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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 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. 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 after speed crystallization were investigated. It was shown that under laser action the initial structure of inclusion-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.


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 105 °C/s and cooling rate of 106 °C/s with action time of (1.0, 2.5, 3.6, 4.2 и 6.0) 103 s.

In 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 (sulfide, 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→m and they have well-developed net of inner interphase boundaries ph-m1→d2. Besides if interphase boundary ph-m1→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→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 \( d_2 \) as a rule have time to melt (or to dissolve) fully in the matrix phase \( \text{ph-m1} \) of inclusion. Under action of convective flows in micrometallurgical bath the liquid phases of inclusion are mixed though often remnants of phase \( d_2 \) 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 liqutation are observed connecting with presence of traces of sojourn of former dispersed phase \( d_2 \). If phases of inclusion have different temperatures of melting that low-melting phase \( \text{ph-m1} \) (sulphide, silicate) is melted in the moment of laser action but high-melting phase \( d_2 \) (oxide, nitride) can to melt fully or partly. In the time of happens the interaction of components of phase \( \text{ph-m1} \) of inclusion with metal matrix of steel promoting the saturation of areas near inclusion with elements of phase \( \text{ph-m1} \) of inclusion and also with elements of dispersed phase \( d_2 \) 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 \( d_2 \) and also with formation of liqutation zones revealing with special micro-spectral analysis.

Interphase boundaries \( \text{ph-m1} \leftrightarrow \text{d2} \) are not precise or at all disappeared owing to dissolution of dispersed phase \( d_2 \). Special micro-spectral analysis shown that near these boundaries in both phases of inclusion the content of elements of neighbour 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 \( \text{ph-m1} \) of inclusion is base and it determines the behavior of all inclusion. Phase \( \text{ph-m1} \) contacts with metal matrix of steel and also with dispersed phase \( d_2 \) across boundaries \( \text{ph-m1} \leftrightarrow \text{d2} \).

Sequence of heavy distortion areas on the surfaces of “non-metallic” matrix of inclusion \( \text{ph-m1} \) and dispersed phase \( d_2 \) and also of the movement of interphase boundaries \( \text{ph-m1} \leftrightarrow \text{liquid steel matrix} \), \( d_2 \leftrightarrow \text{liquid steel matrix} \) and also \( \text{ph-m1} \leftrightarrow \text{d2} \) 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 \( d_2 \) 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 \( \text{ph-m1} \) and \( d_2 \) 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 \( \text{ph-m1} \) and dispersed phase \( d_2 \) the heavy disordered areas are formed too (Fig. 2, b). Evidently one of phases of inclusion (\( \text{ph-m1} \)) is melted scarcely earlier than phase \( d_2 \) and nucleuses of melting of the phase \( \text{ph-m1} \) promote disordering and melting of interphase boundaries \( \text{ph-m1} \leftrightarrow \text{d2} \) inside inclusion. The whole disordered areas (areas of melting) of the phase \( d_2 \) pass into liquid phase \( \text{ph-m1} \) (Fig. 2, c). The former boundary \( \text{ph-m1} \leftrightarrow \text{d2} \) 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 \( \text{ph-m1} \) 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 \( d_2 \) (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 liqutation 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](image.png)

*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 \( \text{ph-m1} \leftrightarrow \text{d2} \), 5 – zone of saturation of phase \( \text{ph-m1} \) with elements of phase \( d_2 \), 6 – zone of saturation of phase \( d_2 \) with elements of phase \( \text{ph-m1} \), 7 – initial position of boundary inclusion-matrix, 8 – initial position of boundary \( \text{ph-m1} \leftrightarrow \text{d2} \) inside inclusion \( \text{ph-m1} \leftrightarrow \text{d2} \)
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 liquidation 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 passaged 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.

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 $H_{nm}^m$ were discovered however in each zone of saturations the “splashes” of $H_{nm}^m$ values are detected.

<table>
<thead>
<tr>
<th>Inclusion, steel, $H_{nm}$ x 10, MPa</th>
<th>Phases of inclusion (state under laser action: L – liquid; M – melted)</th>
<th>State of steel matrix under laser action, $H_{nm}$ x 10, MPa</th>
<th>$H_{nm}$, x 10, MPA and (K_i) in zones</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Fe,Mn)S+ TiCN, E3</td>
<td>(Fe,Mn)S (L)</td>
<td>L, 290</td>
<td>516 (1.78) / 447 (1.54) / -</td>
</tr>
<tr>
<td>MnOSiO2+ MnO, 60G</td>
<td>MnO (L)</td>
<td>L, 620</td>
<td>1128 (1.82) / 868 (1.4) / 806 (1.3)</td>
</tr>
<tr>
<td>FeO-TiO2+ TiCN, 08T</td>
<td>FeO-TiO2 (L)</td>
<td>L / M, 280</td>
<td>451 / 395 (1.61) / 403 / - / -</td>
</tr>
<tr>
<td>MnOSiO2+ Cr2O3, 08H</td>
<td>MnO (L)</td>
<td>L / M, 295</td>
<td>543 / 493 (1.84) / 407 / - / -</td>
</tr>
</tbody>
</table>

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 - 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

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 $H_{nm}^m$ and far from them $H_{nm}$, as well as the coefficient (K_i) at a pulse energy of 25 J and an exposure time of 3.6. 10^-3 s
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.

5. Literature.
Structure and magnetic properties of Mn$_{1-x}$Fe$_x$NiGe (0.05 ≤ x ≤ 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 Mn$_{1-x}$Fe$_x$NiGe (0.05 ≤ x ≤ 0.60) solid solutions are studied. It has been established that MnNiGe is an antiferromagnet with a Néel temperature $T_N$ ≈ 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 Mn$_{1-x}$Fe$_x$NiGe solid solutions, study the features of the crystal structure, and determine the values of fundamental magnetic characteristics.

