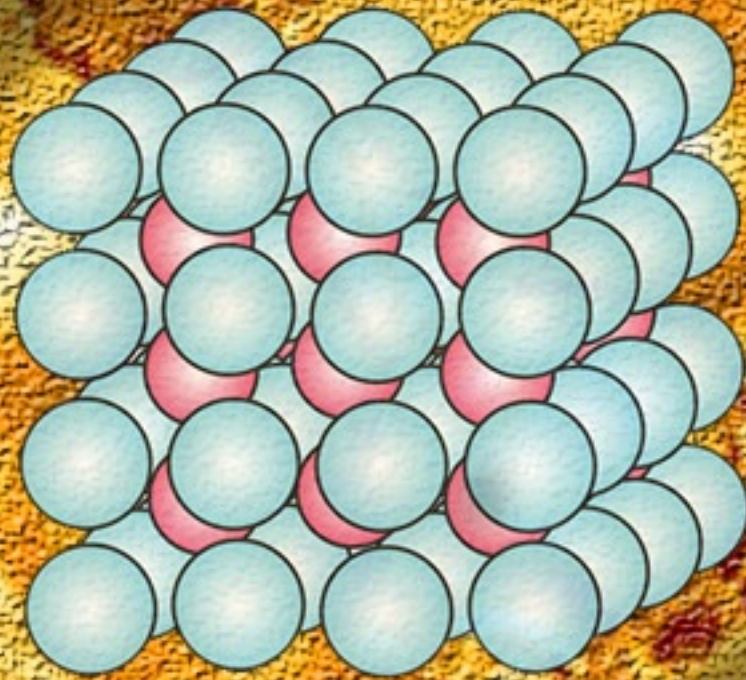


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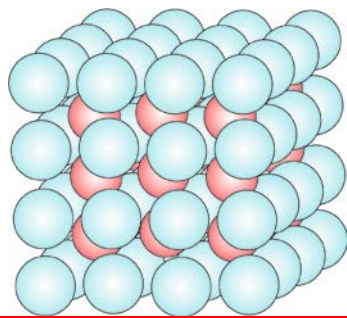
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Transformation of heterophase inclusions “dispersed phases are in non-metallic matrix” in steels under laser action

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Abstract. Melting and crystallization of heterophase non-metallic inclusions “dispersed phases are in non-metallic matrix” was investigated. Mechanism of melting of the inclusions “dispersed phases are in non-metallic matrix” and inclusion-matrix boundaries under contact laser melting with steel matrix in the conditions of abnormal mass transfer connecting with formation of zones with high dislocation density and also with electron and electro-magnetic interaction between inclusion and steel matrix was proposed. That allows to create the possibilities for the influence on the inclusion-matrix boundaries and also on the chemical and phase composition of surface layer of non-metallic inclusions “dispersed phases are in non-metallic matrix”. Peculiarities of structure of non-metallic inclusions after speed crystallization were investigated. It was shown that under laser action the initial structure of inclusion-steel matrix boundaries transits into unstable equilibrium high-energy condition that cause development of the dissipation processes connecting with aspiration of system inclusion-matrix to the state with minimum of the free energy. In the result of the system inclusion-matrix transits to the state of unstable equilibrium which determines structure and properties of laser-quenched interphase boundary. Processes of melting, fusion and dissolution of non-metallic inclusions “dispersed phases are in non-metallic matrix” and also of the melting of steel matrix play the great role in transformation of interphase inclusion-matrix boundaries under laser action.

KEYWORDS: NON-METALLIC INCLUSIONS “DISPERSED PHASES ARE IN NON-METALLIC MATRIX”, STEEL, STRENGTHENING, LASER TREATMENT

1. Introduction.

In steels, heterophase types of inclusions are often present [1 - 9]. For heterophase inclusions, the presence of internal interphase boundaries is characteristic, which, along with the inclusion-matrix interphase boundaries, play an important role in the formation of defects, which is very important when analyzing the reliability and durability of products operating in different conditions [1 - 4]. In heterophase inclusions “dispersed phases are in non-metallic matrix” dispersed particles of an excess second phase (oxides, nitrides, carbonitrides, silicates, etc.) d2, which precipitated from a supersaturated liquid or solid solution, are

present in the “non-metallic” matrix (sulfide, oxide, silicate, etc.) f-m1 (“non-metallic” matrix) (Fig. 1). Such inclusions are dispersed composite formations. Inclusions of this type can be not only two-, but also multiphase, if they contain dispersed particles of several types having different shapes and sizes.

The goal of this investigation was to research the processes of melting, dissolution, crystallization of the heterophase non-metallic inclusions “dispersed phases are in non-metallic matrix” in hyper-nonequilibrium conditions and the influence of these inclusions on the peculiarities of structural changes in steel matrix and its strengthening under laser treatment.

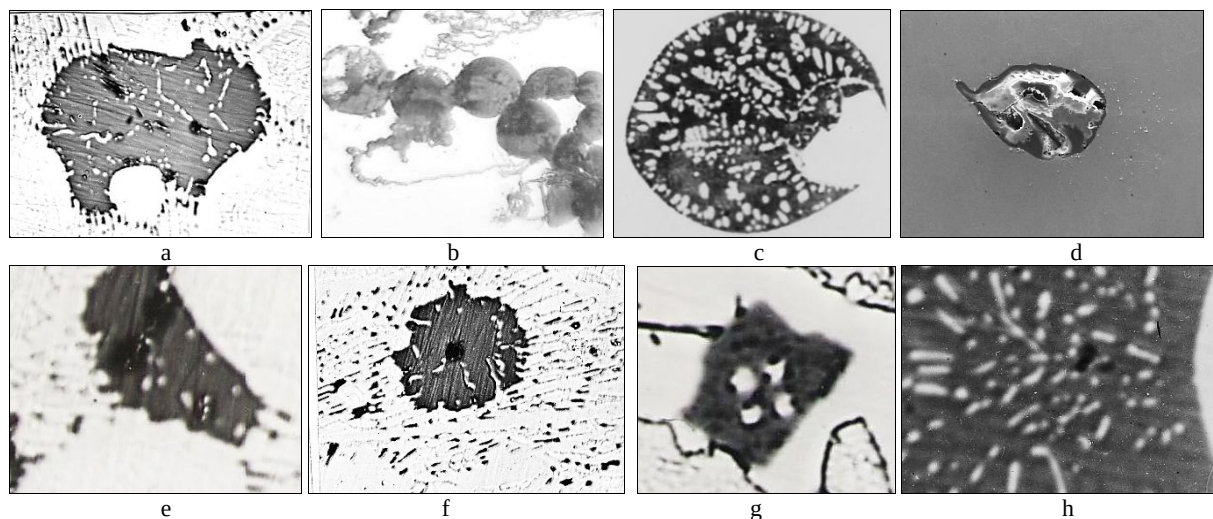


Figure. 1. Non-metallic inclusions “dispersed phases are in non-metallic matrix” before laser action; x600

2. Materials and Procedures.

Specimens made of wheel steel R7, 08Yu, 08T, 08Kp, 08Ch18N10T, ShCh15, NB-57, 12GS, E3 were irradiated by laser in GOS-30M installation with an excitation voltage of 2,5kV and pulse energy of 10, 18, 25 and 30J at heating rate of 10^5 °C/s and cooling rate of 10^6 °C/s with action time of (1,0, 2,5, 3,6, 4,2 и 6,0) 10^{-3} s. heterophase non-metallic inclusions “dispersed phases are in non-metallic matrix” were identified by metallographic, X-ray microspectral and petrographic methods, [10 - 17]. Distribution of elements and nanohardness of steel matrix near inclusions were determined.

3. Results and discussion.

Inclusions “dispersed phases are in non-metallic matrix” represent the dispersal composites when in “non-metallic” matrix

ph-m1 (sulphide, silicate, oxide) present dispersed particles of second phase d2. These phases can to have different temperatures of melting or both be high-melting and low-melting but it is possible the combination of high-melting and low-melting phases too. These inclusions are differed from another that their basic phase ph-m1 contacts with steel matrix across interphase boundary $ph-m1 \leftrightarrow m$ and they have well-developed net of inner interphase boundaries $ph-m1 \leftrightarrow d2$. Besides if interphase boundary $ph-m1 \leftrightarrow m$ in contact with basic phase ph-m1 is not unbroken because the disperse phase d2 also has contact with steel matrix across discrete boundaries $d2 \leftrightarrow m$.

Investigation of inclusions “dispersed phases are in non-metallic matrix” was shown the both phases in the moment of laser action are melted fully or partly. Their behavior is differed from with degree of melting. If both phases ph-m1 and d2 are high-melting that phase ph-m1 is fused or melted in dependence on

temperature regime. Dispersed phase d2 as a rule have time to melt (or to dissolve) fully in the matrix phase ph-m1 of inclusion. Under action of convective flows in micrometallurgical bath the liquid phases of inclusion are mixed though often remnants of phase d2 are shown. If both phases of inclusion are low-melting they are melted and mixed. The oversaturated liquid solutions are formed and crystallized with big speed. In such inclusions the zones of liquation are observed connecting with presence of traces of sojourn of former dispersed phase d2. If phases of inclusion have different temperatures of melting that low-melting phase ph-m1 (sulphide, silicate) is melted in the moment of laser action but high-melting phase d2 (oxide, nitride) can to melt fully or partly. In the time of happens the interaction of components of phase ph-m1 of inclusion with metal matrix of steel promoting the saturation of areas near inclusion with elements of phase ph-m1 of inclusion and also with elements of dispersed phase d2 being in surface area of inclusion. That promotes the rise of level of chemical inhomogeneity of saturated zones in steel matrix in the difference from analogous processes happing under melting of the first and second types of heterophase inclusions. In inclusions after rapid crystallization the heterogeneous distribution of elements is observed connecting with presence of traces of dispersed phase d2 and also with formation of liquation zones revealing with special micro-spectral analysis.

Interphase boundaries ph-m1 $\leftrightarrow$ d2 are not precise or at all disappeared owing to dissolution of dispersed phase d2. Special micro-spectral analysis shown that near these boundaries in both phases of inclusion the content of elements of neighbouring phase is risen. That bears witness about mutual exchange with atoms in the moment of melting of inclusion “dispersed phases are in non-metallic matrix”. Examining the peculiarities of laser melting of inclusions “dispersed phases are in non-metallic matrix” it is follow to note that matrix phase ph-m1 of inclusion is base and it determines the behavior of all inclusion. Phase ph-m1 contacts with metal matrix of steel and also with dispersed phase d2 across boundaries ph-m1 $\leftrightarrow$ d2.

Sequence of heavy distortion areas on the surfaces of “non-metallic” matrix of inclusion ph-m1 and dispersed phase d2 and also of the movement of interphase boundaries ph-m1 $\leftrightarrow$ liquid steel matrix, d2 $\leftrightarrow$ liquid steel matrix and also ph-m1 $\leftrightarrow$ d2 inside inclusion in the process of melting one can to present with next image (Fig. 2). On the surfaces of non-metallic matrix of inclusion and also on the dispersed phase d2 saturating with elements of steel matrix the heavy disordered areas (the areas of melting) are formed (Fig. 2, a). The whole these areas pass into liquid steel matrix saturating it with elements of phases of inclusion. Position of the

inclusion-steel matrix boundary having different areas near phases ph-m1 and d2 is changed owing to melting (Fig. 2, b) in dependence on character of mass transfer between each phase of inclusion and steel matrix. On the surfaces of non-metallic matrix of inclusion ph-m1 and dispersed phase d2 the heavy disordered areas are formed too (Fig. 2, b). Evidently one of phases of inclusion (ph-m1) is melted scarcely earlier than phase d2 and nucleuses of melting of the phase ph-m1 promote disordering and melting of interphase boundaries ph-m1 $\leftrightarrow$ d2 inside inclusion. The whole disordered areas (areas of melting) of the phase d2 pass into liquid phase ph-m1 (Fig. 2, c). The former boundary ph-m1 $\leftrightarrow$ d2 represents liquid zone of interaction of components of both phases of inclusion corresponding with convective flows. In these zones the complicated chemical compositions under rapid cooling after laser action are formed.

Grain boundaries of phase ph-m1 of inclusion contacting with liquid steel matrix are exposed to the active interaction and mass transfer of elements so they must to melt or dissolve more quickly than body of grains. So it is possible the separation of this phase individual fused grains containing melted particles of dispersed phase d2 (Fig. 2, d). Under action of shock waves such complexes are distributed in liquid steel matrix (Fig. 2, e). Evidently phases of such heterophase inclusion do not melt always. High-melting phases can to melt fully or partly, low-melting phases are melted fully.

In inclusions “dispersed phases are in non-metallic matrix” the zones of laser crystallization with liquation causing owing to the mixing of components of both phases in the moment of melting are formed. In non-metallic matrix of some inclusions the areas with regular distribution of raised and reduced concentration of elements of both phases of inclusion were discovered. Analysis of these areas bears witness about possibility of the rate decomposition of liquid or solid solution. For inclusions “dispersed phases are in non-metallic matrix” after speed crystallization the appearance of ultra small variation in grain size, formation of nano-structure state and also of amorphous and mixed amorphous-nanocrystalline structures are typical. Among inclusions “dispersed phases are in non-metallic matrix” more tendency for amorphization have silicate phases of non-metallic matrix since owing to the interaction of elements of both phases of inclusions in the moment of melting the complicated silicate systems are formed. These silicate systems solidify under speed cooling as amorphous silicate glasses. Moreover inclusions containing phases with B, Ni, Si are subjected to amorphization.

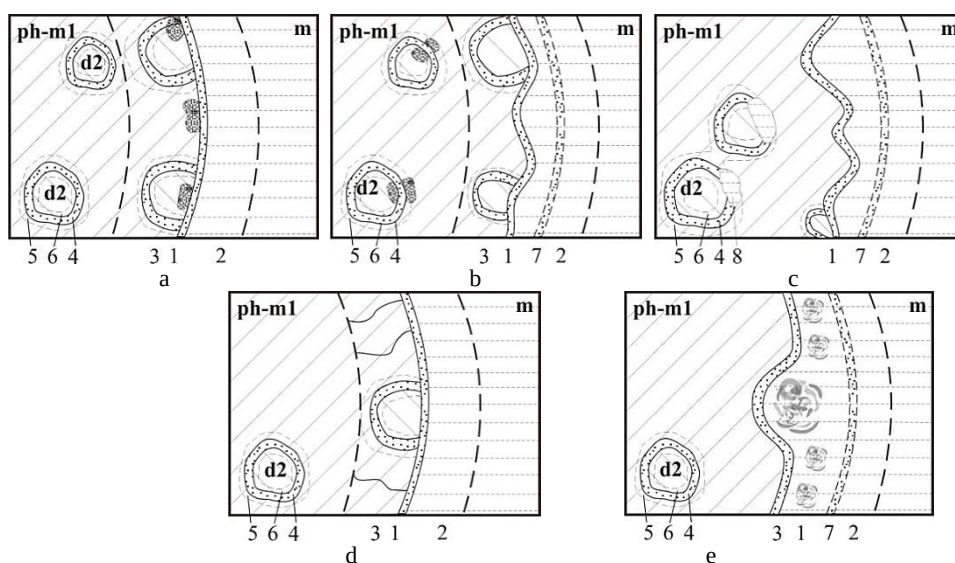


Figure 2. Schemes of laser melting of heterophase inclusions “dispersed phases are in non-metallic matrix”: 1 – inclusion-matrix boundary, 2 – zone of steel matrix saturation with elements of inclusion, 3 – zone of saturation of inclusion with elements of steel matrix, 4 – boundary ph-m1 $\leftrightarrow$ d2, 5 – zone of saturation of phase ph-m1 with elements of phase d2, 6 – zone of saturation of phase d2 with elements of phase ph-m1, 7 – initial position of boundary inclusion-matrix, 8 – initial position of boundary ph-m1 $\leftrightarrow$ d2 inside inclusion ph-m1 $\leftrightarrow$ d2

In the process of melting of both phases of inclusion “dispersed phases are in non-metallic matrix” and also of steel matrix happens the mixing of liquid phases under action of hydrodynamics forces and temperature gradients. In micrometallurgical bath (local zones of inclusion and steel matrix) the nonequilibrium oversaturated heterogeneous liquid solution is formed. In the process of speed crystallization more probable the realization of mechanism of unselective crystallization of inclusions. The results of this crystallization are the fixing of high-temperature phases of inclusions, formation of ultra dispersed grains structure or nano-structure, or solidification with formation of zones of amorphous state. Separation of liquid or solid solution in inclusions can leads to decomposition (possibly with spinodal mechanism) in solid state or to the formation new dispersed particles in inclusions non always corresponding to the chemical composition and structure of initial phase d2 of inclusions. In steel matrix near inclusions “dispersed phases are in non-metallic matrix” the “satellite” particles of new phases were appeared that is typical for the conditions of laser treatment of steels [2]. On the boundaries inclusion-matrix of steel new phases in the shape of layers with different chemical compositions were appeared too [1, 8].

Near inclusions “dispersed phases are in non-metallic matrix” formation of saturated zones of steel matrix is controlled

with the phase-matrix ph-m1 of inclusions which is the basic source of alloying of steel matrix (Fig. 3, a – c, 4). But the influence of dispersed phase d2 creating the heterogeneities of saturated zones is great too. In the results near these inclusions the composite liquation zones of complex types with different structure are formed: the layer type with cascade “spot” distribution of elements having structure of heterogeneous solid solution in the each zone with the “splashes” of quantity of elements; the layer type with cascade-dispersed distribution of elements having structure of heterogeneous solid solution in the each zone with the “splashes” of quantity of elements and with dispersed particles of “satellite” inclusions and also with nondissolved phase d2. Characteristic sign of saturated zones is their complex character and “splashes” of quantity of elements passed from the phase d2 and also presence of remnants of nondissolved phase d2. The “splashes” of quantity of elements in the inclusions of “eutectics” and “dispersed phases are in non-metallic matrix” have different nature. Evidently change of regime of laser treatment will allows to regulate the structures of these composite zones in the steel matrix near heterophase non-metallic inclusions. There are also “satellite” particles (Fig. 3, d), the composition of which differs from the chemical composition of the initial dispersed phase d2 of inclusion.

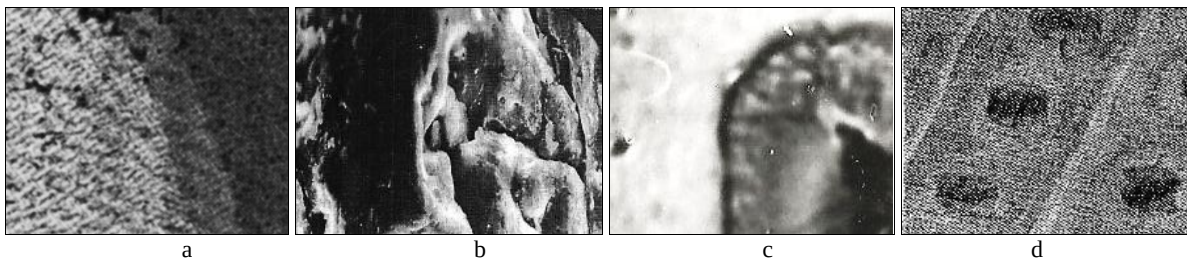


Figure 3. Zones of interaction between inclusions “dispersed phases are in non-metallic matrix” and steel matrix under laser action: a - (Fe,Mn)S+ TiCN, steel E3, b, d - MnO·SiO₂+Cr₂O₃, steel 08Yu, c - (Fe,Mn)S+ TiCN, steel E3; x500x6

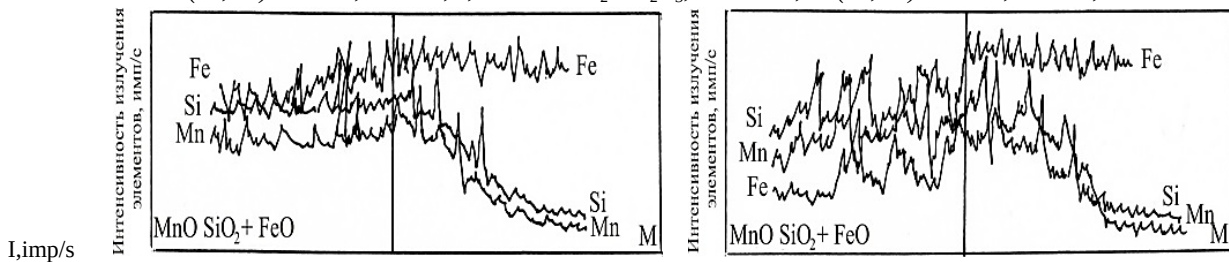


Figure 4. Distribution of elements near inclusions of the “dispersed phases are in non-metallic matrix” type after laser action

The results of a study of the distribution of nanohardness in the zones of saturation of the steel matrix adjacent to inclusions of the “dispersed phases are in non-metallic matrix” type showed that the nanohardness is much higher than its average value for the matrix far from the inclusions (Table 1). The level of nanohardness of each zone of the metal matrix is determined by the type of steel, since the

degree of hardening in the process of laser action depends on its composition and structure. The cascades of nanohardness values of steel matrix away from inclusions H_m^{inc} were discovered however in each zone of saturations the “splashes” of H_m^{inc} values are detected.

Table 1. The values of the nanohardness of the saturation zones of steel matrix near the “dispersed phases are in non-metallic matrix” type of inclusions H_m^{inc} and far from them H_m , as well as the coefficient (K_i) at a pulse energy of 25 J and an exposure time of $3.6 \cdot 10^{-3}$ s

inclusion, steel, H_m , x 10, MPa	Phases of inclusion (state under laser action: L – liquid; M – melted)	State of steel matrix under laser action, H_m , x 10, MPa	H_m^{inc} , x 10, MPa and (K_i) in zones		
			1	2	3
(Fe,Mn)S+ TiCN, E3	(Fe,Mn)S (L) TiCN (M)	L, 290	516 (1,78)	447 (1,54)	- -
MnO·SiO ₂ + MnO, 60G	MnO·SiO ₂ (L) MnO (L)	L, 620	1128 (1,82)	868 (1,4)	806 (1,3)
FeO-TiO ₂ + TiCN, 08T	FeO-TiO ₂ (L) TiCN (M)	L / M, 280	451 / 395 (1,61) / (1,41)	403 / - (1,44) / -	- / - - / -
MnO·SiO ₂ + Cr ₂ O ₃ , 08H	MnO·SiO ₂ (L) Cr ₂ O ₃ (M)	L / M, 295	543 / 493 (1,84) / (1,67)	407 – (1,38) / -	- / - - / -

4. Conclusions.

The main factor for strengthening the phase-adjacent type of "dispersed phases are in non-metallic matrix" the steel matrix is its microalloying from internal sources, which are the phases of ph-m1 and d2 of nonmetallic inclusion. In this case, by forming local liquation zones near each inclusion phase, saturation zones of a cascade-type and cascade-spotted- type steel matrix are created, which are layered composite regions near the phase differences of nonmetallic inclusions

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Structure and magnetic properties of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ ($0,05 \leq x \leq 0,60$) solid solutions

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Abstract: Intermetallic alloys and solid solutions having magnetostructural phase transitions are of interest for theory and practice due to the presence of magnetoresistance, magnetocaloric and magnetostriction effects. MnNiGe -based alloys and solid solutions are convenient model objects for studying static and dynamic distortions of the crystal lattice, since magnetostructural transformations of both the first and second kind realized in them. The features of the relationship of magnetic properties and changes in the crystalline structure of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ ($0,05 \leq x \leq 0,60$) solid solutions are studied. It has been established that MnNiGe is an antiferromagnet with a Néel temperature $T_N \approx 346$ K. Substitution of Mn ions with iron ones causing a decrease in the parameters of the MnNiGe unit cell leads to the emergence of a ferrimagnetic state and in some cases to a manifestation of ferromagnetic ordering of magnetic moments.

Keywords: INTERMETALLIC ALLOYS, SOLID SOLUTIONS, MAGNETIZATION, FERRIMAGNETS

1. Introduction

It is known that the crystalline, magnetic and electronic subsystems of materials are closely related. A striking manifestation of this relationship is the phase transformations induced by external influences in various solid-state objects, which are now being actively investigated. In particular, magnetic phase transformations in magnets lead not only to changes in the magnetic order, but are also accompanied by changes in the symmetry of the crystal lattice and local electronic splitting of magnetoactive bands. This can lead, in particular, to a colossal magnetocaloric effect, which turns out to be important for practical use in cooling devices - magnetic refrigerators operating at room temperature. Multicomponent alloys of 3d-transition elements, including Heusler alloys, in which phase transformations induced by external influences (electric and magnetic fields, pressure, temperature) are observed with manifestation of special physical properties (spin rearrangement of the system, its electronic instability, a giant magnetocaloric effect, etc.), have recently caused increased interest in connection with the revealed prospects of their practical use.

Alloys based on ternary compounds MnNiGe , MnCoGe , MnZnSb , due to the presence of magnetic and structural phase transformations in a wide temperature range, have properties and effects that are in demand in the development of new microelectronic devices. Among them are such as the giant magnetocaloric effect, magnetoresistance, magnetostriction, shape memory effect induced by a magnetic field [1-13]. By selecting the elements of substitution or alloying in ternary alloys MnNiGe , MnCoGe , one can control the properties, creating new states with spontaneous magnetization, form conditions for changes in magnetoelastic interactions [14-16]. From the point of view of fundamental science, alloys and solid solutions based on MnNiGe are interesting model objects for determining the values of static and dynamic distortions of the crystal structure, since phase transformations of both the first and second kind are realized in them.

The aim of this work is to synthesize $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions, study the features of the crystal structure, and determine the values of fundamental magnetic characteristics.

2. Experimental part

Polycrystalline samples of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ ($0,05 \leq x \leq 0,60$) solid solutions were synthesized by solid-phase reaction method. The mixture with the required ratio of the powders of the initial elements in evacuated quartz ampoules was heated to a temperature of 1323 K. The resulting sintered samples were subjected to homogenizing annealing at 1223 K, followed by quenching. For the studies, the compositions $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ were synthesized with a concentration step of 5 (before $x = 0,30$) and 10 mol.% (after $x = 0,30$). The crystal structure and phase composition studies of the samples after each stage of the synthesis was carried out at room temperature by X-ray diffraction in Cu K α - radiation.

The temperature dependences of the specific magnetization $\sigma = f(T)$ and the reciprocal of the magnetic susceptibility $1/\chi = f(T)$ were

studied in a magnetic field with an induction $B = 0,86$ T by the ponderomotive method [17] in the temperature range of $\sim 80 - 800$ K.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solution powders obtained at 300 K in the range of angles $20^\circ \leq 2\theta \leq 95^\circ$ after all stages of the synthesis by the method of solid-phase reactions in evacuated quartz ampoules.

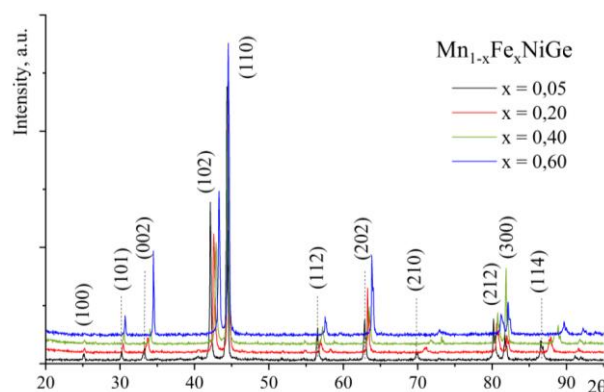


Fig. 1 X-ray diffraction patterns of obtained after all stages of the synthesis $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solution powders.

It was found that at a room temperature the $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ ($0,05 \leq x \leq 0,60$) solid solutions have a hexagonal crystallographic Ni_2In ($B8_2$) type structure of the $P6_3/mmc$ space group. There is a fairly smooth variation in the angular positions of diffraction reflections and redistribution of their intensities in the concentration range $0,05 \leq x \leq 0,60$, which is typical for solid solutions with cationic substitution. The concentration dependences of parameters a , c and unit cell volume V of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions are shown in Figure 2.

