





## INVESTIGATION OF THE STRUCTURAL COMPOSITION OF Fe-Mn-Si-Ti-Al-NC ALLOYS AND THE SOLUBILITY OF ELEMENTS IN $\alpha$ -IRON<sup>†</sup>

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The study of the structural components of Fe-Mn-Si-Ti-Al-N-C with the carbon content of 0.50-0.60% (wt.), Silicon 0.80-0.90% (wt.), Manganese 0.90-0.95% (wt.), Aluminum - 0.20-0.30% (wt.), Titanium - 0.02-0.03% (wt.), Nitrogen - 0.015-0.02% (wt.), the rest - iron. Microstructural, micro-X-ray spectral and X-ray phase analyzes were used to determine the structural state of the alloys. It is shown that after crystallization and a number of phase transformations the structure of the alloy was presented  $\alpha$ -iron alloyed with cementite, oxides, nitrides and carbonitrides. Using the quasi-chemical method, the free energy dependence of the solid solution of  $\alpha$ -iron alloyed with silicon, manganese and titanium was obtained. In  $\alpha$ -iron, it can dissolve up to 0.016% (at.) Carbon, manganese up to 1.3% (at.), Silicon - 1.0% (at.), and titanium up to 0.5% (at.), which is consistent with experimental results.

**Keywords:** complex alloying of steel with aluminum, titanium and nitrogen; inclusions; oxides; nitrides; carbonitrides; ferrite; free energy of ferrite.

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It is known that alloying elements have an effect on phase transformations and the formation of excess phases in steels. Alloying elements can be divided into (where) stabilizing carbides and ferrite in the formation of perlite [1]. Carbide-forming elements include Mn, V, Ti, Cr and Mo [2-3], while non-carbide-forming elements such as Si, Al, Ni and Co [1-3] have high concentrations in the  $\alpha$ -Fe phase. The authors found that there is a strong repulsive force between Si and Mn atoms in  $\alpha$ -Fe structure of BCC [4]. Si atoms predominantly dissolve in  $\alpha$ -Fe and push Mn atoms into cementite. For Fe-4.18C-0.71Mn-0.42Si and Fe-4.16C-0.72Mn-1.82Si alloys, the distribution coefficient between the ratio of the concentration of manganese in cementite and silicon in ferrite was 3.66 ... 8.16, depending on the content of these elements in steel. The manganese content in the ferrite of Fe - 4.18C - 0.71Mn - 0.42Si and Fe - 4.16C - 0.72Mn - 1.82 Si alloys was 0.7% (at.), Silicon - 0.8... 3% (at.), and in manganese cementite - 2.0% (at.), and silicon 0.1% (at.) [4].

With the silicon content of 0.95% (at.) in the cementite of both alloys, its content is  $0.06 \pm 0.01\%$  (at.) and the silicon content of 0.22% (at.) is  $0.09 \pm 0.02\%$  (at.), respectively [1]. The content of Mn in  $\alpha$ -Fe and in the cementite of the alloy with the content of 0.95% silicon is  $0.41 \pm 0.02\%$  (at.) and  $1.60 \pm 0.03\%$  (at.), and for the alloy with the content of 0.22% (at.) Si -  $0.50 \pm 0.04\%$  (at.) and  $1.45 \pm 0.31\%$  (at.), respectively [1].

Studies of the content of alloying elements in the ferrite of Fe-3.2Mn-1.0Al-1.2 C alloy showed that the content of manganese in  $\alpha$ -iron - 3... 10% (at.), Aluminum - 3... 9% (at.) and carbon <0.4 % (at.) [5]. In paper [6], it is indicated that the maximum solubility of elements in  $\alpha$ -iron is: carbon - 0.017% (wt.), Manganese - 1.5% (wt.), Silicon - 1.3% (wt.), which is consistent with the results given in paper [7].

The authors of paper [8] note that the microstructure of steel Fe - 1.5% Mn - 0.6% Si - 0.8% C had the ferrite-perlite structure, and Fe - 2 / 2.5% Mn - 0.6% Si - 0.8% C is pearlitic, which had higher hardness. The authors explain the obtained result by the joint effect of Mn and Si on the eutectic point of Fe-Fe<sub>3</sub>C system - both alloying elements shift S point (eutectoid point on the iron-carbon phase diagram) to the higher carbon content, which leads to the increase in the volume fraction of perlite in steel.

It is known that Si and Al inhibit the formation of carbides, and Si is more efficient than aluminum. Phosphorus and sulfur occupy the position of carbon substitution in all carbides, while Si can replace carbon in two of them - Fe<sub>3</sub>C and Fe<sub>5</sub>C<sub>2</sub> [9]. Currently, the literature contains insufficient data on the structural components and features of the phases of high-alloy alloys, in particular, alloys of Fe-Mn-Si-Ti-Al-N-C system.