2. Experimental part

Polycrystalline samples of Mn$_{1-x}$Fe$_x$NiGe (0.05 ≤ x ≤ 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 Mn$_{1-x}$Fe$_x$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 Kα - 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 ~80 – 800 K.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of Mn$_{1-x}$Fe$_x$NiGe solid solution powders obtained at 300 K in the range of angles $20° ≤ 2\theta ≤ 95°$ 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 Mn$_{1-x}$Fe$_x$NiGe solid solution powders.](image)

It was found that at a room temperature the Mn$_{1-x}$Fe$_x$NiGe (0.05 ≤ x ≤ 0.60) solid solutions have a hexagonal crystallographic Ni$_2$In (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 ≤ x ≤ 0.60, which is typical for solid solutions with cationic substitution. The concentration dependences of parameters $a$, $c$ and unit cell volume $V$ of Mn$_{1-x}$Fe$_x$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 Mn$_{1-x}$Fe$_x$NiGe solid solutions.](image)
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 $\rho_{\text{x}}$ of powders of $\text{Mn}_x\text{FeNiGe}$ solid solutions at $T \approx 300$ K are given in Table 1.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$, nm</th>
<th>$c/a$</th>
<th>$c$, nm</th>
<th>$V$, $10^{-2}$ cm$^3$</th>
<th>$\rho_{\text{x}}$, g/cm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.408</td>
<td>1.32</td>
<td>0.539</td>
<td>7.78</td>
<td>7.95</td>
</tr>
<tr>
<td>0.10</td>
<td>0.407</td>
<td>1.31</td>
<td>0.536</td>
<td>7.72</td>
<td>8.01</td>
</tr>
<tr>
<td>0.15</td>
<td>0.407</td>
<td>1.31</td>
<td>0.533</td>
<td>7.68</td>
<td>8.06</td>
</tr>
<tr>
<td>0.20</td>
<td>0.407</td>
<td>1.30</td>
<td>0.530</td>
<td>7.62</td>
<td>8.12</td>
</tr>
<tr>
<td>0.25</td>
<td>0.407</td>
<td>1.30</td>
<td>0.529</td>
<td>7.61</td>
<td>8.14</td>
</tr>
<tr>
<td>0.30</td>
<td>0.406</td>
<td>1.30</td>
<td>0.527</td>
<td>7.55</td>
<td>8.21</td>
</tr>
<tr>
<td>0.40</td>
<td>0.407</td>
<td>1.29</td>
<td>0.525</td>
<td>7.56</td>
<td>8.22</td>
</tr>
<tr>
<td>0.50</td>
<td>0.407</td>
<td>1.28</td>
<td>0.521</td>
<td>7.50</td>
<td>8.27</td>
</tr>
<tr>
<td>0.60</td>
<td>0.406</td>
<td>1.28</td>
<td>0.519</td>
<td>7.43</td>
<td>8.35</td>
</tr>
</tbody>
</table>

The temperature dependences of the specific magnetization of some $\text{Mn}_x\text{FeNiGe}$ solid solutions are shown in Figure 3.

![Fig. 3 Temperature dependences of the specific magnetization of $\text{Mn}_x\text{FeNiGe}$ solid solutions in a magnetic field of 0.86 T.](image)

Cationic substitution in the $\text{Mn}_x\text{FeNiGe}$ 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 $\sim 8.0 \text{ to } 36 \text{ A m}^{-1} \text{kg}^{-1}$ 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):

$$\mu = \frac{\sigma \cdot M}{N_a} \mu_B,$$

where $\sigma$ is the value of the specific magnetization at nitrogen temperature, $M$ is the molar mass, $\mu_B$ 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 $\text{Mn}_x\text{FeNiGe}$ system were determined using the dependence of the square of the specific magnetization $\sigma^2 = f(T)$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\mu_{\text{Fe}}$, A m$^{-1}$ kg$^{-1}$</th>
<th>$T_c$, K</th>
<th>$\Delta \mu_{\text{Fe}}$, $\mu_B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>13.69</td>
<td>272</td>
<td>0.46</td>
</tr>
<tr>
<td>0.10</td>
<td>34.53</td>
<td>183</td>
<td>1.15</td>
</tr>
<tr>
<td>0.15</td>
<td>36.07</td>
<td>153</td>
<td>1.20</td>
</tr>
<tr>
<td>0.20</td>
<td>30.55</td>
<td>148</td>
<td>1.02</td>
</tr>
<tr>
<td>0.25</td>
<td>20.38</td>
<td>143</td>
<td>0.68</td>
</tr>
<tr>
<td>0.30</td>
<td>13.90</td>
<td>137</td>
<td>0.46</td>
</tr>
<tr>
<td>0.40</td>
<td>9.45</td>
<td>-</td>
<td>0.32</td>
</tr>
<tr>
<td>0.50</td>
<td>7.98</td>
<td>-</td>
<td>0.27</td>
</tr>
<tr>
<td>0.60</td>
<td>7.85</td>
<td>-</td>
<td>0.26</td>
</tr>
</tbody>
</table>

4. Summary

Solid solutions of $\text{Mn}_x\text{FeNiGe}$ 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 $\text{Mn}_0.80\text{Fe}_{0.20}\text{NiGe}$ to 137 K for $\text{Mn}_0.15\text{Fe}_{0.85}\text{NiGe}$ solid solution.

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A composite magnetic material with insulating anticrosive coatings

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Abstract: We have studied electromagnetic and corrosive properties of new soft-magnetic composite materials made from iron powder ASC 100.29 and Atomet 1001HP, surface of which is encapsulated by insulating anticorrosive oxide coating. The results demonstrate that the use of such materials in power supplies, chokes, transformers, stators and rotors of electrical machines and other devices ensures their stable operation under various conditions.

Keywords: SOFT-MAGNETIC COMPOSITE MATERIAL, IRON POWDER, INSULATING COVER, HIGH-FREQUENCY TRANSFORMERS, STATORS AND ROTORS OF ELECTROMACHINES

1. Introduction

Composite materials with the necessary operational properties are widely used in components of various mechanisms and machines in such branches of industry as electrical engineering and electronics. Since the final properties of the products depend on the methods of the starting materials treatment, it is necessary to exactly select the conditions for obtaining composite soft magnetic materials to ensure a controlled chemical composition and structure, which in turn guarantees the required physical and functional properties.