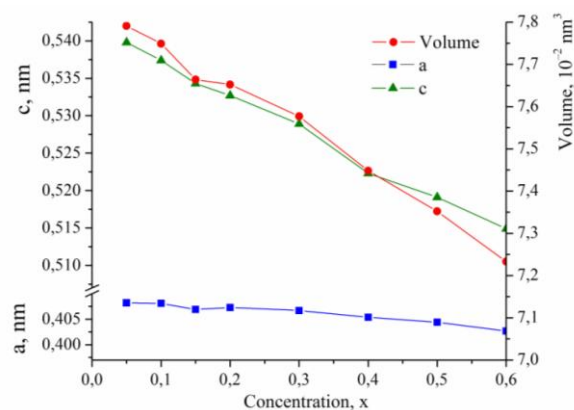


Fig. 2 Concentration dependences of parameters $a = f(x)$, $c = f(x)$, $V = f(x)$ change of the hexagonal unit crystal cell of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions.

The numerical values of the quantities characterizing the sizes of the hexagonal unitary crystal cells a and c , the ratio of the c/a axes, the values of the unit cell volumes V and the X-ray density ρ_{ren} of powders of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions at $T \sim 300$ K are given in Table 1.

Table 1: Values of a and c , c/a ratio, values of unit cell volumes V and X-ray density ρ_{ren} of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions.

x	a , nm	c , nm	c/a	V , 10^{-2} nm^3	ρ_{ren} g/cm^3
0.05	0,408 ₁	0,539 ₁	1,32	7,78	7,95
0.10	0,407 ₈	0,536 ₂	1,31	7,72	8,01
0.15	0,407 ₆	0,533 ₇	1,31	7,68	8,06
0.20	0,407 ₁	0,530 ₉	1,30	7,62	8,12
0.25	0,407 ₂	0,529 ₇	1,30	7,61	8,14
0.30	0,406 ₅	0,527 ₄	1,30	7,55	8,21
0.40	0,407 ₄	0,525 ₇	1,29	7,56	8,22
0.50	0,407 ₄	0,521 ₉	1,28	7,50	8,27
0.60	0,406 ₅	0,519 ₅	1,28	7,43	8,35

The variation of the $a = f(x)$, $c = f(x)$, $V = f(x)$ dependences in Fig. 2 demonstrates that the change in the unit crystal cells parameters at ~ 300 K with a change in the concentration x of the Fe content in the synthesized samples agrees with the Vegard rule for continuous series of solid solutions. A decrease in the parameters a and c upon cationic substitution is most likely a consequence of the difference in the ionic radii of the divalent manganese cations (0.91-0.80) Å and iron (0.82-0.74) Å.

The temperature dependences of the specific magnetization of some $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions are shown in Figure 3.

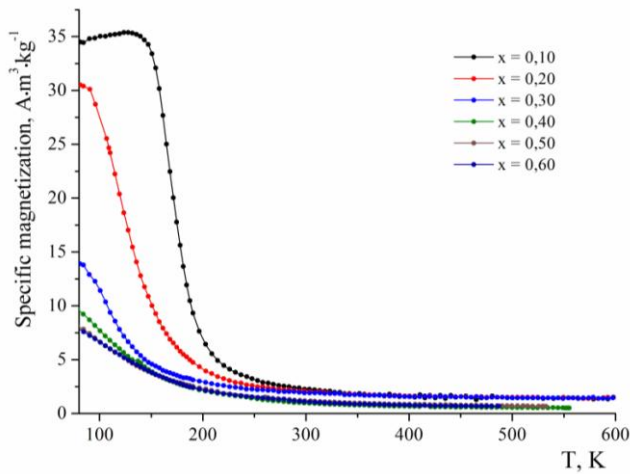


Fig. 3 Temperature dependences of the specific magnetization of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions in a magnetic field of 0.86 T.

Cationic substitution in the $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ system already at 10% substitution of iron for manganese leads to degradation of the antiferromagnetic ordering. The dependences $\sigma = f(T)$ of some compositions indicate the retention of a significant fraction of the antiferromagnetic component at temperatures $T < 150$ K. At concentrations $x > 0.10$, solid solutions exhibit the presence of an uncompensated magnetic moment with a specific magnetization of ~ 8.0 to $\sim 36 \text{ A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$ at $T = 80$ K. Table 2 shows the values of the magnetic moments of solid solutions calculated from the values of the specific magnetization at 80 K, using formula (1):

$$\mu = \frac{\sigma \cdot M}{N_A} \mu_B, \quad (1)$$

where σ is the value of the specific magnetization at nitrogen temperature, M is the molar mass, μ_B is the value of Bohr's

magneton, N_A is Avogadro's constant. The temperatures of the "magnetic order - magnetic disorder" phase transformation in solid solutions of the $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ system were determined using the dependence of the square of the specific magnetization $\sigma^2 = f(T)$.

Table 2: Specific magnetization at 80 K, Curie temperatures and average magnetic moments of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ solid solutions.

x	$\sigma_{80\text{K}}$, $\text{A} \cdot \text{m}^2 \cdot \text{kg}^{-1}$	T_C , K	$\mu_{80\text{K}}$, μ_B
0.05	13.69	272	0.46
0.10	34.53	183	1.15
0.15	36.07	153	1.20
0.20	30.55	148	1.02
0.25	20.38	143	0.68
0.30	13.90	137	0.46
0.40	9.45	-	0.32
0.50	7.98	-	0.27
0.60	7.85	-	0.26

4. Summary

Solid solutions of $\text{Mn}_{1-x}\text{Fe}_x\text{NiGe}$ system in the concentration range $0.05 \leq x \leq 0.60$ by the solid state reaction method were synthesized. X-ray diffraction studies have shown that the samples are single-phase at room temperature. It was found that an increase in the concentration of iron in solid solutions leads to a decrease in the size of the unit crystal cell. It is revealed that the temperature of the phase transformation "magnetic order - magnetic disorder" of the studied samples decreases with an increase in the concentration x of substitution of manganese by iron ions from 272 K for $\text{Mn}_{0.95}\text{Fe}_{0.05}\text{NiGe}$ to 137 K for the $\text{Mn}_{0.70}\text{Fe}_{0.30}\text{NiGe}$ solid solution.

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Layered heat resistant (Nb–V) composites with intermetallic hardening, obtained by diffusion welding

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Abstract: The microstructure and characteristics of the heat resistance of layered composites of Nb–V alloys and intermetallic compounds with aluminum are presented. The composites obtained by diffusion welding under pressure of packages of aluminum foils and foils of niobium alloys with 5, 10, and 15 at. % vanadium had structures representing an alternation of viscous-plastic layers and reinforcing layers of aluminides. The composites were characterized by a viscous-plastic nature of fracture and higher values of strength at room temperature and temperatures up to 1300°C, in comparison with composites without vanadium.

KEYWORDS: LAYERED COMPOSITE, NIOBIUM-VANADIUM ALLOY, INTERMETALLIC COMPOUND, HEAT RESISTANCE, DIFFUSION WELDING, REACTIVE DIFFUSION, MULTILAYER STRUCTURE, STRENGTH, CREEP

1. Introduction

There is an objective need for the development of new-generation structural heat-resistant materials. Niobium alloys are one of the few major contenders for this role. Interest in alloys lies in the production of machine parts and mechanisms from them for operation in a loaded state at temperatures up to 1300°C and, possibly, higher. The requirements for materials are high values of strength, creep resistance, and phase stability at operating temperatures in combination with good crack resistance at room temperature and low density [1, 2].

At present, nickel superalloys remain the most common material for manufacturing, for example, turbine blades. However, their operational properties came very close to the theoretical limit and their further increase became objectively impossible [3, 4]. Instead of Ni alloys, alloys based on the systems Nb–Si, Nb–Al, Mo–Si and some others are being investigated [5–10]. At this point it is necessary to explain that the mentioned works refer to cast alloys. But they do not in the least reflect the real scale of published works devoted to high-temperature alloys obtained by various melting technologies. The heat-resistant composite considered in this communication is formed using a technology that has no analogs with melt methods.

The combination of Nb-alloy and its compounds with Al, Si and C in the structure of the composite reduces its density in comparison with the density of niobium and its alloys, due to the relatively low density of aluminides [8]. But, since all intermetallics are brittle, especially under normal conditions, the problem of crack resistance of the material arises, which, however, is not insurmountable. The optimal organization of the composite structure is capable of providing it with acceptable fracture toughness at room temperature.

For the formation of a layered structure of heat-resistant materials based on the Nb–Al system, the methods of layer-by-layer spraying are widely used in world practice [11–14]. In Russia, for materials with layered structures, the solid-phase technology is more accepted, which consists in diffusion welding of artificially formed multilayer packages or in diffusion welding and subsequent rolling of packages, in particular, on a vacuum rolling mill and then rolling at room temperature [15, 16]. In such a method, the satisfactory crack resistance required by laminated composites is achieved by alternating brittle layers of intermetallic compounds with relatively plastic layers of base metal solid solutions. If we bear in mind the scale of technologies for producing a composite in the future, then we believe that spray technologies are inferior to technologies of diffusion welding and rolling.

In this work, we use melting methods only to obtain niobium-vanadium alloys.

Despite a fairly large number of works on high-temperature materials of a new generation, there are no data in the literature on the effect of various metals, in particular, vanadium, on the structure and mechanical characteristics of layered Nb composites. According to the data of a fairly large number of works on the effect of vanadium on the mechanical properties of cast alloys, alloying with vanadium leads to an improvement in their ductility. Similar studies have been undertaken in this work.

2. Materials, diffusion welding of bags and research methods

Nb- and V-rolled products were used as starting metals, from which niobium alloys with 5, 10, and 15 at. % Vanadium were smelted by the method of levitation at argon pressure $(0.35\text{--}0.45)\times 10^5$ Pa in a suspended state with a rotating frequency electromagnetic field ~ 200 kHz. After holding in the liquid state for 1–2 min, the field was turned off, and the samples fell under the action of gravity into a Cu mold weighing 480 g with an inner “flat cavity” 4 mm thick and 20 mm long, where the ingot crystallized under quenching conditions. The resulting ingots in the form of plates with a thickness of 4 mm were inserted into stainless steel capsules for protection against possible oxidation and rolled on a vacuum rolling mill with preheating to 1000°C and a degree of deformation of $\sim 50\%$. After hot rolling, the samples were removed from the capsules and rolled at room temperature to a strip 150 μm thick.

Multilayer packages were assembled from alternating foils of rolled Nb–V ingots and Al foils 12 μm thick, laid in two layers. The calculated thickness of the package was ~ 2 mm. The formation of the layered structure of the composites was carried out in the process of diffusion welding (DW) of multilayer packets, which was carried out on a unit with a graphite heater, designed for a maximum load of 10 T and a temperature of up to 1700°C. The package to be welded was placed between the movable and fixed punches. Two layers of Graflex graphite tape were laid between the outer surfaces of the package and the punches. The welding temperature was controlled by a (W–Re) thermocouple.

The packages were welded in a vacuum of at least 10^{-4} Torr, first at 500°C for 1 h and a pressure of 4.1 MPa. Then the temperature was increased to 1700°C, and the bag was kept for 15 minutes without pressure, and then for another 15 minutes under a pressure of 30.6 MPa. After welding, the packages had dimensions $35\times 20\times 2$ mm.

The resulting laminated composites were cut into rods for structural studies and mechanical tests for three-point bending and fracture toughness. After cutting, all surfaces of the samples were first subjected to abrasive grinding and then polishing.

Microstructure studies and local X-ray spectral analysis (LXSA) were carried out on digital scanning electron microscopes Tescan VEGA-II XMU and CamScan MV230 at an accelerating voltage of 20 kV and an electron probe current of 200 pA. Размер зонда – 0,16 μm . The characteristic X-ray spectra were processed using a software package developed by Oxford Instruments, the calculation part of which is based on the PAP matrix correction algorithm [17].

Test samples of the short, with a loading rate of 0.5 mm/min, and long durability was carried out at temperatures of from 20 to 1300°C according to the scheme 3-point bending in the vacuum chamber, combined with the test machine «Instron», a high purity argon. To ensure the proper rigidity of the tooling during temperature tests, the supports were made of special heat-resistant ceramics based on silicides of refractory metals.

Ultimate strength [18] σ_B was determined at maximum load P according to the well-known formula: $\sigma_B = 3PL/2bh^2$, where P – load, L – distance between supports, b and h – width and height of the sample, respectively.

The creep of the composites was investigated on samples with dimensions $2.5 \times 2 \times 20$ mm at 1300°C in an argon atmosphere.

Determination of the relative strain rate $\dot{\varepsilon}$ in the section of steady-state creep was carried out on the basis of the problem of rod bending (Figure 1).

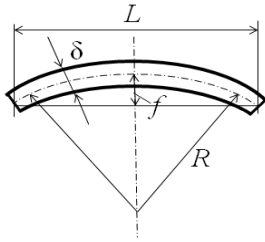


Figure 1. Rod with thickness δ in bending: f – deflection, R – bending radius

According to this task $f = R - \sqrt{R^2 - \frac{L^2}{4}}$ (1), where L is the distance between the supports. For the case when $R \gg L$: $f = R - R(1 - \frac{1}{8} \frac{L^2}{R^2})$ (2), where $R = \frac{1}{8} \frac{L^2}{f}$. Then the relative

deformation ε is equal to: $\varepsilon = \frac{2\pi(R + \frac{\delta}{2}) - 2\pi R}{2\pi R} = \frac{\delta}{2R}$ (3) With the same designs of the initial packages and modes of DS, the macro- and microstructures of the composites (Nb5V) / Al and (Nb15V) / Al differed significantly (Fig. 4.). Substituting the expression for R in (3), we obtain $\varepsilon = \frac{\delta}{2} \frac{1}{\frac{1}{8} \frac{L^2}{f}} = \frac{4\delta}{L^2} f$ and $\dot{\varepsilon} = \frac{\partial \varepsilon}{\partial t} = \frac{4\delta}{L^2} \frac{\partial f}{\partial t} = \frac{4\delta}{L^2} \dot{f}$ (4).

We used the following form of the dependence of the creep rate on stress and temperature: $\dot{\varepsilon} = \frac{4\delta}{L^2} \dot{f}$ (5), where $\dot{\varepsilon}$ – strain rate (s^{-1}), $\dot{f}$ – deflection rate (mm/s), δ – specimen height (mm) and L – distance between supports (mm).

3. Experimental results

3.1. Microstructure of composites

The melted and rolled Nb–V alloys had a homogeneous structure of continuous solid solutions of Nb and V without any other structural components.

The cross-sectional structure of the composite with the Nb–5 at. % V (Fig. 2, a) was an alternation of light layers up to $100 \mu\text{m}$ thick and thin (about $10 \mu\text{m}$) dark layers. At higher magnification, they had three layers (Fig. 2, b)

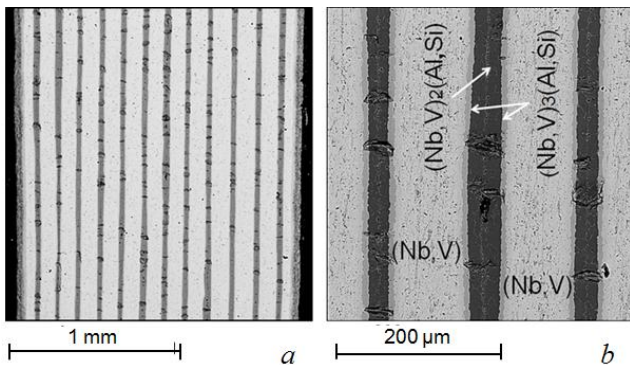


Figure 2. Macro- (a) and microstructure (b) of the layered composite Nb5V/Al based on the alloy Nb–5 at. %V after DW

According to local X-ray diffraction data (Fig. 3, a), the structure of diffusion layers in the (Nb5V)/Al composite consisted of a $(\text{Nb,V})_2(\text{Al,Si})$ compound layer $30\text{--}35 \mu\text{m}$ thick enclosed between two thin ($5\text{--}8 \mu\text{m}$) by layers of the compound $(\text{Nb,V})_3(\text{Al,Si})$. In both intermetallic compounds, silicon was found at a level of 0.5 at. %, which was present in aluminum as an impurity. Regarding the distribution of vanadium, we can say that its presence in niobium is limited to 4 at. %, and in layers of intermetallic compounds $(\text{Nb,V})_3(\text{Al,Si})$ and $(\text{Nb,V})_2(\text{Al,Si})$ – 0.5 and 1 at.%, respectively.

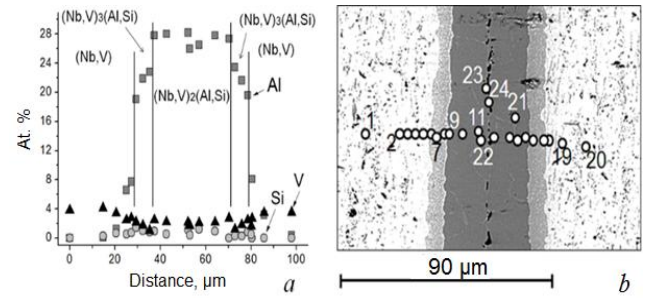


Figure 3. Results of local XS-analysis (a) and microstructure of the interaction zone between the layers of alloy and aluminum (b) in the layered composite Nb5V/Al after diffusion welding: 1–24 – points local XSA-analysis

The microstructure of the layer formed as a result of the mutual diffusion of aluminum and the alloy is shown in Fig. 3, b. Note the presence in the central part of the $(\text{Nb,V})_2(\text{Al,Si})$ compound layer of a line of dark inclusions of Al_2O_3 oxide (23 and 24 – points of local XSA).

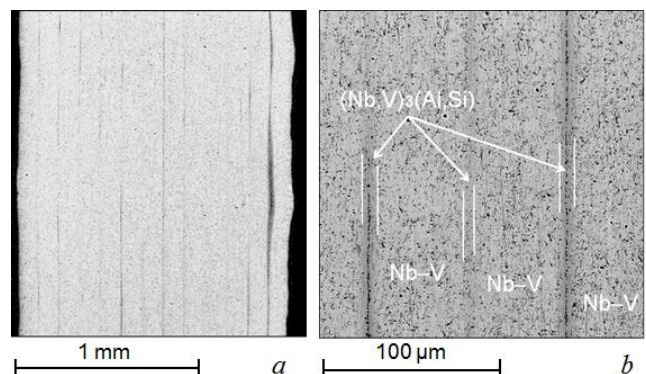


Figure 4. Macro- (a) and microstructure (b) of a layered composite Nb15V/Al based on an alloy Nb–15 at. %V after DW

Similar studies are presented for a composite based on an Nb – 15 at. %V. With the same designs of the initial packages and modes of DW, the macro- and microstructures of the composites (Nb5V)/Al and (Nb15V)/Al differed significantly (Fig. 4).

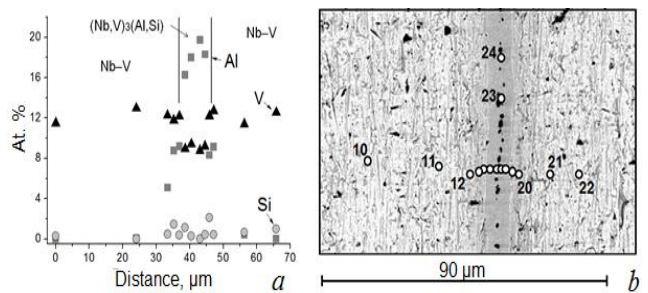


Figure 5. Results of local XS-analysis (a) and microstructure of the interaction zone between the layers of the alloy and aluminum (b) in the layered Nb15V/Al composite after diffusion welding: 1–24 – points of local XSA-analysis

The layered structure of the composite with 15 at. % vanadium is characterized by "diffuseness" of the macro- and microstructure with an almost complete absence of interlayer boundaries (Fig. 4, b). In addition, it can be noted that the "saturation" of the niobium - vanadium alloy layers with ultradispersed inclusions is significantly higher than in the composite with 5 at. %V (compare Figs. 2, b and 4, b). This is most likely due to the presence of finely dispersed carbide inclusions formed during the welding of packets due to the presence of CO in the atmosphere of a chamber with a graphite heater. Confirmation of this can be obtained when compared to composites microstructure layers of Nb-V alloys at high magnification (cp. Fig. 3, b and 5, b). It is clear that the Nb15V/Al composite contains a significantly larger amount of light gray needle-like inclusions than the Nb5V/Al composite.

The results of the LXS-analysis of the composite with 15 at. % vanadium, shown in Fig. 5, a showed that the layer formed during diffusion welding is a compound $(\text{Nb,V})_3(\text{Al,Si})$, in which 8 at% vanadium is dissolved. Vanadium is present in the layers of the (Nb-V)-alloy in an amount of 12 at. %. Local analysis points 23 and 24 (see Fig. 5, b) show Al_2O_3 inclusions in the center of the $(\text{Nb,V})_3(\text{Al,Si})$ -layers.

Summarizing the results of microstructural studies, it can be noted that:

- the layered structure of the composites consisted of viscous-plastic layers of (Nb-V)-alloys and strengthening intermetallic layers of $(\text{Nb,V})_3\text{Al}$ and $(\text{Nb,V})_2\text{Al}$ compounds with a low silicon content;
- the solubility of vanadium in the layers of the intermetallic compound $(\text{Nb,V})_3(\text{Al,Si})$ was ~ 0.5 in the Nb5V/Al composite, from 3 to 4 – in the Nb10V/Al composite, and 8 at. % – in the Nb15V/Al composite;
- the vanadium concentrations in the layers of the intermetallic compound $(\text{Nb,V})_2(\text{Al,Si})$ were at the level of ~ 1 and ~ 5 at% for the composites Nb5V/Al and Nb10V/Al, respectively.

In addition, in the diffusion zones of composites with alloys Nb-5 and 10 at. %V, a full set of intermetallic compounds of the Nb-Al system could be observed, such as: $(\text{Nb,V})_3(\text{Al,Si})$, $(\text{Nb,V})_2(\text{Al,Si})$ and $(\text{Nb,V})(\text{Al,Si})_3$. However, the Nb15V/Al composite contained only the compound $(\text{Nb,V})_3(\text{Al,Si})$, which in places transforms into a "concentrated" solid solution of aluminum in the Nb-15 at. %V alloy. Hence it follows that vanadium accelerates the formation of intermetallic compounds of niobium with aluminum.

3.2. Flexural strength tests

The dependence of the short-term bending strength σ_B of the composites on the test temperature in the range from room temperature to 1300°C is shown in Fig. 6. The strength of the composites, depending on the vanadium content in the Nb-V alloy, showed a monotonic increase from 660 to ~ 1215 MPa both at room temperature and at 1300°C – from ~ 265 to 390 MPa.

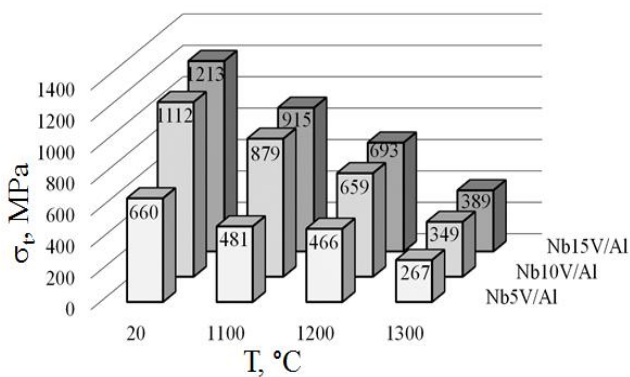
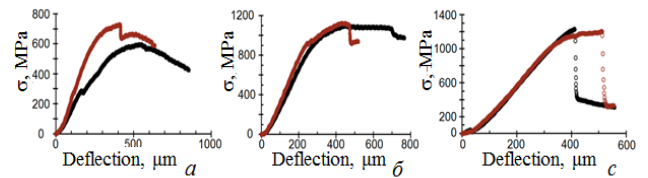


Figure 6. Dependence of the average values of σ_t on the test temperature and vanadium content

Bending tests of composite specimens at room temperature showed a ductile fracture pattern (Fig. 7). The load was applied perpendicular to the layers. The maximum on the load-displacement

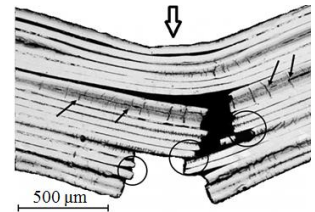


curves corresponded to a deflection without fracture equal to 400 μm . Almost all composite samples of alloys Nb-5 and 10 at. %V continued to bend without destruction, up to a deflection of 700–800 μm .

Figure 7. Typical test curves for laminated composites at room temperature: a – Nb5V/Al, b – Nb10V/Al, c – Nb15V/Al

If the composite had some kind of destruction (see Fig. 7, c), then it was characterized by a "layered" mechanism. Delamination was observed along the brittle intermetallic components of the sample, as less crack-resistant structural elements in the composite (Fig. 8). The arrows also show short transverse cracks in the intermetallic layers. On the contrary, when individual layers of the (Nb-V)-alloy were destroyed, viscous-plastic signs appeared. All the ends of the layers had a thinning of their middle part testifying to this.

Figure 8. The nature of the destruction of the investigated layered composites Nb15V/Al at room temperature



3.3. Creep tests

The experimental dependences for composite specimens that were tested for creep at 1300°C are shown in Fig. 9 and are summarized in table. 1. The so-called 100-hour strength or the magnitude of the stress causing deformation in the composite equal to 1% per 100 hours was estimated.

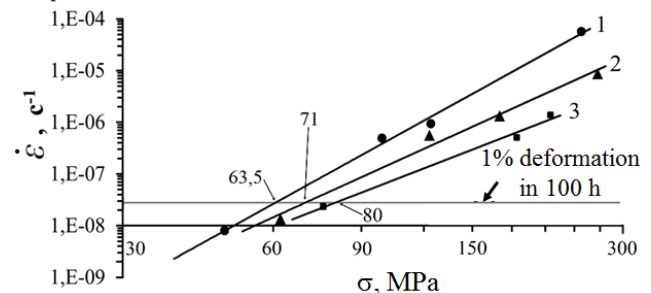


Figure 9. Dependences of the creep strain rate on stress for composites Nb5V/Al (1), Nb10V/Al (2) and Nb15V/Al (3) at a temperature of 1300°C

Tests of composites for creep at 1300°C showed the following results: the magnitude of the stress causing deformation in the composite equal to 1% per 100 h or the so-called 100-hour strength of composites based on niobium alloys with 15, 10, and 5 at. % V was equal to 80, 71 and 63.5 MPa.

Table 1. Results of creep tests of composites

Композит	100-часовая прочность σ_{100} , МПа	Показатель степени, n
Nb5V/Al	63,5	3,75
Nb10V/Al	71,0	4,40
Nb15V/Al	80,0	5,73

However, the exponents n (from 3.75 to 5.73) of the composites are rather large, which indicates the sensitivity of the composites under study to a change in the applied voltage and can negatively affect the operational properties of the material.

3.4. Discussion of the results obtained

Microstructure studies showed that vanadium accelerated reactive diffusion between layers of Nb-V and Al alloys in welded NbV/Al packages. This followed from the fact that under the same

welding conditions in a composite with an Nb–5 at. %V, the interaction zone consisted of $(\text{Nb,V})_2(\text{Al,Si})$ and $(\text{Nb,V})_3(\text{Al,Si})$ layers bounded by explicit phase boundaries. In contrast, in a composite with 15 at. %V, the interaction zone was characterized by an almost complete absence of phase boundaries and consisted only of the compound $(\text{Nb,V})_3(\text{Al,Si})$. The composite of Nb-alloy with 10 at. %V occupied an intermediate position. Compared to other composites, the best strength properties were for the Nb15V/Al composite.

The different solubilities of vanadium in the intermetallic compounds Nb_3Al and Nb_2Al can be explained by referring to the phase diagrams of Nb–Al and V–Al. At atmospheric pressure, the V–Al phase diagram does not contain the V_3Al compound, which is related to the Nb_3Al compound. But on the other hand, it contains a "twin" compound of the Nb_2Al intermetallic compound (33.3 at. % Al) – V_5Al_3 (37.5 at. % Al). Hence, the higher solubility of vanadium in the intermetallic compound Nb_2Al than in Nb_3Al .

The achieved results in terms of strength are comparable with similar data for highly alloyed eutectic alloys of the Nb–Si system [19], but in terms of viscos-plastic properties they are much superior. But the fact is that if the fracture toughness of the composites obtained is calculated according to the generally accepted method after bending tests of notched specimens, then, due to their high plasticity, its calculations will be incorrect. Therefore, we have no numerical values for this characteristic of composites. By the method we used, we tested materials with fracture toughness of $25 \text{ MPa}\cdot\text{m}^{1/2}$ and even more. Such values were considered very high. Returning to niobium-vanadium alloys, one can foresee that their fracture toughness values can exceed $25\text{--}30 \text{ MPa}\cdot\text{m}^{1/2}$.