The aim of this work was to investigate the phase composition of alloys of Fe-Mn-Si-Ti-Al-NC system and to determine the solubility of elements in  $\alpha$ -iron.

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### MATERIALS AND RESEARCH METHODS

The study was performed on alloys of Fe-Mn-Si-Ti-Al-NC system with the carbon content of 0.50-0.60% (wt.), Silicon 0.80-0.90% (wt.), Manganese 0.90-0.95 % (wt.), aluminum - 0.20-0.30% (wt.), titanium - 0.02-0.03% (wt.), nitrogen - 0.015-0.02% (wt.), the rest - iron.

The smelting of the alloy was carried out in the furnace in alundum crucibles in the argon atmosphere. The cooling rate of the alloy after casting was 10 K/s. Metallographic sections of the alloy were made according to standard methods using diamond pastes. Chemical and spectral analysis were used to determine the chemical composition of the alloy [10]. The phase composition of the alloy was determined using the optical microscope "Neofot-21". The main results of micro-X-ray spectral analysis were obtained using the electron microscope JSM-6490 with the scanning prefix ASID-4D and energy-dispersive X-ray microanalyzer "Link Systems 860" with software. X-ray diffraction analysis was performed on DRON-3 diffractometer in monochromatized Fe-K<sub>α</sub> radiation.

### RESULTS AND THEIR DISCUSSION

The microstructure of the alloy in the cast state was represented by perlite and ferrite. Perlite had the fine morphology (Fig. 1, a).

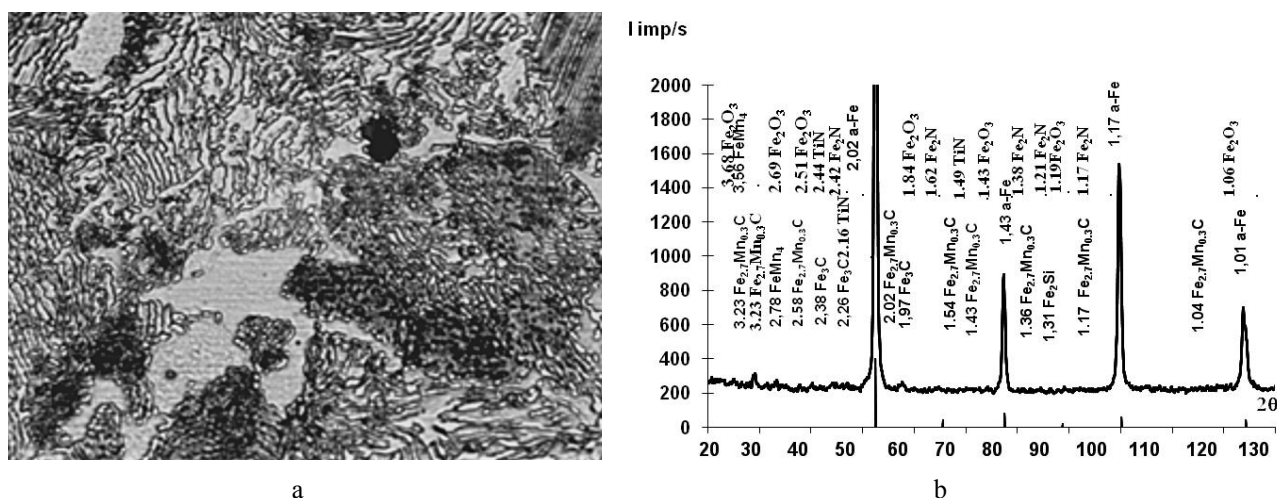


Figure 1. - Microstructure (a) and diffraction pattern (b) of the alloy system Fe-Mn-Si-Ti-Al-NC

In the structure of the alloys were found multilayer inclusions, which had a size of 1.5-2 μm. The formation of the multiphase inclusion begins with the formation of the phase melt  $L \rightarrow \text{Al}(\text{TiFe})_2\text{O}_3$ . This phase additionally contains manganese 2.55% (at.), Silicon 1.0% (at.), Nitrogen 4.23% (at.) (Fig. 2).

