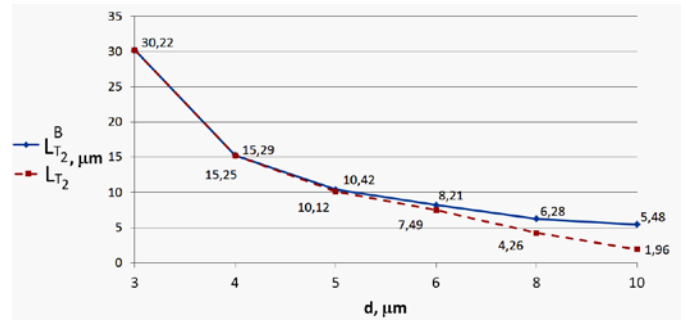


Figure 4 – Zn diffusion depth in polycrystalline Al depending on the average grain size d

— $L_{T_2}^B$ - diffusion depth along the triple junctions;
 - - L_{T_2} - diffusion depth along the grain boundaries.

Therefore, if the grain size in the polycrystalline solid is comparable with the diffusion path along GB, two diffusion fronts are formed in the sample with diffusing substance propagation. The first is the diffusion front along TJ, the second – the diffusion front along GB, which is also formed due to a rapid transfer of the substance along TJs. When decreasing grain size, the penetration depth along TJ and GB increases (L_{T_2} and $L_{T_2}^B$ increase), and both fronts converge. This means that the total depth of the diffusing substance penetration into a sample increases with decreasing average grain size (at constant external conditions). At relatively low temperatures, a small-grained material becomes more permeable to diffusion than a large-grained material. A diffusing substance penetrates into it to a greater depth, and the material is saturated more.

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DEPENDENCES OF PHASE TRANSITIONS TEMPERATURES OF PEROVSKITES ABX_3 ($X = O$ or F) UPON THE INTERATOMIC A-X BOND STRAINS

ЗАВИСИМОСТИ ТЕМПЕРАТУР ФАЗОВЫХ ПЕРЕХОДОВ ПЕРОВСКИТОВ ABX_3 ($X = O$ или F) ОТ НАПРЯЖЁННОСТЕЙ МЕЖАТОМНЫХ СВЯЗЕЙ А-Х

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Abstract. The ferro-, antiferroelectric and rotational phase transitions of known binary perovskite structure oxides (ABO_3) and fluorites (ABF_3) have been considered. Some correlations between their phase transition temperature values, on the one hand, and the interatomic bond A-X ($X = O$ or F) strain values, on the other hand, have been constructed. It has been established that the known perovskite structure binary oxides and fluorites with different phase transition nature, caused of a lot of their composition and structure factors, are conditioned, among another, by the interatomic bond A-X strains in their structure.

KEYWORDS: OXIDES, FLUORITES, PEROVSKITE STRUCTURE, BOND STRAINS, PHASE TRANSITION TEMPERATURE, FERROELECTRICS, ANTIFERROELECTRICS, POTENTIAL TRANSITION

1. Introduction

Solid state binary perovskite structure oxides (PSO) and fluorites (PSF) which compositions are described by the general ABX_3 formula, where $X = O$ or F , have been intensively synthesized and studied and study for more than 60 years [1-5], because some of them undergo structural phase transitions (PT) of different nature at appointed temperatures. Those are ferroelectric (FE) phase transitions, at which polar phases appear in the substance; antiferroelectric (AFE) PT, at which antipolar phases appear as well as ϕ - and ψ -type rotational, R, nonferroelectric ones at which different transformations of the octahedral frame of crystal lattice have place. As effect of the structural PT symmetry O_h^1 of preceding phase reduces abruptly into a lower symmetry and, as rule, transforms to any of its subgroups. Ferroelectrics and their solid solutions are basic of the active functional materials for electronics, and their PTs temperature values play an important role. In this connection, understanding why a compound is ferro- or antiferroelectric or undergoes rotational phase transitions and what its temperatures can depend on is of great theoretical interest as well as has practical implications for directed search of new compounds and materials on its basis with the certain structure and properties.

Is there a common feature of the binary PSO and PSF structure that can determine their PT nature and their temperature values? What a feature is necessary to classify their PTs? The theory of ferroelectricity tries different concepts, values or parameters for this role. They are used to construct some qualitative and quantitative correlations between the PT nature and temperature values, on the one hand, and these parameters, on the other hand. Some of them can be determined only experimentally, others - both experimentally and calculated *a priori*. Why are there no ferroelectric or antiferroelectric phase transitions in fluorites, while there are no symmetric constraints for them? Can polar or antipolar phases appear in those compounds in principle? Why do take place similar rotational phase transitions in both the PSO and the PSF? The aim of this work is to answer the above and other questions using the proposed the interatomic bonds A-O strains, δ_{AO} , or A-F, δ_{AF} , calculated using the perovskite structure quasi-elastic model proposed by Sakhnenko VP in 1972 [6] and to construct some correlations between these quantities, on the one hand, and corresponding PT temperatures, on the other hand.

2. Model and the interatomic bond A-X strain determination

Review briefly the unstrained cation-anion bonds elastic model or quasi-elastic perovskite cell model [1, 6-10]. In its creation, analysis and use participated author too. The internal energy of a crystal is modeled as the elastic energy of deformable cation-anion bonds in perovskite structure. The main assumption of the model is that for any cation-anion bond one can introduce an equilibrium bond length – the length of an unstrained bond A-X or B-X, and their stiffness coefficients. These parameters are assumed to be constants for such cation-anion pairs in every compound ABX_3 belonging to the same structural type.

In the case of a binary perovskite with chemical formula ABX_3 , taking into account 12 A-X and six B-X bonds in the reduced cubic perovskite cell one can write the elastic energy as

$$(1) \quad U = 6k_{AX} \left(\frac{a}{\sqrt{2}} - L_{AX}^0 \right)^2 + 3k_{BX} \left(\frac{a}{2} - L_{BX}^0 \right)^2,$$

where a is the reduced cubic cell parameter corresponding to one ABX_3 formula unit of a usual slightly distorted perovskite cell, L_{AO}^0 and L_{BO}^0 are unstrained bond lengths of the A-X and B-X pairs, and k_{AX} and k_{BX} are their respective stiffness coefficients. In the perovskite compounds the interatomic distances can differ substantially from the respective lengths of the unstrained bonds. According to our estimates, their difference for A-X bond can be up to 25%. Therefore, it is assumed that the equilibrium state corresponds to the minimum of the elastic energy (1).

The stiffness coefficients k_{AX} and k_{BX} can be estimated from the generalization of empirical relations found by Gordy [11] in 1946 from the analysis of molecules, which for the case of perovskites can be simplified to

$$(2) \quad k_{AX} = \frac{n_A}{4} \gamma; \quad k_{BX} = n_B \gamma,$$

where n_A and n_B are valences of the ions A and B, respectively, and γ is a constant. By minimization of the energy U given by equation (1), we obtain the following relation for the reduced lattice constant of the cubic ABO_3 perovskite unit cell:

$$(3) \quad a = \frac{4\sqrt{2}k_{AX}L_{AX}^0 + 2k_{BX}L_{BX}^0}{4k_{AX} + k_{BX}}.$$

Unstrained elastic bond lengths for many chemical elements frequently encountered in perovskite compounds were calculated and are given in the supporting information to this work.

Despite the seeming simplicity of the reviewed model, it allows the prediction of the reduced cubic lattice constants of perovskites with an accuracy of better than 1 %. Another striking conclusion that can be drawn from the model is the equation

$$(4) a_1 + a_4 = a_2 + a_3$$

between the reduced cubic lattice constants a_1 , a_2 , a_3 and a_4 of the perovskite-like compounds with the chemical formulae ABX_3 , $A'BX_3$, $AB'X_3$ and $A'B'X_3$, respectively, where A , A' and B , B' are pairs of cations with equal valences, and X is oxygen or a halogen. As shown in papers [7, 10] the relation (4) holds for more than 50 analyzed sets of perovskites to accuracy better than 1%. This striking relation, who holds for the lattice parameters of completely different perovskites, justifies assumption used in the model.

Substituting in (3) the values k_{AX} and k_{BX} (2) through the valences of the atoms A and B n_A and n_B , we obtain a formula for determining the average parameter $\alpha_{exp} = \sqrt[3]{V_{cell}}$ of the reduced perovskite cell, which can be slightly distorted, that is, differ from the ideal cubic one:

$$(4) \alpha_{calc} = \frac{\sqrt{2n_A L_{AX}^0 + 2n_B L_{BX}^0}}{n_A + n_B}.$$

Expression (4) will be used later to calculate the interatomic bond A-X strains.