4. Conclusions

1. From the data of local X-ray spectral analysis, it followed that vanadium in the intermetallic layers Nb_3Al and Nb_2Al was dissolved in significantly different amounts, respectively:

– 0.5 and 1.0 – in the Nb5V/Al composite with its content in the alloy equal to 4 at. %;
– 3.5 and 5.0 – in the Nb10V/Al composite with its content in the alloy equal to 8 at. %.

2. Mechanical tests of laminated composites for short-term strength showed a monotonic increase in strength with an increase in vanadium content in the Nb–V alloy, both at room temperature and at $1100\text{--}1300^\circ\text{C}$. Mechanical tests of laminated composites for short-term strength showed a monotonic increase in strength with an increase in vanadium content in the Nb–V alloy, both at room temperature and at $1100\text{--}1300^\circ\text{C}$.

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Development of products manufacturing technology based on piezoceramics

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Abstract: A technology has been developed for producing a tubular mover based on piezoceramics PZT-19, PZN-PT-BT, PZN-PT-PZ by dry radial-isostatic pressing used for the production of scanning tunnel microscopes as a manipulator of precise movements.

KEYWORDS: SCANNING TUNNEL MICROSCOPE, TUBULAR MOVER, PIEZOCERAMICS, TECHNOLOGY, DRY RADIAL ISOSTATIC PRESSING

1. Introduction

Materials based on piezoceramics are widely used to create efficient and reliable systems and devices [1–3].

The creation of a scanning tunnel microscope (STM) broke new ground in the development of many areas of contemporary science and technology [4–7]. During the development of STM, the requirements for the microscope design were more fully defined. In general form, it contains a tip with a device for precise movements, a base with a vibration protection system, and a control device for displaying information. Generally, the movement device should provide six degrees of movement: in threes for rough and precise positioning. Piezoceramic manipulators are small-sized and highly rigid, i.e. they have high resonant frequencies; they are easy to manufacture; they are suitable for work in various environments and ultra-high vacuum; they do not set up electromagnetic fields, and make it possible to achieve atomic resolution. The characteristics of the movements for the STM operation can be evaluated as follows:

- a range of precise movements in the X, Y, Z directions – not less than 400 nm;
- a range of rough movements in the X, Y, Z directions – more than 1 mm;
- shot size of movements – up to 1x1 nm;
- resolution in X, Y directions – about 0.1 nm;
- resolution in the Z direction – 0.01 nm;
- thermal drift in the X, Y directions – no more than 0.4 nm/min, in the Z direction – no more than 0.05 nm/min.

The purpose of this work was to develop a piezoceramic-based manufacturing technology for products used for STM as a manipulator of precise movements.

2. Experimental technique

To obtain a tubular mover based on piezoceramics, used for the manufacture of scanning tunnel microscopes as a manipulator of precise movements, pre-synthesized ceramic materials PZT-19, PZN-PT-BT, PZN-PT-PZ were used which were mixed with the addition of 3% binder (polyvinyl acetate adhesive (PVA) for 12-14 hours. Then the powder was dried and granulated.

Ceramic tubular blanks were pressed in O.V. Roman Powder Metallurgy Institute by the method of dry radial isostatic pressing [8], based on the use of an intermediate elastic medium, which separates the molded powder blank and the medium transferring the compaction pressure to the powder through this shell on the ISPR.1 isostatic equipment. The isostat is shown in Figure 1.

The equipment (Figure 1) for the implementation of this method includes a high-pressure pump, a pressing chamber with a hydraulic cylinder for extracting a press tooling (Figure 2) with a molded powder blank, and a vibration stand for compacting the powder in a pressing die (Figure 3). The press tooling for pressing consists of a die (shell) of polyurethane, metal rods with a base, uniformly placed inside the tooling and a fixing nut (Figure 2).



Fig. 1. External view of the isostatic pressing equipment ISPR.1



Fig.2. Press tooling with molded blank assembly

The prepared charge mixture was poured into the cavity of the press tooling and compacted on a vibration stand. The press tooling was placed in isostatic pressing equipment. The pressing was carried out at a pressure of 100 MPa. Then, the pressed blanks were burned at temperatures of 1000 - 1270 °C for 1-2 hours in air.

The burned tubular blanks were cut into sections of the required length, polished, metallized, and polarized. Piezoceramic tubular propelling devices with a length of 40-70 mm and a diameter of 11.2 mm with a wall thickness of 0.5 mm were produced from tubular blanks 450 mm long. The tubular piezoceramic products are shown in Figure 4.



Fig. 3 A vibration stand for powder compaction



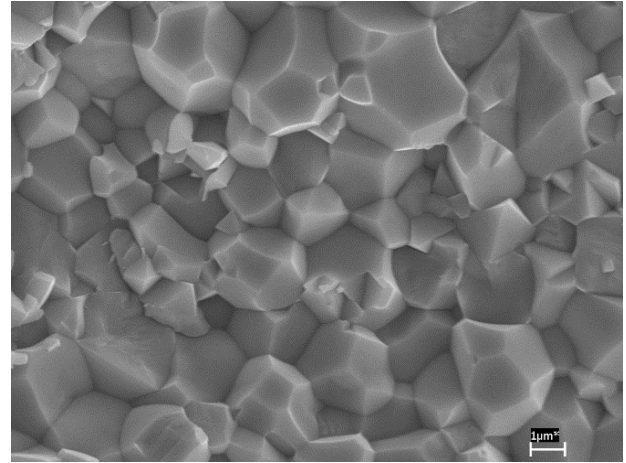
Fig. 4 A view of the blanks of a tubular propelling device for precise movements

3. Results and discussion

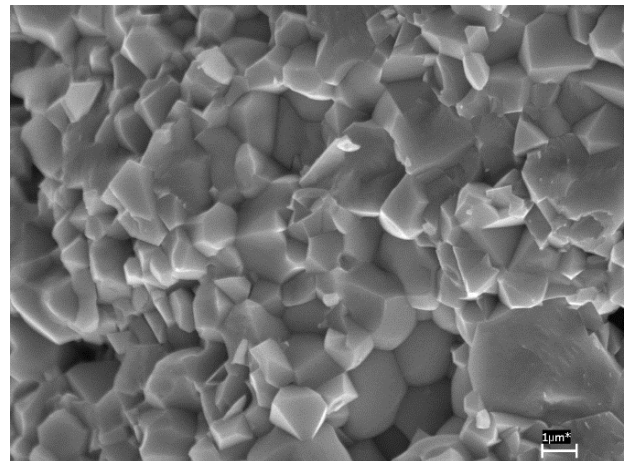
The study of the surface morphology and determination of the grain size of the phases of the studied ceramic materials was carried out using LEO 1455 VP scanning electron microscope of "Carl Zeiss" company. The microstructure of piezoceramic samples of PZT-19, PZN-PT-BT, PZN-PT-PZ materials used for the manufacture of products is shown in Figure 5.

The determination of the electrophysical and piezoelectric parameters of the ceramic samples was carried out according to the standard technique.

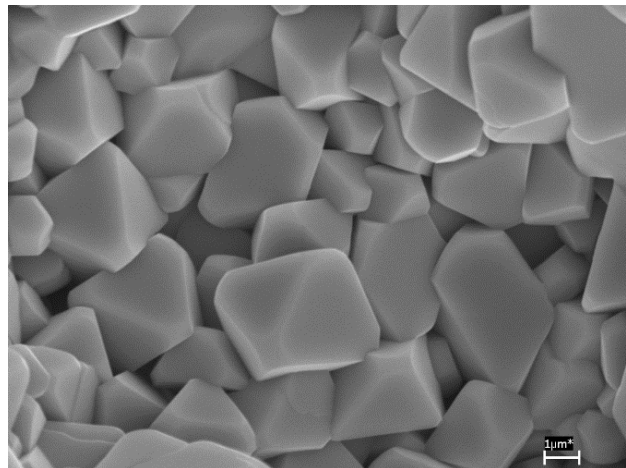
The dependences of the relative elongation on the value of the applied stress for all groups of samples were investigated. According to the data on the field dependences of movement for all groups of materials, graphs were built showing the electromechanical hysteresis for PZT-19 material (Figure 6), for PZN-PT-BT (Figure 7) and for PZN-PT-PZ (Figure 8); piezoelectric coefficients d_{31} are calculated for each material.



a)



b)



c)

Fig. 5 Microstructure of piezoceramic samples of materials: a) PZT-19; b) PZN-PT-BT; c) PZN-PT-PZ

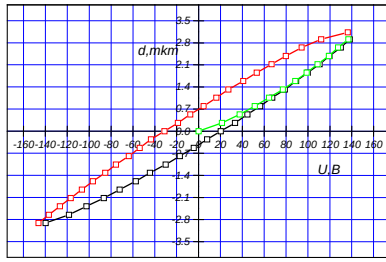


Fig. 6 Electromechanical hysteresis of PZT-19 piezoceramic material

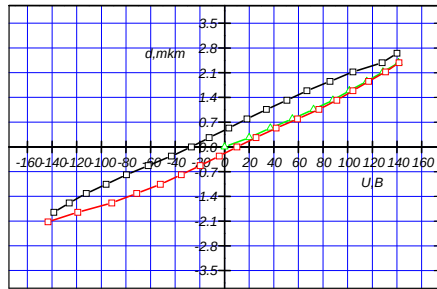


Fig. 7 Electromechanical hysteresis of PZN-PT-BT piezoceramic material

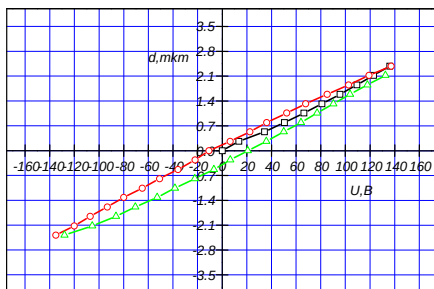


Fig. 8 Electromechanical hysteresis of PZN-PT-PZ piezoceramic material

Based on the research results, the optimization of the production technology of tubular movers was carried out.

As a result, tubular piezoceramic movers were developed with the following characteristics:

external diameter	– 11,2 mm
inner diameter	– 9,8 mm
length of piezoceramic mover	– 70 mm
piezomodule d_{31} at 295 K	– $170 \cdot 10^{-12}$ C/N
scan field at a voltage ± 150 V	– (140×140) nm
bending sensitivity	– 0,5 nm/v
density of piezoceramic material	– $7,68 \text{ g/cm}^3$
mechanical quality factor	– 120
dielectric permittivity	– 1600
polarization	– OD positive or OD negative
type of electrodes	– nickel; copper; copper-nickel.

Conclusion

Based on the results of the research, a technology was developed for obtaining, based on piezoelectric ceramics, PZT-19, PZN-PT-BT, PZN-PT-PZ, by isostatic pressing, tubular propellers) used for the manufacture of scanning tunneling microscopes, as a manipulator of precise movements.

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Effect of TiB₂ additives on sintering temperature, structure and properties of the composite material of the Fe- FeCr800 system

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Abstract: The effect of TiB₂ additives on the sintering temperature, structure, and mechanical properties of materials based on the Fe-FeCr800 system is investigated. It was shown that the introduction of titanium diboride additives leads to the activation of compaction and to a 50–70°C decrease in the sintering temperature of the pressed composites based on iron. It has been studied that the addition of titanium diboride in the range of 0.38–0.74 (% wt.) provides, with a slight increase in hardness, an increase of 20–25% of the flexural strength of the composite 65Fe–35 FeCr800 (wt.), and also provides the formation of a multiphase, microheterogeneous structure of the matrix-filled composite type, which consists of chromium steel of the X6Cr17 type, double iron-chromium carbides M₇C₃, M₃C and complex carboborides of the Me₃(CB) type.

KEYWORDS: POWDER MATERIALS, COMPOSITE, SINTERING, FE800, TiB₂, MICROHARDNESS.

Heterogeneous Fe-Cr-C alloys are marked by a significant difference in the properties of the structural components - carbide and metallic phases in terms of their hardness, strength, ability to plastic deformation, resistance to fracture. By changing the phase composition and heterogeneity of the structure, additional allocations of hard or soft inclusions can be obtained in the structure of ferrochromic alloys by doping and modification. Such hard inclusions can dramatically increase the abrasion resistance, and soft antifriction properties of alloys [1].

Carbide steels, by their properties, are intermediate between hard alloys and tool steels. They are most often based on alloy steels, including stainless steels, and titanium carbide or carbonitride is most often used as a solid component. In contrast to the known solutions, we have proposed an iron-based carbide steel with a high-carbon ferrochrome content of 35(% wt.) and titanium diboride as an alloying additive.

In our previous works [2, 3], it was shown that, as an initial chromium-containing solid component of a powder wear-resistant material based on iron, instead of chromium carbide, high-carbon ferrochrome powder FeCr800 of industrial production can be successfully used. As a result of the active interaction during the sintering of iron with high-carbon ferrochrome, complex iron-chromium are additionally formed in the material structure.

As the most stable compound of boron and titanium, TiB₂ is widely used due to its high melting point, high hardness and excellent wear resistance. By alloying chromium carbide steels Fe-FeCr800 with titanium diboride, materials with enhanced mechanical properties were obtained.

The aim of the work is to investigate the effect of titanium boride additives (0.38–2.2 wt. %) on sintering temperature, mechanical properties, and the structure of chromium carbide steels.

Objects and research methods

Iron powder, high-carbon ferrochrome and titanium boride powder were used as raw materials for the research. High-carbon ferrochrome powder was obtained from FeCr800 lump by mechanical grinding in a jaw crusher and then ball milled.

The source of boron in the mixture was titanium boride and the boron content in the mixture ranged from 0.12 to 0.67(% wt.). The choice of boron as an alloying additive is explained by the fact, that it gives [4] several times stronger effect on iron than carbon,

contributing to grain refinement and significantly increases the wear resistance of white cast iron. In addition, boron forms a low melting Fe-Fe₂B eutectic with iron and can activate the sintering process of a powder carbidosteel containing high carbon ferrochrome.

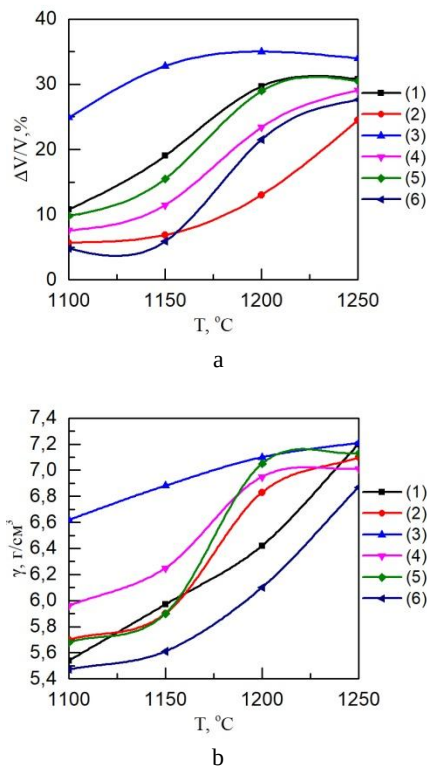
Powder mixtures of materials were prepared by wet milling-mixing in a ball mill in alcohol medium according to the regimes given in [4] article. The samples were pressed in a closed die at 800 MPa. Sintering was carried out in a vacuum electric furnace according to pre-established regimes that ensure the production of materials with maximum density. The mechanical properties of the samples were determined by standard methods for powder materials and hard alloys [5, 6]. The microstructure of the materials was examined on a REM-106I electron microscope. The phase composition of the samples was investigated by X-ray diffraction analysis (XRD) on the diffractometer "UltimaIV, Rigaku" (Japan).

Results and discussion

TiB₂ additives were introduced in an amount of 0.38–2.2 (wt. %), which corresponds to a titanium content of 0.5–2 (wt. %) in the Fe-35% FeCr800 alloy. A study of the effect of sintering temperature with an isothermal exposure of 30 minutes on density and volumetric shrinkage showed (fig. 1) that, with an increase in sintering temperature from 1100 to 1250°C, the density and volumetric shrinkage of the samples increase monotonously. Such a course of dependences is typical for powder materials, the sintering of which occurs first in the solid and then with the participation of the liquid phase.

With an increase in the content of the dopant, the increase in the density and shrinkage of the samples is somewhat inhibited, which is especially noticeable in materials with 1.48 and 2.2% TiB₂. This may be due to the consumption of dopant components (Ti and B) for the formation of complex Fe-Cr-Ti borides.

High values of volumetric shrinkage and density are observed for samples with 0.74 (% wt.) TiB₂. Even at sintering temperatures of 1100 - 1150 °C, the volumetric shrinkage of the material of this composition is 24.9 -32.8%, which is 1.5 times higher than that of the sample of the basic composition. With an increase in sintering temperature to 1200 °C, it reaches 34%, which is the highest value among the samples of all the mixtures given due to the formation of the liquid phase due to melting of the eutectic in the Fe-Cr-BC system (~ 1180 °C), and activation of the sintering process composite.

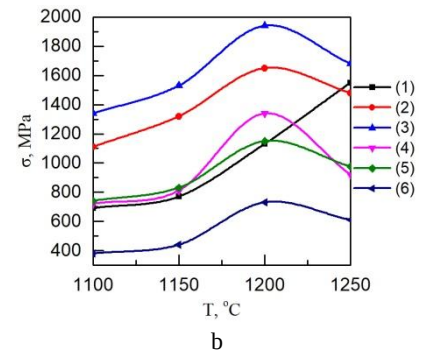
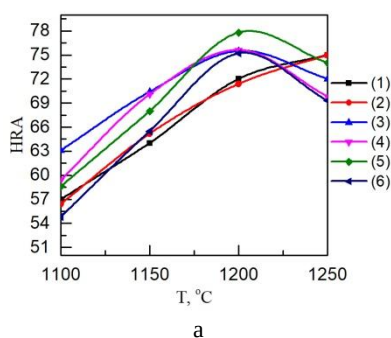


1- 65Fe-35 FeCr800; 2- 64,8Fe-34,8 FeCr 800-0,38TiB₂; 3- 64,6Fe-34,6 FeCr 800-0,74TiB₂; 4- 64,4Fe-34,4 FeCr 800-1,12TiB₂; 5- 64,2Fe-34,2 FeCr 800-1,48TiB₂; 6- 63,9Fe-33,9 FeCr 800-2,2TiB₂ (%wt.)

Figure 1 - Influence of sintering temperature and TiB₂ additives on volume shrinkage (a), density (b) of samples from composite material Fe-35%FeCr 800

With increasing sintering temperature to 1250 °C, the density and volumetric shrinkage of the samples decrease somewhat, which can be explained by the formation of the maximum amount of the liquid phase, therefore, the samples lose their shape and even begin to melt, especially when the TiB₂ content (1.48 and 2.2 %, wt.).

The study of the effect of sintering temperature on the hardness and flexural strength of materials Fe-FeCr800-(0.38-2.2%) TiB₂ showed (fig. 2) that an increase in sintering temperature from 1100 to 1200 °C leads to an increase in hardness and flexural strength of materials with titanium boride additives. With a further increase in sintering temperature to 1250 °C, there is a slight decrease in hardness and flexural strength of composites, which is associated with grain growth, loss of shape, and the beginning of fusion of samples.



1- 65Fe-35 FeCr800; 2- 64,8Fe-34,8 FeCr 800-0,38TiB₂; 3- 64,6Fe-34,6 FeCr 800-0,74TiB₂; 4- 64,4Fe-34,4 FeCr 800-1,12TiB₂; 5- 64,2Fe-34,2 FeCr 800-1,48TiB₂; 6- 63,9Fe-33,9 FeCr 800-2,2TiB₂ (%wt.)

Figure 2 - Influenced sintering temperature and the amount of TiB₂ on the hardness (a) and bending strength (b) of the material Fe-35% FeCr800

Electron studies and local micro X-ray spectral analysis of materials of the Fe- FeCr 800 system doped with TiB₂ showed that their structure is microheterogeneous, multiphase and consists of light gray, gray, dark gray and black phases. Alloying with the addition of TiB₂ affects the structure of the carbide phase of the composite, this is especially noticeable when the TiB₂ content is 0.74-1.48 (wt. %) (fig. 3 b, c). The size of carbides decreases from 8-13 to 4-6 μm. This is explained by the simultaneous action of two factors, on the one hand, boron affects the decrease in the sintering temperature, and on the other hand, titanium additions contribute to the inhibition of grain growth. The results of X-ray microanalysis showed the composition of dark gray phases, indicating that this is complex iron-chromium carbide of the Me₇C₃ type, and the gray phases are carboborides of the Me₃(CB) type.

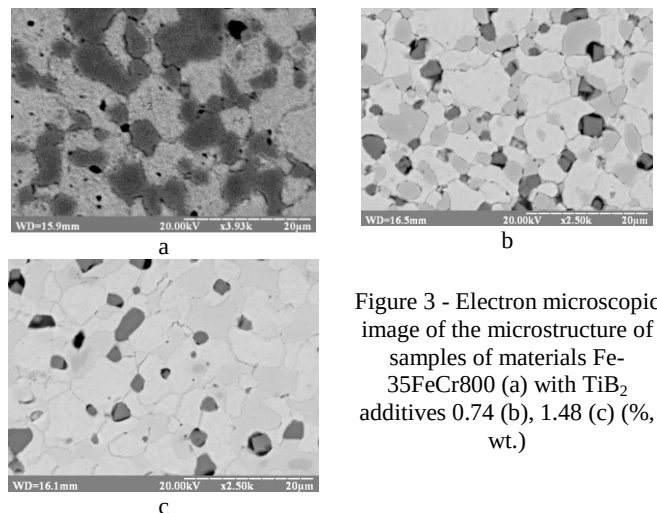


Figure 3 - Electron microscopic image of the microstructure of samples of materials Fe-35FeCr800 (a) with TiB₂ additives 0.74 (b), 1.48 (c) (% wt.)

As the content of boride additives increases from 0.74 to 1.48 (wt. %), the amount of carboborides increases, and the amount of chromium-iron carbides decreases (fig. 3 b, c).

Conclusions

The effect of the alloying addition TiB_2 on the sintering temperature, structure formation and mechanical properties of materials of the Fe-35FeCr800 system (wt. %) was investigated. It has been established that the introduction of a boron-containing additive into the charge of the base material 65Fe-35FeCr800 (wt. %), due to the formation of low-melting iron-based eutectics, reduces the sintering temperature of composites by 50-70°C. It is shown that with an increase in the sintering temperature from 1100 to 1250°C, the density and volumetric shrinkage of the specimens monotonically increase. It was revealed that the use of these additives provides the formation of a multiphase, microheterogeneous structure of a matrix-filled composite consisting of chromium steel, double chromium-iron carbides M_7C_3 , M_3C and complex carboborides of the $\text{Me}_3(\text{CB})$ type. It is shown that the introduction of titanium diboride into the basic composition of the composite in the range of 0.38-0.75 (wt. %) provides, with a slight increase in hardness, an increase of 20-25% in the ultimate flexural strength of the 65Fe-35FeCr800 composite (wt. %).

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The reciprocal lattice of cubical systems of metallic crystals

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Abstract: A study was carried out of the reciprocal lattice of metal crystals with cells *I* and *F* - Bravais type. The X-ray diffraction pattern gives *hkl* for the *F* - unit cell for even values, and for *I* - for $h k l = 2n$ (n is an integer). Transformation centered lattice to *P* - Bravais types choose that other reflexes do not die but they are absent in reciprocal lattice with metallic crystals are absent.

KEYWORDS: METALS, X - RAY ANALYSIS, RECIPROCAL LATTICE (RL), UNIT CELL (UC), POINT (P), WEIGHT OF RL POINT

1. Introduction

In modern crystallographic literature, one can find the statement that the reciprocal lattice depends on the choice of the unit cell of the crystal [1].

At the same time, the radius vector of the reciprocal lattice site can be determined experimentally by calculating the interplanar distance. Consequently, the nodes of the reciprocal lattice can change their indices depending on the choice of the unit cell of the crystal. For cells of a non-primitive type, some reflexes do not go out, because they're points are absent in the reciprocal lattice. This problem requires further study. The problem is relevant for metals of cubic syngony, in which unit cells are of the *F* and *I* types [2].

2. Indices of reciprocal lattice point and unit cell parameters

The engineering industry metallic crystals are described by either hexagonal or cubic lattices. At the first case the unit cell gets to *P* Bravais type. At the second the *F* and *I* types have place.

Parameters of the crystals $(\vec{a})_{i=1,2,3}$ and reciprocal lattices (*RL*) $\vec{a}^*$ are related by condition:

$$(\vec{a}_i^* \cdot \vec{a}_j) = \delta_{ij}, \quad (1)$$

where δ_{ij} (delta functions) is one if $j=i$ and it is zero if $i \neq j$. The indices of basic *RL*-vectors are 100,010, 001. The radius-vector of the *RL*-point $\vec{r}^*$ depends on the interplanar distances vector $\vec{d}$ as $r^* = \frac{1}{d}$. Vectors $\vec{a}$ and $\vec{r}^*$ are paralleling each other.

It was possible to assign a weight for every points of *RL* as

$$F(hkl) = \sum_{j=1}^N f_j \exp 2\pi i(hx_j + ky_j + lz_j), \quad (2)$$

where f_j is atomic scattering factor of *j*-atom [1]. *N* is a number atoms in the unit cell. Indices *hkl* are the sign indices of crystallographic plane in crystal and coordinates point of *RL* and $(x_j y_j z_j)$ are coordinates of *j*-atom. The *hkl* and $(xyz)_j$ depend on the choice of a crystals unit cell.

The coordinates of gemological points in the *I*-cell are (000), $\left(\frac{1}{2} \frac{1}{2} \frac{1}{2}\right)$ and they in *F* - type are (000), $\left(\frac{1}{2} \frac{1}{2} 0\right)$, $\left(\frac{1}{2} 0 \frac{1}{2}\right)$, $\left(0 \frac{1}{2} \frac{1}{2}\right)$.

Let the metallic atoms are placed in these point. According 2 in this case

$$F(hkl) = f \left(1 + \exp \pi i(h+k) \right) + \exp \pi i(k+l) + \exp \pi i(l+h)$$

It means that for *F* - type that to (2) the $F(hkl)$ are none zero for metals with *I* - UC type.

$$F(hkl) = f \left(1 + \exp \pi i(h+k+l) \right)$$

$h+k+l=2n$ (n - integer number). For *F* - type *hkl* may be lither all even or all odd. Then $F\{(001)\}$ in both cases are zero. But

locations of the $(\vec{a}_i^*)_{i=1,2,3}$ haven from (1). One says the X-ray

reflexes with indices (001) die out. The vectors $\vec{r}^*$ in *RL* does not depend on unit cells parameters because they have measure in

absolute scale. In a *F* unit cell we take a point (000), $\left(\frac{1}{2} \frac{1}{2} 0\right)$,

$\left(\frac{1}{2} 0 \frac{1}{2}\right)$, $\left(0 \frac{1}{2} \frac{1}{2}\right)$ and build the unit cell *P* - type.

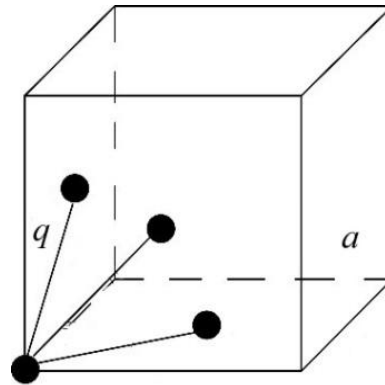


Fig. 1. Transformation the *F* - unit cell to *P* - type.

The parameter *P* - unit cell are $a_p = b_p = c_p = q$.

$$\alpha_p = \beta_p = \gamma_p = 60^\circ.$$

It means the crystallographic coordinates of the basic point in *P* - type Bravais *P*-cell and their $(xyz)_p$ analogis are differens (table 1).

Table 1. The crystallographic coordinates of point on *P* - and *F* basis.