For materials operating in alternating electromagnetic fields, the most important characteristics are magnetic permeability, induction and losses due to magnetization and eddy currents, corrosion resistance [1-5]. The value of electrical resistivity determines the maximal frequency with which the use of this material is advisable. Currently, a number of firms produce composite soft magnetic materials based on various encapsulated iron powders. The insulating layers prevent iron particles from contacting each other. As a result, the properties of the known composite soft magnetic materials are close to the properties of electrical steel. However, the presence of an insulating magnetically disordered substance between individual particles of metal particles leads to a decrease the magnetic permeability of the material to $\mu_m = 100 – 500$, and the magnitude of the magnetic induction is of the order of $B_m = 1.6$ T [6, 7]. The task is to increase magnetic induction and magnetic permeability, reduce the amount of electromagnetic losses of the material. Essential progress in improvement of magnetic properties of composite materials achieve in the present work due to using in quality isolate coverings various magnetic oxide – ferrites. Thus thickness isolation covering of iron particles have been reduced to some nm. The electromagnetic parameters of the obtained materials depend on the size, morphology of the particles and the purity of the initial powders; the chemical composition and thickness of the insulating coatings, from the atmosphere in which the treatment takes place. Also for practical using of such materials it is important to have a good corrosion resistance.

Metal particles with applied insulating coatings are easily oxidized in a humid environment, but oxides on the metal surface significantly reduce the magnetic properties. Traditionally, various protective coatings are applied to metal surfaces to prevent corrosion. However, over time, the protective coating will deteriorate and the metal has to be reworked in order to protect it from corrosion. In addition, anti-corrosion surface treatment is not always effective, since the presence of defects in parts often leads to internal corrosion, which destroys the latter. The applied special insulating corrosion-resistant layers in the composite material have a dual purpose: reduction of electromagnetic losses and protection against oxidation, since each particle is encapsulated. As a result, parts made of composite materials based on encapsulated powder will be protected from both surface and internal corrosion, and the service life of the parts will be determined only by their mechanical wear.

The aim of this work is to study the influence of the synthesis conditions of composite materials based on particles of iron powders with insulating coatings on its electromagnetic and corrosion characteristics.

2. Experimental part

Based on the requirements for the initial powders the water – atomized iron powder Hoganes ASC100.29 (Sweden) was selected as the main object of studies. On the particles of the material were deposited layers of phosphorus, boron, titan oxides using an optimized technique. Purity of ASC100.29 powder is 99.5%. The chemical composition of the powder is presented in the Table 1.

Table 1: Chemical composition of the water-sprayed iron powder ASC100.29 (Sweden).

<table>
<thead>
<tr>
<th>Type of iron powder</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASC100.29 (Sweden)</td>
<td>99,5</td>
<td>0,08</td>
<td>0,04</td>
<td>0,08</td>
<td>0,01</td>
</tr>
</tbody>
</table>

From the calculated and experimental data it was found that, depending on the particle size of the initial metal iron powder, the resulting composite materials can be divided into two classes: low-frequency ($f < 1$ kHz) and high-frequency ($f > 1$ kHz). For subsequent high-frequency applications, powders with a size of less than 100 microns are screened with a separator $S49-1000-1$, for low-frequency ones with a size $> 100$ microns. After separation an insulating layer was applied to the surface of the iron particles.

The deposition procedure included the stage of preliminary mixing of the initial metal powders with a given amount of reagent, which included an alcohol solution of orthophosphoric acid in the ratio of 40% $H_3PO_4$ + 60% ethyl alcohol. Instead of $H_3PO_4$, boride or titanium compounds can be added.

In the next step, the prepared powder was placed in an insulation coating reactor. The powders with the reaction additive were treated in the reaction drum at a pressure of 0.1 to 1.0 atm., heated to a temperature of 150 – 200°C during 15 – 30 min. As a result, a complex coating of ferrite compounds and phosphates formed on the surface of iron particles. The chemical composition in case of phosphorus oxide coatings is a complex system of iron oxides $FeO$, $Fe_2O_3$ and phosphorus oxide $P_2O_5$. A small amount of carbon and silicon are also present. The thickness of the insulating layer on the iron particle depends on the processing time of the powder and the concentration of the alcohol solution of phosphoric acid.

The magnetic permeability of the composites was measured in the frequency range up to 2.0 kHz. To study the features of magnetic properties, cores were made in the form of rings by pressing composite powders under a pressure of 7-8 t/cm². The density of the samples was determined by hydrostatic weighing in distilled water. Measurements of important magnetic characteristics – induction, loss, magnetic permeability – were performed on an express magnetometer. The magnetization dependences of the
obtained samples were recorded, the area of the hysteresis loop in pixels was determined, and losses were calculated. The pixel dimension was determined by measuring the magnetic flux using an F5050 microwebermeter.

The corrosion behavior of composites was investigated by open circuit potential (OCP) and anodic polarization curves (linear and Tafel) using a potentiostat/galvanostat Princeton- PARSTAT 2273 (with a specialized soft “Power Corr”) in a 3.5 wt% NaCl aerated solution at a temperature of 25°C. The electrochemical measurements were performed in a glass cell of 50 ml capacity with thermostated jacket, with a conventional three electrode: Ag/AgCl (with KCl 0.3M) as the reference electrode and a platinum plate as counter electrode, both of them of Radiometer production. The working electrodes each had 1 cm² of exposed surface.

3. Results and discussion

On Fig.1 is shown the static magnetization curve of a composite magnetic material on the basis of powder ASC100.29. It is visible from the resulted data, that process of magnetization as against laminated Si-steel is closed to linear at an induction of saturation ~ 2.2 T. For electrotechnical steel the induction of saturation is closed to 1.8 T.

Comparative investigations of electromagnetic characteristics for materials on base of Hoeganes ASC100.29 and such ones from powders of Micrometals and Atomet companies are carried out. On Fig. 2 are shown the magnetization curves of magnetic-soft materials with isolation magnetic oxide of the iron powders ASC100.29 – a curve 1 and known composite materials with dielectric isolation at use of powders High Flux (HF) – a curve 2 (manufactured by Micrometals, USA).

Presence of isolation backlash between particles of iron in a composite material on the basis of powder ASC100.29 results to that initial value of magnetic permeability has also the maximal value (Fig. 3).