Table 1. Phase transition nature and temperatures and the calculated interatomic bonds A-X strains in oxides and fluorites

PT type, composition, bond A-X and B-X strains ($\delta_{A-X}/\delta_{B-X}$), % and T_{PT} , K			R PT: T_{PT} and final phase	
FE ¹⁾ and *FE ²⁾	AFE ¹⁾ and *AFE	rotational PT, R PT	T_1 , K	G_1
KNbO₃ (-0.2/0.0) $T_{PT} = 708$	NaNbO₃ (15/-2.5) $T_{PT} = 630$	NaNbO₃ (15/-2.5)	914	00 ψ
*KTaO ₃ (0.2/-0) $T_{PT} = 13$	CdTIO₃ (9.1/-4.0) $T_{PT} = 1223$	NaTaO₃ (15.4/-2.6)	903	00 ψ
*SrTiO ₃ (1.4/-0.7) $T_{PT} = 10$	*CdSnO ₃ (12.6/-5.3) $T_{PT} = 1073$	CaTiO₃ (6.2/-2.8)	1533	$\phi\phi\psi$
PbTiO₃ (-1.0/0.5) $T_{PT} = 763$	*CdHfO ₃ (13.8/-5.7) $T_{PT} = 1050$	SrZrO₃ (6.2/-2.8)	1440	00 ϕ
BaTiO₃ (-2.8/1.5) $T_{PT} = 403$	*PbSnO ₃ (2.0/-1.0) $T_{PT} = 400$	SmAlO₃ (-0.3/0.3)	2100	$\phi\phi\phi$
-	*PbHfO ₃ (3.0/-1.4) $T_{PT} = 490$	PrAlO₃ (-0.8/0.9)	1320	$\phi\phi\phi$
-	PbZrO₃ (3.6/-1.6) $T_{PT} = 505$	LaAlO₃ (-1.4/1.4)	770	$\phi\phi\phi$
-	-	NaMgF₃ (13.1/-5.4)	1170	$\phi\psi\phi$
-	-	KMnF₃ (7.0/-3.3)	185	00 ϕ
-	-	KCdF₃ (11.6/-4.8)	488	00 ψ
-	-	KCaF₃ (13.1/-5.6)	560	0 $\phi\psi$
-	-	TlCdF₃ (7.7/-3.5)	191	00 ϕ
-	-	RbCdF₃ (7.7/-3.5)	124	00 ϕ
-	-	RbCaF₃ (9.4/-4.1)	198	00 ϕ

The length of the strained interatomic bonds A-X or B-X differs, sometimes considerably, from their unstrained equilibrium length, and their relative strains can be determined by the formula:

$$(5) \delta_{AX} = \frac{L_{AX} - L_{AX}^0}{L_{AX}^0}, \delta_{BX} = \frac{L_{BX} - L_{BX}^0}{L_{BX}^0},$$

where

$$(6) L_{AX} = \alpha_{calc} / \sqrt{2} \text{ and } L_{BX} = \alpha_{calc} / 2.$$

Expression (5) and (6) will be used to calculate (Table 1) the interatomic bonds A-X strains.

3. Separation of phase transitions of different nature from the interatomic bond A-X strain values

The considered binary oxides and fluorides having phase transitions of various natures together with the calculated interatomic bond strains are shown in Table 1. In its ¹⁾ -in boldface, the formulas of binary oxides and fluorites are identified, the strains of the interatomic bonds in them, the abbreviated names of the established nature of their phase transitions and the bonds A-X strains in binary oxides and fluorites values of their temperatures, while ²⁾ - in the usual font formulas – are written, the value of the interatomic bond strains in them, the abbreviated names of the assumed phase transitions nature and the values of their temperatures, which is also noted by the sign "*".

Таблица 2 - The intervals of calculated values (δ_{AX})_{calc} and (δ_{BX})_{calc} for binary PSO and PSF testing: ferro- (FE), anti-ferroelectric (AFE) and rotational (R) ϕ - and ψ -types PT and intervals of their experimental temperatures (T_{PT})_{exp}

PT nature	Intervals (δ_{AX}) _{calc} , % and PT temperatures (T_{PT}) _{exp} , K		Intervals (δ_{BX}) _p , % and PT temperatures (T_{PT}) _{exp} , K	
	from	up to	from	up to
Ferro- and antiferroelectric PT of PSO				
FE	$\delta_{AO} = -2.8$; $T_{PT} = 393$	$\delta_{AO} = -0.2$; $T_{PT} = 763$	$\delta_{BO} = 0.0$; $T_{PT} = 763$	$\delta_{BO} = 1.5$; $T_{PT} = 393$
AFE	$\delta_{AO} = 1.8$; $T_{PT} = 400$	$\delta_{AO} = 15.0$; $T_{PT} = 638$	$\delta_{BO} = -5.7$; $T_{PT} = 1070$	$\delta_{BO} = -1.0$; $T_{PT} = 400$
Rotational PT of ϕ- и ψ-types of PSO				
R PT	$\delta_{AO} = -1.6$; $T_{PT} = 700$	$\delta_{AO} = 6.2$; $T_{PT} = 1440$	$\delta_{BO} = -2.8$; $T_{PT} = 1440$	$\delta_{BO} = 1.4$; $T_{PT} = 700$
ϕ -type	$\delta_{AO} = 6.2$; $T_{PT} = 1533$	$\delta_{AO} = 15.4$; $T_{PT} = 914$	$\delta_{BO} = -2.8$; $T_{PT} = 914$	$\delta_{BO} = -2.5$; $T_{PT} = 1533$
ψ -type				
Rotational PT of ϕ- и ψ-types of PSF				
R PT	$\delta_{AF} = 7.7$; $T_{PT} = 124$	$\delta_{AF} = 9.4$; $T_{PT} = 198$	$\delta_{BF} = -4.1$; $T_{PT} = 198$	$\delta_{BF} = -3.3$; $T_{PT} = 124$
ϕ -type				
R PT	$\delta_{AF} = 11.6$; $T_{PT} = 488$	$\delta_{AF} = 13.1$; $T_{PT} = 560$	$\delta_{BF} = -5.6$; $T_{PT} = 560$	$\delta_{BF} = -4.8$; $T_{PT} = 488$
ψ -type				

In the structures of the majority of binary PSO, as in the structures of the binary PSF, bonds A-O or A-F are stretched ($\delta_{AO} > 0$ or $\delta_{AF} > 0$), and B-O or B-F bonds are compressed ($\delta_{BO} < 0$ or $\delta_{BF} < 0$), in comparison with the tightest packing of atoms. Nevertheless, several PSO, among which there are famous ferroelectrics KNbO₃, PbTiO₃ and BaTiO₃ (See Table 1), have compressed interatomic A-O bonds and, on the contrary, though slightly but stretched B-O bonds.

The calculated values are the intervals of variation of the computed δ_{AO} or δ_{AF} (Table 2) and the intervals of the experimental temperatures of the corresponding PTs of various nature for the PSO and the PSF, which are quite clearly separated from each other in the values δ_{AO} or δ_{AF} in the case of FE and AFE PT (Fig. 1), and on the generalized diagram the line of the polynomial trend of degree 6 most accurately describes this dependence. Nevertheless, it can be seen that the trend of degree 6 more accurately describes this dependence for AFE PT.

4. Correlations between the phase transition temperatures and the interatomic bond A-X strains

Several correlations on the diagrams (δ_{AO} , T_{PT}) or (δ_{AF} , T_{PT}) are constructed to determine how the nature of the observed PT of these compounds can be connected with their interatomic bond strain values. Taking into account the fairly clear separation of phase transitions in terms of δ_{AO} or δ_{AF} values it is established that, firstly, in the binary ferroelectric PSO structures (Fig.1) the interatomic A-O bonds are compressed i.e. $\delta_{AO} < 0$, in contrast to the always stretched interatomic bonds A-O in the structure of every PSF, i.e. $\delta_{AO} > 0$ [11]. Secondly, in the PSF the interatomic A-F bonds are stretched always and much stronger, and the B-F bonds are more compressed than in ferroelectric PSO, which possibly interfere with the appearance of ferroelectric properties in it. Is this not the answer to one of the posed in the introduction questions, in particular, about the reason for the absence of ferro- and antiferroelectric phase transitions in PSO? However, the sum of the dipole polarizabilities of atoms in each PSF composition are noticeably lower [12] than for any PSO, and, of course, lower, than for ferroelectric PSO, which can also be one more reason of the ferroelectric properties absence for PSF.

Third, in comparison with ferroelectric PSO, in virtual ferroelectrics KTaO_3 and SrTiO_3 the interatomic A-O bonds are already slightly stretched, i.e. $\delta_{AO} > 0$. Nevertheless, the introduction of other A or B atoms into the corresponding sublattices, for example, in the solid solutions of the systems $\text{KTaO}_3\text{-LiNbO}_3$ or $\text{KTaO}_3\text{-KNbO}_3$ [13-15], together with the inevitable decreasing of the average interatomic bond A-O strains led to the appearance of any ferroelectric properties. By values of its interatomic bond A-O strains its closer to AFE PSO section, which starts from PbSnO_3 (See Fig 1) and ends on NaNbO_3 , which has the most stretched interatomic bonds A-O ($\delta_{NaO} = 15\%$) among antiferroelectric PSO.