X_p	000	100	010	001
X_F	000	$\frac{1}{2} \frac{1}{2} 0$	$0 \frac{1}{2} \frac{1}{2}$	$\frac{1}{2} 0 \frac{1}{2}$

The general view of relation between d and $abc, \alpha\beta\gamma, hkl$ is the next:

$$\frac{1}{d^2} = \frac{\begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \frac{k}{b} & 1 & \cos\alpha \\ \frac{l}{c} & \cos\alpha & 1 \end{vmatrix} + \frac{1}{b} \begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \cos\gamma & \frac{k}{b} & \cos\alpha \\ \cos\beta & \frac{l}{c} & 1 \end{vmatrix} + \frac{1}{c} \begin{vmatrix} \frac{h}{a} & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \frac{k}{b} \\ \cos\beta & \cos\alpha & \frac{l}{c} \end{vmatrix}}{\begin{vmatrix} 1 & \cos\gamma & \cos\beta \\ \cos\gamma & 1 & \cos\alpha \\ \cos\beta & \cos\alpha & 1 \end{vmatrix}} \quad (3)$$

It means, that all parameters of the right part this equation (known as quadratic formula) must be changed, but d is an experimental parameter which depend on only crystal structure [2, 6]. Then this formula gives possibility to construct relation between parameter of unit cells and indices of X-ray reflexes for distinguishing unit cell for a crystal.

The relation $d = f(hklabc\alpha\beta\gamma)$ is (2). Let indices of $F-UC$ are hkl and they are in $P-UC$ are HKL . Then for the same:

$$\frac{h^2 + k^2 + l^2}{a^2} = \frac{\frac{H}{q} \begin{vmatrix} H/q & 1/2 & 1/2 \\ K/q & 1 & 1/2 \\ L/q & 1/2 & 1 \end{vmatrix} + \frac{K}{q} \begin{vmatrix} H/q & 1/2 & 1/2 \\ 1/2 & K/q & 1/2 \\ 1/2 & L/q & 1 \end{vmatrix} + \frac{L}{q} \begin{vmatrix} H/q & 1/2 & 1/2 \\ 1/2 & 1 & K/q \\ 1/2 & 1/2 & L/q \end{vmatrix}}{\begin{vmatrix} 1 & 1/2 & 1/2 \\ 1/2 & 1 & 1/2 \\ 1/2 & 1/2 & 1 \end{vmatrix}} \quad (4)$$

But $q = \frac{\sqrt{2}a}{2}$ then

$$(h^2 + k^2 + l^2) = 3(H^2 + K^2 + L^2) - 2(HK + KL + LH), \quad (5)$$

The relations between $F-UC$ and $P-UC$ it is possible to see in the table 2.

Table 2. The relation between indices of cubic F – Bravais unit cell and P – unit cell for the same crystal.

$\{HKL\}$	$\sum h_i^2$	$\{hkl\}$	$\{HKL\}$	$\sum h_i^2$	$\{hkl\}$
100	3	111	311	19	331
110	4	200	321	20	420
111	3	111	322	19	331
200	12	222	330	36	600
210	11	311	331	27	333,511
211	8	220	332	24	422
220	16	400	333	27	511,333
221	11	311	400	48	444

222	12	222	410	43	533
300	27	511,333	411	36	600
310	24	422	420	44	622

We can see that points of RL for $F-UC$ with mixed even-odd indices are absent.

The table 3 contains the indices of vertices $P-UC$ (HKL) and according to them indices of cubic RL .

Table 3. The vertices of $P-UC$ (HKL) and their analogies in cubic RL (hkl)

No	1	2	3	4	5	6	7	8
HKL	000	100	110	010	001	101	111	011
hkl	000	$\bar{1}11$	002	$1\bar{1}1$	$11\bar{1}$	020	111	200

The displacement $P-UC$ in cubical RL is given on figure 2.

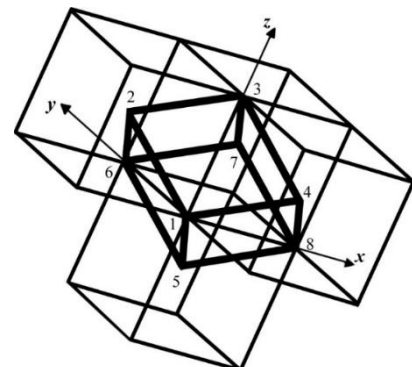


Fig. 2. Relation between $P-UC$ and cubic RL (number Bravais unit cell accordingly tabel 3)

Thus if one takes the F – in three closed packing the point of RL with mixed even-odd indices are absent. In this case needs to cubic super cell with parametr $\vec{a}_{js}^* = 2\vec{a}_j^*$ (see (1)). S – indices super cell. The thesis about super unit cell are followed from analyses of I and C – type UC [3, 4].

For the cubic I – unit cell the points as a basis it is taken the radius-vector of the point 100 and 010 and $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ (fig.3).

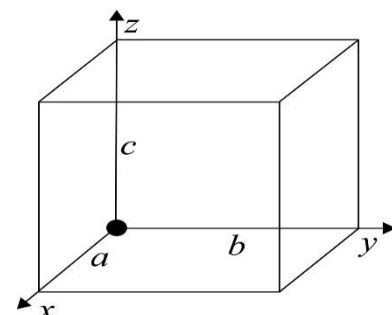


Fig. 3. Basis-vector in the $I-UC$

If parameter of $I-UC$ are $a = b = c, \alpha = \beta = \gamma = 90^\circ$.

Then parameters of $P - UC$ are $A=B=a$, $C = a \frac{\sqrt{3}}{2}$,

$\cos \alpha_p = \cos \beta_p = \frac{1}{\sqrt{3}}$, $\gamma_p = 90^\circ$. Then formula (3) for

$P - UC$ is the next:

$$\frac{1}{d^2} = \frac{\begin{vmatrix} \frac{H}{a} & 0 & \frac{1}{\sqrt{3}} \\ \frac{K}{a} & 1 & \frac{1}{\sqrt{3}} + \frac{K}{a} \\ \frac{2L}{a\sqrt{3}} & 0 & 1 \end{vmatrix}}{\begin{vmatrix} 1 & \frac{H}{a} & \frac{1}{\sqrt{3}} \\ 0 & \frac{K}{a} & \frac{1}{\sqrt{3}} + \frac{2L}{a\sqrt{3}} \\ \frac{1}{\sqrt{3}} & \frac{2L}{a\sqrt{3}} & 1 \end{vmatrix}} = \frac{\begin{vmatrix} 1 & 0 & \frac{1}{\sqrt{3}} \\ 0 & 1 & \frac{1}{\sqrt{3}} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & 1 \end{vmatrix}}{\begin{vmatrix} 1 & 0 & \frac{H}{a} \\ 0 & 1 & \frac{K}{a} \\ \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{2L}{a\sqrt{3}} \end{vmatrix}} \quad (6)$$

where HKL are the indices of $P - RL$ for $P - UC$. For $I - UC$ as before the signs of indices are hkl . From formulas $\frac{1}{d^2} = f(hkl, a)$

and $\frac{1}{d^2} = \varphi(HKL, a)$ we obtain the relation between hkl and HKL for the same interplane distance.

$$h^2 + k^2 + l^2 = 2(H^2 + K^2 + 2L^2 + HK - 2KL - 2HL) \quad (7)$$

The basis of $P - UC$ of RL are 001, 010, 100 and indices of the other vertex of UC are 110, 101, 011, 111 and 000. For these $P - UC$ of RL with unit cell in crystal and for several of the indices HKL there are relations in the table 4.

Table 4. Relations between indices HKL (P – type unit cell) and hkl (I type – unit cell).

HKL	$h^2+k^2+l^2$	hkl
001	4	200
010	2	110
100	2	110
110	6	211
101	2	101
011	2	101
111	2	110
200	8	220
002	16	400
210	14	321
201	8	202
211	10	310
112	14	123
300	18	411
003	36	600
310	26	510
301	14	321
103	32	440
311	14	312
113	18	411
400	32	440
004	64	800

The first seven points (plus (000) – point) are the vertices of $P - UC$ in RL . At the hkl column the forms of crystallographic planes indices are presented.

One can see that independently of indices of $P - RL$ points corresponding them indices the same points in $I - RL$ always have the even sum.

The cubic metals are presented in the table 5 [5, 6].

There are the metals with F – and I – type of unit cell. Therefore there are the parameter a for all objects.

Table 5. Unit cell parameters of metals with face centered and internal centered Bravais unit cell

F				I			
№	elem ent	element number in the Periodic table	a, A	№	elem ent	element number in the Periodic table	a, A
1.	Li	3	4,379	1.	Li	3	3,509
2.	Al	13	4,049	2.	Na	11	4,290
3.	Ca	20	5,582	3.	K	19	5,344
4.	Mn	25	3,855	4.	Ti	22	3,306
5.	Fe	26	3,646	5.	V	23	3,025
6.	Co	27	3,544	6.	Cr	24	2,884
7.	Ni	28	3,523	7.	Mn	25	3,075
8.	Cu	29	3,614	8.	Fe	26	2,866
9.	Sr	38	6,084	9.	Rb	37	5,710
10	Rh	45	3,804	10	Y	39	3,90
11	Pd	46	3,890	11	Zr	40	3,600
12	Ag	47	4,085	12	Nb	41	3,300
13	La	57	5,285	13	Mo	42	3,147
14	Ce	58	5,162	14	Cs	55	6,079
15	Yb	70	5,486	15	Ba	56	5,019
16	Ir	77	3,836	16	La	57	4,26
17	Pt	78	3,923	17	Ce	58	4,11
18	Au	79	4,078	18	Pr	59	4,13
19	Pb	82	4,950	19	Nd	60	4,13
20	Ac	89	5,311	20	Sm	62	4,07
21	Th	90	5,084	21	Eu	63	4,582
22	Pu	94	4,637	22	Gd	64	4,06
23	Am	95	4,894	23	Hf	72	3,545
				24	Ta	73	3,302
				25	W	74	3,165
				26	Tl	81	3,882
				27	U	92	3,524

3. Conclusion

Thus it in the crystal lattice the centered unit cell (F , I , C – types) are taken then it needs to analyses super unit cells. For F and $I - UC$

$$\left(\vec{a}_s^* \cdot \vec{a} \right)_j = 2 \text{ and for } C - UC \left(\vec{a}_s^* \cdot \vec{a} \right) = \left(\vec{b}_s^* \cdot \vec{b} \right) = 2 \text{ but } \left(\vec{c}_s^* \cdot \vec{c} \right) = 1.$$

For complicated structures n may be more then 2. For the diamond $\left(\vec{a}_s^* \cdot \vec{a} \right) = 4$.

To speak that some reflexes die out is not true because according with then points of RL are absent.

The reciprocal lattices of crystals are the displacement the point with $\vec{r}^*$ are determined by crystals. For the RL conception of centering does not used. The centered may be only unit cells of non – primitive Bravais types (F , I , C , AB). In these cases it need to take the super unit cell.

The localization of the point RL must be analyses on the base of P – type unit cell. In this case it is possible to see that same reflexes do not died but their point RL are absent (for I -type $h+k+l=2n+1$ and for F -type hkl must be the same evens.

About this conclusion it is necessary to remember when one analyses the energetic properties of crystals because the weight of

RL – points related with wave vector. The later is used for example for investigation of wave function.

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Influence of physicochemical and structural factors on cast materials – foundry methodology. Part I

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Abstract: A scientific methodology for foundry has been developed in order to have a constant connection between foundry and the continuous development of solid state physics. This is achieved through the continuous expansion of the minimum scientific knowledge based on the historical development of metal physics, solid state physics, and today mathematics is placed in the first place. Metal science is a pure application of metal physics and solid state theory based on foundry, today it is materials science. The natural mathematical theory of foundry is the theory of thermal conductivity describing phase transitions of the first and second kind through Stefan-type problems - solidification together with modern software products for descriptions.

Keywords: SCIENTIFIC METHODOLOGY, THEORY SOLID STATE PHYSICS, SOFTWARE PRODUCTS

1. Introduction – first order phase transition

The mathematical base of the casting is mathematical tasks of Stefan [1] and Schwartz [2]. The open thermodynamic system (OTS) is: V_{SYS} is the sum of cast volumes of liquid V_{CL} , surface front S_{Front} and solid V_{CS} phases, mold volume V_M with it boundary surfaces B_{WS} and B_M . The task of Stefan-Schwartz in 3D for numerical investigation by Finite Elements Method is: heat conductivity equation (1, 1) and initial conditions (1, 1, 2); Stefan's boundary condition at front (1, 2) with growth velocity front liquid/solid (1, 2, 1); mold boundary condition at work surface (1, 3); mold/environment boundary condition (1, 4):

$$V_{SYS} = (V_{CL} \cup S_{Front} \cup V_{CS}) \cup B_{WS} \cup (V_M \cup B_M), \quad (OTS)$$

$$(c + SFQ_m) \frac{\partial T}{\partial t} = \lambda \Delta T, \text{ in } V_{SYS} \quad (1, 1)$$

$$T_L(x, y, z, t) = \text{const}_L, T_M(x, y, z, t) = \text{const}_M, \quad (1, 1, 2)$$

$$-\lambda_L \nabla T_{L|S_F} = \rho_S R Q_m - \lambda_S \nabla T_{S|S_F}, \text{ or} \quad (1, 2)$$

$$R = [\lambda_L \nabla T_{L|S_F} - \lambda_S \nabla T_{S|S_F}] / \rho_S Q_m, \quad (1, 2, 1)$$

$$-\lambda_C \nabla T_{C|B_{WS}} = \alpha_{B_{WS}} (T_{C|B_{WS}} - T_{M|B_{WS}}) = -\lambda_M \nabla T_{M|B_M}, \quad (1, 3)$$

$$-\lambda_M \nabla T_{M|B_M} = \alpha_{B_M} (T_{M|B_M} - T_{En}) - \lambda_M \nabla T_{M|B_M} = \alpha_{B_M} (T_{M|B_M} - T_{En}), \quad (1, 4)$$

where T is the temperature of cast, liquid, solid, mold (C, L, S, M); the thermophysical coefficients of the (OTS): conductivity, capacity, density (λ, c, ρ); SF is source heat function, Q_m is latent heat at the melting temperature T_m .

1.1. Crystallography – Methodology [4 and 3]

Crystal symmetry data: The description of the crystal structure: is through periodic atomic rows to build the *elemental cell* and forms *bases*. Mathematics remarks: crystal lattice is an abstraction: the crystal structure is formed of important "lattice" and "lattice points" are equivalent (LB); according to Bravais: points of a regular periodic structure is eq. (2, 1) by ξ, η and ζ are the axes of the coordinate system in 3D space, which is generally acute-angular; the same arrangement of atoms in a crystal lattice by the vectors a, b and c of primitive translation for every two points r and r' is eq.(2, 2) and eq.(2, 3); bases of N atoms or ions (particles) and located to the lattice point so $0 \leq x_i, y_i, z_i \leq 1$ is defined as eq.(2, 4); together with the presented on the figures 1 and 2:

$$\text{lattice} + \text{basis} = \text{of crystal structure.} \quad (LB)$$

$$\sin^2(\pi \xi/a) + \sin^2(\pi \eta/a) + \sin^2(\pi \zeta/a) = 0, \quad (2, 1)$$

$$r' = r + n_1 a + n_2 b + n_3 c, \text{ or} \quad (2, 2)$$

$$T = n_1 a + n_2 b + n_3 c = n_1 a_1 + n_2 a_2 + n_3 a_3, \quad (2, 3)$$

$$r_j = x_j a + y_j b + z_j c. \quad (2, 4)$$

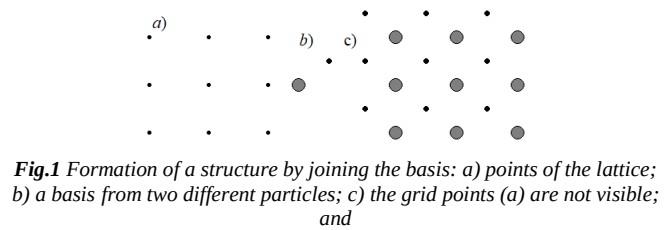


Fig.1 Formation of a structure by joining the basis: a) points of the lattice; b) a basis from two different particles; c) the grid points (a) are not visible; and

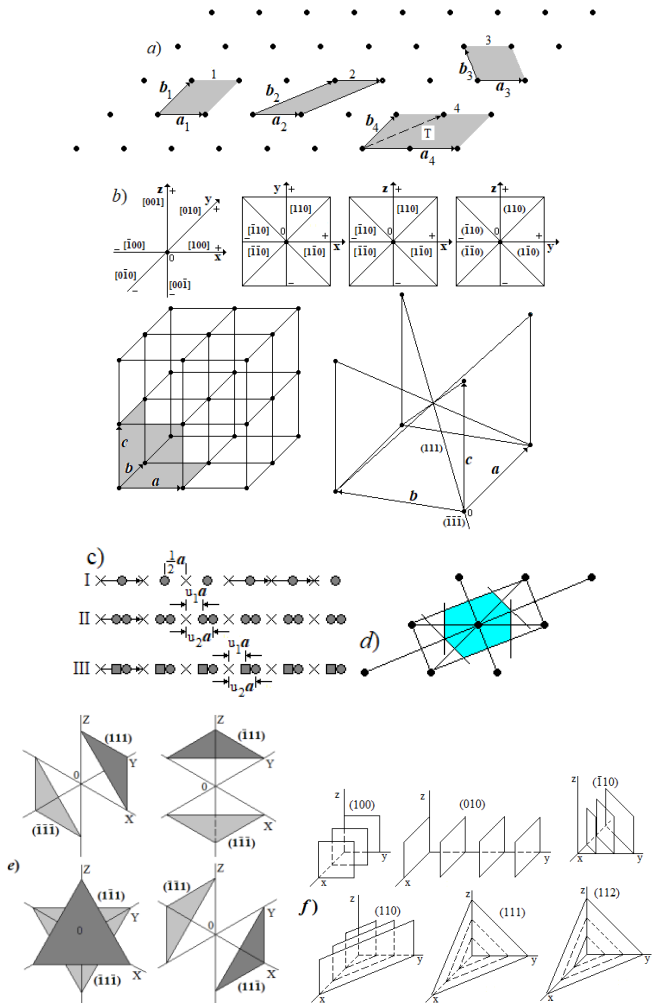


Fig.2 Important crystallographic markings: Primitives cells: a) Geometric idea: Points of 2D crystallographic lattice, where a and b are primitives vectors of primitive translation T . Vectors a_4 and b_4 are not primitive translation vectors; b) Primitive cell on a 3D crystal lattice; Direction indices $[uvw]$ are projections of vectors on the coordinate axes;

axis indexes (+x) is [100] and (-x) is $\bar{1}00$, axis indexes (+y) is [010] and (-y) is $0\bar{1}0$, axis indexes (+z) is [001] and (-z) is $00\bar{1}$; diagonals indexes on the orthogonal surfaces: diagonal (+xy) is [110] and diagonal (-xy) is $\bar{1}\bar{1}0$; diagonal (+yz) is [011] and diagonal (-yz) is $0\bar{1}\bar{1}$; (+xz) is [101] and diagonal (-xz) is $\bar{1}0\bar{1}$; Diagonal indices in the volume of the quadrants of an orthogonal coordinate system: diagonals indexes in the positive quadrant (+x, +y, +z) are [111]; in the negative quadrant (-x, -y, -z) are $\bar{1}\bar{1}\bar{1}$; diagonal indexes in the other quadrants: (+x, -y, +z) are $1\bar{1}1$; (-x, -y, +z) are $\bar{1}\bar{1}1$; (-x, +y, +z) are $\bar{1}11$; (+x, -y, -z) are $1\bar{1}\bar{1}$; (-x, -y, -z) are $\bar{1}\bar{1}\bar{1}$; (-x, +y, -z) are $\bar{1}1\bar{1}$. The indices of the diagonals in the volumes of these quadrants form a group $\{111\}$ and are obtained by displacement (relocation) the indexes ± 1 ; c) Atomic rows of three different structures: (x) are the points location in the lattice; (●) and (■) are two kinds of atoms; a is a vector of constant magnitude and direction. In all three rows I, II and III, the points are connected to each other by the vector of primitive translation a. I. Primitive (smallest) first-order basis: the distance between the atom (●) and the lattice point (x) is a/2; II. Primitive second-order basis: between two identical atoms (●●) and lattice point (x) we have two distant one is u_1a and second is u_2a ; III. Primitive third-order basis: two different atoms (●■) and the lattice point (x), one at a distance u_1a and the other at a distance u_2a . d) A primitive Wigner-Seitz cell is a small volume around a point in the crystal structure obtained as follows: this point connects to its first neighbors by straight lines divided in half by perpendicular planes; e) Atoms on a plane form an atomic plane, and parallel atomic planes form a group through Miller indices (hkl), where h is cut from x-axes, k is cut from y-axes and l is cut from z-axes. In positive quadrant (+x, +y, +z) are (hkl) and in negative quadrant (-x, -y, -z) are $\bar{h}\bar{k}\bar{l}$; group: (111), $\bar{1}\bar{1}\bar{1}$, $\bar{1}11$, $1\bar{1}\bar{1}$, $11\bar{1}$, $\bar{1}\bar{1}1$, 111 , $\bar{1}\bar{1}\bar{1}$; f) Characteristic of this scheme [3, 4] for a cube: 1. for parallel and uniformly oriented planes, the Miller indexes are (hkl) are the same. A similar rule is true in the relations between the direction indexes [uvw]; 2. A plane parallel to one of the coordinate axes has an index 0 for this direction: [uvw], [0vw] and [u0w]; 3. A plane passing through the origin of the coordinate system shall be recorded by means of the indices of a plane parallel to it, crossing from the coordinate axes cuts of finite length. Example: a side of a cube perpendicular ($\perp$) to the axis (x) is written with Miller indexes so (hkl) = (100) i.e. $h = 1$, $k = 0$ and $l = 0$. At ($\perp$) to the axis (y) indexes (010); and

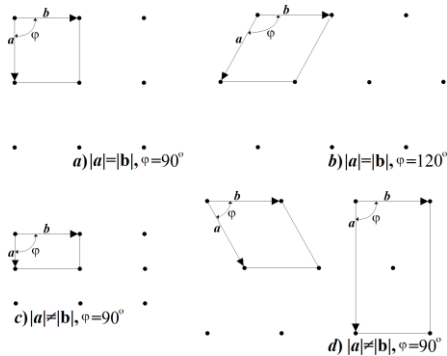


Fig.3 Bravais' basic 2D lattices [4]: a) square; b) hexagonal; c) rectangular; d) centered rectangular; and

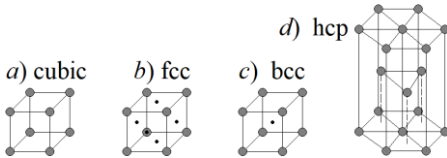


Fig.4 Primitive 3D cells [4].

Elementary fourteen cells space lattices of Bravais with [Crystallographic system (CS); Number cells in system (NCS); Symbol cells (SC); Characteristics of the elementary cells (CEC)] in an important Matrix of the „Bravais knowledge“ as follows:

CS	NCS	SC	CEC
Triclinic	1	P	$a \neq b \neq c; \alpha \neq \beta \neq \gamma$
Monoclinic	2	P, C	$a \neq b \neq c; \alpha = \gamma = 90^\circ \neq \beta$
Rhombohedral	4	P, C, I, F	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
Tetragonal	2	P, I	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$
Cubic	3	P, I, F	$a = b = c; \alpha = \beta = \gamma = 90^\circ$
Trigonal	1	R	$a = b = c; \alpha = \beta = \gamma < 120^\circ, \neq 90^\circ$
Hexagonal	1	P	$a = b \neq c; \alpha = \beta = 90^\circ \neq \gamma = 120^\circ$

where types of cells (NCS) are C is wall centered is not a primitive cell, F is a wall-centered primitive cell, I is a volume-centered (internally-centered) primitive cell, P is a primitive elementary cell, R is a primitive rhombohedral elementary cell; (CEC): a, b, c are vectors of the crystallographic axes, and α, β, γ are angles between coordinate axes. For every (CS) is needed: Elemental cell volume (cell); Atomic radius – defined by half of the distance between the first neighbors in the crystal of the pure chemical element; Number of points in the grid of a cell; The volume of the primitive cell; The number of points on (c) the grid per unit volume; The number of first neighbors; The distance between the first neighbors; The number of neighbors, after the first neighbors, i.e. the second neighbors; The distance to the neighbors, after the second neighbors.

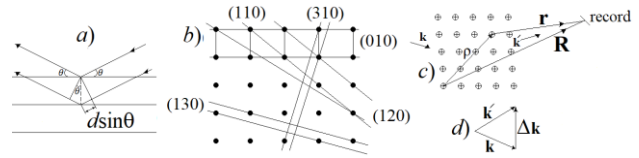


Fig. 5 Necessary rays measurement [4]: a) diffraction; b) reflecting atomic planes of crystal structure (cubic); c) $p + r = R$ or $r = R - p$; d) scattering vector $\Delta k = k' - k$ (elastic scattering $k' = k$) and each point of the lattice may be a scattering center.

External observation method – Electron microscope (resolution 2 Å) [4] with uses X-rays with wavelength to diffract in the crystal structure: X-ray eq. (2, 5); Neutrons: eq.(2, 6); Electrons eq.(2, 7); Bragg's law (Fig. 5) eq.(2, 8) with condition (2, C):

$$\epsilon = hc/\lambda \text{ and } \lambda(\text{\AA}) = 12,4/\epsilon(\text{eV}), \quad (2,5)$$

$$\epsilon = h^2/2m_n\lambda^2; (\epsilon = p^2/2m_n) \text{ and } \lambda(\text{\AA}) \approx 0,28/[\epsilon(\text{eV})]^{1/2}, \quad (2,6)$$

$$\epsilon = h^2/2m\lambda^2; \text{ and } \lambda(\text{\AA}) \approx 12/[\epsilon(\text{eV})]^{1/2}, \quad (2,7)$$

$$2d\sin\theta = n\lambda, \quad (2,8)$$

$$\lambda \leq d; \lambda = 1,54 \text{ (\AA)} \text{ at } \theta = 11^\circ \text{ and lattice parameter } 4 \text{ (\AA)}, \quad (2,C)$$

vector and amplitude of diffraction (2, 9); Laue's condition scattering (2, 10); Basic vectors (2, 11) inverse lattice and elementary cell volume $b.c \times a = c.a \times b = a.b \times c$; position of nodes of the grid $\rho_{mnp} = ma + nk + pl$; Fourier space in position of nodes and inverse lattice vectors $G = hA + kB + lC$; scalar multiplication of vectors $G \cdot \rho_{mnp}$ (2, 12); electron concentration in the Fourier crystal - analysis for periodic distributions (2, 13), (2, 13, 1), (2, 13, 2); (2, 14) is new view of eq. (2, 13) by n_G , which is also in integral (2, 14, 1) equal to the volume V for $\Delta k = G$ and if $\Delta k = 0$ then the integral is equal 0:

$$\Delta k = k' - k, \text{ and amplitude } \mathcal{A} = \sum_{mnp} \exp[-2\pi i(mh + nk + pl)], \quad (2,9)$$

$$a.\Delta k = 2\pi h, b.\Delta k = 2\pi k, c.\Delta k = 2\pi l, \quad (2,10)$$

$$A = 2\pi \frac{b \times c}{a \cdot b \times c}, B = 2\pi \frac{c \times a}{a \cdot b \times c}, C = 2\pi \frac{a \times b}{a \cdot b \times c}, \quad (2,11)$$

$$G \cdot \rho_{mnp} = 2\pi(hm + kn + lp) = 2\pi \cdot (\text{integer}), \Rightarrow \exp(iG \cdot \rho_{mnp}) = 1. \quad (2,12)$$

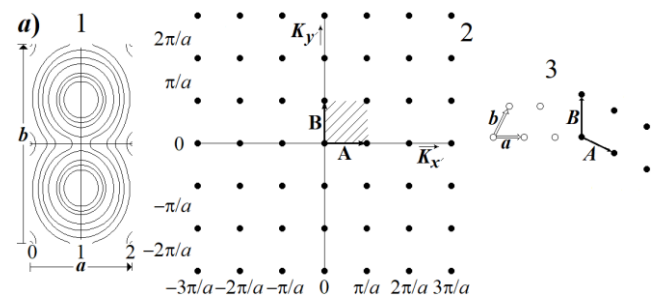
$$n(\rho) = \sum_K n_K e^{iK \cdot \rho}, \text{ only at } K \equiv G, \quad (2,13)$$

$$n(\rho + \rho_{mnp}) = \sum_K n_K \exp(iK \cdot \rho) \exp(iK \cdot \rho_{mnp}). \quad (2,13,1)$$

$$K \cdot (ma + nk + pc) = 2\pi \cdot (\text{integer}) \text{ such as } G \cdot \rho_{mnp} = 2\pi, \quad (2,13,2)$$

$$n(\rho) = \sum_G n_G \exp(iG \cdot \rho), \quad (2,14)$$

$$\int dV n(\rho) \exp(-i\rho \cdot \Delta k) = \sum_G n_G \int dV \exp(iG \cdot \rho) \exp(-i\Delta k \cdot \rho); \text{ and } \quad (2,14,1)$$



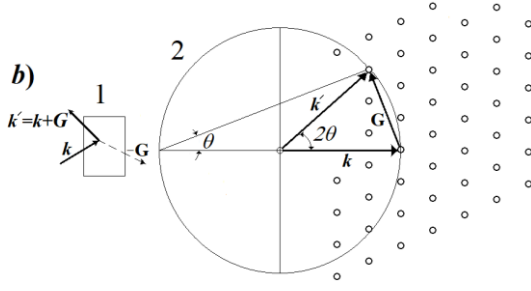


Fig. 6. Example of Fourier analysis of periodic distribution in a crystal [4]: **a)** Geometric idea of Fourier space: 1 - a rectangular primitive cell with axes $\mathbf{a}$ and $\mathbf{b}$ and a basis of two identical atoms. The contour lines connect places with the same concentration of electrons n_G i.e. charge distribution; 2 - Probability density by Fourier row for electron distribution in the crystal n_G (see eq. (2, 16) and eq. (2, 16, 1), where G is the inverse lattice vector), i.e. in the nodes of the inverse lattice ($K_x \perp a$, $K_y \perp b$) the values of the Fourier coefficients $|n_G| \cdot 10^3$ in the space $K_x \in [0 \pm 3\pi/a]$, $K_y \in [0 \pm 2\pi/a]$ are indicated; 3 - Vectors $\mathbf{a}$ and $\mathbf{b}$ of crystal lattice and vectors $\mathbf{A}$ and $\mathbf{B}$ of two-dimensional inverse lattice. The hatched area is the cell on the inverse lattice; **b)** Ewald's construction: 1 is a crystal, $\mathbf{k}$ is an incident photon, $\mathbf{k}'$ is a diffracted photon, $-\mathbf{G}$ is a wave vector of the crystal experiencing emission, 2 - the points $\bigcirc$ are nodes of the crystal inverse lattice, $\mathbf{k}' = \mathbf{k} + \mathbf{G}$, $k = 2\pi/\lambda$, $\mathbf{G}$ - inverse vector lattice.