As against it for powders of iron with a ferrite covering initial permeability $\mu_0 = 80-100$, and the maximal permeability $\mu_m = 800 – 1000$.

Magnetic properties of a composite material essentially depend on pressure of pressing or density of a product. Magnetization curves in a frequency range up to 2000 Hz practically coincide and have identical behavior for a magnetic material on basis ASC100.29.

![Fig. 1 Static magnetization curves of a composite magnetic material on the basis of powder ASC100.29.](image1)

![Fig. 2 Magnetization curves of soft magnetic materials with isolation magnetic oxide powders of iron ASC100.29 – a curve 1 and known composite materials with dielectric isolation at use of powders High Flux (HF) – a curve 2 (manufactured by Micrometals, USA).](image2)

![Fig. 3 Field dependencies of induction and magnetic permeability of the soft magnetic material on basis of ASC100.29.](image3)

![Fig. 4 Total energy losses per cycle as a function of frequency for examined magnetic cores at magnetic induction $B = 1.0$ T (1 – ASC100.29, 2 – Atomet 1001HP).](image4)

![Fig. 5 Frequency dependencies of the inductance and Q-factor of the composite magnetic material (Fig 5) show that in frequencies range 100 Hz ÷ 10 MHz the inductance practically does not change its value. The value of Q-factor reaches its maximum in the range of ~ 20–30 kHz. With use of the developed composite materials on the basis of powders of iron ASC100.29 pre-production models of invertors power supplies up to 10 kW in a frequency range up to 100 kHz are developed, chokes of various purpose, the pre-production model of the electric motor for a frequency range up to 2000 Hz is developed.

Reliability and stability of work in various conditions of power supplies on transformers with the core on base of the composite material, determined by high value of temperature Curie – is higher 800°C and a magnetic induction of saturation 2.1 T, compensates expenses for the additional charge of a copper wire and the losses connected to it for sources with capacity less than 1 kW.
The results of the study of electrochemical corrosion in the form of the parameters calculated from the linear polarization (LP) and Tafel dependencies are presented in table 2. It follows from the table that for a composite based on a powder with grain over 100 microns, the corrosion rate is 0.982 mm/year, and for a composite with a grain of 20-100 microns – 0.485 mm/year. This fact can be explained by following. The experimental data on the corrosion of some metals and metal alloys, including iron-based ones, indicate that the grain size practically does not affect the corrosion rate. The exception is cases where at the grain boundaries of the metal the conditions are such that corrosion can acquire an intergranular character. The increase in grain size in such alloys creates a great possibility of the appearance of intergranular corrosion and can significantly enhance it: the total length of the boundaries of coarse-grained metal is less than that of fine-grained metal, and, therefore, the intensity of corrosion per unit length of the grain boundary will be greater.

**Table 2: Electrochemical corrosion parameters determined from the Tafel curves obtained in 3.5 wt% NaCl at 28°C.**

<table>
<thead>
<tr>
<th>Type of iron powder</th>
<th>E_{OCP} (V)</th>
<th>R (Ω)</th>
<th>E_{corr} (V)</th>
<th>I_{corr} (A)</th>
<th>CR (mm/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>composite based on powder with grain over 100 microns</td>
<td>-0.574</td>
<td>88.231</td>
<td>-0.657</td>
<td>190.9×10^-6</td>
<td>0.982</td>
</tr>
<tr>
<td>composite based on powder with grain 20-100 microns</td>
<td>-0.561</td>
<td>59.079</td>
<td>-0.582</td>
<td>61.23×10^-6</td>
<td>0.485</td>
</tr>
</tbody>
</table>

**4. Summary**

A method of synthesis of composite materials based on iron powders, the particles of which are coated with a nanoscale layer of phosphides, has been developed, which includes the stage of preliminary mixing of the initial metal powders with a given amount of an alcohol solution of orthophosphoric acid in the ratio 40%H$_3$PO$_4$ +60% ethanol. The method makes it possible to reduce the lubricant content to 0.01 – 0.10%, which makes it possible to obtain subsequently a high-quality molded product from a soft magnetic composite material with a density of 7.50 – 7.65 g/cm$^3$ and, as a result, having high electromagnetic characteristics.

The carried out preliminary researches of a composite magnetic material on the basis of powders of iron ASC100.29, surface of which is capsulated by ferrite and phosphides, have shown perspectives of their application in engineering. Unique specific parameters of a soft magnetic composite material – a magnetic induction of saturation 2.1 T, work in a frequency range up to 100 kHz at Curie temperature from above 800°C allow using it in high speed valve and valve-jet electro machines and as chokes and high-frequency transformers. A powder-based composite with a grain size d > 100 mkm has less corrosion resistance. The corrosion rate in this case is 2 times higher, due to the fact that in this case there is a manifestation of intergranular corrosion.

**5. Acknowledgments**

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**6. References**

Thermodynamics of soot formation by methane combustion

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Abstract: The report deals with the process of soot formation by methane combustion. They are analysed by comparing thermodynamic quantities directly related to the thermal stability and/or reactivity of the atomic-molecular system - average entropy, enthalpy, free Gibbs energy, thermal capacity and thermodynamic energy.

Keywords: SOOT, METHANE, THERMODYNAMICS

1. Introduction

It is customary to refer to soot [1] as a non-chemically bound carbon (preferably in amorphous form) obtained by incomplete combustion and/or thermal decomposition of hydrocarbons.

Soot formation is highly dependent on the composition of the fuel. This process is intensified due to the secondary thermal destruction. This is especially true for arenas and their derivatives. The delocalization of the chemical bond in the benzene nucleus (of naphthalene > benzene > aliphatic (from its formation aliphatic are arranged in the form: alkanes < alkenes < alkynes)). Another factor that significantly affects the process is the type of flame.

The soot formation [2] during the combustion of less hydrogen-saturated molecules is mainly due to the secondary thermal destruction. This is especially true for arenas and their derivatives. The delocalization of the chemical bond in the benzene nucleus (of the type sp$^2$) redistributes the energy (in the form of heat) into the molecule to all structure-determining atoms. Due to the inability to access sufficient oxidant, individual atomic-molecular residues decompose and subsequently agglutinate into larger, over-atomic structures.