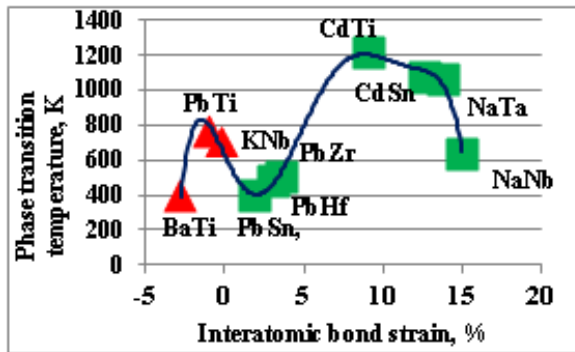


Fig.1. Correlation between the interatomic bond A-O strains in the PSO and the temperature of their FE and AFE phase transitions: FE - red triangles; AFE - green squares

Fourthly, for each δ_{AO} or δ_{AF} values individual interval of certain PT nature there is a maximum T_{PT} : in the ferroelectric PSO δ_{AO} interval - at the point PbTiO_3 equal to 763 K; in the antiferroelectric PSO δ_{AO} interval (See Fig. 1) - at the point CdTiO_3 equal to 1223 K. Fifthly, a situation with the dependences T_{PT} of different rotational phase transitions are more complicated (Fig. 2). With increasing δ_{AO} and/or δ_{AF} , the ϕ -type rotational PT temperatures increase almost precipitously and after a certain δ_{AO} real representatives on the narrow interval ends, as if forming a kind of automatically built-in by the program "virtual" (without representatives) dome in the temperature range, certainly above the melting points for such solid state substances. The maximum of this trend can shift to high temperatures up to ~ 9000 K. Temperature T_{PT} dependence for PSO with the rotational ϕ -type PT starts from the temperature LaAlO_3 $T_{PT} = 770$ K, closed to the maximum temperature for ferroelectrics PbTiO_3 with $T_{PT} = 763$ K, and ends on SmAlO_3 with the maximum among real such PSO $T_{PT} = 2100$ K. That above virtual dome is by its greatest middle part locates between the ferroelectric and antiferroelectric

intervals δ_{AO} (see Fig. 2) starting from $\delta_{AO} = -0.3\%$ for SmAlO_3 and ending on $\delta_{AO} = 6.0\%$ for SrZrO_3 on the decline of this dependence.

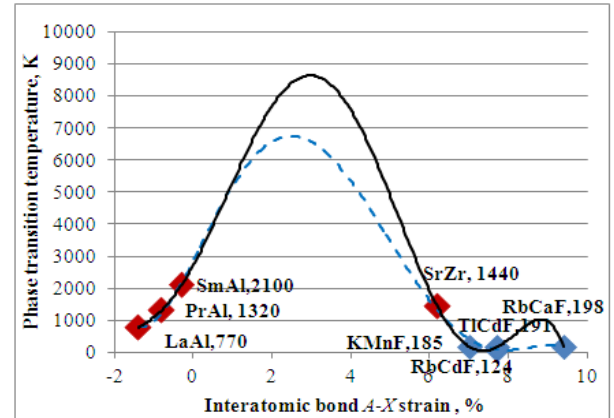


Fig. 2. Correlation between the PSO interatomic bond A-O and PSF A-F strains and the temperatures of their rotational phase transitions ϕ -type: T_{PT} of the PSO - dark red rhombuses; PT of the PSF - blue rhombuses; approximation by a polynomial trends of degree 5 - blue curve; of degree 6 - black one

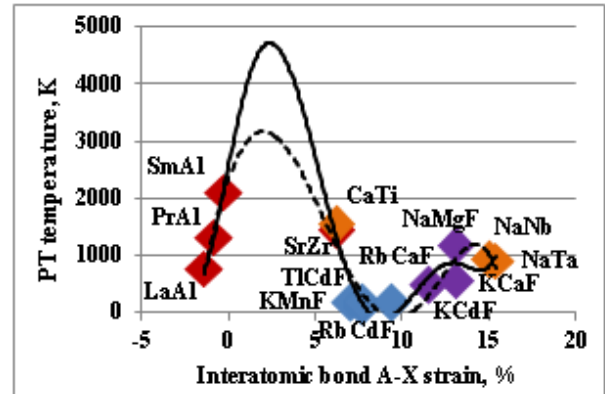


Fig. 3. Generalized correlation between the PSO interatomic bond A-O and PSF interatomic bond A-F strains, on the one hand, and the temperatures of their rotational phase transitions ϕ - and ψ -type PT: ϕ -type of the PSO - dark red and PT of the PSF - blue rhombuses; PT ψ -type of the PSF - purple rhombuses and PT of the PSO - orange rhombuses; PT ψ -type of the PSF - purple rhombuses and PT ψ -type of the PSO - orange rhombuses

In principle, in order to describe well the dependence of the T_{PT} of PSO rotational ϕ -type PTs as a δ_{AO} function, a polynomial trend of degree 2 is suitable. Constructed general dependences for PSO and PSF (See Fig. 2) are well approximated by polynomial trends of the fifth or sixth degree, where the author dared to combine the dependencies for PSO and PSF on two different intervals in general dependence. Sixthly, after the previous interval, no longer overlapping with its, but into the antiferroelectric PSO interval, the PSF rotational ϕ -type PT interval starts from $\delta_{AO} = 7.0\%$ for KMnF_3 and ends on $\delta_{AO} = 9.4\%$ for RbCaF_3 , which T_{PT} is very low in comparison with T_{PT} for antiferroelectric PSO: less than 200 K.

However, if in this diagram (See Fig. 2), devoted to the rotational ϕ -type PT, we add the T_{PT} temperatures of the rotational PTs of the ψ -type, both for the PSO and the PSF (Fig. 3) that above the virtual maximum will greatly decrease. Such construction with the combination of different FPs and different objects is completely justified because the R PTs of ψ -type are observed quite rarely both among the PSO and the PSF, although they are fairly well separated by the values of δ_{AX} . It turns out that these dependencies and the temperatures of their PTs are somehow interrelated, since they can be described by one common curve.

5. Conclusions

Thus, all binary PSO and PSF that undergo phase transitions of different nature can be separated by the values of their interatomic bond A-X strains. Phase transitions of every nature under consideration: the ferroelectric, antiferroelectric, and rotational ϕ - and ψ -types, are located on separate intervals of their interatomic bonds A-X strain values. At the same time, ferroelectrics are quite clearly separated from antiferroelectrics. The δ_{AX} intervals of ferroelectric PTs overlapped with rotational ϕ -type PTs for PSO are partially, as well as AF PTs for PSO with rotational ϕ - and ψ -types PT. Thus, the answer to the most important question posed in the Introduction was found: the structure general argument δ_{AO} was found and tested for all the considered binary PSO and PSF: interatomic bond A-X strains, which can be calculated *a priori* from a quasi-elastic perovskite type structure model. The same parameter can be proposed for other perovskite-like structures. Moreover, here it is clearly demonstrated not only that the temperatures of PTs, which are experimentally determined in various laboratories of the world and fixed in recognized monographs and reference books [1 - 5], depend on these values of interatomic bond strains, but also rather difficult. Nevertheless, one can assume their appearance.

It seems that the temperatures of PTs of different nature in the respective interval of δ_{AX} vary in one scenario: with increasing of the interatomic bond A-O or A-F strain values, to some extent, the of each nature PT temperature, T_{PT} , increases to a certain maximum, after which it decreases. When the A-O bond is strongly compressed, as, for example, in BaTiO_3 ($\delta_{AO} = -2.8\%$), the B-O bond is relatively small, but stretched, which, generally speaking, is not typical for this connection in the structures of the PSO. That is why, when the ferroelectrics BaTiO_3 was discovered, the "stretching" of the Ti-O bond in it was considered [2] as the cause of its FE state, which distinguished it not only from non-ferroelectric PSO, but also from other ferroelectrics with the perovskite structure. They talked [1 - 3] about some "freedom" for the Ti atom, which determines the nature of BaTiO_3 PT as FE PT. Nevertheless, as the stretching of B-O bonds from BaTiO_3 to PbTiO_3 decreases (see Fig. 1) and moreover, with decreasing contraction of the A-O bond, the temperature of its FE PT and even the value of the spontaneous polarization, P_s , that is one of the main ferroelectric state characteristics, is higher than their values for BaTiO_3 .

It seems that the cause of the FE state is just the contraction of the A-O bond, as in PbTiO_3 or KNbO_3 with higher temperatures of the FE PT, than for BaTiO_3 , rather than the stretching of the B-O bond, as was thought about BaTiO_3 . Moreover, the increasing of the interatomic bond A-O stretching in the future leads to the absence of ferroelectricity already in SrTiO_3 and KTaO_3 with the interatomic bonds A-O comparatively small strains and then the strain starting already from 2%, leads to the AFE PT in PbSnO_3 , PbHfO_3 , PbZrO_3 , et al. At some the A-O bond strain, its elasticity goes over a certain limit, after which the temperature of the AFE PT drops sharply. The shown separation of different nature phase transitions into separate intervals for binary perovskites of ABX_3 can be carried out for ternary and more complex perovskites, as well as representatives of other structural families.