Fourier analysis [5] eq.(F, 1) and distribution of electron concentration in a crystal eq.(n, 1) is theorem [4]: for an arbitrary function eq.(2, 13) having a translational periodicity in a lattice is described by a Fourier series only if the quantities $\mathbf{K}$ appearing in the order are vectors of the inverse lattice $\mathbf{G}$:

$$\begin{aligned} \frac{1}{2}a_0 + \sum_{k=1}^{\infty} (a_k \cos k\tau + b_k \sin k\tau) &= \sum_{k=-\infty}^{\infty} c_k e^{ikt}, \text{ and for the coefficients,} \\ a_k &= \frac{1}{\pi} \int_{-\infty}^{\infty} f(\tau) \cos k\tau d\tau, \quad b_k = \frac{1}{\pi} \int_{-\infty}^{\infty} f(\tau) \sin k\tau d\tau, \\ c_k &= \bar{c}_k = \frac{1}{2\pi} \int_{-\infty}^{\infty} f(\tau) \sin k\tau, \quad (k = 0, 1, 2, \dots). \end{aligned} \quad (F, 1)$$

Mathematics

Physics

$$\begin{aligned} n(\mathbf{x}) &= C_0 + \sum_{k=1}^{\infty} (C_p \cos p\mathbf{x} + S_p \sin p\mathbf{x}), \quad C \text{ and } S \text{ are real number,} \\ n(\mathbf{x}) &= n_0 + \sum_{p \neq 0} n_p e^{ip\mathbf{x}} = n_0 + \sum_{p > 0} [n_p (\cos p\mathbf{x} + i \sin p\mathbf{x}) + n_{-p} (\cos p\mathbf{x} - i \sin p\mathbf{x})], \\ C_p &= \mathcal{A}\{n_p + n_{-p}\}; S_p = i n_p - i n_{-p} = -\mathcal{T}(n_p + n_{-p}); n_p^* = n_{-p}. \end{aligned} \quad (n, 1)$$

The row (n, 2) $\Rightarrow$ (n, 1) estimating complex coefficients n_p and n_{-p} . Geometrically, diffraction is represent: 1. frequency - ω , ω' ; 2. wave vector $\mathbf{k}$, $\mathbf{k}'$; ω , $\mathbf{k}$ - incident ray; ω' , $\mathbf{k}'$ - scattered ray. In elastic scattering - the quantum energy of X-ray does not change (E, 1); dispersion ratios of electromagnetic waves in vacuum (E, 2); diffraction condition (E, 3); a photon in a vacuum has an energy impulse $\hbar\omega$ equal to $\hbar\omega/c$ or $\hbar k$; periodic distribution of electrons modulates plane wave in crystal (E, 3, 1) and wave vector $\mathbf{k} + \mathbf{G}$ and photon with impulse $\hbar(\mathbf{k} + \mathbf{G})$; for impulse condition: after entering the beam crystal gives impulse $-\hbar\mathbf{G}$ (Fig.6 b); the emission rate of a crystal with a mass of 1 g. for the reflection with a vector of the inverse lattice with a length of 1.10^{-8} cm is (E, 3, 2); a new record (E, 3) by $k'^2 = (\mathbf{k} + \mathbf{G})^2$ and is reported $k' = k$; eq.(E, 4) equivalents of eq.(2,8):

$$\begin{aligned} \hbar\omega' &= \hbar\omega, \\ \omega' &= ck \text{ and } \omega' = ck \Rightarrow k' = k, \\ \Delta\mathbf{k} &= \mathbf{G} \text{ or } k' = k + G, \\ e^{ik \cdot r} &\rightarrow e^{ik \cdot r} \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G} \cdot r}, \\ v &= \hbar G / M \approx 10^{-19} \text{ cm/s,} \\ 2\mathbf{k} \cdot \mathbf{G} + G^2 &= 0. \end{aligned} \quad (E, 1) \quad (E, 2) \quad (E, 3) \quad (E, 3, 1) \quad (E, 3, 2) \quad (E, 4)$$

Important for the different types of lattices [4] (see Fig.6 and Fig.7: the inverse lattice and the volume of the primitive cell are built, i.e. the Wigner-Seitz cell for the inverse lattice, which contains only one node located in the center of the cell, and is the first Brillouin zone for the corresponding lattice. The Brillouin construction represents the wave vectors $\mathbf{k}$ of all incident rays that are reflected by the crystal by Bragg diffraction:

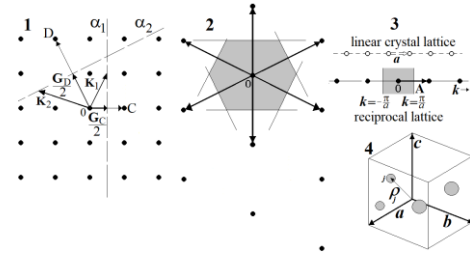


Fig. 7. 1. Reciprocal lattice: points C, D ; reciprocal vectors $\mathbf{G}_C, \mathbf{G}_D$ bisected by perpendicular planes (α_1 and α_2 boundary of dotted lines of the dotted border lines of the Wigner-Seitz zone in reciprocal lattice); K_1, K_2 arbitrary vectors satisfy the diffraction conditions; 2. Brillouin's zones (see 1); 3. 1D crystal and reciprocal lattices basic vector $\mathbf{A}$ with length $2\pi/a$; and the shortest inverse vectors are $\mathbf{A}$ and $-\mathbf{A}$; intersecting planes (lines) perpendicular through the middle of the vectors $\mathbf{A}, -\mathbf{A}$ are the boundaries of the first Brillouin zone at $k = \pm\pi/a$; 4. Structure factor: the position of the j -atom in the elementary cell with vectors $\rho_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$; and

vector $-\mathbf{G}$ is also a vector of the inverse lattice (see Fig.6.b.1 and Fig.7.1) and for this in (E, 4) we put $-\mathbf{G}$ instead of $\mathbf{G}$ and get:

$$\begin{aligned} 2\mathbf{k} \cdot \mathbf{G} &= G^2, \\ \mathbf{k} \cdot (\mathbf{G}/2) &= (G/2)^2. \end{aligned} \quad (ZB, 1) \quad (ZB, 1.1)$$

Structural factor of the basis: Crystal lattice reflections are determined by eq.(2, 10). An atom consists of a nucleus surrounded by electrons whose distribution in the crystal is $n(\rho)$ eq.(2, 16). The intensity of the reflections depends on the composition of the atoms in the elementary cell, i.e. by the number and arrangement of atoms and the distribution of electron density in the cell. Used: 1. the reflections describe the nodes of the inverse lattice eq. (2, 13) denoted by (h, k, l) ; 2. Superposition of functions of electron density c_j bound to the individual atom- j (see Fig.7, 4). Algorithm [4] (Fig.7, 4): vector $\rho_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$ starting at a node with vector ρ_{mnp} eq.(2, 12) on the lattice mnp ; selected the initial node of coordinates $\rho_{000} = 0$; vector of the atom- j (position) is $\rho_j + \rho_{mnp}$; the function $c_j(\rho - \rho_j - \rho_{mnp})$ determines the concentration of electrons in the vicinity of the atom- j in the cell mnp and $n(\rho) = \sum_{mnp} \sum_j c_j(\rho - \rho_j - \rho_{mnp})$ eq.(RI, $n(\rho)$), in the first summation $j = 1, \dots, s$ is on all atoms of the basis, and the second is on the number of all nodes of the lattice M^3 ; scattering amplitude by superposition $\mathcal{A}_{\Delta k} = \sum_{mnp} \sum_j \int dV c_j(\rho - \rho_j - \rho_{mnp}) \exp(-i\rho \cdot \Delta k)$ as $\int dV c_j(\rho - \rho_j - \rho_{mnp}) \exp(-i\rho \cdot \Delta k) = f_j \exp[-i(\rho_j + \rho_{mnp}) \cdot \Delta k]$ and $\rho' \equiv (\rho - \rho_j - \rho_{mnp}) \Rightarrow$ eq.(RI, $\mathcal{A}_{\Delta k}$) and atomic scattering factor of (form factor) eq.(FF):

$$\begin{aligned} n(\rho) &= \sum_{mnp} \sum_j c_j(\rho - \rho_j - \rho_{mnp}), \\ \int dV c_j(\rho - \rho_j - \rho_{mnp}) \exp(-i\rho \cdot \Delta k) &= f_j \exp[-i(\rho_j + \rho_{mnp}) \cdot \Delta k], \\ \mathcal{A}_{\Delta k} &= \sum_{mnp} \sum_j \int dV c_j(\rho - \rho_j - \rho_{mnp}) \exp(-i\rho \cdot \Delta k), \\ f_j &= \int dV c_j(\rho') \exp(-i\rho' \cdot \Delta k), \end{aligned} \quad (RI, n(\rho)) \quad (RI, n(\rho), 1) \quad (RI, \mathcal{A}_{\Delta k}) \quad (FF)$$

From eq.(2, 9) and $\rho_{mnp} = m\mathbf{a} + n\mathbf{b} + p\mathbf{c} \Rightarrow$ if $\Delta\mathbf{k}$ satisfies the condition $\rho_{mnp} \cdot \Delta\mathbf{k} = 2\pi(\text{integer}) \Rightarrow$ the sum of eq.(2, 9) of the scattering amplitude $\mathcal{A}$ in the crystal lattice with the M^3 nodes gives $\mathcal{A}_{\max} = M^3$ and new notation eq.(RI, $\mathcal{A}_{\Delta k}$, 1) and max scattering amplitude in inverse lattice $\mathcal{A}_G$; $\mathcal{L}_G$ of structure factor basis (SFB):

$$\begin{aligned} \mathcal{A}_{\Delta k} &= \sum_{mnp} \exp(-i\rho_{mnp} \cdot \Delta k) \left(\sum_j f_j \exp(-i\rho_j \cdot \Delta k) \right) \text{ or } \mathcal{A}_G = M^3 \mathcal{L}_G, \\ \mathcal{L}_G &= \sum_j f_j \exp(-i\rho_j \cdot \Delta k). \end{aligned} \quad (RI, \mathcal{A}_{\Delta k}, 1) \quad (SFB)$$

An arbitrary reflection is called (h, k, l) in inverse lattice when the scalar multiplication $\rho_j \cdot \mathbf{G}$, where ρ_j is [(see Fig.1.4) $\rho_j = x_j \mathbf{a} + y_j \mathbf{b} + z_j \mathbf{c}$] and $\mathbf{G}$ is eq.(2, 13) and:

$$\begin{aligned} \rho_j \cdot \mathbf{G} &= (x_j \bar{a} + y_j \bar{b} + z_j \bar{c}) \cdot (\hbar \bar{A} + k \bar{B} + l \bar{C}) = 2\pi(x_j h + y_j k + z_j l), \\ \mathcal{L}(hkl) &= \sum_j f_j \exp[-i2\pi(x_j h + y_j k + z_j l)], \end{aligned} \quad (hk l) \quad (SF, hkl)$$

f_j the scattering ability of the individual atom- j in elementary cell. A classic notion of scattering by a single atom. In the scattering of the single atom, the effect of interference inside the atom eq.(FF, G) within the density limits $c(r)$ is reported; $r \propto G \Rightarrow r.G = r.G \cos \alpha$, with spherical symmetry of $c(r)$ with respect to the origin of the coordinate system (Fig.7.4) integrates by $d(\cos \alpha)$ in $[-1, 1]$ eq. (FF, G, 1); the magnitude of the atomic scattering factor is eq.(FF, G, 2); if the charge is at the beginning of the coordinate system (Fig.7.4) $r_j = 0 \Rightarrow r.G = 0$ and in the boundary case $(\sin Gr)/1 = 1 \forall G$ we have eq. (FF, G, 3); where Z is the number of electrons in the atom and therefore [4]: f_G is the ratio of the amplitude of radiation, actually scattered by the distribution of electrons in the atom, to the amplitude of radiation, of the scattering of an electron located at a point:

$$f_G = \int dV c(\rho) e^{-ir.G}, \quad (FF, G)$$

$$f_G = 2\pi \int r^2 dr d(\cos \alpha) c(r) e^{-iGr \cos \alpha} \\ = 2\pi \int dr r^2 c(r) \frac{e^{ir.G} - e^{-ir.G}}{iGr}, \quad (FF, G, 1)$$

$$f_G = 4\pi \int dr c(r) r^2 (\sin Gr / Gr), \quad (FF, G, 2)$$

$$f_G = 4\pi \int dr c(r) r^2 \equiv Z. \quad (FF, G, 3)$$

A simple harmonic oscillator [3] (Fig. 8) describes chaotic motion of an atom around equilibrium position in a crystal lattice is eq.(3, 1) to axes (x, y, z) of N is $N/3$; The solution is eq.(3, 2): where α is the coefficient of elasticity; u is the distance of the oscillation of the atom in the equilibrium position (node) from the crystal lattice; ω is the angular frequency eq.(3, 3); ν is Einstein's frequency eq. (3, 4); **Hooke's law** – elastic deformation of a cube with edge a_0 extends (lengthened by a length $\Delta a = a_0$), i.e. a cube with edge a_0 under the force F becomes a parallelepiped, which in the direction of force is extended to $2a_0$ eq.(3,5);

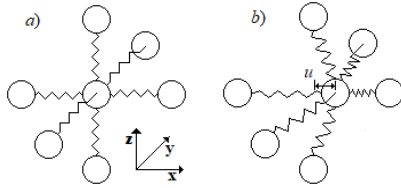


Fig. 8 Oscillator [3]: **a)** atom in equilibrium; **b)** the atom is displaced at a distance u in the direction x . First approximation, there is no displacement y, z ; and

$$m(d^2 u / dt^2) = -\alpha u, \quad (3, 1)$$

$$u = A_0 \cos \sqrt{\alpha/m} t, \quad (3, 2)$$

$$\omega = \sqrt{\alpha/m}, \quad (3, 3)$$

$$\nu = (1/2\pi) \sqrt{\alpha/m} \quad (3, 4)$$

$$Y(\Delta a / a_0) = F / a_0^2. \quad (3, 5)$$

At room temperature the atom is in the equilibrium position p_0 , and at high temperature it changes in time t with magnitude $u(t)$ is eq.(MA, T); it is assumed that the mean value of the high temperature scattering amplitude is eq.(A, T), where G is vector equal to the change of the wave vector at reflection, $\langle \dots \rangle$ is the average at temperature equilibrium; decomposition in order exponential multiplier is $\langle \exp(-iu.G) \rangle$ [4] and the wave scattering intensity is eq.(RI,T):

$$\rho(t) = \rho_0 + u(t), \quad (MA, T)$$

$$\langle A \rangle = A_0 \langle \exp(-iu.G) \rangle, \quad (A, T)$$

$$I = I_0 \exp \left[-\frac{1}{3} \langle u \rangle^2 G^2 \right]. \quad (RI, T)$$

For eq.(RI, T) I_0 is the intensity of scattering radiation at a fixed grid the exponential multiplier is called the *Debye-Waller multiplier*. Atomic standard deviation $\langle u^2 \rangle$ and the mean value of the potential energy for a classical harmonic oscillator (Fig. 8) $\langle U \rangle$ in 3D space at thermal equilibrium is $(3/2)k_B T \Rightarrow$ eq.(RI, T, U), where C is a force constant; M is the mass of the atom; ω is the angular

frequency of the oscillator and we use $\omega^2 = C/M$ [3]; and the intensity of the scattered radiation is eq.(RI, T, 1), where h, k, l are indexes in expression $G = hA + kB + lC$:

$$\langle U \rangle = \frac{1}{2} C \langle u^2 \rangle = \frac{1}{2} M \omega^2 \langle u^2 \rangle = \frac{3}{2} k_B T. \quad (RI, T, U)$$

$$I(hkl) = I_0 \exp \left[-\frac{k_B T G^2}{M \omega^2} \right], \quad (RI, T, 1)$$

And for a quantum oscillator $\langle u^2 \rangle \neq 0$ and at $T=0$ due to zero oscillations; the model of an independent harmonic oscillator is used for the oscillation of the atom: at $T = 0$ K this motion can be described by zero energy $3\hbar/2\omega$. This is the energy of a 3D quantum harmonic oscillator in its ground state, related to the value of the classical energy of the same oscillator, located at rest, i.e. (without oscillation or movement). The potential energy of the oscillator is half the energy of a classical oscillator at thermal equilibrium eq.(RI,T,U) and we have eq.(RI,T,U,1 or eq.(RI,T,U,2) $\Rightarrow$ eq.(RI,T,2):

$$\langle U \rangle = \frac{1}{2} M \omega^2 \langle u^2 \rangle = \frac{3}{4} \hbar \omega, \text{ or } \quad (RI, T, U, 1)$$

$$\langle u^2 \rangle = 3\hbar/2M\omega, \quad (RI, T, U, 2)$$

$$I(hkl) = I_0 \exp \left[-\frac{k_B T G^2}{M \omega^2} \right], \quad (RI, T, 2)$$

1.2. Thermodynamics – Methodology [3, 4 and 7]

State of ideal gas in open thermodynamic system (cube - volume V , temperature T and pressure P) [3, 7]: **Heat energy** of solid body eq. (4, 1) and **Debye temperature** eq.(4, 2); pressure P (hits the atoms in the walls with velocity v) and it is assumed of force acting on the walls $F = P$ eq.(4, 3) i.e. atoms motion p and transmitting in impulse of $2p$ [3, 7] eq.(4, 3, 1); the kinetic energy E of each atom is $E = (1/2)mv^2$ and eq.(4, 3, 2), and energy gas eq.(4, 3, 3); **Heat capacity (classical model)** eq.(4, 3, 3); The thermal capacity of ideal one atomic gas is **3 cal/mole K** independent of T and experiment agreement [3, 7]; **The thermal energy** is equal to $kT/2$ to all degrees of freedom, relative to x, y, z coordinates in 3D space. Equation (4, 3, 4) is very important but not used for solid [3]. With each normal oscillation in the system, the heat energy $kT/2$ falls to the limit case - high temperatures [3]. An atom oscillates at a constant sum of kinetic E_T and potential energy E_P i.e. $\text{const} = E_T + E_P$; E_T changes $(0 \div E_T)$ - period; the middle kinetic energy is $E_T/2 = kT/2$; heat energy in a closed volume of atomic gas is $kT/2$, gas have no potential energy; **for oscillator the total kinetic energy is $E_T = kT$** ; then total energy for each solid consisting of N atoms is eq. (4, 3, 5); for the molar heat capacity of a solid is eq.(4, 3, 6) generally correct, but used for quantitative ratios not always accurately. The absorption of heat energy by the oscillator allows the determination of the amplitude and max displacement $u_{\max}$ and converts the potential energy into a potential one $E_T^{\text{potential}} = (\alpha u_{\max}^2)/2$ and eq.(4, 3, 7) and eq.(4, 3, 8).

$$C_v = (\partial E / \partial T)_v, \quad (4, 1)$$

$$\theta_D = (\hbar v_D / k), \quad (4, 2)$$

$$PV = RT, \quad (4, 3)$$

$$P = (N/3)mv^2, \quad (4, 3, 1)$$

$$P = (2/3)NE, \quad (4, 3, 2)$$

$$E_{\text{GAS}} = 3RT/2N, \quad (4, 3, 3)$$

$$C_v = 3R/2 \text{ or } C_v = 3k/2, \quad (4, 3, 4)$$

$$E_{\text{Solid}} = 3NkT, \quad (4, 3, 5)$$

$$C_{v, \text{Solid}} = 3Nk = 3R, \quad (4, 3, 6)$$

$$E_T^{\text{potential}} = (\alpha u_{\max}^2)/2, \quad (4, 3, 6.1)$$

$$u_{\max} = (2E_T^{\text{potential}} / \alpha)^{1/2}, \quad (4, 3, 7)$$

$$u_{\max}^{\text{room temperature}} = 0.2 \text{ \AA} [3]. \quad (4, 3, 8)$$

The behavior of atoms considered as a whole is considered through Newton's macroscopic mechanics, but atoms internal structure is

described by quantum mechanics [3, 4] – purpose of this work.

2. Fundamentals of Material Science

Heisenberg's uncertainty principle: in physics there are such pairs of variables for which a final error occurs in their general definition; the quantitative record is [3] eq.(5):

$$(\Delta p_x)(\Delta x) \geq \hbar, \text{ (Heisenberg's uncertainty principle, 5, 1)}$$

$$(\Delta p_y)(\Delta y) \geq \hbar, \quad (5, 2)$$

$$(\Delta p_z)(\Delta z) \geq \hbar, \quad (5, 3)$$

$$(\Delta E)(\Delta t) \geq \hbar, \quad (5, 4)$$

where p_x, p_y, p_z - impulse and coordinates; E, t - energy and time; $\hbar$ is Plank's constant. A probability of particle behavior is introduced by setting a wave function eq.(6, 1), eq.(6, 2). The probability is a real quantity, ψ in the general case it is a complex quantity and to determine the density of the probability it is necessary to multiply ψ by the complex conjugate ψ^* [3]:

$$\text{Probability density} = \psi^*(x, t) \psi(x, t), \quad (\text{Wave functions, 6, 1})$$

$$\psi^*(x, t) \psi(x, t) dx \text{ is probability an particle } \in (x, x + dx) \text{ at the moment } t$$

$$\int_{-\infty}^{\infty} \psi^*(x, t) \psi(x, t) dx = 1. \quad (\text{Wave functions, 6, 2})$$

A method for determining the probabilistic behavior of the particle is: some wave function is set; the Schrödinger equation is used to determine the wave function. Basic law of physics [3] - Schrödinger's equation explaining phenomena is eq.(7, 1) in 1D case and 3D eq.(7, 2), where $\hbar$ is Plank's constant; m is particle mass; $V(x)$ - potential energy; For time-independent potential energy V , then the wave function eq.(7, 3) is a partial solution for the Schrödinger equation independent of time is eq.(7, 4) [3]:

$$\frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi(x, t)}{\partial x^2} + V(x) \psi(x, t) = \frac{-\hbar}{2\pi i} \frac{\partial \psi(x, t)}{\partial t}, \quad (7, 1)$$

$$\frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(x, y, z) \psi = \frac{-\hbar}{2\pi i} \frac{\partial \psi}{\partial t}, \quad (7, 2)$$

$$\psi(x, t) = \psi(x) e^{(-2\pi/\hbar)Et}, \quad (7, 3)$$

$$\frac{-\hbar^2}{8\pi^2 m} \frac{\partial^2 \psi(x)}{\partial x^2} + V(x) \psi(x, t) = E \psi(x), \quad (7, 4)$$

Eq.(7, 4) is very important (3). For $V(x) = 0$, the Schrödinger equation is eq. (7, 5) and describes a harmonic oscillator when replacing time with x . One solution is the function (7, 6), which is replaced by a time-dependent function of the type (7, 6, 1) describing a traveling wave. Eq. (7, 6, 2) also depicts a traveling wave with phase velocity ω/k . The function (7, 6, 1) is compared with the equation of a string (7, 6, 3) oscillating with moving in the direction y (3). The wave function of the type eq.(7, 6, 1) when writing (7, 6, 4) two basic relations are obtained (7, 6, 5) and (7, 6, 6) [3]:

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m E}{\hbar^2} \psi = 0, \quad (7, 5)$$

$$\psi = \exp \left[i x \sqrt{8\pi^2 m E / \hbar} \right], \quad (7, 6)$$

$$\psi(x, t) = \exp \left[\frac{-2\pi i}{\hbar} (Et - x \sqrt{2mE}) \right], \quad (7, 6, 1)$$

$$y = \sin(kx - \omega t), \quad (7, 6, 2)$$

$$y = e^{i(kx - \omega t)} \text{ and } \Rightarrow \quad (7, 6, 3)$$

$$\psi = e^{i(kx - \omega t)}, \quad (7, 6, 4)$$

$$E = \frac{\hbar \omega}{2\pi}, \quad (7, 6, 5)$$

$$k = \frac{2\pi p}{\hbar}, \quad (7, 6, 6)$$

frequency ω is expressed by the energy of the system (7, 6, 5); the constant k is also a function of the system energy $k = (8\pi^2 m)^{1/2} E / \hbar$. But the energy in the considered case is only kinetic then $E = p^2 / 2m$,

where p is the particle impulse (7, 6, 6). The ratio (7, 6, 5) is called *Einstein ratio* and the ratio (7, 6, 6) is called *de Broglie ratio*.