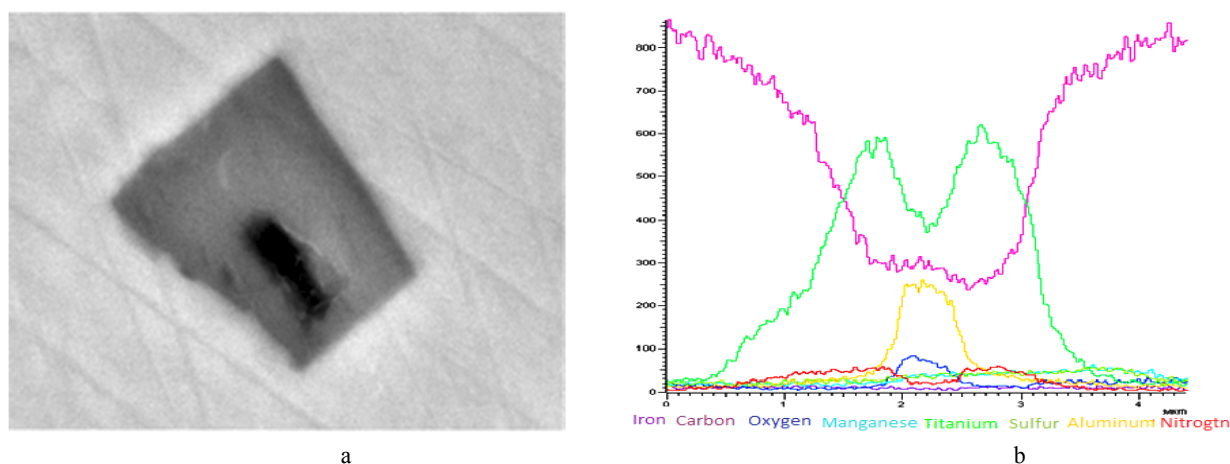


Figure 2. Microstructure of multiphase inclusion (a) and diffractogram of chemical elements distribution (b)

The phase  $(\text{Ti}_{0.3}\text{Fe}_{0.2})(\text{N}_{0.3}\text{C}_{0.2})$  is placed around it, with stereometry of TiN phase. The formation of the phase  $(\text{Ti}_{0.3}\text{Fe}_{0.2})(\text{N}_{0.3}\text{C}_{0.2})$  occurs by peritectic reaction –  $L + \text{Al}(\text{TiFe})_2\text{O}_3 \rightarrow (\text{Ti}_{0.3}\text{Fe}_{0.2})(\text{N}_{0.3}\text{C}_{0.2})$ . This phase is alloyed with manganese up to 2.4% (at.), Silicon up to 0.3% (at.), Aluminum up to 2.0% (at.). It should be noted that the nitrides that were formed during the crystallization of this alloy contained sulfur up to 0.9% (at.). In addition, the following inclusions were identified in the microstructure using X-ray phase and micro-X-ray diffraction analyzes: oxides -  $\text{Fe}_3\text{AlO}_2$  with FeO stereometry,  $(\text{FeAl})_2\text{O}_3$  with  $\text{Fe}_2\text{O}_3$  stereometry,  $\text{F}_{21}\text{Ti}_{18}\text{O}_{24}\text{N}_{17}\text{C}_{17}$ ,  $\text{Fe}_{40}\text{Al}_{15}\text{O}_{31}$ ; nitrides -  $\text{FeTiN}$  with stereometry TiN,  $\text{Ti}_2\text{FeN}$  ( $\text{Ti}_{41}\text{Fe}_{26}\text{N}_{27}$ ); carbonitrides -  $\text{Fe}_{50}\text{N}_{15}\text{C}_{30}$ ,  $\text{Fe}_3\text{NC}_2$ ,  $\text{Fe}_3\text{Ti}_2\text{N}_3\text{C}$  ( $\text{Fe}_{20}\text{Ti}_{28}\text{N}_{35}\text{C}_{15}$ ),  $\text{FeTiNC}$ ,  $\text{Fe}_2(\text{NC})$ , which were alloyed

with manganese up to 0.5% ( at.), silicon 1.0% (at.), titanium up to 5.0% (at.). At doping the iron alloys with manganese, silicon and titanium, any pure carbides of manganese, silicon and titanium do not exist, but there are complex carbides [11]. In addition, the formation of  $Fe_{2.7}Mn_{0.3}C$ , carbide was determined in the structure and phase  $FeMn_4$ ,  $Fe_2Si$ .

It should be noted that the inclusions found in the microstructure were located not only along the grain boundaries, but also in the pearlite grain.

The presence of ferrite was observed around the inclusions and along the boundaries of pearlite. On the diffraction pattern, the  $\alpha$ -iron lines were shifted toward larger angles compared to pure  $\alpha$ -iron (Fig. 1, b). The obtained result can be explained by the fact that the ferrite is alloyed with manganese, silicon, titanium, aluminum and the lattice parameter of  $\alpha$ -iron changes. Micro X-ray spectral studies of the surface of the samples performed in this work showed that ferrite could contain up to 1.0% (at.) Manganese, 1.7% (at.) Silicon, 1.0% (at.) Titanium, 0.032% (at.) Carbon.