Author want to finish the message with the prophetic words of Professor Fesenko EG, stated by him in the monograph [1] in a free translation of the author: "The study of regularities and connections is greatly facilitated by the simplicity of the structural type of perovskite, so we can expect that they will be successful and will form an important stage in the near future in the development of solid-state physics and crystal chemistry. This will make it possible not only to explain the physical properties of the PSO and to solve the problem of computational design and creation of new highly effective materials on the basis of PSO, but also to make important generalizations that go far beyond the family limits to the boundless "sea" of ion-covalent crystals. "

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EXPERIMENTAL DATA AND SIMULATION BY THE FINITE ELEMENT METHOD OF THE CYLINDRICAL STEEL SHAFT QUENCHING IN WATER

ЕКСПЕРИМЕНТАЛНИ ДАННИ И СИМУЛИРАНЕ ПО МЕТОД НА КРАЙНИТЕ ЕЛЕМЕНТИ НА ЗАКАЛЯВАНЕТО НА ЦИЛИНДРИЧЕН СТОМАНЕН ВАЛ ВЪВ ВОДА

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Abstract: In the present work, the process of water quenching of a steel cylindrical body imitating a stepped shaft is considered. The cooling function was determined experimentally, based on which the heat transfer coefficient was determined according to an existing methodology. The results obtained are used as input data for simulation using the finite element method. Results are obtained for the cooling functions at different points in two sections of the shaft. The results of the simulation are compared with the CCT curves and with the measured hardness at these points.

Keywords: STEEL C45, WATER QUENCHING, FINITE ELEMENT ANALYSIS, COOLING FUNCTION, HEAT TRANSFER COEFFICIENT

1. Introduction

Heat treatment is the most common and most effective method to altering the properties of metals and their alloys [1]. The most commonly thermally treated metal alloys are those of iron, and the most commonly used in the thermal process is quenching. A responsible transition (where more than 90% of the waste is obtained) when quenched is the cooling transition. The reason for this is that during cooling due to the large temperature gradient in the different points of the cooled object and the formation of the final structure and properties of the articles, conditions are created for the occurrence of large internal mechanical stresses. One way to reduce the risk of inadmissible strain or destruction due to an increase in stresses above the yield strength while at the same time achieving total quenching is the right choice of cooling environment and the conditions under which it works.

Appropriate modeling and simulation of different quenching cooling processes can provide reliable information about the temperature distribution of the volume of the objects under investigation as a function of the time directly related to the changes in structure occurring during the cooling process. Due to the flexibility of the method and the possibility of an easy and rapid change of the introduced data on the cooling characteristics of the environments used for quenching, it is possible to simulate different cooling conditions for short time and to choose those which guarantee the highest quality of the heat-treated products [2-7].

The choice of the boundary of the mathematical model is dictated by various considerations: choice of method of solving the mathematical task, knowledge of the physical properties of the volume consideration, knowledge of the specific boundary condition, etc. In this work, only the solid steel body is considered and for the definition of the mathematical model, it is necessary to know the heat transfer coefficient (HTC). It is possible to determine it by lumped-heat-capacity method or by inverse method [8].

The ABAQUS [9] commercial program for finite elements analysis has been chosen for use because it is possible to create custom subroutines.

2. Methodology of Experiment

In the work were used cylindrical test bodies imitating a stepped shaft – Fig. 1, The material of shaft is C45 steel (1.0503, EN 10083-2), and the chemical composition determined by quantum analysis is shown in Table 1.

Two test pieces were made, with the type K thermocouple (Chromel/Alumel) mounted in the geometric center of one. The test piece made in this way serves to obtain the cooling curves (T-t curves), recording and using LabVIEW software application for

data process. After obtaining the cooling curves, the calculation of HTC α is made using the equation:

$$\alpha = V \cdot G \cdot \frac{c_p}{(\Delta t \cdot F)}, \quad (1)$$

with dimensionality W/m^2K , where V is the cooling rate in $^{\circ}C/s$, G in kg is the mass, c_p in J/kg.K is the specific heat capacity, Δt in $^{\circ}C$ is the temperature difference between the heated body and the cooling fluid, and F in m^2 is the contact area.

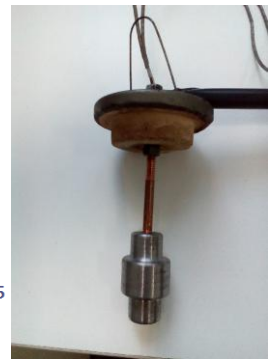
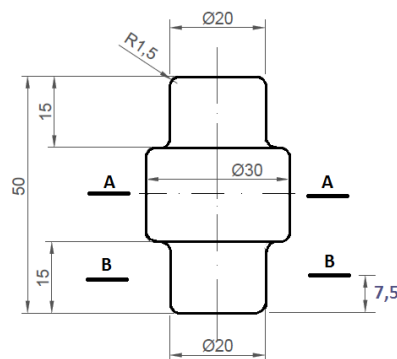


Fig. 1. Shape and dimensions of the quenched body

Table 1. Chemical composition of the quenched body

Element	C	Si	Mn	S	P
Contents %	0,46	0,35	0,71	0,041	0,04

As a cooling medium, tap water was used with an initial temperature of 15 $^{\circ}C$ and volume 1 liter.

The test body is heated to a temperature of 857 $^{\circ}C$ (temperature recommended for quenching of the used steel) in a laboratory furnace and oxidation medium and then transferred to the cooling bath. Three attempts were made, and after each attempt, the test body was cleaned with sandpaper. The recorded cooling curves are averaged and the results is used as the starting point for calculation of HTC.

The second sample is heat treated in a manner identical to that described above. After cooling for quenching, it is cut in the manner shown in Fig. 1. The determination of the hardness distribution in its volume was made after polishing the surfaces by the Vickers method with load of 10 kg. The results obtained for the hardness were converted to Rockwell hardness scale "C" (HRC).

Due to technical limitations, no cooling data has been taken of the surface of the body, but only at the central point.

3. Mathematical and numerical models

The quenching of steel in water is considered as a problem for transient heat transfer [10], in which using the temperature equilibrium condition and the Fourier law, the following equation is obtained:

$$\text{div}(\lambda \cdot \text{grad}(T)) + Q = V\rho\dot{U}. \quad (2)$$

In this equation, λ is a symmetric second-order conductivity tensor, T is a temperature, Q is an internal heat volumetric source, V is the volume of the body, ρ is the density, and $\dot{U}$ is the variation over time of the specific enthalpy.

The boundary conditions are described by the equations for the heat flux on the outer surface and the heat flux of the convection of the body, respectively:

$$q = q(\mathbf{x}, t), \quad (3a)$$

$$q = \alpha(T - T^0), \quad (3b)$$

where the vector $\mathbf{x}$ describes the position in time t , and T^0 is the temperature of the cooling fluid.

The initial condition is:

$$T(\mathbf{x}, t = 0) = 857^\circ \text{C}. \quad (4)$$

The solution of equation (2) under conditions (3a), (3b), and (4) was done using the finite element method [10]. Spatiol discretization is realized through standard Galerkin approach for energy balance:

$$\begin{aligned} \int_V \rho \dot{U} \delta T dV + \int_V \frac{\partial \delta T}{\partial \mathbf{x}} \cdot \lambda \cdot \frac{\partial T}{\partial \mathbf{x}} dV = \\ = \int_V \delta T r dV + \int_{S_q} \delta T q dS, \end{aligned} \quad (5)$$

In this equation δT is the variation of the temperature, satisfying the boundary condition in outer surface and the volume.

The body is discretized with finite elements with shape functions and functions of temperature:

$$T = N^n(\mathbf{x})T^n, \quad (6)$$

where n is the node number in discrete element, and N is the interpolating functions, dependent from the type of the finite element.

The integration of the time, τ , is done by equation:

$$\dot{U}_{\tau+\Delta\tau} = (U_{\tau+\Delta\tau} - U_\tau) / \Delta\tau. \quad (7)$$

4. Finite element model

A 3D geometrical model of the body was created in ABAQUS. The discretization is made with 20013 tetrahedral elements with one nod in the middle of the edges (typ DC3D10 in ABAQUS). This number of elements is enough for convergence according Draganov at all. [11].

The heat conductivity coefficient and the specific heat capacity are non-linear temperature functions set out in Table 2. For the density of the steel, a value of 7850 kg/m³ is adopted.

Table 2. Physical properties

Temperature, °C	300	400	600	800	1000
Specific heat capacity, J/kg.K	469	506	521	660	616
Conductivity, W/(m.K)	48	47	41	37	32

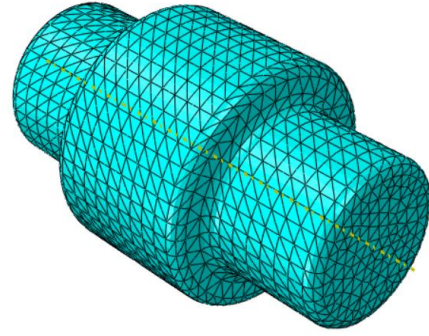


Fig. 2. Discretization

The initial temperature of the shaft is 857 °C. The temperature of the cooling fluid - T^0 , is 15 °C, and the HTC is a non-linear function of the temperature (time) and is tabled in 1000 steps, according to the experiment – Fig. 3.

5. Results and discussion

The cooling temperature obtained experimentally is replaced in equation (1) and the HTC function is obtained – Fig. 3 (red color, continuous curve) that applies to the central point of the shaft. In order to be transferred to the border of the body, a iterative procedure was performed. As a proximity criterion, the ratio between the temperature at the center point of the experiment and from the simulation was chosen. A subroutine was created for interpolation of the temperature and HTC values obtained experimentally in the simulation time points. The HTC determined in the manner described above is shown in Fig. 3 with a blue color and a broken line.