Energy quantization [3]: a particle in a potential pit [3]. Wave function ψ in 1D pit $0 \leq x \leq L$, is of the view eq.(7, 7) at $x=0$ $\psi(0)$ and at $x=L$ $\psi(L)=0 \Rightarrow \psi(L)=\sin kL=0$ eq.(7, 7, 1); k accepts only these values from the condition eq.(7, 7, 2) i.e. k accepts only discrete values $\Rightarrow$ energy E also assumes discrete values eq.(7, 7, 3); the uncertainty condition for a maximum nonlocalized particle (i.e. with minimum energy) is eq.(7, 7, 4) and taking into account $E = p^2 / 2m$ for energy we have eq.(7, 7, 5):

$$\psi(x) = \begin{cases} \sin kx \\ \cos kx \end{cases}, \quad (7, 7)$$

$$\psi(L) = \sin kL, \quad (7, 7, 1)$$

$$k = \frac{n\pi}{L} \quad n = 1, 2, \dots, \infty, \quad (7, 7, 2)$$

$$E = \frac{\hbar^2 k^2}{8\pi^2 m} = \frac{\hbar^2 n^2}{8\pi^2 L^2}, \quad n = 1, 2, \dots, \infty, \quad (7, 7, 3)$$

$$(\Delta x)(\Delta p) = (L)(2p) = \hbar. \quad (7, 7, 4)$$

$$E = \frac{\hbar^2}{8mL}. \quad (7, 7, 5)$$

Particle in 3D potential pit [3]: the Schrödinger equation is eq.(8, 1); The potential and zero values at the pit boundaries is eq.(8, 2); and eq.(8, 1) $\rightarrow$ eq.(8, 3) with boundary condition eq.(8, 2); ψ -function is eq.(8, 4):

$$\frac{-\hbar^2}{8\pi^2 m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + V(x, y, z) \psi = E \psi, \quad (8, 1)$$

$$V = 0 \begin{cases} 0 < x < L \\ 0 < y < L, \psi = 0 \\ 0 < z < L \end{cases} \begin{cases} x = 0, L \\ y = 0, L \\ z = 0, L \end{cases}, \quad (8, 2)$$

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m E}{\hbar^2} \psi = 0, \quad (8, 3)$$

$$\psi(x, y, z) = \psi_1(x) \psi_2(y) \psi_3(z), \quad (8, 4)$$

$$\left(\frac{1}{\psi_1} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{\psi_2} \frac{\partial^2 \psi}{\partial y^2} + \frac{1}{\psi_3} \frac{\partial^2 \psi}{\partial z^2} \right) + \frac{8\pi^2 m E}{\hbar^2} = 0, \quad (8, 5)$$

Eq.(8, 5) turns into system of differential equations (8, 5, 1)

$$\begin{aligned} \frac{1}{\psi_1} \frac{\partial^2 \psi_1}{\partial x^2} &= -k_1^2, \\ \frac{1}{\psi_2} \frac{\partial^2 \psi_2}{\partial y^2} &= -k_2^2, \\ \frac{1}{\psi_3} \frac{\partial^2 \psi_3}{\partial z^2} &= -k_3^2, \\ k_1^2 + k_2^2 + k_3^2 &= \frac{8\pi^2 m E}{\hbar^2}, \end{aligned} \quad (8, 5, 1)$$

The system differential equations with exponential or sinusoidal solutions depending on the values of the constants k - real or complex eq.(8, 6)

$$\begin{aligned} \psi_1 &= e^{\pm i k_1 x}, \\ \psi_2 &= e^{\pm i k_2 y}, \\ \psi_3 &= e^{\pm i k_3 z}. \end{aligned} \quad (8, 6)$$

If $\forall k$ is apparent, then the solution is a real exponent and the boundary conditions (8, 2) are not satisfied, therefore only sinusoidal solutions are possible. The boundary conditions in a three-dimensional potential well are satisfied by the set of functions (9) [3]:

$$\begin{aligned}\psi &= A \sin k_1 x \sin k_2 y \sin k_3 z, \\ k_1 &= \frac{n_1 \pi}{L}, \quad n_1 = 1, 2, \dots, \\ k_2 &= \frac{n_2 \pi}{L}, \quad n_2 = 1, 2, \dots, \\ k_3 &= \frac{n_3 \pi}{L}, \quad n_3 = 1, 2, \dots, \\ E &= \frac{-\hbar^2}{8\pi^2 m} (n_1^2 + n_2^2 + n_3^2).\end{aligned}\quad (9)$$

The term quantum state means the state of the system described by a partially linear independent solution of the Schrödinger equation. One main result is that the description of the motion of a particle in a 1D potential pit [3]. The motion of a particle in a 1D potential well requires only one quantum number. Therefore, the motion of a particle and in a 3D potential well the ψ -function depends on three quantum numbers n_1, n_2, n_3 . Three quantum numbers appear because the partial differential 3D equation is divided into three independent equations and each of them leads to a new quantum number. The energy also depends on three quantum numbers eq.(9). Quantum state and degeneration [3]: The ψ -function when a particle moves in a 3D potential well is denoted by $\psi(n_1, n_2, n_3)$ and characterizes the possible states of the system, physically different from all other states or functions. The discrete states of particle energy in potential wells eq. (7, 7, 3) and eq. (9) have discrete values called discrete spectra [3]. According to Eq. (8, 5, 1) and Eq. (9), energy data can be obtained by specifying several combinations of quantum numbers. According to data from [3] for different levels in the 3D case the notation is (n_1, n_2, n_3) and an example of three ψ -functions of one level are:

$$\begin{aligned}\psi_{112} &= A \sin \frac{\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{2\pi z}{L}, \\ \psi_{121} &= A \sin \frac{\pi x}{L} \sin \frac{2\pi y}{L} \sin \frac{\pi z}{L}, \\ \psi_{211} &= A \sin \frac{2\pi x}{L} \sin \frac{\pi y}{L} \sin \frac{\pi z}{L}.\end{aligned}\quad (10)$$

3.2 CASTEP and First order phase transition

In fundamental works [3, 4, 6, 8] the foundry methodology is embedded. The casting process consists of two parts: casting and solidification, but from the point of view of physics, hydrodynamics and first order phase transition. Work [3] covers all areas of foundry - a major branch of materials science. The idea and methodology of the book [3] is "to build a bridge between metallurgical engineers and theoretical physicists." This basic direction in our opinion today is: mathematics; mathematical physics and theoretical physics in materials science. Work [4] is a theoretical book and is an accurate image of mathematics applied in-depth explanation of the microscopic mechanisms of physical phenomena in solid state physics. A concrete example is based on the mathematical field of differential and integral calculus [5]: Fourier series and Fourier integrals in [4] the concept of "Fourier space" was introduced. Work [7] applied Nernst's theorem to a solid for atomic heat capacity and compared it with Debye's formula derived by quantum theory.

Energy fluctuation of chaotic systems: Boltzmann energy fluctuation eq.(EF, 1): p is the probability of an atom staying in a state with energy E ; k is the Boltzmann constant; T is the temperature; $A(T)$ is a physical characteristic of the system such that the integral of the probability of staying in one state is equal to one. The probability of an atom being in two arbitrary states is eq.(EF, 2); Helmholtz free energy of system is eq.(FE): E is internal energy; T is absolute temperature; S is entropy:

$$\begin{aligned}p(E) &= (A) e^{-E/kT}, & (EF, 1) \\ p(E_1)/p(E_2) &= e^{-E_1/kT} / e^{-E_2/kT}, & (EF, 2) \\ F &= E - TS. & (FE)\end{aligned}$$

Eq. (EF, 2) describes the distribution of the atoms of a solid body by levels of different energy states at any given time under the condition of constancy of the total energy. Atoms are distributed by levels of oscillation energy in different ways. A quantitative

measure of these modes is entropy when it is maximal (*in other words, maximal chaos*). Hence a system is in a stable state when the internal energy is minimal. The exact condition for equilibrium of an arbitrary system is a tray: sustainability state = of minimum free energy, i.e. $F = \min$. **Defects in the crystals:** **point** - violations of the lattice in isolated from each other points of the lattice: **vacations** - nodes of the lattice without atoms in them; **embedding atoms** - only atoms placed between the atoms in the lattice nodes; **impurity atoms** - atoms of different types, occupying places in the lattice; **linear defects: dislocations** - have a noticeable length in only one direction; surface defects of two types: external (boundary surface) - imperfections due to the fact that the surface of the solid body borders on another phase; internal (boundary surface) - surfaces on which there is a transition from one spatial orientation of the crystal lattice to another. There can be an infinite variety of boundaries between two adjacent grains. The energy of an atom in the ground state is E_{GS} ; the energy of high fluctuation for vacation formation is $E_v > E_{GS}$ and relative probability of vacation formation is $\exp(-E_v/kT)$ i.e. in a crystal lattice of Z atomic nodes, the number of vacations Schottky eq.(V, 1); the number of embedded n_i in the volume of a crystal (with N atomic nodes) Frenkel eq.(V, 2), where a is integer (normally not great) which characterizes the amount of identical internodes in the calculation of one atom of the lattice; local expansion - dilatation to the end of the dislocation Δ eq.(dil) [3], where b is Burger vector; r is radial distance from a point to a dislocation line, θ angle between two atomic rows; displacement corresponding to the helical surface equation eq.(dis, 1); energy dislocation of the hollow cylinder U_D eq.(dis, 2), μ is displacement module for the given material; l is length; if r_0 is equal to a distance of one or two interatomic rows then the ratio r_1/r_0 is about $5 \cdot 10^{-3}$ [3]:

$$n_v = N e^{-E_v/kT}, \quad (V, 1)$$

$$n_i = a N e^{-E_i/kT}, \quad (V, 2)$$

$$\Delta = \frac{\Delta V}{V} = \frac{b}{r} \sin \theta, \quad (dil)$$

$$u_z = \frac{b}{2\pi} \theta, \quad (dis, 1)$$

$$U_D = \frac{\mu b^2 l}{4\pi} \ln \frac{r_1}{r_0}. \quad (dis, 2)$$

The atoms in the crystal lattice move: through thermal oscillations and elementary acts of transition from node to node - diffusion. It is influenced by: 1. Crystallographic and geometric characteristics; 2. Temperature. Diffusion is a set of chaotic movements of atoms - in the form of oscillation and transition of atoms from one node of the crystal lattice to another. The averages of the chaotic unequal atomic "jumps" are statistically estimated and are the reason for moving an atom over a long distance. The diffusion in the crystals are: vacation movements; movements of embedded atoms; exchange of places between two atoms; ring-shape exchange between four atoms. Diffusion in solid solution alloys - diffusion of small atoms located between the nodes: Energy for overcoming the barrier is E_m , frequency for jump f_m of an atom in an elementary crystal cell of Z equivalent neighboring atoms is $\exp(-E_m/kT)$ at v is of order 10^{13} Hz eq.(Dif, 1) and atom exchange vacation is f eq.(Dif, 2); 1D diffusion eq.(Dif, 1d); 3D diffusion eq.(Dif, 3d); new 1D eq.(1d, 1); diffusion coefficients eq.(D, 1) and eq.(D, 2):

$$f_m = Z \exp(-E_m/kT), \quad (Dif, 1)$$

$$f = Z v e^{-E_m/kT} e^{-E_v/kT}, \quad (Dif, 2)$$

$$\sqrt{\bar{X}^2} = \sqrt{f t d^2}, \quad D = f d^2 / 2, \quad \sqrt{\bar{X}^2} = \sqrt{2 D t}, \quad (Dif, 1d)$$

$$(\bar{R}^2)^{1/2} = (\bar{X}^2 + \bar{Y}^2 + \bar{Z}^2)^{1/2}, \quad (\bar{R}^2)^{1/2} = (f d^2 t)^{1/2}, \quad (Dif, 3d)$$

$$(\bar{X}^2)^{1/2} = \left(\frac{\bar{R}^2}{3} \right)^{1/2} = \left(\frac{d^2 f t}{3} \right)^{1/2}, \quad D = \frac{f d^2}{6}, \quad (Dif, 1d, 1)$$

$$D = Z \frac{d^2 v}{6} e^{-(E_v + E_m)/kT}, \quad (D, 1)$$

$$D = D_0 e^{-Q/kT}. \quad (D, 2)$$

CASTEP [6 and 8] is academic and commercial software product created in TCM Group of Cavendish Laboratory of

Cambridge. CASTEP [6 and 8] is redesign 1999-2001 and adapted for parallel computers (calculations) by researchers at the Universities of York, Durham, St. Andrews, Cambridge and Rutherford Labs. Theories used [8]: Density functional theory DFT - principles and method to determine the ground state electronic structure of a system; Methodology of electronic structure calculation: use a set one-electronic Schrödinger (Kohn-Sham) equation solved by plane-wave pseudopotentials; The wave functions are extended by a set of plane wave bases defined using periodic boundary conditions and Bloch's theorem; Use *ab initio* pseudopotential in the required wording; Mathematical schemes are used to directly reduce the energy to obtain self-electron wave functions and the corresponding charge density.; Tasks [8]: *Total energy in point; Electronic structure; Geometry optimisation; Molecular dynamics; Transition states; Phonons; Electric field response; Exchange and correlations.* The amount of total energy is of major interest and of extreme interest is its reaction to external influences. This reaction can be compared to an experiment. In case of system disturbances, the total energy can be expanded as a series of disturbances. Thus a wide range of physical properties become available to us; if the second-order energy is calculated with respect to the given disturbance, Perturbation $\rightarrow$ Physical quantity can be obtained [8]:

PERTURBATION	PHYSICAL QUANTITY
Atomic position $\rightarrow$	Phonons
Electric field $\rightarrow$	dielectric properties
Magnetic field $\rightarrow$	NMR
Lattice parameters $\rightarrow$	Elastic constants
k-point $\rightarrow$	Born charges.

First order phase transition and classical theory and CASTEP is shown of Fig. 9 [15 and 16]:

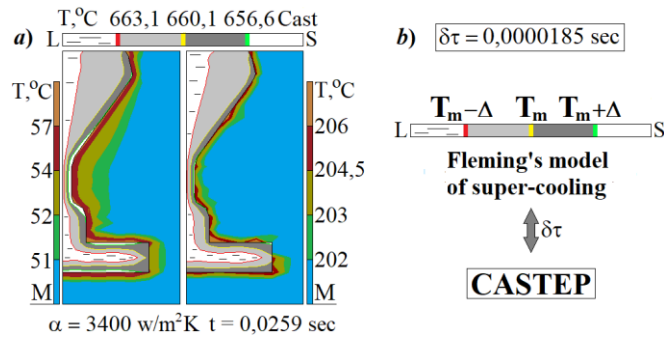


Fig. 9 First order phase transition 3D by Finite elements method, Fleming's super-cooling [15 and 16] and CASTEP i.e. application of CASTEP in foundry: a) First order of phase transition in a sample for spectral chemical analysis and influence of the mold initial temperature 51 °C and 206 °C; b) Generalize solution in transition zone $T_m \pm \Delta$ in one step of time $\delta\tau = 0,0000185\text{sec}$, T_m is melting point; Fleming's super-cooling and CASTEP.

In the work [10] data on the rate of growth of dendrites depending on the supercooling of the bath with melt are cited. The physics of supercooling in front of the top of the dendrites is Fleming's model as the sum [10]: *the effect of the radius of curvature of the top of the dendrites + supercooling necessary for atomic jump through the interfacial surface + supercooling of the melt to separate and dissipate the heat of crystallization.*

In [16] 1D classical Stefan's problem is developed with taking into account a super-cooled zone with dissipation of the hidden heat of melting Q_m ; the boundary $x_1(t)$ is liquid/(super-cooled zone) and the other $x_2(t)$ is (super-cooled zone)/solid; boundaries move according to two laws of the square root with coefficients K_1 and K_2 and at speeds R_1 and R_2 :

$$R_1 = \frac{[\lambda_1 \nabla T_{x_1-0} - \lambda_2 \nabla T_{x_2+0}]}{\rho_1 Q_m}, R_2 = \frac{[\lambda_1 \nabla T_{x_1-0} - \lambda_2 \nabla T_{x_2+0}]}{\rho_2 Q_m}, \quad (V_{\text{ZONE}})$$

$$x_1(t) = K_1 \sqrt{t}, \quad x_2(t) = K_2 \sqrt{t}. \quad (S_{\text{ZONE}})$$

To describe the state of the atoms in the moving cooled zone, we suggest using the CASTEP software by multiscale approach: Stefan's problem is solved and at any moment CASTEP is used:

$$t = \sum \delta\tau \Rightarrow, at \forall \delta\tau \{T_1(x_1, \delta\tau), T_2(x_2, \delta\tau)\} \Leftrightarrow \text{CASTEP}.$$

Here t is the time process as a sum of small steps $\delta\tau$. We know the solidification temperature field and at each time step we calculate the state of the atoms in the transition zone. And the end: 1. Stefan's task [1] and Stefan-Schwartz's task are complemented by the Stefan type task developed in [16]; 2. Work [16] offers a good opportunity for analysis of the transition state of atoms from a liquid state to a solid state through the software product CASTEP. Historically, the fundamental basis of metal science [9] is metal physics [11] and the theory of solids [3, 4]. Here we note that [13] is a natural methodological and fundamental continuation of work [9]. The mathematical basis of foundry is the theory of thermal conductivity - problems of Stefan [1, 2, 7 and 16], and phase transitions of the first and second order, considered theoretically and engineering in [10]. In [12] with quantum field theory of a solid body, elementary excitations in solid and interactions between them are considered. Scientific methodology is based on [14] with a focus on foundry.

3. Conclusions

1. A foundry methodology has been developed based on historical developments and new advances in solid state physics and the CASTEP software product.
2. The first order phase transition in the sample casting for chemical spectral analysis presents the basic idea of the interaction *solidification and evaluation of structures* through CASTEP.

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Casting of body parts with complex geometry in 3D printed sand forms

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Abstract: The intensive development of turbochargers power at the end of the decade and two years after the announcement of the latest results of this development, "Breakthrough: Nitrogen Oxides (NOx) 10 times below the predicted for 2020 limits" still there is no data for the rehabilitation of the contemporary diesel engine. The progress made by the multiplication of turbochargers in bi-turbo, three-turbo and four-storied turbo has been underestimated and neglected in the shadow of the publicity for electric, hybrid and gasoline vehicles.

The article offers progressive technical solutions for casting of aluminum crankcase for turbochargers of new generation through the rational use of 3D printed sand molds. The research and application in the foundry of new 3D printer technologies gives the opportunity to realize casting with new and additional functions due to their complicated geometry and their high geometric accuracy.

Keywords: ALUMINUM ALLOY, COMPRESOR HOUSING, 3D PRINTED SAND, HIGLY COMPLEX GEOMETRY, GAZ PERMEABILITY

1. Introduction

The need to reduce air pollution from internal combustion engines [1] significantly changed the complexity of aluminium alloys castings. In the new versions [2] the turbochargers are loaded with new functions and are carriers of new elements related to the improvement of combustion [3]. This change in geometry can be summarized as an obligation to add additional cores with more complex geometry to the standard structures.

Conventional foundry methods can not accurately realize the geometry drawn and required by the new designs. These old methods impose numerous geometric changes: tearing the inner form from monobloc to a few simpler cores. It is also imperative to distort the internal and external walls with the so-called foundry slopes in the direction "wherever is possible". If these and other changes are rejected by the creators of the desired shape, the foundry tools (core boxes, models, moulds) cannot be realized. The creators of the new form are forced to retreat back.

Another problem occurs after the individual constituent elements are being established. The assembly (gluing) of several separate simple cores to achieve the desired complex internal shape, worsens the accuracy and stability of the dimensions. Unsatisfactory accuracy becomes visible too late after the casting – after the machining or even later – during the final tests.

2. Research

The use of segments of 3d-printed sand has certain advantages, the first one is that there is no need for foundry slopes to reproduce a geometric shape. A second important advantage is that it makes possible the realisation of all complex forms, in a single mono-bloc if there are no other prescriptions.

The purpose of this work is to find and to describe other advantages of the printed sand forms, valid for all types of substances used to bind sand grains during the printing.

The research was done on castings with high geometric complexity of inner shapes (sometimes external), as the housings of various turbochargers.

The following 3 figures present different experimental elements:

- Fig. 1 shows 3 photos of Carters for turbochargers, moulded into sand moulds, realized in industrial 3d-printers
- Fig. 2 shows 3 pictures of two different cores with complex geometry, impossible to be realized in conventional technologies;
- Fig. 3 presents photo of other cores difficult to realize by conventional technology- narrow cooling channels with extremely precise and complex shape, with a minimal machining over-thickness at the entrance and the exit on each side.

In the narrow space between the different elements of compact combustion engines, each millimetre is carefully foreseen. Installing or dismantling to replace wrong elements is unacceptable. The over-thickness for machining is minimum and the casting part could be scrapped if it is more or not enough:

- The rupture of the core during the casting;

- Causes leakage due to "lack of material" on the surface of the seals.



Fig.1 Photos of aluminium parts casted in to 3D-printed sand. The moulds are made up of segments printed in industrial printers.

Finding a successful technical solution for the removal of gases in a safe direction would make unnecessary the search for other complications in the opposite direction – how to improve the density.



Fig. 2 Photos of 3d-printed sand segments:
a) Two views of central-core in 3D-printed sand;
b) 3D-printed core "Monobloc" with the highest complexity

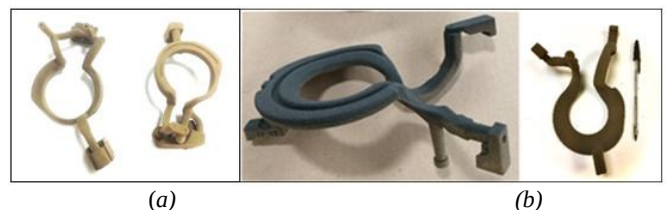


Fig. 3 Photos of another type of 3d-printed sand segments:
(a) Photos of the same sand core for a cooling channel in aluminium cast part - top view (left) and bottom view (right);
(b) Photo of another core of a cooling channel with a complex geometric shape. (Pen on the right is a witness to the scale)

When using 3 d-printed forms for aluminium castings, it should be reported that the casting of these alloys is at relatively low temperatures (below 760 °c). This advantage helps to abandon old perceptions that the binder is determined by the foundryman. Today it is time to progress through:

- Completion of the outdated discussions about the type and percentage of the binder. It is already optimised by the printing experts, and separately for each binder.

- All binders, whether or not based on furan, phenol or inorganic resins/substances, when they come into contact with the liquid metal, heat and emit gases, regardless of whether the process is degradation, burning or evaporation.
- Avoid hermetically closing of the printed segments into each other.
- Avoid the blocking of the possibilities for removal of the gases (or vapours) that have been caused during casting and solidification. Sometimes specialists are doing the opposite – useless deepening in details about the chemical processes, but not to be removed, but with the only goal to search for new arguments for maintaining the old discussions.
- To make simple "paths" to avoid increased pressure of the formed gas, through its evacuation from critical places or at critical moments, without complicating the reflections about the chemical process for the formation of this gas.

In order to find efficient solutions, the current work is inspired by the process of producing sand cores "Croning" [4], rather specialised in aluminium castings. In the realization of the cores for aluminium castings with "Croning" process is searched for a cores' structure and choice of the appropriate machine, in which to empty the core's interlayer, keeping only one shell of a few millimetres left in contact with the heated sand core box. These numerous cases existed in turbochargers from the very beginning of the turbocharger supply in the '70s of the 20th century. Besides what already exists in the "Croning"-process, the idea of making a two-layered core is used in this case. In contrast to an old idea of applying a sand with different sizes, in the case here, the second layer of the core is from the same sand, but it is done so that the presence of resin in the inner layer is avoided. It doesn't matter whether the resin is on furan, phenol or inorganic base.

The following figure Fig.4 is a diagram of a typical sand shape with permeability activated [5].

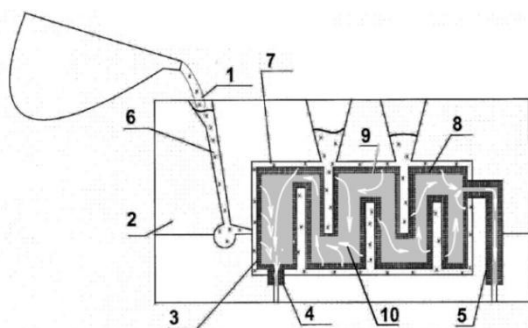


Fig.4 Diagram of sand form made up of segments, printed in industrial 3D printers, with permeability activated.

The indications are as follows: 1-liquid metal; 2 - Sand form of 3d-printed segments (upper and lower forms, inserts or other parts); 3 - Core (one of the 3d-printed segments); 4,5 - Marks of the core; 6 - runner; 7 - casting part; 8 - layer of the printed segment that contains the resin; 9 - The other layer of the printed segment that does not contain resin; 10 - direction of evacuation of gases (or steam, or smoke from combustion, if it exists). The two layers (8) and (9) are a constituent part of the core (3).

In the cases where the surface of the core is almost entirely surrounded by the hardening liquid metal, the gas (from evaporation, decomposition, or burning of the resin) is formed very quickly in contact with the liquid metal. Permeability activation allows this gas, formed during filling and hardening, to be evacuated inside the segment. This gas is then routed to the outside of the form by channels specially designed for its evacuation.

If this activation does not exist, if it is blocked or destroyed for various other reasons, the absence of outlet increases the pressure inside the core and the gas created (no matter how it is formed-from evaporation, decomposition, or burning resin) begins to penetrate the opposite direction-to the liquid or partially hardened metal.

The sand moulds for this study have been printed by industrial 3D printers provided for the presentation of services accessible in Europe "articles of 3d-printed sand" [6].

On Fig. 5 A picture of a slender 3 D-printed form is shown, taken approximately 2 minutes immediately after casting. At the front and alongside we observe traces of gas leaving the shape. Evacuation of this gas is calm, evenly without thrusts or combustion. The white colour of this gas is probably due to products from the decomposition of the resin to carbon dioxide and other ingredients which have not been able to be glued to the sand grains through which they pass until they cool or leave the form on the pathways of activation of the permeability.

The cast part is an aluminium turbo compressor housing.



Fig.5 Picture of 3D-printed sand mould, taken almost 2 minutes after casting.

White spots on both sides of the form indicate the evacuation of gas, which is emitted by the contact of the core with the liquid metal, through the specially made channels, following the pathways for activation of permeability sequentially.

This result is confirmed by numerous other castings for turbochargers.

The solution found is also confirmed for other types of castings for the automotive industry, such as differential clutch casings, gearbox casings, steering gearboxes, steering deck casings, hybrid vehicle deck casings [7], other specific cases, pump bodies, mouldings for cylinder heads of combustion engines, electric engine bodies etc.

3. Conclusions

1. The use of 3d-printed molds for aluminum complex-geometric casting parts is possible and essential to achieve the exact form without any "adjustment" to conventional foundry requirements.

2. The production of casting parts with high geometric complexity in 3d-printed forms is more advantageous in terms of time and global budget (price of foundry coreboxes, pattern plates or other tools and price of casting).

3. The application of 3d-printed moulds is a modern casting process that requires specific knowledge and training specially adapted to the users and the training of 3d-design teams is very important

4. The use of 3d-printed molds for castings, easily produced by conventional methods, is useless and unjustified, makes no sense for industrial needs.

5. The production of cast parts in 3d printed sand moulds is entirely digital after learning of all the specifics of this casting

process. With this technology, it is possible to produce good and without any defects part from the first casting. The only condition is that the development of the process optimization is also done by the digital way and carried out by virtual casting professionals.

6. The use of 3d-printed forms in parallel with gravitational aluminum diecastings can find successfully stable and fast solutions waiting for the industrial development of "direct" printing [9] of aluminum products.

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Technological first-order phase transition base of foundry and material science

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Abstract: Technological first-order phase transition is obtain base process of material science by numerical experiments at use of finite elements method (FEM). The history of movement and the geometry of the front in the first-order phase transition are investigated. A free first-order phase transition was investigated to estimate the local place of the liquid residue. Mathematical model is Stefan-Schwartz task in 3D case. The corresponding temperature fields of a free and technological first-order phase transition are presented. Engineering information is local phase transition conditions is shown of macro-level with the local transition time and volume at the front is assumed.

Keywords: STEFAN-SCHWARTZ TASK, 3D FEM, FREE AND TECNOLOGICAL FIRS-ORDER PHASE TRANSITION

1. Introduction – fundamentals processes of material science

Some of the basic processes of material science are phase transitions [3, 5, 7, 12, 16, 17, 18 and 19]. Our institute has been developing technologies and equipment for foundry production for more than 40 years on the basis of the Angel Balevski and Ivan Dimov method for injection molding (certificate No.187 / 1961 y. P. 181 [12]). The gas counter-pressure casting method allows precise volume and surface formation of castings [12]. Investigation of gas-, hydro- and thermodynamic processes in conditions of gas counter pressure casting and their influence for controlling the formation of castings [7, 12].