Thus, additional alloying with titanium and aluminum leads to the decrease in the content of manganese silicite in ferrite in comparison with the data given in [6-7]. Pearlite cementite was alloyed with manganese up to 2.0% (at.), Titanium 1.2% (at.), Silicon 1.2% (at.), And aluminum 0.4% (at.).

It is known that the lattice parameter of the BCC of iron at room temperature has the numerical value of 2,862 Å [12]. As can be seen from table 1, additional doping of the Fe-Mn-Si-C alloy with titanium, aluminum and nitrogen leads to the increase in the lattice parameter of  $\alpha$ -iron [6]. The obtained result can be explained by the fact that in the  $\alpha$ -iron lattice it is possible to replace iron atoms with manganese, silicon, titanium or aluminum.

**Table 1.** Lattice parameter, crystallite size, dislocation density, degree of microstresses in  $\alpha$ -Fe

Lattice parameter, Å	Block sizes L, Å	Degree of microstress	Dislocation density, cm <sup>-2</sup>
2.867	1184	$1.05 \cdot 10^{-3}$	$28 \cdot 10^{10}$

The structure of  $\alpha$ -Fe has the volume-centered lattice and belongs to the spatial group  $O_h^9 - Im\bar{3}m$  with 8 atoms in the first coordination sphere [13]. Each atom of the BCC lattice has six tetrahedral and three octahedral pores. Of the six atoms surrounding the octahedral pore, two are closest to the others. The arrangement of carbon atoms in the BCC lattice can be described as follows: the arrangement of carbon atoms in the octahedral pore, which has four nearest metal atoms at the distance of 2.02 Å, and two at the distance of 1.43 Å, each metal atom has 8 neighbors, which are located on distances of 2.48 Å from each other.

To determine the solubility limit of manganese, silicon, aluminum, titanium in  $\alpha$ -iron and the effect of these elements on the solubility of carbon, the quasi-chemical method was used [14].

The interaction of Fe-Fe, Fe-C, Fe-Si, Fe-Mn, Fe-Al, Fe-Ti and Fe-V<sub>a</sub> atoms, where V<sub>a</sub> is the vacancy which can be considered as follows: the interaction energies of atomic pairs  $v_{FeFe}, v_{FeSi}, v_{FeVa}, v_{FeMn}, v_{FeAl}, v_{FeTi}$ . The energy of interaction between metal and carbon atoms at the distance of 2.02 Å is denoted by  $-v_{FeC}, v_{SiC}, v_{TiC}, v_{MnC}$ . For carbon atoms located at the distance of 1.43 Å  $-v_{FeC}^1, v_{SiC}^1, v_{TiC}^1, v_{MnC}^1$ . The results presented in paper [7] were used for numerical values of the interaction energy of pairs of atoms.

The free energy of ferrite can be determined by the formula:  $F = E - kT \ln W$ , where E is the internal energy of ferrite, W is the thermodynamic probability of the placement of atoms in the nodes of the crystal lattice of ferrite,  $k = 1.38 \cdot 10^{-23}$  J / K is the Boltzmann constant, T is the absolute temperature. Thus, the free energy of ferrite is determined as follows:

$$\begin{aligned}
 F = & -8(N_{Fe}N_{Ti}v_{FeTi} + N_{Fe}N_{Fe}v_{FeFe} + N_{Mn}N_{Fe}v_{MnFe} + N_{Si}N_{Fe}v_{SiFe}) \\
 & -4(N_{Fe}N_Cv_{FeC} + N_{Mn}N_Cv_{MnC} + N_{Si}N_Cv_{SiC} + N_{Ti}N_Cv_{TiC} + N_{Fe}N_{Va}v_{FeN_{Va}}) - \\
 & -2(N_{Fe}N_Cv_{FeC}^1 + N_{Mn}N_Cv_{MnC}^1 + N_{Si}N_Cv_{SiC}^1 + N_{Ti}N_Cv_{TiC}^1 + N_{Fe}N_{Va}v_{FeN_{Va}}^1) - \\
 & -kT(8(N_{Fe} + N_{Mn} + N_{Si} + N_{Ti} + N_{Va})(\ln(N_{Fe} + N_{Mn} + N_{Si} + N_{Ti} + N_{Va}) - 1) - \\
 & -8N_{Fe}(\ln N_{Fe} - 1) - 8N_{Mn}(\ln N_{Mn} - 1) - 8N_{Si}(\ln N_{Si} - 1) - 8N_{Ti}(\ln N_{Ti} - 1)) - \\
 & -4(N_C + N_{Va})(\ln(N_C + N_{Va}) - 1) - N_C(\ln N_C - 1) - \\
 & -N_{Va}(\ln N_{Va} - 1)
 \end{aligned}$$