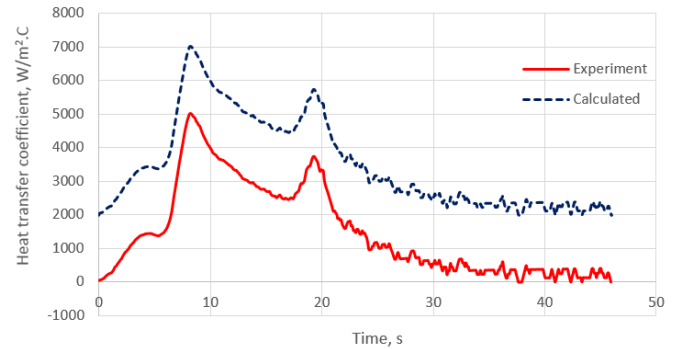


Fig. 3. Heat transfer coefficient

In the second iteration step, a satisfactory approximation was obtained, with the maximum difference between the temperature at the center point of the experiment and the simulation at temperature above 300 °C being 2.67%. In Fig. 4 is a diagram of the temperature distribution in 6.026 s.

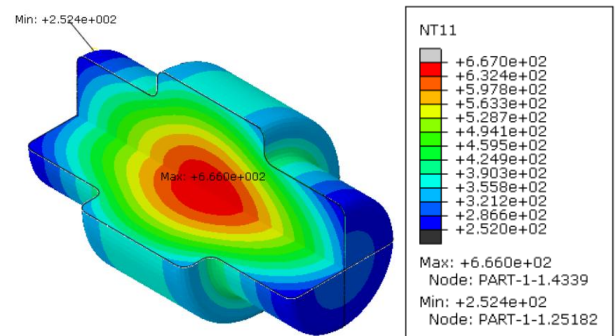


Fig. 4. Температурно поле в 6,026 s

In Fig. 5 shows the CCT diagram of steel 45 [12] with the cooling curves imposed on it at selected five points in sections A and B obtained after simulation. In the initial comparison of the obtained cooling curves with the thermokinetic diagram, there is a discrepancy between the fields in which they fall and the measured hardness results. For the correct positioning of the cooling curves relative to the conversion curves, the values for the time of curves obtained in the simulations must be multiplied by a factor of 0.5. The coefficient is established after determining the hardness at the selected points – Fig. 6, with 1 being the function of hardness in section B, with 2 – section A, and 3 – hardness in half-martensitic zone

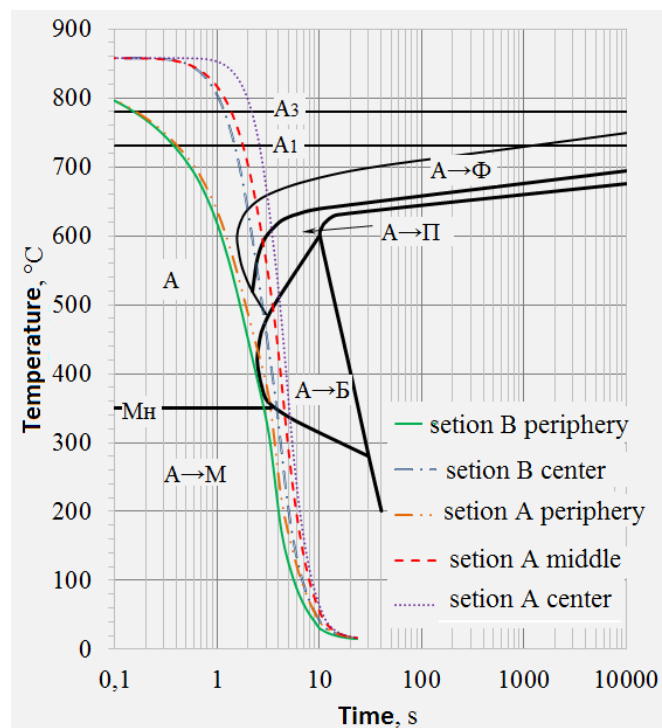


Fig. 5. Thermokinetic diagram for steel 45 and the location to the simulated cooling curves

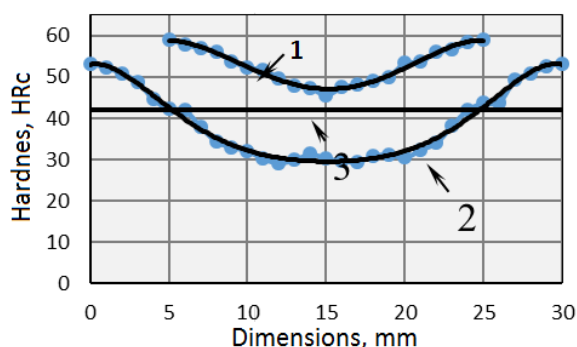


Fig. 6. Hardness

6. Conclusion

The hardness distribution found is logical due to the differences in the studied cross-sections. As can be seen from the figure 6, the cross section of 20 mm in diameter there is a total quenching and when the cross-section increases to 30 mm, the hardened structure (with a hardness greater than HRc 42) is at a depth of 5.5 mm.

The numerical simulation by finite element method based on the transfer of the HTC from central point to the shaft boundary gives a quality plausible result in terms of the expected stiffness that will allow the predictability of the quenching depth in bodies with similar configurations.

The reasons for inconsistency of the experimental cooling curve either the measured hardness may be many, but in this case it is most likely due to poor contact of the thermocouple with the test body. Once the coefficient is established, the resulting simulated cooling curves show a very good match between the expected and hardnesses obtained and can be used to predict the stiffness of bodies with similar shape and size made of different grades of steel for which a thermodynamic breakage diagram of the supercooled austenite.

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ELECTRON-BEAM REMELTING OF Ni-Cr-Al-Y ALLOYS FOR MANUFACTURING OF CATHODES FOR ION-PLASMA COATING

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Abstract: An experimental electron-beam technology for obtaining tube billets from NiCrAlY alloys used as cathodes for the deposition of heat-resistant coatings by the ion-plasma method has been developed. It is established that coatings applied to gas turbine blades of aircraft engines using cathodes of electron beam melting meet the requirements of Motor-Sich JSC TU for this type of products.

Keywords: ELECTRON-BEAM MELTING, HEAT-RESISTANT ALLOYS, COATINGS ON GAS TURBINE BLADES, ION-PLASMA COATING.

1. Introduction

NiCrAlY materials are used to protect high-temperature nickel-based heat-resistant alloys from high-temperature oxidation, in particular, they are widely used as an internal bonding metal layer in thermal barrier coatings on gas turbine engine (GTE) blades, performing not only protective functions, but also reducing the difference in coefficient of thermal expansion between base and ceramic outer layer. Rigid conditions for the operation of gas turbine blades, associated with the multiple change of the thermal regime under the influence of gas streams saturated with combustion products of the fuel, give rise to special requirements for the quality of coatings on the base material. The search for optimal technologies for the formation of a qualitative layer applied to the blade material, begun as early as the late 1980s. last century, showed the high efficiency of the ion-plasma method with the use of cathode-cast tube castings made of high-purity NiCrAlY alloys [VIAM RF, is available by <https://viam.ru/review/2725>].

In most cases cast billets are subjected to rolling, drawing, mechanical and other types of processing for the subsequent manufacture of tubular products. Naturally, the use of multiple technological redistribution leads to a significant increase in the cost of products, and therefore the development of technologies that allow to obtain blanks with subsequent minimal mechanical, thermal and other treatments remains the main problem of their production. System studies on the development of technologies for the production of tube billets from copper, zirconium, titanium and other alloys are held at the Paton Institute of Electric Welding, NAS of Ukraine, Physical and Technological Institute of Metals and Alloys, International Campain "ANTARES", etc. [1-3].

A promising direction in the development of this technology is the use of electron beam melting (EBM), widely used to produce ingots (slabs) of metals and high purity alloys [4]. However, obtaining high-quality pipe billets from heat-resistant nickel-base alloys is a rather complicated technical problem due to the substantial difference in the physico-chemical characteristics of the alloy components and technological difficulties in obtaining hollow articles from these alloys [5, 6].

Therefore, at the initial stage of the introduction of ion-plasma equipment in 1981 (the MAP-1 unit with a vacuum-arc evaporation method - the development of the Institute of Aviation Materials (Russian Federation), ingots of the appropriate alloys were used for the production of cathodes, which were subjected to drilling and subsequent machining of the inner and outer parts hollow billets to the required geometric dimensions.

This technology is extremely time-consuming and costly, especially in the manufacture of cathodes made from alloys МЗП 6 and СДП 2 (Ni-basis; 18-24 % Cr, 10-14% Al; 0.4-1% Y; % by weight), with increased hardness and brittleness [7, 8]. About 50% of the metal goes to waste, re-melted. To optimize the technological process, the Institute of Aviation Materials proposed a method for

producing cast pipe products from nickel and / or cobalt-based alloys, including melting the charge materials and casting the melt in a vacuum into a preheated casting mold in the form of a ceramic shell with a sprue-feeding system or a mold of casting graphite with a casting bowl (fig. 1), and subsequent machining of the workpiece [9].