On Fig. 1 is shown the base geometric diagram of the casting process by the method of the „GP“ [19]:

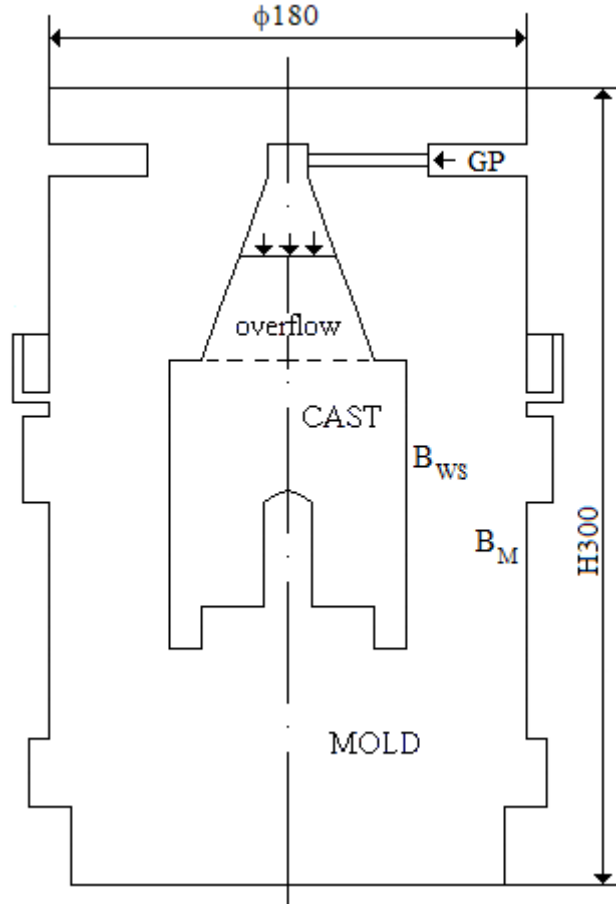


Fig. 1 Geometrical diagram of open thermodynamics system (OTS): Mold and cavity for Cast and overflow with overall dimensions diameter $\phi = 180$ mm and height $H = 300$ mm. The volume V_{SYS} is the sum of cast volumes of liquid V_{CL} , surface front S_{Front} and solid V_{CS} phases, mod volume V_M with it boundary surfaces B_{ws} and B_M .

The casting method „GP“, the first-phase phase method runs under high gas pressure [19].

The mathematical base of the casting is mathematical tasks of Stefan [1] and Schwartz [2]. The open thermodynamic system (OTS) of Fig. 1 is:

$$V_{SYS} = (V_{CL} \cup S_{Front} \cup V_{CS}) \cup B_{ws} \cup (V_M \cup B_M)$$

The task of Stefan-Schwartz in 3D for numerical investigation by Finite Different Method, Finite Elements Method and so on is:

- Equation of the heat conductivity:

$$(c + SFQ_m) \frac{\partial T}{\partial t} = \lambda \Delta T \quad \text{in } V_{SYS}, \quad (1, 1)$$

- Stefan's boundary condition (S_F):

$$-\lambda_L \nabla T_{L|S_F} = \rho_S R Q_m - \lambda_S \nabla T_{S|S_F}, \quad (1, 2)$$

And growth velocity of solid phase:

$$R = [\lambda_L \nabla T_{L|S_F} - \lambda_S \nabla T_{S|S_F}] / \rho_S Q_m, \quad (1, 2, 1)$$

- Boundary condition at the mold's work surface (B_{ws}):

$$-\lambda_C \nabla T_{C|B_{ws}} = \alpha_{B_{ws}} (T_{C|B_{ws}} - T_{M|B_{ws}}) = -\lambda_M \nabla T_{M|B_M}, \quad (1, 3)$$

- Boundary condition mold-environment (B_M):

$$-\lambda_M \nabla T_{M|B_M} = \alpha_{B_M} (T_{M|B_M} - T_{En}), \quad (1, 4)$$

- Initial conditions at $t = 0$:

$$T_L(x, y, z, t) = \text{const}_L, T_M(x, y, z, t) = \text{const}_M, \quad (1, 5)$$

where T is the temperature with indexes for the cast (C) liquid (L) and solid (S) phases and mold (M); V_{SYS} is the sum of cast volumes of liquid V_{CL} , surface front S_{Front} and solid V_{CS} phases, mod volume V_M with it boundary surfaces B_{ws} and B_M . the thermophysical coefficients of the (OTSF) are: thermal capacity (c), density (ρ); S_F is function of the heat source, Q_m is latent heat of the melting at the melting temperature T_m .

The mold (Fig. 1) is for "GP" casting method [19], in which the cast is formed under high gas pressure. The study of temperature changes in operation [19] was made using the MAGMASoft software package. The solution of Stefan-Schwartz task is for maximum heat transfer: coefficient of heat transfer $\alpha = 56000$ w/m²sK at the mold boundary B_{ws} and B_M ; mold initial temperature $T_M(x, y, z, 0) = 72^\circ$ C is introduce on Fig.2, where the initial temperature of the mold and the temperature field of the first-order free phase transition at a time are shown The technological model of eq.(1) is solved by using a software package of (FEM) created at our institute of M. Dimitrov and S. Bushev.

The purpose of this work is to consider the phase transition of the first order of basic process in foundry.

2. Free process of first-order phase transition in foundry

A free first-order phase transition process in the casting process is carried out by **uniform and constant heat exchange** throughout the working and external surfaces of the mold.

In Fig. 2 is shown cross section of car wheel formation at FREE first-order phase transition

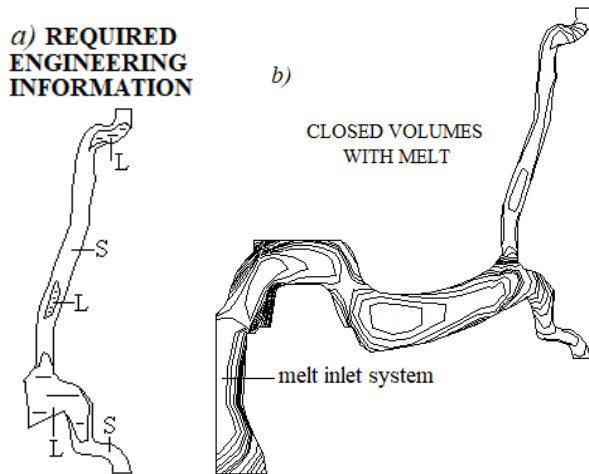


Fig. 2 Methodology of the example of the car wheel formation at free first-order phase transition and heat unit (closed volumes with melt): a) ice cast [20]; b) history of phase transition of Al [21].

A major engineering interest (Fig. 2) is the temperature field of a first-order phase transition is the location and geometry of the interfacial surface [1, 2, 3, 5, 7 and 12] separating the volumes of the liquid and solid phases in the formed cast. In Fig. 3, the initial temperature of (OTC) and the temperature field of a free first-order phase transition with the front (zone) of phase transformation at time $t = 0, 6475$ sec are presented:

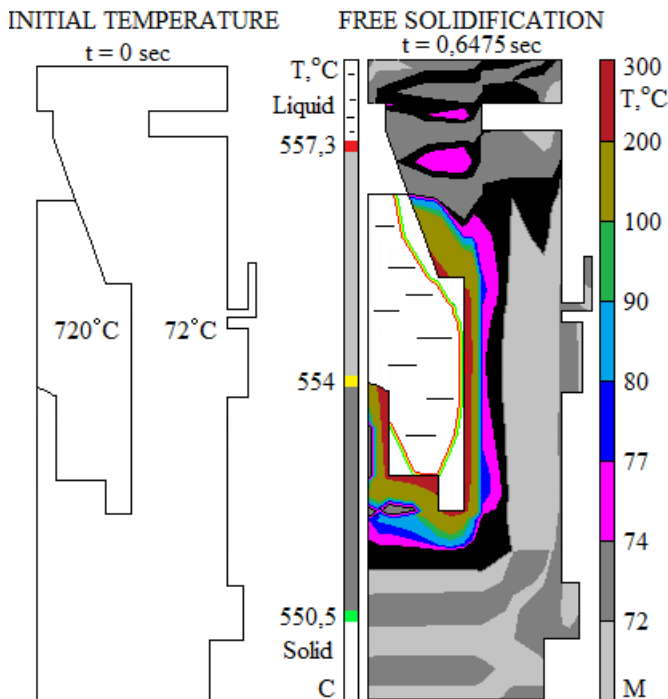


Fig. 2 Initial (OTC) casting temperature and shape with a temperature field of free first kind of phase transition at time $t=0.6475$ sec together with the volumes of liquid and solid phases separated by the phase transition front (zone).

The correct engineering answer is the history of the phase transition front (zone) movement from free first-order phase transition in the time is present:

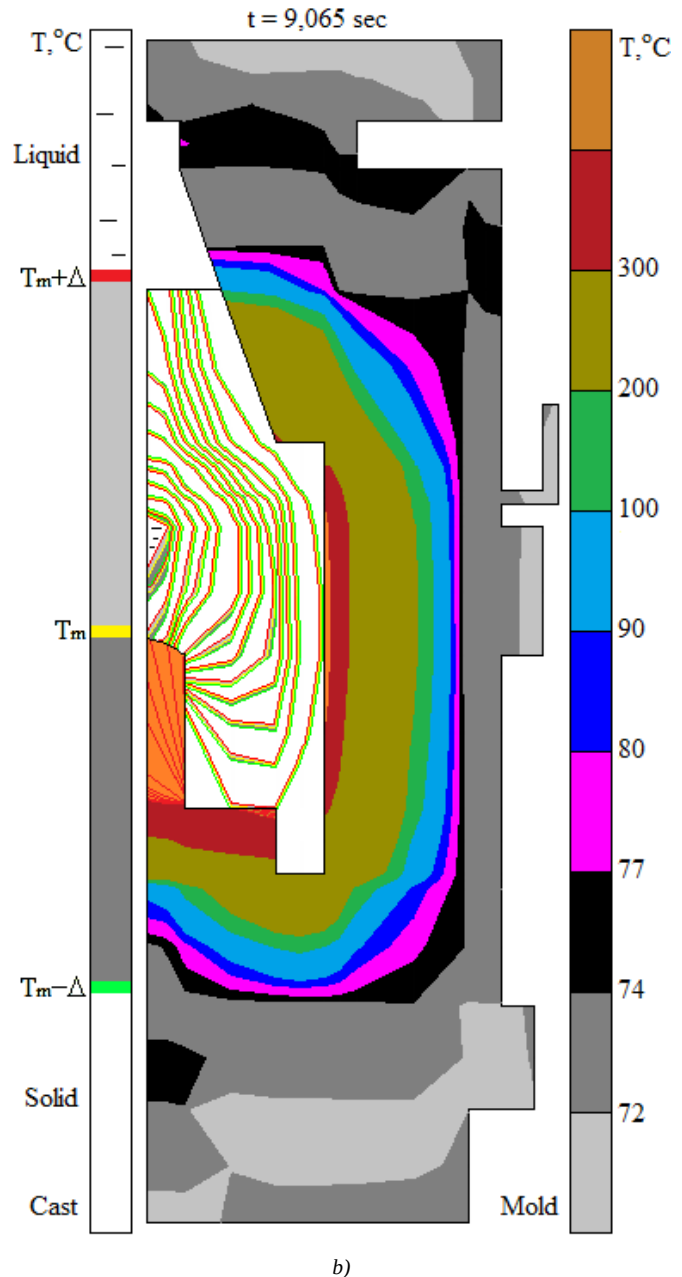
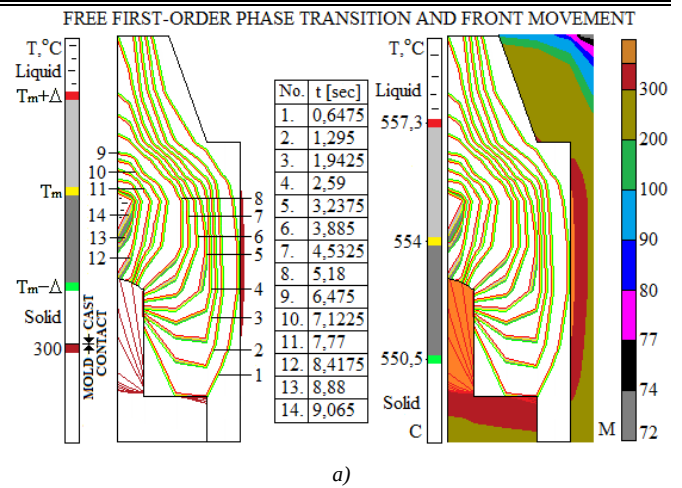


Fig. 3 Initial condition and a temperature field of free first-order phase transition in the end time $t = 9,065$ sec of numerical experiment: a) history of the movement boundary phase transition front (zone) with 14-in transition; table with 14-in times; the temperature field in a little layer at the mold work surface contact; b) full temperature field of the system at the end time = 9,065 sec of the numerical experiment.

The overflow does not fulfill its purpose.

3. Technological first-order phase transition in foundry

In Fig. 4 is the methodology for a technological first-order phase transition based on [20]:

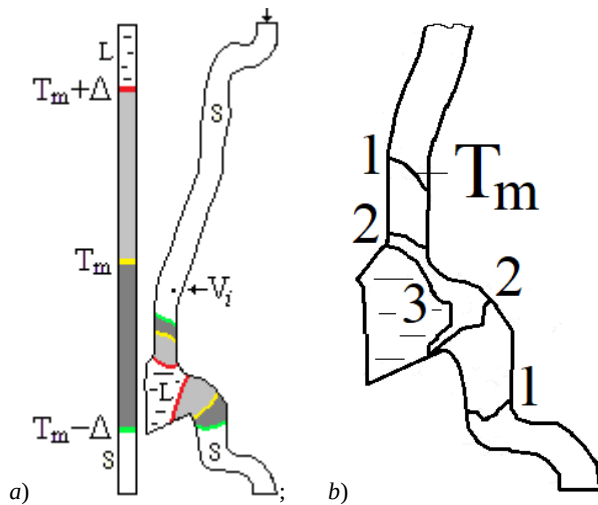


Fig. 4 Technological first-order phase transition in foundry [20]: a) ↓ is cooling place; the volumes of liquid (L) and solid (S) phases separated by the phase transition front (zone) ($T_m - \Delta$, T_m , $T_m + \Delta$) with removable of thermal unit; V_i is micro-volume; b) sketch for work [20] history of movable isothermal surface (front) T_m in tree time 1, 2, 3 at technological removal of thermal unit.

The basic purpose of the foundry methodology is to move the front of a first-order phase transition: from a cold region to a warm region without closed liquid volumes. Here (see Fig. 1) we have an overflow whose volume must to finish the first-order phase transition in the warm overflow. On Fig.5 we used initial temperature of the mold:

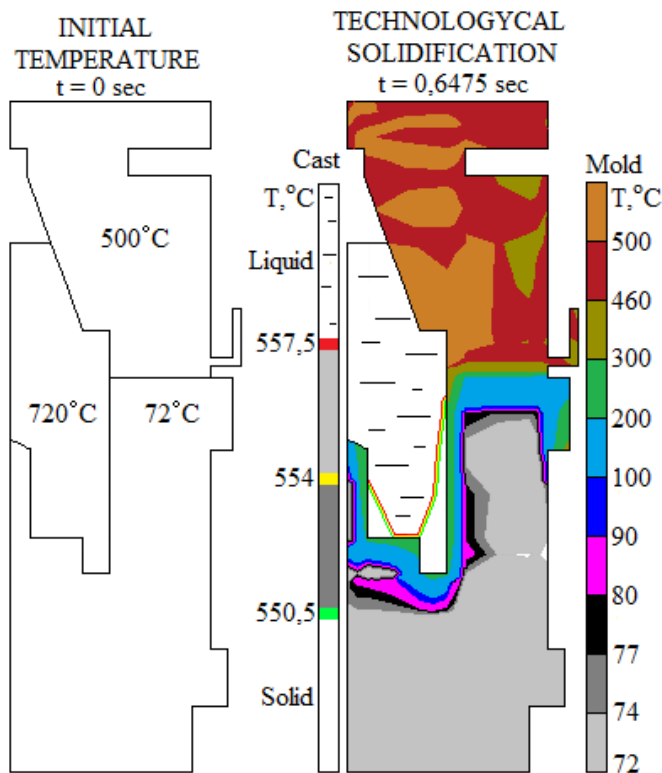


Fig. 5 Initial temperature of the mold is of two area cold with 72° C and hot – 500° C. In hot part of the mold is located the overflow. The temperature field of the OTS in the time $t = 0,6475$ sec.

The numerical experiment is the same - the history of the motion of the first-order phase transition front and is presented in Figs. 6:

TECHNOLOGICAL MOVEMENT FIRST-ORDER PHASE TRANSITION

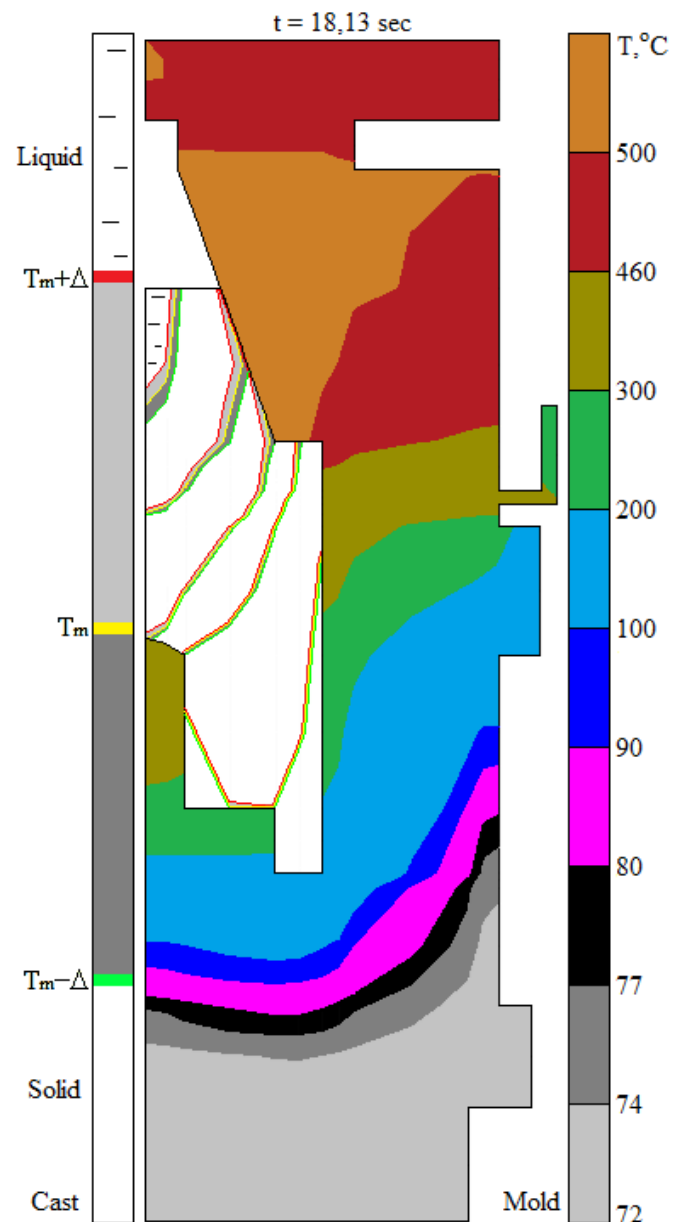
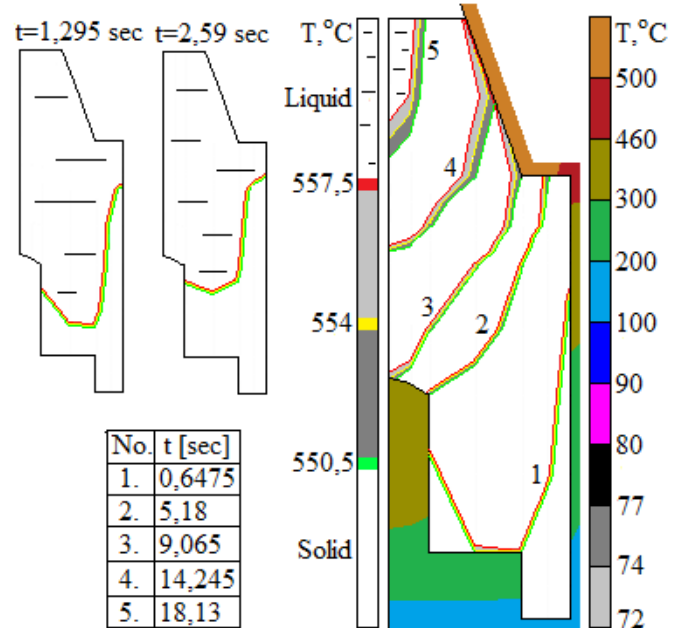


Fig. 6 History of the front moving the first-order phase transition:

a) detailed history of front moving and is ending in the overflow volume;
the last temperature field at the contact surface cast/mold; b) the last
temperature field of the OTS in the time $t = 18,13$ sec.

From Fig. 6 follows that the overflow in the hot area of the mold we have technological first-order phase transition and is ending in the overflow volume.

4. Technological first-order phase transition – cast structure

Engineering information [6, 3, 5, 7, 9, 12] from calculated front of first-order phase transition is: geometry, thickness, correlation volume V_i , characteristic time τ_{ch} (or local t_f) of phase transition on Fig. 7:

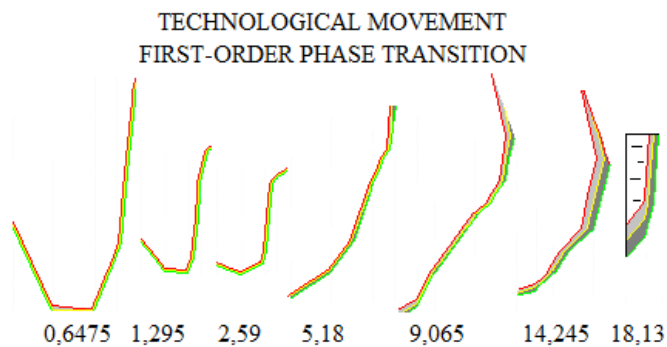


Fig. 7 The history of the technological first-order phase transition and local difference between the two temperatures $T_m - \Delta$ and $T_m + \Delta$ in the fronts at: 0,6475sec; 1,295sec; 2,59sec; 5,18sec; 9,065sec; 14,245sec; 18,13sec;

$$t_f = \Delta\mu / RVT_{S[Front]}, \quad (2, 1)$$

$$\tau_{ch} = V_i^{2/d} / D = \Delta\mu / RVT_{S[Front]} = t_f, \quad (2, 2)$$

where $\Delta\mu$ is thermodynamic driving force; $d = 1, 2, 3$; D is Diffusion coefficient. The volume V_i we suggest it to be considered as a cell needed to work with the CASTEP [22] software product, which is available for crystallization processes. CASTEP is software to perform calculations on the first principle of quantum mechanics for the study of the properties of the crystal surfaces in the solid state [22]. This software can calculate five tasks: energy; geometry optimization; molecular dynamics; elastic constants; study of transition-state [22]. The task of CASTEP – study of transition-state is connect with [3, 5, 6, 7, 9, 11, 12, 20 and 21]. Elastic constants task of CASTEP is connect with [8]. Technological first-order phase transition is two levels: 1. Macro-level Stefan-Schwartz [1, 2] and eq. (1) and eq. (2); 2. Meso-level [4, 6, 10, 13, 14, 15].

Stefan-Schwartz problems and CASTEP software covered theoretical and applied material science [16, 17 and 18]. J. From all of this it follows that even the smallest family foundry requires scientific support based on the Stefan-Schwartz problem and [1 and 2], which can be provided by a relevant industrial branch, such as MACHINE BUILDING.

. Conclusion

The technological process of a first-order phase transition is obtained at the macro-level based on the history of geometry and the movement of its front. A local volume is defined at the front to describe this transition and at meso-levels using CASTEP software.

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Complete set of radioisotope densitometer with ionising radiation source of cesium-137 and calibration of the radioisotope densitometers

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Abstract: Research on charging a radioisotope density meter (Endress + Hauser AG, Sweden) with ionizing radiation source of cesium-137 types GCs7.021.1, GC 7.012.8 and calibrating radioisotope densitometers on stands with liquid simulators based on mixtures of bromoform and ethyl alcohol. Calibrated radioisotope densitometers were used to determine the density of the pulp emulsion in the technological line of the State Enterprise «Navoi Mining and Metallurgical Combine» (Bessopan industrial site, Zarafshan city, Republic of Uzbekistan).

The paper presents studies on the development of a method for calibrating a radioisotope level meter (Berthold Technologies GmbH & Co. KG) under the conditions of the presence of natural radionuclides in the composition of gas condensate and powdered polyethylene intermediate product at the gas production enterprise of the JV «Uz-Kor Gas Chemical», «Ustyurt Gas Chemical Complex» (Kirk-kyz settlement, Republic of Karakalpakstan).

KEYWORDS: GAMMA SOURCE BLOCK, IONIZING RADIATION SOURCE CESIUM-137, DETECTOR BLOCK, INFORMATION PROCESSING AND ANALYSIS BLOCK, LIQUID SIMULATOR, CALIBRATION OF RADIOISOTOPE DENSITOMETER, NATURAL RADIONUCLIDES, INTERMEDIATE POWDERED POLYETHYLENE PRODUCT, GAMMA BACKGROUND, LEAD SHIELD FOR DETECTOR BLOCK, CALIBRATION OF RADIOISOTOPE LEVEL GAUGE.

Introduction

Radioisotope density meters and radioisotope level gauges are designed for non-contact measurement of the density or level of liquids and dispersed systems (suspensions, emulsions, slurries) of various compositions in closed tanks and pipelines and their principle of work is the same. The principle of operation of radioisotope densitometers and radioisotope level gauge is based on the registration of residual gamma radiation from radiation ionizing source after it passes through pipeline or tank and. The degree of attenuation of gamma radiation from the thickness and density (or level) of the pipe wall material, the length of the gamma radiation path depends on the controlled environment and the density (or level) of the controlled environment. Radioisotope densitometers and radioisotope level gauges measure constant value of gamma radiation.

One of the following ionizing radiation source is used in radioisotope densitometers and radioisotope level gauges: cesium-137, americium-241, cobalt-60, curium-244, which are placed in a lead shielding container with a collimator on pipeline or tank, and a detector block is permanently located on their opposite side. However, Cs-137 and Co-60 ionizing radiation sources are often used. Radionuclide Cs-137 has half-life of 30, 2 years and gamma energy of 661.6 keV and radionuclide Co-60 has half-life of 5.3 years and gamma energies 1.1732 MeV, 1.3325 MeV [1]. It is more expedient to use the Cs-137 source because of its longest half-life and energy of gamma radiation, not required powerful lead shielding in the gamma-radiation source block in order to ensure the radiation safety of personnel.

The import of Cs-137 ionizing radiation sources into the Republic of Uzbekistan from abroad is associated with some difficulties, such as: obtaining a license from the Ministry of Foreign Economic Relations and Trade, the cost of training, servicing and disposal of sources after the expiration of their service life.

The aim of the study is to complete ionizing radiation sources Cs-137 of the GCs7.021.1 and GCs7.012.8 types with radioisotope densitometers (Endress + Hauser AG, Sweden) and development of methods for calibrating radioisotope density meters in laboratory conditions for their further use in the technological line of the State Enterprise «Navoi Mining and Metallurgical Combine».

Radioisotope level gauges (Berthold Technologies GmbH & Co. KG) were purchased and installed on polyethylene production lines at the gas production enterprise JV «Uz-Kor Gaz Chemical», «Ustyurt Gas Chemical Complex» for measuring of level of powdered polyethylene intermediate product in closed tanks. However, these radioisotope level gauges did not work properly, namely there was an abnormal situation and there was a difference

between the level of the product as measured by the radioisotope level gauge and the actual level of the product and the problem was that it was impossible to accurately calibrate the radioisotope level gauges.

The purpose of the study was to study the reasons for the error in measuring the level of technological intermediate product with radioisotope level gauge and develop methods for calibrating radioisotope level meter.

Decision of considered problems

The Institute of Nuclear Physics of the Academy of Sciences has Cs-137 radiation ionization sources of the GCs7.021.1 type with activity of 82.7 mCi and GCs7.012.8 type with activity of 8.56 mCi, which have zero duty cycle, however, their assigned terms of use have expired.

It was necessary to carry out work to check the tightness of the Cs-137 sources (GCs7.021.1 and GCs7.012.8) and extend their service life, as well as to carry out work on charging the sources in the blocks of gamma sources of radioisotope densitometers. To test the tightness of Cs-137 sources (GCs7.021.1 and GCs7.012.8) and extend their service life, a method for testing the tightness of sources was developed.

To calibrate radioisotope densitometers, a technique was used to calibrate a radioisotope density meter based on liquid simulators based on mixtures of bromoform and ethyl alcohol.

To solve the problem of accurate calibration of radioisotope level gauges investigations of monitoring of natural radionuclides at the facilities of the gas processing enterprise JV «Uz-Kor Gas Chemical», «Ustyurt Gas Chemical Complex», as well as spectrometric analysis of samples of gas condensate and powdered polyethylene intermediate product were carried out.