Determining the mechanism of soot formation is difficult to model using mathematical and statistical methods. The difficulty is to describe the thermodynamic relationships of each of the frequently changing factors during the process. With the development of quantum theory, some difficulties are minimized.

Semi-empirical methods [3] of quantum chemistry are based on the Hartree-Fock formalism, but they make many approximations and derive some parameters from empirical data. They are very important in computational chemistry for characterizing large molecules, where the complete Hartree-Fock method [4] without approximations is too complex and slow. The use of empirical parameters seems to allow some incorporation of the effects of electronic correlation [5] into the methods.

The purpose of this report is to characterize the methane combustion process (the simplest hydrocarbon) from the point of view of molecular thermodynamics by semi-empirical quantum chemical methods.

2. Methodology

2.1. Write the combustion equation to carbon on methane [6]:

2.2. Compilation of Z-matrices of all starting materials and reaction products [7]:

2.3. MM2 [8] is applied to minimize the force fields [9] of the individual atoms in the molecules under normal conditions;


2.5. Determination of molecular thermodynamic quantities describing [13] the nature of processes [14];

- Entropy;
- Enthalpy;
- Free Gibbs Energy;
- Thermal Energy [15];
- Thermal capacity.

Each value of the source methane is determined by:

1) 240K and 1bar; 240K and 10bar; 240K and 20bar; 240K and 55bar; 300K and 1bar; 300K and 10bar; 300K and 20bar; 300K and 55bar; 340K and 1bar; 340K and 10bar; 340K and 20bar; 340K and 55bar;

2) the carbon produced is determined by: 1170K and 1 bar; 1170K and 10bar; 1170K and 20bar; 1170K and 55bar; 1370K and 1bar; 1370K and 10bar; 1370K and 20bar; 1370K and 55bar; 1570K and 1bar; 1570K and 10bar; 1570K and 20bar; 1570K and 55bar.

Data should be presented graphically and analyzed [16].

3. Results

3.1. Write the combustion equation to carbon on methane

The soot formation of methane combustion can be schematically represented as:

3.2. Compilation of Z-matrices of all starting materials and reaction products

Z-matrices of the molecules of methane, oxygen, carbon and water are created.

3.3. MM2 is applied to minimize the force fields of the individual atoms in the molecules. The created Z-matrices (3.2) of the methane, oxygen, carbon and water molecules are subjected to MM2 modification under normal conditions.

3.4. Conducting molecular dynamics of the resulting Z-matrix with minimized force fields

Methane and oxygen molecules (via the resulting Z-matrices of point 3.3) are subjected to molecular dynamics at T = 1173K for 30sec. The new Z-arrays thus obtained serve as a starting point for subsequent processes.

3.5. Determination of molecular thermodynamic quantities describing the nature of processes:

1) The data (Fig.1) from the change in entropy, enthalpy, free Gibbs energy, thermal energy and thermal capacity when burning methane at temperatures of 240 ÷ 340K and pressures 1 ÷
with increasing temperature and pressure, the average entropy of methane decreases. This could be attributed to the fact that its concentration is lower than that of the oxidizer (air). The average enthalpy of the system is probably increasing, but based on the expansion of the combustion products (CO₂ and H₂O);

- enthalpy is expected to increase with increasing ambient temperature and remain unchanged as pressure increases. The latter is the result of maintaining the ratio \( P \cdot V = \text{const} \), which is confirmed by the fact that the volume around the methane molecules is increasing (even if the medium remains unchanged);

- free Gibbs energy decreases with increasing temperature, but increases with increasing pressure (at the same temperature). Therefore, as the critical temperature approaches, the spontaneity of chemical processes (including decomposition) increases;

- thermal energy and thermal capacity is directly proportional to the increase in temperature and remains relatively constant when the pressure changes. The thermodynamic dependence described in the change of enthalpy is also valid here.

2) Values (Fig.2) for entropy, enthalpy, free Gibbs energy, thermal energy and thermal capacity for methane combustion at temperatures of 1170 - 1570K and pressures 1 - 55bar at excess oxygen,

- thermal energy up to 1570K is subject to the dependence in 3.5(I). After reaching its critical temperature, it decreases and thus displaces the reaction to produce amorphous carbon, in this case carbon soot.

4. Conclusion

By using semi-empirical quantum methods apparent is illustrated thermodynamics of soot formation combustion of methane. The data obtained using the methodology presented is not inconsistent with current scientific research in the field.

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Effect of TiB$_2$ additives on sintering temperature, structure, and properties of the composite material of the Fe-FeCr800 system

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Abstract: The effect of TiB$_2$ 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 M$_7$C$_3$, M$_2$C and complex carboborides of the Me$_6$(CB) type.

KEYWORDS: POWDER MATERIALS, COMPOSITE, SINTERING, FECR800, TiB$_2$, 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, TiB$_2$ is widely used due to its high melting point, high hardness and excellent wear resistance. By alloying titanium 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 carbonitride which is especially noticeable in materials with 1.48 and 2.2% TiB$_2$.

Results and discussion

TiB$_2$ 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% TiB$_2$.

High values of volumetric shrinkage and density are observed for samples with 0.74 (% wt.) TiB$_2$. This may be due to the consumption of dopant components (Ti and B) for the formation of complex Fe-Cr-Ti borides.

Conclusion

The effect of TiB$_2$ 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 M$_7$C$_3$, M$_2$C and complex carboborides of the Me$_6$(CB) type. The choice of boron as an alloying additive is explained by the fact, that it gives 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-Fe$_2$B eutectic with iron and can activate the sintering process of a powder carbide steel 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).
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 TiB$_2$ content (1.48 and 2.2 %, wt.).

The study of the effect of sintering temperature on the hardness and flexural strength of materials Fe-FeCr 800-(0.38-2.2%) TiB$_2$ 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.

Electron studies and local micro X-ray spectral analysis of materials of the Fe-FeCr 800 system doped with TiB$_2$ showed that their structure is microheterogeneous, multiphase and consists of light gray, gray, dark gray and black phases. Alloying with the addition of TiB$_2$ affects the structure of the carbide phase of the composite, this is especially noticeable when the TiB$_2$ 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 Me$_7$C$_3$ type, and the gray phases are carboborides of the Me$_3$(CB) type.