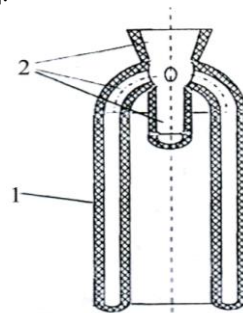


Fig. 1. The design of the ceramic shell mold for casting of tube billets: 1- tubular shell part; 2 - gating system with molding cup [9]

In the technological process, a two-chamber induction furnace with a melting and casting chamber and a charging chamber is used, which are separated by a vacuum gate providing a vacuum of 0,6 Pa in the melting chamber. Form before pouring it is necessary to warm up to a temperature of 950-1000 °C. The casting in the mold is carried out at a melt temperature of 1420-1600 °C at a speed of 20-50 kg / min. Cooling of the casting to a temperature equal to or less than ½ the melting point of the alloy is carried out in a vacuum, the subsequent - in the air. It should be noted that the use of vacuum induction melting in the manufacture of blanks has a number of significant drawbacks.

Among them:

- degree of refining of liquid metal is lower in comparison with electron-beam melting;
- need to produce single shell molds, as well as sprue-feeding systems and pouring bowls;
- need to heat and maintain the required temperature of the ceramic or graphite shell shape;
- interaction of molten metal with a ceramic or graphite material, leading to contamination of the casting;
- the difficulty of providing and maintaining high melt overheating;
- the difficulty of ensuring a high rate of pouring liquid metal.

Reducing the casting speed leads to the formation of foundry defects of the "non-braze" type, due to the high rate of crystallization on the walls of the metal jet shape, the oxidation of its surface, which does not allow obtaining a reliable metallurgical connection between the primary casting and the crystallized icicle of the primary metal on the inner surface of the mold.

These shortcomings are not inherent in the EBM method, which, as is known, is the most promising method of metal refining and degassing in vacuum [1, 4]. Therefore, in Research Association "ELTEHMASH" (Vinnitsa, Ukraine) together with the Frantsevich

Institute for Problems of Materials Science of National Academy of Sciences of Ukraine mastered the experimental production of tubular cathodes for ion-plasma spraying of NiAlCrY alloy coatings. An important role in the development of the technology of manufacturing tubular type cathodes was played by the urgent need in Ukraine for import substitution of similar products from the Russian Federation.

2. Materials and experimental procedure

The melting of tubular billets from M3Π 6 and M3Π 7 alloys was carried out in 2 stages on an electron beam installation L-4, developed and manufactured by SA "ELTEHMASH" [10]. The unit is equipped with 4 gas-discharge electron guns with a cold cathode of 100 kV each. In the first stage, according to [8], ingots of alloys (table 1) were prepared in the form of cylindrical billets with a diameter of 100 mm and a length of 250 ... 300 mm.

Table 1

Chemical composition of ingots after electron-beam remelting

Alloys	Content of elements, % (wt.)			
	Cr	Al	Y	Ni
M3Π 6	18...24	11...14	0,4...1	basis
M3Π 7	18...24	4...6	0,4...1	basis

In the working chamber of the installation L-4, a crucible was installed to melt the tube-type blanks (Fig. 2). The necessary number of ingots of a given chemical composition was placed in the chamber of the horizontal feeder of the charge into the melting zone (not shown in Fig. 2). Before the start of the process (step 2), the water-cooled rod with seed was transferred to a copper water-cooled cylindrical mold at a height of 10 ... 15 mm from its upper edge. In this case, the rod was fixed in such a way that there was no gap between it and the crystallizer, as well as a copper water-cooled cylindrical mandrel arranged coaxially with the crystallizer and fixed by means of a special traverse through which water is circulated.

Otherwise, it is possible to shed liquid metal, which makes it impossible to carry out the technological process. The diameter of the mandrel in the lower part is slightly less than in the upper part, which excludes jamming and deformation of the mandrel walls when it is removed from the cast preform. This ensures the production of cylindrical metal tubular castings of different chemical composition, since during crystallization of the alloy, subsequent cooling of the casting and its thermal shrinkage, its jamming and deformation of the mandrel walls are excluded. The preforms of the nickel alloy are alloyed into an intermediate vessel - the liquid metal is gradually merged through the spout of the intermediate capacity into the crystallizer. The height of the filling is 9 ... 11 mm. In connection with the presence of a traverse, which serves to fix the copper mandrel and the supply of cooling water to it to prevent its destruction under the action of an electron beam, heating of the metal surface in the crystallizer is carried out by means of two electron guns **1, 2** (Fig. 1, b). The beams of the guns are scanned according to the program (scanning frequency 50 Hz, current for each gun 0.8 ... 1 A), forming two heating zones in the form of osculating semirings (Fig. 2, b). When the power control of electron beam heaters is separately controlled, a significant temperature gradient can occur in the heating zones, which under certain conditions leads to cracking and jamming of the casting in the crystallizer.

Therefore, during the formation of the pipe blank, synchronous regulation of the gun power is performed to maintain the material surface in the crystallizer in a liquid state at approximately the same temperature. After holding the first portion of the filled metal in the crystallizer for 6-8 seconds, the workpiece is pulled at a speed of 1 mm / s, while simultaneously filling the next portion of the metal and controlling its height by the sensor to 9...11 mm, the total yield of the crystallized part of the casting from the crystallizer.

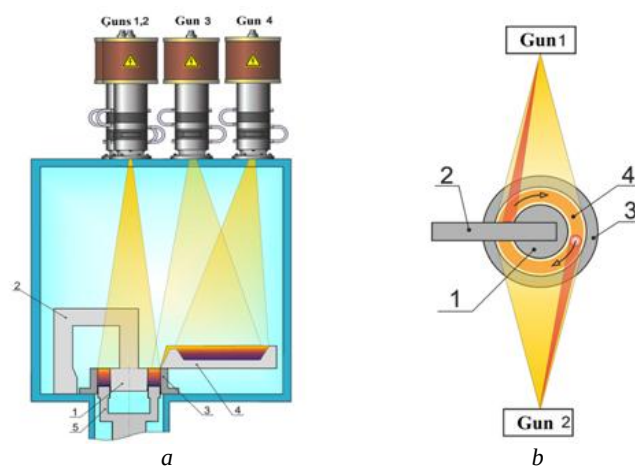


Fig.2. Scheme of the crystallizer design for the manufacturing of tube billets by ELF (a) method and the heating scheme of the melt bath by two electron guns with sweeps of rays in the form of semirings (b - top view): 1 - water cooled mandrel, 2 - traverse; 3 - water-cooled crucible; 4 - intermediate capacity; 5 - water-cooled rod with seeding

3. The results and discussion

Thus, the tubular blank with outer and inner diameters outside 198 mm, and inside 114 mm and length $L = 358...360$ mm is formed during 240...250 min. It is completely drawn out of the crystallizer and cooled in a vacuum to a temperature of 300 °C. After cooling to room temperature, the workpiece is machined to diameters outside 180 mm and inside 140 mm and $L = 348...352$ mm. The chips after chemical cleaning, drying and compacting are reused as a starting material for melting the tube-type blanks. The appearance of the billet after melting and machining is shown in fig. 3.

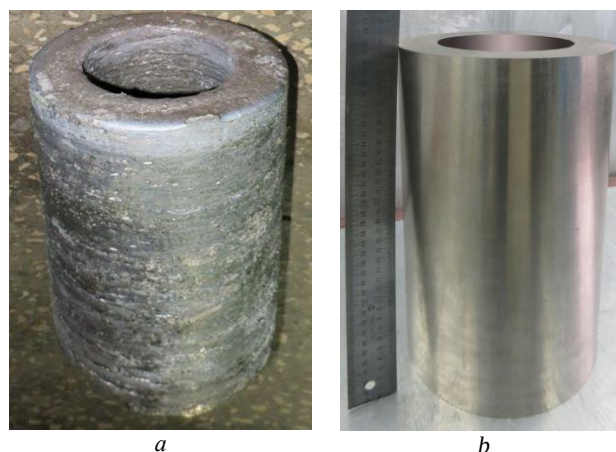


Fig. 3. General view of the tube billet produced by electron-beam remelting (a) and those after machining (b)

The chemical composition of pipe billets fully meets the specifications for cathodes according to TU U 27.4-200113410.002-2001 [8] and TU U 1-92-113-87 [11]. Visual inspection and control of geometric dimensions confirms the compliance of cathodes with the requirements of the drawing in accordance with TU 6823-21-38 (JSC "Motor Sich", Ukraine). The phase composition of the materials of the tube billets was determined on a DRON-4 diffractometer by shooting in K_{Cu} filtered radiation in the range of angles $2\theta = 20-100$ deg with silicon as a reference. Recording of diffractograms was carried out with scanning in steps of 0.05 deg. According to the analysis results for the cast material from the M3Π 7 alloy, the formation of a solid solution based on nickel is characteristic. The phase composition of the M3Π 6 alloy is more complicated. The main constituents of the material are the heat-resistant β (NiAl) and γ' (Ni₃Al) phases, as well as the α -solid solution based on chromium

(fig. 4). A typical microstructure of cast billets from МЗП 7 (a) and МЗП 6 (b) alloys is shown in fig. 5.

Portion filling and rapid crystallization of the melt lead to the formation of a dispersed structure. At approximately the same content of Ni, Cr, and Y in alloys, the dispersion of structural elements increases with increasing aluminum content from 4-6 % by weight (МЗП 7) to 10-14 % by weight (МЗП 6), which contributes to the formation of new phases. It should be noted that МЗП 7 alloy is characterized by a smooth transition from a fine-grained structure in the zones adjacent to the cooled surfaces of the mandrel and crystallizer to a coarse-grained structure formed in the central regions of the casting. For casts of alloy МЗП 6, this phenomenon is less pronounced.