The results of radiation monitoring and gamma spectrometric analysis show that the samples of the technological products (gas condensate and powdered polyethylene intermediate product) contain natural radionuclides Ra-226, Ra-228 and the products of their radioactive decay Bi-214, Pb-214, Ac-228, which accumulate in closed technological tanks and products to increased gamma background. Because of this, errors occur when measuring the level of an intermediate free-flowing powdery product with a radioisotope level gauge. Because of this, errors occur when measuring the level of an intermediate free-flowing powdery product with a radioisotope level gauge. Under these conditions, for accurate calibration of the radioisotope level gauge, a special lead shield on the surface of the detector unit housing.

Results and discussion

The manufacturer of radioactive sources (All-Union Association of Isotopes "Isotope", Russia) for testing the tightness of a new of radiation ionizing sources recommended the use of radiometric method for testing a sealed Cs-137 source, in which the radioactive source is immersed in 7-10% nitric acid heated to 900 C⁰, for 1 hour [2]. However, this leak test method is impractical for end-of-life Cs-137 sources due to the potential for surface corrosion from nitric acid. To check the tightness of the Cs-137 sources (GCs7.021.1 and GCs7.012.8), a 10% solution of phosphoric acid was used, which, unlike nitric acid, forms a protective film on the surface of the Cs-137 source capsule, which protects the source from corrosion. According to the proposed method, in a protective box, the Cs-137 source was placed in a solution of phosphoric acid (10%) and the source was kept in this immersion liquid for 1.0 hour at temperature of 25 C⁰ [3]. Then, in the cuvette, the activity of the acid extract was measured on radiometric pulse analyzer with scintillation counter (photomultiplier tube with NaI crystal) or gamma-beta spectrometers "Radek", MKGB-01 (Russia).

The activity of the measured acid extract is calculated using the formula:

$$A = A_c \cdot \frac{N_1}{N_2} \quad (1)$$

where: A_c - activity of the control solution with the radionuclide Cs-137 with known activity; N_1 - count rate from acid solution; N_2 - count rate from control solution.

Source is considered leakproof if the activity of the acid extract does not exceed 185 Bq (5 nCi) [4, 5]. If the activity of the radionuclide Cs-137 that passes into the immersion liquid exceeds 185 Bq, then the source is considered to be depressurized and must be buried in specialized radioactive waste disposal facility.

The results of tests for the tightness of the Cs-137 sources of ionizing radiation showed that both sources are hermetic, i.e. the activity of the Cs-137 radionuclide in immersion liquids is not higher than 165 Bq (5 nCi).

Thus, it was concluded that the sources of cesium-137 GCs7.021.1 and GCs7.012.8 are hermetically sealed and meet the requirements of international standards [4, 5] and they can be used for completing radioisotope densitometers.

The calculated activity of the Cs-137 sources (GCs7.021.1 and GCs7.012.8) at the date of their use were determined by the formula:

$$A_t = A_0 \cdot \exp(-\lambda \cdot t) \quad (2)$$

where: A_t - activity of Cs-137 source on date 10/12/2019; A_0 - initial activity of Cs-137 source according to the passport; λ - Cs-137 radioisotope decay constant of $2.296 \cdot 10^{-2}$ /year; t - time (years) elapsed since the certification of Cs-137 sources according to the passport.

Table 1 and table 2 shows the technical data of the closed gamma radiation source of Cs-137 type GCs7.012.8 and GCs7.021.1.

Table 1. Technical data and characteristics of closed gamma radiation source with radionuclide of Cs-137 type GCs7.012.8, passport No. 10203, serial No. IXE.

Name, characteristic and unit of measurement	Data
1. Working surface	bottom
2. Measured value of the exposure dose rate in the direction of the perpendicular surface at distance of 1 m from it with the ratio of the diameter of the cylindrical channel of the collimator of the installation type VU-01 to its length equal to 0.6, A/kg	$1.6 \cdot 10^{-10}$
3. Confidence limits of the total error of the results of measuring the exposure dose rate of the source with probability of 0.95, in %	± 15
4. Month and year of exposure dose rate	12.2019

measurement	
5. Activity of the radionuclide Cs-137 in the source, Bq	$3.17 \cdot 10^8$, 8.56 mCi
6. External dimensions of the source, mm diameter height	6.0 10.0
7. Capsule material, type of stainless steel	12X18N10T
8. Dimensions of the active part of the source, mm diameter height	5.0 7.0
9. Source tightness	tight
10. The level of radioactive contamination of the source with radioactive substances when determined by the smear method, Bq, no more	185

Table 2. Technical data and characteristics of closed gamma radiation source with radionuclide of Cs-137 type GCs7.021.1, passport No. 22338, serial No. 190.

Name, characteristic and unit of measurement	Data
1. Working surface	bottom
2. Measured value of the exposure dose rate in the direction of the perpendicular surface at distance of 1 m from it with the ratio of the diameter of the cylindrical channel of the collimator of the installation type VU-01 to its length equal to 0.6, A/kg	$1.43 \cdot 10^{-9}$
3. Confidence limits of the total error of the results of measuring the exposure dose rate of the source with probability of 0.95, in %	± 15
4. Month and year of exposure dose rate measurement	12.2019
5. Activity of the radionuclide Cs-137 in the source, Bq	$3.06 \cdot 10^9$, 82.7 mCi
6. External dimensions of the source, mm diameter height	8.0 12.0
7. Capsule material, type of stainless steel	12X18N10T
8. Dimensions of the active part of the source, mm diameter height	6.0 6.5
9. Source tightness	tight
10. Level of radioactive contamination of the source with radioactive substances when determined by smear removal, Bq, not more than	185

After issuing a certificate of the tightness of the Cs-137 sources, work was carried out to charge the Cs-137 sources in the blocks of gamma sources of radioisotope densitometers.

Charging of the Cs-137 GCs7.012.8 radioisotope density meter was straightforward as the size of the source slot allows the Cs-137 source to be linked to the gamma source block. However, to charge the GCs7.021.1 gamma source block, it was necessary to increase the size of the source socket in the gamma source block. For free placement of the Cs-137 GCs7.012.8 source ($\varnothing=7$ mm and $h=10$ mm) in the source socket ($\varnothing=8$ mm, $h=12$ mm), the source socket in the gamma source block was increased on drilling machine to dimensions ($\varnothing=10$ mm, $h=13$ mm), which made it possible to charge the Cs-137 source into the gamma source unit of the radioisotope density meter.

In the protective box, work was carried out to remotely charge the Cs-137 source in the blocks of gamma sources of radioisotope

density meters, for this, the source was placed in the source socket of the gamma source block, the cover of the source socket was closed, and the source protective locking mechanism was transferred from the "open" position to "open" position to "closed" position.

Dosimetric control of the exposure dose rate of gamma radiation by calibrated dosimetric device SRP-88 N was carried out. When charging the gamma source block with source of Cs-137 GCs7.021.1, the measured equivalent dose rate of gamma ionizing radiation at distance of 0 m from the surface was 55 $\mu\text{Sv/h}$, and measured equivalent dose rate of gamma ionizing radiation at distance of 1.0 m was 0.5 $\mu\text{Sv/h}$. For the purpose of radiation safety, density meters must comply with the requirements of radiation safety standards and the basic sanitary rules for ensuring radiation safety (SanPiN No. 0193-06). In radioisotope devices intended for use in an industrial environment, the equivalent dose rate of ionizing radiation in any direction (except for the direction of direct gamma radiation) should not exceed: on the surface of a gamma source block with a charged ionizing radiation device - 100 $\mu\text{Sv/h}$ (10 mR/h); at a distance of 1 m from the gamma source block - 3 $\mu\text{Sv/h}$ (0.3 mR/h) [6].

Thus, the measured doses fully comply with the requirements of sanitary standards and additional lead protection of the gamma source unit is not required.

Calibration of radioisotope densitometers

It is shown in [7] that petroleum ether, gasoline, benzene (0.650-0.860 g/cm³), water-alcohol solutions (0.870-0.950 g/cm³), sulfuric-wine solutions (0.960-1.010 g/cm³) sulfuric-water solutions (0.960-1830 g/cm³) and Thule solutions (1.840-2,000 g/cm³) are usually used for liquid imitators. However, these liquid simulators have aggressive properties and are highly toxic to personal health.

To calibrate the radioisotope density meter, calibration stands with liquid simulators were used. To obtain liquid simulators, tribromomethane CHBr₃ stabilized with resorcinol and ethyl alcohol (C₂H₅OH) were mixed in glass vessels [8].

The approximate ratios of the components of the liquid simulators of the controlled environment are set in Table 3.

Table 3. Approximate ratios of the components of the liquid simulators of the controlled environment.

Simulator number	Density value, kg /m ³	Simulator percentage	
		bromoform	alcohol
1	800	0,5	99,5
2	1000	10,0	90,0
3	1200	19,5	80,5
4	1400	29,0	71,0
5	1600	38,5	61,5
6	1800	48,0	52,0
7	2000	57,5	42,5
8	2200	67,0	33,0
9	2400	76,5	23,5
10	2600	86,0	13,0
11	2800	95,6	4,5

Hydrometers [9] were used as auxiliary instruments, with the help of which the densities of liquid simulators were measured.

For the manufacture of calibration stands for simulators by welding, square containers and cylindrical containers were made from sheet steel.

Calibration stands for liquid simulators were in the form of square containers with dimensions: height is 15 cm, width is 40 cm, length is 324 mm, wall thickness is 8 mm.

Calibration stands simulators in the form of cylinder, plugged at both ends, have dimensions: width is 40 cm, diameter is 10 mm.

Calibration stand simulators have threaded heads ($\varnothing=20$ mm and $\varnothing=32$ mm) for filling them with liquid simulators.

Development of lead screen for gamma source collimator

Radioisotope density meter was equipped with Cs-137 ionizing radiation source of the GCs7.021.1 type (activity 82.7 mCi).

To meet the requirements of the radioisotope density meter specification [10], lead shield was developed to reduce the activity of the Cs-137 GCs7.021.1 source (activity=82.7 mCi) to the activity of the Cs-137 GCs7.012.8 source (activity=8.56 mCi). Lead shield 15 mm thick in front of the collimate of gamma source block was installed. The thickness of the lead shield was determined experimentally by dosimetric measurements.

Dosimetric measurement #1: The gamma-radiation source unit with charged Cs-137 GCs7.012.8 source (activity = 8.56 mCi) is located at distance of 45 mm from the empty (without liquid simulator) simulator stand, and the detector block is located at distance of 100 mm from it. The collimator of the gamma source block was set to the "open" position, and the dose rate of gamma radiation was measured with dosimeter IdentiFiender Target (Thermo Fisher Scientific, USA) at 3 points from the detector block.

Measured point 1 is at distance of 5 mm from the initial part of the detector block (beginning of the detector), point 2 is at distance of 200 mm from the initial part of the detector block (middle of the detector), point 3 is at distance of 395 mm from the initial part of the detector unit (end of detector).

Dosimetric measurement #2.

The gamma-radiation source block with charged Cs-137 GCs7.021.1 source (activity=82.7 mCi) is located at distance of 45 mm from the empty (without liquid simulator) simulator stand, and the detector unit is located at distance of 100 mm from it. The collimator of the gamma source block was set to the "open" position, and the dose rate of gamma radiation was measured with dosimeter IdentiFiender Target (Thermo Fisher Scientific, USA) at 3 points from the detector block as described above. Dosimetric measurement #3.

Gamma source block with charged Cs-137 GCs7.021.1 source (activity = 82.7 mCi) and lead 15 mm thick installed in front of the collimator was installed at a distance of 45 mm from the empty simulator stand. The detector block is located at distance of 100 mm from the empty (without liquid simulator) simulator stand. The collimator of the gamma source block was set to the "open" position, and the dose rate of gamma radiation was measured with dosimeter IdentiFiender Target (Thermo Fisher Scientific, USA) at 3 points from the detector block as described above.

Table 4 shows the results of dosimetric measurements of the exposure dose rate of gamma radiation from Cs-137 sources.

Table 4: Results of dosimetric measurements of the exposure dose rate of gamma radiation from Cs-137 sources (GCs7.012.8 and GCs7.021.1).

No.	Type of source Cs-137	Measured point number	Radiation exposure dose, $\mu\text{Sv/h}$
1.1	GCs 7.012.8 (activity =8.56 mCi)	1	6,6
1.2	-/-	2	7,6
1.3	-/-	3	5,6
			average: 6.6
2.1	GCs 7.021.1 (activity =87.2 mCi)	1	32
2.2	-/-	2	30,1
2.3	-/-	3	30,7
			average: 30.9
3.1	GCs 7.021.1 (activity =87.2 mCi)	1	6,4

	+ lead screen with thickness 15 mm		
3.2.	-//-	2	6,8
3.3.	-//-	3	6,5
			average: 6.6

As can be seen from table 4, when using a lead shield in front of the collimator, the average dose of gamma radiation from the GC7.021 source is 6.6 $\mu\text{Sv/h}$, which is equal to the average dose of gamma radiation from the GCs7.012.8 source (6.6 $\mu\text{Sv/h}$) and 15 mm thick lead shield reduces the activity of the source GCs7.021 (87.2 mCi) until the activity of the source GCs 7.012.8 (8.56 mCi).

Thus, in the block of gamma source of radioisotope density meter with ionizing radiation source Cs-137 GCs7.021.1 with activity of 87.2 mCi, lead screen 15 mm thick was installed in front of the collimator.

Calibration of radioisotope densitometers in laboratory conditions on the calibration stands of the simulator with liquid simulators was carried out.

To calibrate the radioisotope density meter, first a gamma-source unit with a charged Cs-137 GCs7.021.1 source with a lead shield 15 mm thick is located, then a simulator stand with a liquid simulator was placed, and then the detector block was installed in the same way as shown in Figure 1 [10].

Fig.1. Sketch of clamp for attaching a radioisotope density meter to a process pipe.

To calibrate the radioisotope density meter, the gamma source block with charged Cs-137 GCs7.021.1 source was placed on tripod (height=50 mm) with horizontal collimator, lead screen 15 mm thick was installed in front of it and at distance of 45 mm simulator stand with liquid simulator of known density filled to full, and detector block was located at a distance of 100 mm from the simulator stand.

Then, according to the operating instructions for the radioisotope density meter [11], the detector unit was connected to the processing and information unit with a connecting cable, and the detector unit was connected to a 220 V electrical network.

Radioisotope densitometer software built into the microchip allows the radioisotope densitometer to be calibrated at 9 different densities, while we calibrate the radioisotope densitometer at 3 densities for optimal performance. For calibration were used: liquid simulator # 1 with a density of 1.118 g/cm^3 , liquid simulator # 2 with density of 1.415 g/cm^3 and liquid simulator # 3 with a density of 1.715 g/cm^3 . The radioisotope density meter has been calibrated, i.e. the number of electrical impulses (frequency) arising in the detector, transmitted to the information processing and analysis unit, corresponds to the measured density of the liquid simulator.

For the fluid simulator to fluctuate, each calibration of the radioisotope density meter was waited for 30 minutes, and the density of each simulator fluid was measured for 30 minutes. When calibrating a radioisotope density meter, the density value of the liquid simulator and the density value in percentage (%) were obtained on the display of the information processing and analysis unit.

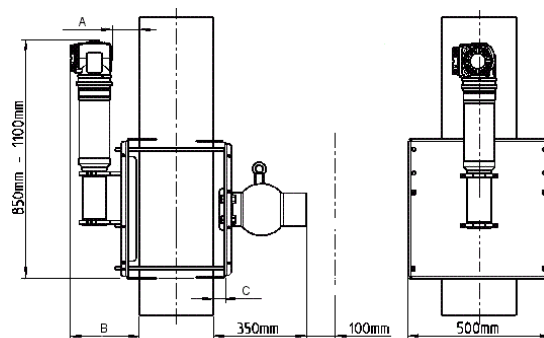
Table 5 shows the technical characteristics of the calibrated radioisotope density meter (serial number P 9007001064 FHX-40) and its operating parameters.

Table 5. Technical characteristics of the calibrated radioisotope density meter (serial number P 9007001064 FHX-40) and its operating parameters.

#	Name, type	Value
1.	Gamma source block, No. PA 00040113F	Weight= 40 kg
2.	Source Cs-137 GC _s 7.021.1, serial No. 190	Activity=87,2 mCi

3.	Lead screen in front of the collimator	Thickness=15 mm
4.	Scintillation detector block FM G60, No. P 900A50100F	Length=400 mm
5.	Process pipe inner diameter	$\varnothing=308$ mm
6.	Process pipe wall thightness	h=8 mm
7.	Input pulp emulsion density parameters: minimum pulp density maximum pulp density	1.200 g/cm^3 1.600 g/cm^3
8.	DC output electrical signals	lower density limit I=4.0 mA upper density limit I=20.0 mA

In Figure 2 shows the photographs of the calibration process of the radioisotope density meter (serial number P 9007001064 FHX-40).



$\varnothing$	A	B	C
200	95	255	35
250	100	260	40
300	100	260	45
350	110	270	50
400	110	270	55





Fig. 2. Calibration of a radioisotope density meter (serial number P 9007001064 FHX-40)

As shown in the figure 2, the top photo shows the block gamma source; lead shield 15 mm thick; simulator stand with liquid simulator No. 2 with density of 1.415 g/cm³; detector block; connecting cable; information processing and analysis block with closed lid; the bottom photo shows: information processing and analysis block with an open lid; display with the image of density of liquid simulator No. 2 with density of 1.415 g/cm³.

In Figure 3 shows the curve of the dependence of the current strength on the density of the radioisotope density meter.

Density of liquid simulator, g/dm³

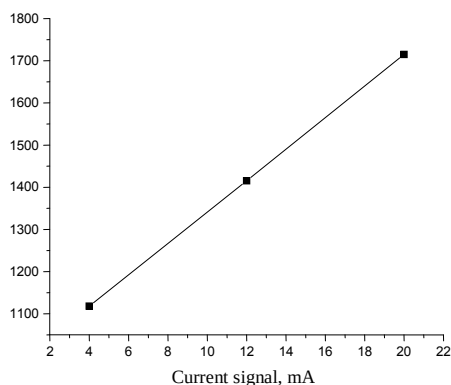


Fig. 3. Curve of the current strength on the density of the radioisotope densitometer.

As seen from Fig. 3 radioisotope density meter (serial no. P 9007001064 FHX-40) is calibrated to the operating mode at 3 density points, where at a pulp density of 1.118 g/cm³ analog signal current appears in the 4.0 mA connector, and at pulp density of 1.715 g/cm³ the electric current of the analog signal in the connector is 20.0 mA.

Table 6 shows the technical characteristics of the calibrated radioisotope density meter (serial No. P 9006E01064 FHX-40-V1B).

Table 6. Technical characteristics of the calibrated radioisotope density meter (serial number P 9006E01064 FHX-40-V1B) and its operating parameters.

#	Name, type	Value
1.	Gamma source block, No. PA 00030113F	Weight= 40 kg
2.	Source Cs-137 GC ₇ 7.021.1, serial No. IXE	Activity=8.56 mCi
3.	Scintillation detector block FM G60, No. 900A20100F	Length=200 mm
4.	Process pipe inner diameter	Ø=159 mm
5.	Process pipe wall thickness	h=10 mm
6.	Input pulp emulsion density parameters:	

	minimum pulp density	1.200 g/cm ³
	maximum pulp density	1.500 g/cm ³
7.	DC output electrical signals	lower density limit: I=4.0 mA upper density limit: I=20.0 mA

In Figure 4 shows the photographs of the calibration process of the radioisotope density meter (serial No. P 9007001064 FHX-40).



Fig. 4. Calibration of the radioisotope densitometer (serial No. P 9006E01064 FHX-40-V1B).

As shown in the Fig. 4, the top photo shows the block gamma source (with charged source of Cs-137 GC₇7.012.8, activity is 8.56 mCi); cylindrical simulator stand with liquid simulator No. 3 with density of 1.694 g/cm³; detector block; the down photo shows display of information processing and analysis block with open lid; display with the image of density of liquid simulator No.3 with density of 1.6907 g/cm³.

Calibration of radioisotope level gauge

At the gas production enterprise of the JV «Uz-Kor Gas Chemical» «Ustyurt Gas Chemical Complex», on the polyethylene production line, radioisotope level meters (Berthold Technologies GmbH & Co. KG) are used, which did not accurately measure the level of the intermediate powdered polyethylene product in closed tanks.

Monitoring of natural radionuclides at the technological facilities of the gas processing enterprise was carried out by dosimetric devices Identi Fiender Target (Thermo Fisher Scientific, Inc., USA), Radiagem 2000 (Canberra, USA), Polimaster DKG-RM (Expert Scientific and Technical Center, Belarus) and spectrometry analysis of the objects (samples of primary gas condensate and intermediate loose powdered product) were carried out on gamma-beta spectrometers "Radek", MKGB-01 (Russia) with software Ascinti.

Radiation monitoring of natural radionuclides at the technological facilities of this gas production enterprise showed that at some technological installations (filtering equipment F-5201 A)

there is a multiple (more than 800 times) excess of background gamma radiation (12 mR/h or 0.86 C/kg). In addition, natural radionuclides are contained in gas condensate and in a powdery intermediate polyethylene. Studies have shown that natural radionuclides accumulate in closed containers together with intermediate powdered polyethylene product.

Study of the literature has shown that as a result of the extraction, storage and transportation of oil and gas at oil and gas production enterprises, natural radionuclides Ra-226, Th-232, and their fission products are extracted from the bowels of the earth, which are collected in the form of radioactive deposits on the inner surface of technological equipment [12, 13]. Specific activity of natural radionuclides was determined from analytical lines with the energy of analytical peaks of gamma radiation 242 keV, 295 keV, 352 keV of the decay product of Ra-226 of the radionuclide Pb-214 and from analytical lines with the energy of analytical peaks of gamma radiation 609 keV, 1120 keV and 1764 keV of the product of the decay of Ra-226 of the radionuclide Bi-214 [14].

Specific activity of the natural radionuclide Th-232 was determined from analytical lines with the energy of analytical peaks of gamma radiation of 583.2 keV, 2614.5 keV of the decay product of Th-232 of the radionuclide Tl-208 and analytical lines with the energy of analytical peaks of gamma radiation 338.3 keV of Th-232 decay products of the Ac-228 radionuclide [15].

The results of gamma-spectrometric analysis showed that in formation waters, liquid gas condensate from the Urga and Surgil gas fields, as well as in the powdery intermediate polyethylene product of gas condensate processing, there is mainly radioactive contamination with natural radionuclides Ra-226, Th-232 and their daughter radionuclides Bi-214, Pb-214, Ac-228, and natural radionuclides are absent in the final technological products (ethylene and propylene granules) (see Table 7).

Table 7. Results of gamma spectrometric analysis of investigated samples.

Investigated sample	Specific activity of natural radionuclide, Bk/kg			
	²²⁶ Ra	²¹⁴ Pb	²¹⁴ Bi	²²⁸ Ac
Formation water from separator	162±40	30±5	35±6	32±9
Formation water from buffer capacity	153±42	33±5	52±8	28±8
Gas condensate	-	25±3	15±1	-
Intermediate powdered polyethylene product	25±5	20±4	25±5	28±8
Granules ethylene	-	-	-	-
Granules propylene	-	-	-	-

Table 7 shows that in liquid propylene gas condensate and intermediate powdery polyethylene product, there are impurity radionuclides Pb-214, Bi-214, Ac-228 with a total specific activity of 37-40 Bq / kg and this concentration does not exceed the requirements of sanitary standards of SanPIN. 0193-06 [16]. However, despite the fact that the daughter fission products of natural radionuclides have short half-lives (²¹⁴Bi – T_{1/2}=19.8 min, ²¹⁴Pb – T_{1/2}= 26.8 min, ²²⁸Ac – T_{1/2}=6.13 hours) when they are present in the powdery intermediate polyethylene product and gradually accumulate in closed tanks during the gas processing process, they multiply the overall background of gamma radiation and the gamma radiation of the Cs-137 source of the gamma source of the radioisotope density meter.

Thus, natural radionuclides negatively affect the operation of radioisotope level gauge, namely, on the information processing and analysis unit (electronic panel board)

radioisotope densitometer, an increase or decrease in the electric analog current in the 0-5.0 mA and 4.0-20.0 mA connectors occurs and errors in measuring the level of the technological product occur.

The calibration curve of the signal current versus the level of an intermediate polyethylene powder product in the presence of short-lived natural radionuclides with normal signal current and abnormal signal current is shown in Figure 5.

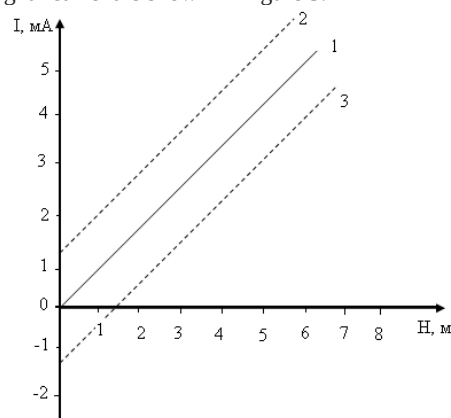


Fig. 5. Calibration curve of signal current (*I*) from level (*H*) of intermediate powdered polyethylene product in close tank: 1 – normal calibration curve; 2,3 – abnormal calibration curve.

To solve this problem, 2 methods have been developed for accurate calibration (adjustment) of the radioisotope level gauge.

The first method consisted in the fact that a signal current correction unit was developed, designed to rectify an analog current signal and supply it to an electronic panel unit in connectors 0-5.0 mA and 4.0-20.0 mA [17].

Figure 6 shows a functional diagram of the signal current correction unit.

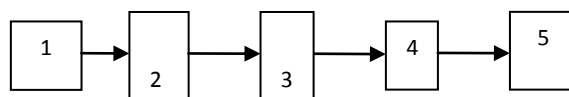


Fig. 6. Functional diagram of the signal current correction unit: 1 – block gamma source with Cs-137 source; 2 – intermediate powdered polyethylene product; 3 – detector block; 4 – signal current correction unit; 5 – electronic panel board.

The second method turned out to be more effective and in order to eliminate errors (errors) when measuring the level of a powdery bulk polyethylene intermediate in closed containers, the body of the radioisotope level gauge detection unit was wrapped in special lead shield 0.9 mm thick. The required thickness of the lead shield was determined by the dosimetry method. The lead shield made it possible to exclude an increase in the gamma background, to reduce the activity of natural radionuclides to zero.

Thus, as a result of the use of a lead shield on the surface of the detection unit, an accurate calibration of the radioisotope level gauge was achieved, which ensured the spoiled operation of the radioisotope level gauge.

Conclusion

Sources of ionizing radiation Cs-137 (GCs7.021.1 and GCs7.012.8) were tested for tightness. The source socket in the gamma source block was enlarged, ionizing radiation source of Cs-137 GCs7.021.1 (# 190) into the gamma source block of the radioisotope density meter (serial number P 9007001064 FHX-40) was charged, screen was installed in front of the collimator of the gamma source block made of 15 mm thick lead sheet. Ionizing

radiation source of Cs-137 GCs7.012.8, (# IXE) into the gamma sources block of the radioisotope densitometer (serial No. P 9006E01064 FHX-40-V1B) was charged.

In laboratory conditions calibration of the radioisotope densitometers at the simulators stands with liquid simulators was made.

In the radioisotope densitometers, when the lower pulp density ($\rho=1.200 \text{ g/cm}^3$) is reached, electrical signal appears in the 4.0 mA connector, and when the upper pulp density ($\rho=1.600 \text{ g/cm}^3$ and $\rho=1.500 \text{ g/cm}^3$) is reached electrical signal appears in the 20.0 mA connector, which indicates the serviceability of both radioisotope density meters. After calibrating radioisotope densitometers and installing them on technological production lines of the State Enterprise «Navoi Mining and Metallurgical Combine», the data of measurements of the density of the pulp emulsion will be displayed on computer monitors in real time.

The results of radiation monitoring showed that natural radionuclides are present inside some technological equipment of the JV «Uz-Kor Gas Chemical», «Ustyurt Gas Chemical Complex» and these natural radionuclides are contained both in the gas condensate and in the intermediate powdery polyethylene product, therefore, there is a multiple increase in the background gamma radiation. Natural radionuclides accumulate together with the technological product in closed tanks and lead to erroneous operation of the radioisotope level gauge.

To solve the problem of calibrating the radioisotope level gauge, a 0.9 mm thick lead shield was installed on the surface of the radioisotope level gauge detection unit, which ensured accurate calibration (adjustment) of the radioisotope level gauge and ensure its proper operation.

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