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-$35$FeCr$_800$ system (wt. %) was investigated. It has been established that the introduction of a boron-containing additive into the charge of the base material $65$Fe-$35$FeCr$_800$ (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$_7$C$_3$, M$_3$C and complex carboborides of the Me$_3$(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 $65$Fe-$35$FeCr$_800$ composite (wt. %).

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ISO 4498-1-90 “Metal sintered materials, excluding solid alloys. Determination of apparent hardness. The materials are mainly with uniform hardness across the cross-section”.
6. ISO 3327 “Alloys are solid. Determination of the tensile strength at the transverse bend”.

17
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 aluminium are presented. The composites obtained by diffusion welding under pressure of packages of aluminium 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 (0.35–0.45)×10^4 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 crystalized 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 ~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 35×20×2 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 зоны – 0.16 мм. 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] $\sigma_0$ was determined at maximum load $P$ according to the well-known formula: $\sigma_0 = 3PL/2bh^2$, 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 2.5×2×20 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).

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 $R \gg L$: $f = R - R(1 - \frac{L^2}{8R^2})$ (2), where $R = \frac{L^2}{8f}$. Then the relative deformation $\varepsilon$ is equal to: $\varepsilon = \frac{2\pi(\frac{L^2}{8})^{\frac{1}{2}} - 2\pi R}{2\pi} \frac{\dot{\varepsilon}}{2\pi}$ (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 $\varepsilon = \frac{\delta}{2\pi R} = \frac{4f}{\delta R} f$ and $\dot{\varepsilon} = \frac{\delta \dot{f}}{\delta t} = \frac{4f \delta f}{\delta t} f$ (4).

We used the following form of the dependence of the creep rate on stress and temperature: $\dot{\varepsilon} = \frac{4f \delta f}{\delta t} f$ (5), where $\delta$ – strain rate (s$^{-1}$), $f$ – deflection rate (mm/s), $\delta$ – 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 µm thick and thin (about 10 µm) dark layers. At higher magnification, they had three layers (Fig. 2, b).

According to local X-ray diffraction data (Fig. 3, a), the structure of diffusion layers in the (Nb5V)/Al composite consisted of a (Nb,V)$_2$(AlSi) compound layer 30–35 µm thick enclosed between two thin (5–8 µm) layers of the compound (Nb,V)$_3$(AlSi). 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 (Nb,V)$_3$(AlSi) and (Nb,V)$_2$(AlSi) – 0.5 and 1 at. %, respectively.

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 (Nb,V)$_2$(AlSi) compound layer of a line of dark inclusions of Al$_2$O$_3$ oxide (23 and 24 – points of local XSA).

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

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 XS-analysis

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 XS-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 (Nb,V)(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 Al2O3 inclusions in the center of the (Nb,V)(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 (Nb,V)3Al and (Nb,V)2Al compounds with a low silicon content;
- the solubility of vanadium in the layers of the intermetallic compound (Nb,V)3(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 (Nb,V)2(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: (Nb,V)3(Al,Si), (Nb,V)2(Al,Si) and (Nb,V)(Al,Si)3. However, the Nb15V/Al composite contained only the compound (Nb,V)2(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 σt 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](image)

**Figure 6.** Dependence of the average values of σt 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](image)

**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](image)

**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](image)

**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>
<thead>
<tr>
<th>Композит</th>
<th>100-часовая прочность σt</th>
<th>Показатель степени n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb5V/Al</td>
<td>63,5</td>
<td>3,75</td>
</tr>
<tr>
<td>Nb10V/Al</td>
<td>71,0</td>
<td>4,40</td>
</tr>
<tr>
<td>Nb15V/Al</td>
<td>80,0</td>
<td>5,73</td>
</tr>
</tbody>
</table>

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 (Nb, V)3(Al, Si) and (Nb, V)3(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 (Nb, V)3(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 Nb3Al and Nb2Al 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 V2Al compound, which is related to the Nb2Al compound. But on the other hand, it contains a “twin” compound of the Nb3Al intermetallic compound (33.3 at. % Al) – V2Al (37.5 at. % Al). Hence, the higher solubility of vanadium in the intermetallic compound Nb3Al than in Nb2Al.

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 visco-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 MPa 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 25–30 MPa m^{1/2}.

4. Conclusions
1. From the data of local X-ray spectral analysis, it followed that vanadium in the intermetallic laminated Nb5V/Al and Nb10V/Al 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 1100–1300°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 1100–1300°C.

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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» (Bessospan 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 Chemicals», «Usturt 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 1.732 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 completely 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», «Usturt 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 Gaz Chemicals», «Usturt 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 °C, 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 °C [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:

\[ A = A_0 \times \frac{N_1}{N_2} \]  
(1)

where: \( A_0 \) - 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:

\[ A_t = A_0 \times \exp(-\lambda t) \]  
(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; \( \lambda \) - Cs-137 radioisotope decay constant of \( 2.296 \times 10^{-4} \) 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.

<table>
<thead>
<tr>
<th>Name, characteristic and unit of measurement</th>
<th>Data</th>
</tr>
</thead>
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<tr>
<td>1. Working surface</td>
<td>bottom</td>
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<tr>
<td>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</td>
<td>( 1.6 \times 10^{10} )</td>
</tr>
<tr>
<td>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 %</td>
<td>±15</td>
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<tr>
<td>4. Month and year of exposure dose rate measurement</td>
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</tbody>
</table>