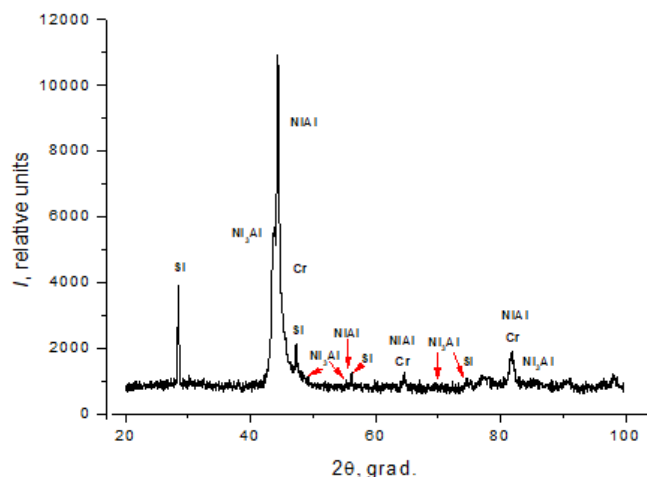


Fig. 4. Phase composition of the alloy tube billet from МЗП 6

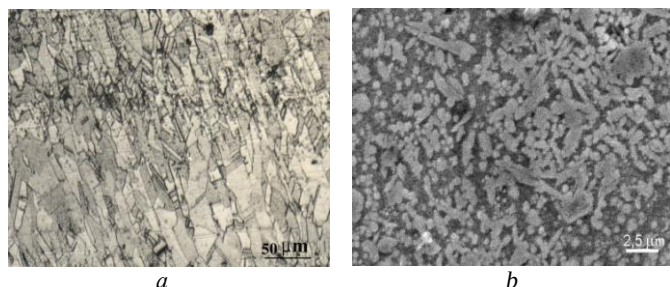


Fig. 5. Microstructure of cast billets from alloys МЗП 7 (a) and МЗП 6 (b)

Experimental work was carried out to evaluate the possibility of using experimental cathodes in Joint-stock company “Motor-Sich” joint-stock company. In comparative studies on the application of coatings on the surface of the blades, two castings of the production of the Research Association “ELTEHMASH” from the МЗП 2 alloy and one serial sample of the same composition from the СДП 2 alloy (batch production RF) were used. Coating was carried out on the АПН-250. The installation with an experimental cathode worked stably, all technological parameters corresponded to the parameters of the serial technology. On the coated blades, a roughness control was performed, which showed that the roughness was $R_a = 1.63 \dots 2.88$ per shear, and $R_a = 0.67 \dots 3.2$ - on the flow surfaces of the shelves. ЛЮМ-10B control of blades with a coating showed that they meet the requirements of TU-222-TU-20 of Joint-stock company “Motor-Sich”. The conducted studies confirmed that the structure and thickness of the test coatings correspond to coatings obtained using serial cathodes.

Conclusions

1) An experimental electron-beam technology for the production of tubular cathodes for ion-plasma coatings has been developed.

2) The performance characteristics of coatings on blades obtained by spraying experimental cathodes correspond to the characteristics of standard coatings.

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EFFECT OF THERMAL-CYCLIC DEFORMATION AND HEAT TREATMENT ON THE STRUCTURE AND ELECTRICAL PROPERTIES OF CтЗ

ВЛИЯНИЕ ТЕРМОЦИКЛИЧЕСКОЙ ДЕФОРМАЦИИ И ТЕРМИЧЕСКОЙ ОБРАБОТКИ НА СТРУКТУРУ И ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА СТАЛИ CтЗ

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Abstract: The results of the effect of preliminary thermal-cyclic deformation on the microstructure of hot-rolled low-carbon steel Cm3nc are presented. It is shown that the regime of thermal-cyclic rolling leads to a decrease in the average grain size of ferrite from 8 to 6 microns in comparison with the structure of steel after industrial production. There is a decrease in the size of pearlite colonies and their volume fraction in the structure of steel after using thermal-cyclic deformation. The results of the effect of heat treatment: normalization and tempering on the electrical resistivity of the hot-rolled carbon steel sheet Cm3nc produced using thermal-cyclic mode of deformation processing (DTCT). DTCT preliminary thermal-cyclic was rolled (5 cycles at a reduction of 10-15 % in each cycle and cooled to a temperature below the Ar1). And normalizing annealing was carried out in the range from 100 to 900 °C increments to 100 °C for 1 hour. The possibility to reduce the magnitude of the specific electrical resistance of the hot-rolled steel manufactured using DTCT mode through the use of subsequent normalizing at 700 °C on average 10 %, and by annealing – no more than 5 %. A further increase in the time of normalization at 700 °C to 3, 5 and 10 hours has no significant effect on the value of the electrical resistance of the steel subjected DTCT. However, the downward trend in resistivity is maintained. Overall reduction of electrical resistivity of the hot-rolled steel Cm3nc by using mode DTCT and subsequent normalizing at 700 °C for 1 hour is more than 12 %.

KEYWORDS: STEEL, STRUCTURE, DEFORMATION, THERMAL-CYCLIC ROLLING, ANNEALING, NORMALIZING, ELECTRICAL RESISTIVITY.

1. Introduction

In the field of electro-technical material engineering low-carbon steel can be attributed to the most available and cheap materials exhibiting good mechanical tensile properties. However its application is restrained by increased specific electric resistance compared to copper and aluminum alloys. It is well-known that for structurally sensitive properties, that together with mechanical characteristics include specific electric resistance, a combined impact of temperature and deformation is efficient [1-5]. To such impacts one can attribute deformation thermal-cyclic treatment (DTCT), which is represented by thermal-cyclic treatment combined with various types of deformation in the range of low or high temperatures [1,6]. Such combined treatment leads to intensification of diffusion processes occurring at preset temperature fluctuations with application of stresses and deformations, accumulation of structural changes occurring in cycles and connected with bulk effects of phase transformations, difference in thermal-physical characteristics of phases etc. Ultimately these processes provide for formation of optimal structure and improvement of physical and mechanical properties of steels, cast irons, aluminum alloys and other materials [6-15]. A reserve for reduction of specific electric resistance could be subsequent thermal treatment to obtain better equilibrium structure with reduced amount of crystallographic defects and lower level of internal stress [12,17], normalizing and annealing in the first place. Therefore the objective of the study was researching impact of various modes of normalizing and annealing onto specific resistance of hot-rolled CтЗnc steel, manufactured with application of DTCT.

2. Material and methods

Low carbon commercial quality CтЗnc steel served as material for research. The steel was produced at “Novokuznetsk integrated steel plant (NKMK)” JSC. Chemical composition of

steel was determined on ARL 4460 emission spectrometer. Results are presented in Table 1.

In order to roll sheet with application of DTCT a slab was cut out from ingot with dimensions of 165×500×1800 mm. Thermal-cyclic rolling of slab was performed at “NKMK” JSC on sheet rolling mill 500. One cycle of thermal-cyclic slab and billet rolling included heating up to 1300 °C, holding for 2-2,5 h, reduction of 10-15 % and air-cooling down to temperature below Ar1. There were 5 treatment cycles performed, at that in the 1st and 3rd cycles cooling was down to 500-550 °C, and in the remaining cycles – down to 50-100 °C. Reduction by cycles was performed by the pattern of 165→140→120→110→100→90 mm and further down to sheet thickness of 5 mm according to “NKMK” JSC sheet rolling mill process. Upon reaching breakdown length of 2500 mm it was cut into two halves 1200-1250 mm each. Samples were cut out from the sheet received with the dimensions of 5×20×100 mm and thermally-cyclic rolled down to thickness of 4, 3, 2 and 1 mm over 1-5 treatment cycles. Rolling was performed on the laboratory mill of 20 kW capacity with plain rolls of 250 mm diameter. Prior to deformation the samples were heated to 850 °C and held during 30 minutes, cooled down to rolling temperature of 750 °C. Reduction ratio in cycles for various thicknesses equaled 20, 25, 30 and 50 % correspondingly. Annealing of sheet samples was performed in resistance furnaces SNOL 2.2, 5.2/12,5-I1. Optical microscopes LaboMet-I1 and OLYMPUS-GX51F were used for studies of steel microstructure, and NORMA M88a unit assembled on the basis of Thompson bridge circuit was applied to measure electric resistance. Samples for electric resistance measurement had square section with 1-5 mm sides and 100 mm length. Procedural error of specific resistance measurement made $0,05 \cdot 10^{-8} \Omega \cdot m$.