### 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.

<table>
<thead>
<tr>
<th>Name, characteristic and unit of measurement</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Working surface</td>
<td>bottom</td>
</tr>
<tr>
<td>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</td>
<td>( 1.43 \times 10^{9} )</td>
</tr>
<tr>
<td>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 %</td>
<td>±15</td>
</tr>
<tr>
<td>4. Month and year of exposure dose rate measurement</td>
<td>12.2019</td>
</tr>
<tr>
<td>5. Activity of the radionuclide Cs-137 in the source, Bq</td>
<td>3.06 \times 10^{4}, 82.7 mCi</td>
</tr>
<tr>
<td>6. External dimensions of the source, mm diameter height</td>
<td>8.0, 12.0</td>
</tr>
<tr>
<td>7. Capsule material, type of stainless steel</td>
<td>12X18N10T</td>
</tr>
<tr>
<td>8. Dimensions of the active part of the source, mm diameter height</td>
<td>6.0, 6.5</td>
</tr>
<tr>
<td>9. Source tightness</td>
<td>tight</td>
</tr>
<tr>
<td>10. Level of radioactive contamination of the source with radioactive substances when determined by smear method, Bq, no more than</td>
<td>185</td>
</tr>
</tbody>
</table>

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 capsule, which protects the source from corrosion, to be linked to the gamma source block. However, to make it possible to charge the Cs-137 source into the gamma source block, it was necessary to increase the size of the source socket in the gamma source block. The level of radioactive contamination of the source with radioactive substances when determined by the smear method, Bq, no more than 185.

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.
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 μSv/h, and measured equivalent dose rate of gamma ionizing radiation at distance of 1.0 m was 0.5 μSv/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. 0.193-06). 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 μSv/h (10 mR/h); at a distance of 1 m from the gamma source block - 3 μSv/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.

<table>
<thead>
<tr>
<th>Simulator number</th>
<th>Density value, kg/m³</th>
<th>Simulator percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>bromoform</td>
</tr>
<tr>
<td>1</td>
<td>800</td>
<td>0,5</td>
</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>10,0</td>
</tr>
<tr>
<td>3</td>
<td>1200</td>
<td>19,5</td>
</tr>
<tr>
<td>4</td>
<td>1400</td>
<td>29,0</td>
</tr>
<tr>
<td>5</td>
<td>1600</td>
<td>38,5</td>
</tr>
<tr>
<td>6</td>
<td>1800</td>
<td>48,0</td>
</tr>
<tr>
<td>7</td>
<td>2000</td>
<td>57,5</td>
</tr>
<tr>
<td>8</td>
<td>2200</td>
<td>67,0</td>
</tr>
<tr>
<td>9</td>
<td>2400</td>
<td>76,5</td>
</tr>
<tr>
<td>10</td>
<td>2600</td>
<td>86,0</td>
</tr>
<tr>
<td>11</td>
<td>2800</td>
<td>95,6</td>
</tr>
</tbody>
</table>

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 (D=20 mm and Ø=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).

<table>
<thead>
<tr>
<th>No.</th>
<th>Type of source Cs-137</th>
<th>Measured point number</th>
<th>Radiation exposure dose, μSv/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>GS7.012.8 (activity=8.56 mCi)</td>
<td>1</td>
<td>6.6</td>
</tr>
<tr>
<td>1.2</td>
<td>/-/-</td>
<td>2</td>
<td>7.6</td>
</tr>
<tr>
<td>1.3</td>
<td>/-/-</td>
<td>3</td>
<td>5.6</td>
</tr>
<tr>
<td>2.1</td>
<td>GS7.021.1 (activity=87.2 mCi)</td>
<td>1</td>
<td>32</td>
</tr>
<tr>
<td>2.2</td>
<td>/-/-</td>
<td>2</td>
<td>30.1</td>
</tr>
<tr>
<td>2.3</td>
<td>/-/-</td>
<td>3</td>
<td>30.7</td>
</tr>
<tr>
<td>3.1</td>
<td>GS7.021.1 (activity=87.2 mCi)</td>
<td>1</td>
<td>6.4</td>
</tr>
</tbody>
</table>
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 μSv/h, which is equal to the average dose of gamma radiation from the GCs7.012.8 source (6.6 μSv/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.

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

<table>
<thead>
<tr>
<th>#</th>
<th>Name, type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Gamma source block, No. PA 00040113F</td>
<td>Weight= 40 kg</td>
</tr>
<tr>
<td>2.</td>
<td>Source Cs-137 GC7.021.1, serial No. 190</td>
<td>Activity=87.2 mCi</td>
</tr>
</tbody>
</table>
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/cm$^3$; 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/cm$^3$.

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

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/cm$^3$ an analog signal current appears in the 4.0 mA connector, and at pulp density of 1.715 g/cm$^3$ 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.

<table>
<thead>
<tr>
<th>#</th>
<th>Name, type</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Gamma source block, No. PA 00030113F</td>
<td>Weight= 40 kg</td>
</tr>
<tr>
<td>2.</td>
<td>Source Cs-137 GC,7.0121.1, serial No. IXE</td>
<td>Activity=8.56 mCi</td>
</tr>
<tr>
<td>3.</td>
<td>Scintillation detector block FM G60, No. 900A20100F</td>
<td>Length=200 mm</td>
</tr>
<tr>
<td>4.</td>
<td>Process pipe inner diameter $\Omega=159$ mm</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Process pipe wall thickness h=10 mm</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Input pulp emulsion density parameters:</td>
<td></td>
</tr>
</tbody>
</table>

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 GC7.012.8, activity is 8.56 mCi); cylindrical simulator stand with liquid simulator No. 3 with density of 1.694 g/cm$^3$; 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/cm$^3$.

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 this gas production 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 Ascenti.

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 Ci/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.

<table>
<thead>
<tr>
<th>Investigated sample</th>
<th>Specific activity of natural radionuclide, Bk/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>226Ra</td>
</tr>
<tr>
<td>Formation water from separator</td>
<td>162±240</td>
</tr>
<tr>
<td>Gas condensate</td>
<td>-</td>
</tr>
<tr>
<td>Intermediate powdered polyethylene product</td>
<td>25±5</td>
</tr>
</tbody>
</table>

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 – T½=19.8 min, 214Pb – T½=26.8 min, 228Ac – T½=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.

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.

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 (GC7.021.1 and GC7.012.8) were tested for tightness. The source socket in the gamma source block was enlarged, ionizing radiation source of Cs-137 GC7.021.1 (ID 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 GCs 7.012.8, (# 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.

References:

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).
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.

![Fig. 3 A vibration stand for powder compaction](image1)

![Fig. 4 A view of the blanks of a tubular propelling device for precise movements](image2)

![Fig. 5 Microstructure of piezoceramic samples of materials: a) PZT-19; b) PZN-PT-BT; c) PZN-PT-PZ](image3)
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**: $170 \times 10^{-12}$ C/N
- **Scan field at a voltage $\pm 150$ V**: $(140 \times 140)$ nm
- **Bending sensitivity**: 0.5 nm/v
- **Density of piezoceramic material**: 7.68 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.

**References**

Quality Control of the Concrete Pavement Constructions for Mother Theresa Airport

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Abstract: Nowadays, roads and airports are the most used ways of communication to connect people to each other inside and outside of Albania. Based on it, infrastructure has been a key parameter to develop economy and social life of Albania. The request of the people to use the roads and airports is increasing every year which has made the government to concentrate on the infrastructure improvement and development. The most common problem comes from Mother Theresa airport due to non-formal management control. Due to it, our research work will be focused on the quality control of the concrete pavement constructions of the Mother Theresa Airport.

Keywords: CONCRETE PAVEMENT CONSTRUCTIONS, PORTLAND CEMENT, QUALITY CONTROL, AIRPORT, INFRASTRUCTURE

1. Introduction

Nowadays, roads and airports are the most used ways of communication to connect people to each other inside and outside of Albania. Based on it, infrastructure has been a key parameter to develop economy and social life of Albania. The request of the people to use the roads and airports is increasing every year which has made the government to concentrate on the infrastructure improvement and development. More quality is needed to meet the requirements of the current transport infrastructure of concrete or asphalt used in these transport routes. More efficient methods for road monitoring and structural assessment have been needed to ensure good care and provide an adequate road maintenance solution.

In general, the design and construction of airport concrete pavement requires consideration of many features, including the concrete quality, construction method, performance of concrete under service conditions and the economy [1, 2]. In Albania, the most common problem comes from Mother Theresa airport due to non-formal management control. Structural condition and quality control are the main factors to be considered for road maintenance planning. In aviation runway at Mother Theresa airport are often managed informally, based on the judgment and experience of the staff. Experience has shown that there are three important steps that are particularly helpful in managing airport runways such as:

- Inventory of all runways
- Periodic assessment of the condition of all runways.
- Use condition assessments to set priorities for projects and consideration of alternative options.

Based on it, our research work will be focused only in the quality control of the concrete pavement constructions of the Mother Theresa Airport. In the current paper we need to be concentrate on the accredited laboratory testing by using only compression test of the concrete.

2. Materials for Production of the Concrete

The Portland cement has been prepared for our research work. For the production of Portland cement, various minerals of natural origin can be used, as well as industrial products. The main minerals for this purpose are minerals which contain the main components of Portland cement such as: calcium oxide (main ingredient), silicon oxide, aluminum oxide and iron oxide. We have used three important steps for production of the Portland cement which are as follows:

- Preparation of raw material;
- Production of clinker;
- Production of cement

Table 1 depict raw materials where carbonates have hardness according to the degree of Mohs.

Table 1: Raw materials in the mixture.

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>CaCO3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure limestone</td>
<td>96-100</td>
</tr>
<tr>
<td>Limestone</td>
<td>90-96</td>
</tr>
<tr>
<td>Argil limestone</td>
<td>75-90</td>
</tr>
<tr>
<td>Mergel</td>
<td>40-75</td>
</tr>
<tr>
<td>Mergel Argil</td>
<td>10-40</td>
</tr>
<tr>
<td>Argil</td>
<td>0-4</td>
</tr>
</tbody>
</table>

3. Sample preparation

The prepared samples has been casted in three cube-shaped molds with dimensions 150x150x150 mm and another sample in a mold with dimensions 100x100x500 mm. All mixtures were compacted on a vibrating machine to ensure that the samples have been mixed correctly. For best results, the concrete should be vibrated as well as possible so that the results are as accurate as possible. The Fig. 1 depict the machine that make compact the mold.

Fig. 1 Compact molding machine

After compaction, all samples are stored for one day in molds at room temperature. The samples are then opened and stored as can be seen in the Fig. 2.
Afterward, an increasing compressive force is applied over the sample until its destruction appears determining the maximum force. Concrete can withstand compressive strength in the range of 3 - 35 MPa, which is suitable for our applications like airport runways. The test was conducted at 28 days of the conservation process. The compression test is the quantity that is indirectly determined by the measurement which depends on the force applied to the sample. Sample stress $\sigma$ of uniaxial compressive strength is evaluated as the ratio of maximum applied force $F_{\text{max}}$ and sample cross-sectional area $A$ in the beginning of the test according to equation (1) [3].

$$\sigma = \frac{F_{\text{max}}}{A}$$

(1)

### 5. Measurement Results

Based on our measurement we will show in the Table 2 the dimensions of the sample and in the Table 3 the compressive strength results.

<table>
<thead>
<tr>
<th>Sample (No)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Height (mm)</th>
<th>Weight (g)</th>
<th>Density ($\text{kg/m}^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>8200</td>
<td>2430</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>8260</td>
<td>2447</td>
</tr>
</tbody>
</table>

Table 2. Dimensions of the samples.

<table>
<thead>
<tr>
<th>Sample (No)</th>
<th>Day</th>
<th>Age of Sample</th>
<th>Crush</th>
<th>Load (kN)</th>
<th>$\sigma$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2020</td>
<td>&gt; 28</td>
<td>Normal</td>
<td>622.1</td>
<td>27.6</td>
</tr>
<tr>
<td>2</td>
<td>2020</td>
<td>&gt; 28</td>
<td>Normal</td>
<td>603.3</td>
<td>26.8</td>
</tr>
</tbody>
</table>

Table 3. Compressive strength results

From the above results of the performed tests we have seen that the values of compressive strength of the concrete sample come out within the predicted values.

### 6. Conclusions

This papers briefly describes the quality control of the concrete pavement construction for Mother Theresa airport in Albania. Also we have been focused on the sample preparation of concrete and one of the important quality control factor that is compressive strength test. The future research work will be concentrate to the other quality controls for aviation airport such as wet permeable test and flexural test concrete.

### 7. References