Table 1. Chemical composition of treated Cm3nc steel

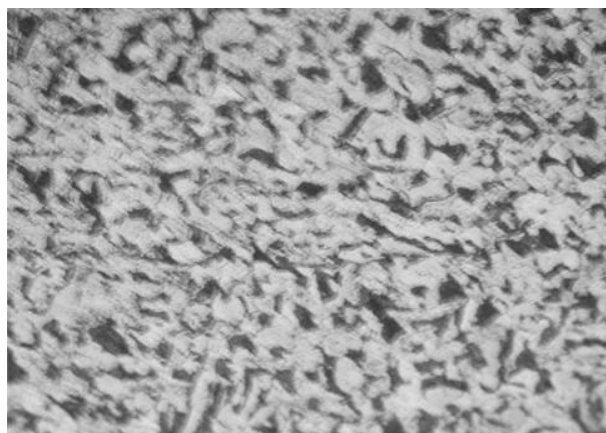
Steel grade	Heat №	Elements ratio, % (weight.)								
		C	Mn	Si	P	S	Cr	Cu	Ni	Fe
CтЗnc	060886	0,19	0,54	0,07	0,013	0,028	0,3	0,07	0,03	rem.

3. Results and discussion

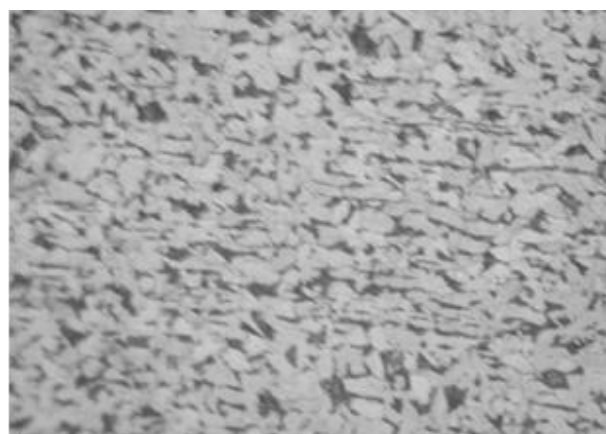
Microstructure of hot rolled sheet from Cr3nc steel rolled in industrial mode and with application of thermal-cyclic deformation consists of evenly distributed ferritic grains and pearlite colonies [12]. However, preliminary thermal-cyclical rolling leads to certain reduction of ferrite average grain size from 8 down to 6 μm compared with grain within structure of a sheet produced in industrial mode, as well as to reduction of pearlite colonies size and their volume ratio (fig. 1).



a



b



B

Fig. 1 – Effect of deformation thermal-cyclic treatment onto microstructure of sheet Cr3nc steel, produced by a – industrial process (sheet thickness 5 mm); b – with application of preliminary thermal-cyclic rolling (sheet thickness 5 mm); c – with application of preliminary and subsequent thermal-cyclic rolling (sheet thickness 1 mm); $\times 200$

Determination of specific electric resistance of sheet steel indicated that after preliminary DTCT (rolling) its value is $16,8 \cdot 10^{-8}$

$\Omega \cdot \text{m}$, which is 3-5 % lower, than in sheet steel of industrial production. Effect of deformation cycles onto specific electric resistance of steel produced with DTCT, at further thermal-cyclic rolling from 5 to 1 mm is shown in fig. 2.

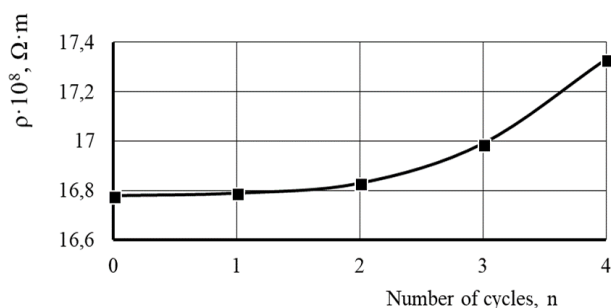


Fig. 2 – Effect of number of deformation cycles onto specific electric resistance of hot rolled Cr3nc steel produced with application of DTCT

It can be noted that increasing the number of deformation cycles increases specific resistance of rolled sheet, which is apparently related with extension of grain junction lines in structure of deformed steel and incomplete relief of work hardening in thin sheets. For instance, determination of average size of ferrite grains and pearlite colonies displayed their reduction after the 4th deformation cycle down to value of 2-3 μm . At that, increase of deformation degree in cycle leads to more intensive growth of specific electric resistance of samples cut out of rolled material.

A reserve for reduction of specific electric resistance of hot rolled steel could be subsequent thermal treatment that allows obtaining better equilibrium structure compared to deformed metal condition [17]. Therefore the effect was studied of temperature and normalizing and annealing time onto the value of specific resistance of hot rolled Cr3nc steel. Treatment temperature was altered within the range of 100 to 900 $^{\circ}\text{C}$ with pitch of 100 $^{\circ}\text{C}$ and holding time of 1 h. Results of determining specific resistance of samples from hot rolled Cr3nc steel in normalized and annealed states are drawn in fig. 3.

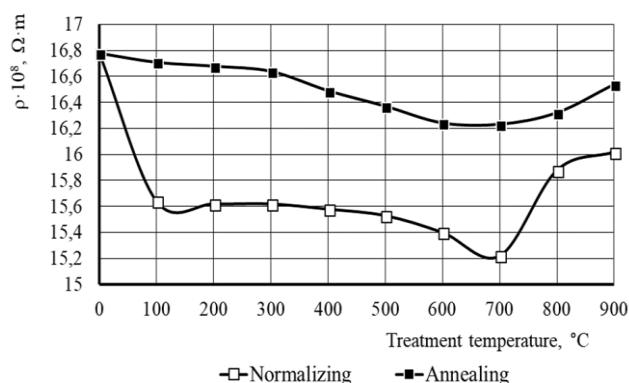


Fig. 3 – Effect of annealing and normalizing temperature onto specific electric resistance of hot rolled Cr3nc steel produced with application of DTCT

It is established that with the increase of treatment temperature for both normalizing and annealing modes value of specific electric resistance is reduced until temperature reaches 700 $^{\circ}\text{C}$. At that in normalized samples specific electric resistance is 6 % lower compared to the annealed ones, and its absolute value makes $15,22 \cdot 10^{-8} \Omega \cdot \text{m}$. Increase of specific electric resistance of steel with the increase of normalizing and annealing temperature up to 900 $^{\circ}\text{C}$ may be related with coalescence at this temperature of cementite present in pearlite component after DTCT in dispersed form.

Further on the effect was studied of holding time of steel samples at optimal treatment temperatures: for normalizing – 700 °C, for annealing – 600 °C. Optimal treatment temperature corresponds to minimal value of specific electric resistance of samples. Results of determining specific resistance of sheet Cr3nc steel produced in industrial mode and with application of DTCT, after annealing and normalizing at various holding times, are shown in fig. 4.

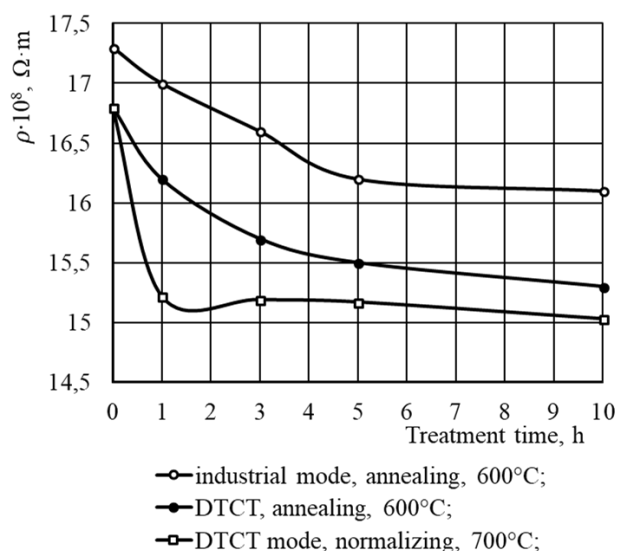


Figure 4 – Effect of thermal treatment time onto specific electric resistance of sheet Cr3nc steel produced in industrial mode and DTCT mode

It is demonstrated that sequential increasing of holding time at annealing and normalizing up to 10 h leads to reduction of specific electric resistance of sheet industrial steel and steel produced with application of DTCT. Variation regularity of specific electric resistance at annealing for experimental and industrial steel is the same: however, reduction level varies. After annealing DTCT treated steel has specific resistance 5÷6 % lower, and minimal value corresponds to annealing time of 10 h and makes $15,3 \cdot 10^{-8} \Omega \cdot m$.

Increasing of normalizing time at 700°C up to 3, 5 and 10 h does not significantly affect the value of specific electric resistance of hot rolled steel produced with application of DTCT, although retains a trend to its reduction. Thereby overall reduction level of specific electric resistance of hot rolled steel due to application of DTCT mode and subsequent normalizing at 700 °C within 1÷10 h averages 10-13 %.

4. Conclusions

1. Application of preliminary thermal-cyclic rolling allows reducing specific electric resistance in sheet Cr3nc steel by 3÷5 % compared to industrial mode.
2. Application of high reduction ratios (20-50 %) in DTCT cycles for hot rolled Cr3nc steel to produce sheet of less than 5 mm thickness leads to increase in specific electric resistance in proportion to number of cycles and degree of deformation.
3. Combination of DTCT with subsequent annealing at 600 °C within 1÷10 h for hot rolled Cr3nc steel reduces specific electric resistance by 4-6 % on average as compared to industrial production process.
4. Introduction of sequential normalizing at 700 °C within 1÷10 h allows reducing the value of specific electric resistance of DTCT treated hot rolled Cr3nc steel by the average of 9-10 %.

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