To calculate the solubility of carbon in  $\alpha$ -iron, we need to find the solution of the system of equations:

$$\frac{\partial F}{\partial N_C} = 0, \quad \frac{\partial F}{\partial N_{Va}} = 0, \quad \frac{\partial F}{\partial N_{Si}} = 0, \quad \frac{\partial F}{\partial N_{Mn}} = 0, \quad \frac{\partial F}{\partial N_{Fe}} = 0, \quad \frac{\partial F}{\partial N_{Ti}} = 0. \quad (1)$$

The resulting system of equations (1) is transcendental. Usually the solution of such equations can be obtained graphically or numerically. But in the framework of this problem, it is expedient to consider the asymptotic solution of the equations. To do this, we present the logarithm included in each of the equations of system (1) in the form of Taylor series (this is acceptable under the conditions of its convergence):

To obtain the asymptotic estimate of the solution of system (1), it suffices to consider the first two terms of the development of logarithms.

The results of solving the system of equations showed that in  $\alpha$ -iron it could dissolve in 0.016% (at.) Carbon, manganese up to 1.3% (at.), Silicon - 1.0% (at.), and titanium up to 0.5% (at.). It should be noted that additional alloying of Fe-Mn-Si-C alloy with titanium, aluminum and nitrogen leads to the decrease in the content of silicon, manganese and carbon in  $\alpha$ -iron [6-7].

The obtained results can be explained by the fact that additional alloying of Fe-Mn-Si-C alloy with titanium, aluminum and nitrogen promotes the formation of complex carbides of oxides, nitrides and carbonitrides, and reduces the content of doped elements in  $\alpha$ -iron.

## CONCLUSIONS

1. The analysis of the phase composition of alloys of Fe-Mn-Si-Ti-Al-NC system with the carbon content of 0.50-0.60% (wt.), Silicon 0.80-0.90% (wt.), Manganese 0, 90-0.95% (wt.), Aluminum - 0.20-0.30% (wt.), Titanium - 0.02-0.03% (wt.), Nitrogen - 0.015-0.02% (wt.), the rest - iron. It is determined that after crystallization and a number of phase transformations the structure of the alloy was presented by  $\alpha$ -iron, alloyed with cementite, oxides, nitrides and carbonitrides.

2. Using the quasi-chemical method we obtain or the dependence of the free energy of the solid solution of  $\alpha$ -iron doped with silicon, manganese and titanium. It was found that in  $\alpha$ -iron it can dissolve in 0.022% (at.) carbon, manganese up to 1.6% (at.), Silicon - 1.0% (at.), and titanium up to 0.5% (at.), which is in agreement with the experimental results.

3. It is established that the maximum solubility of carbon, manganese, titanium and silicon in  $\alpha$ -iron of Fe-Mn-Si-C alloys is lower in comparison with their solubility in the corresponding binary systems.

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## ДОСЛІДЖЕННЯ СТРУКТУРНОГО СКЛАДУ СПЛАВІВ СИСТЕМИ Fe-Mn-Si-Ti-Al-N-C ТА РОЗЧИННОСТІ ЕЛЕМЕНТІВ В $\alpha$ -ЗАЛІЗІ

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В роботі проведено дослідження структурних складових сплавів системи Fe-Mn-Si-Ti-Al-N-C з вмістом карбону 0,50-0,60 % (мас.), силіцію 0,80-0,90 % (мас.), мангану 0,90-0,95 % (мас.), алюмінію – 0,20-0,30 % (мас.), титану – 0,02-0,03 % (мас.), азоту – 0,015-0,02 % (мас.) решта – залізо. Для визначення структурного стану сплавів використовували мікροструктурний, мікροрентгеноспектральний та рентгенофазовий аналізи. Показано, що після кристалізації та низки фазових перетворень структура сплаву була представлена  $\alpha$ - залізом, легованим цементитом, оксидами, нітридами та карбонітридами. З застосуванням квазіхімічного методу отримали залежність вільної енергії твердого розчину  $\alpha$ -заліза легованого силіцієм, манганом та титаном. В  $\alpha$ -залізі може розчинятись до 0,016 % (ат.) карбону, мангану до 1,3 % (ат.), силіцію – 1,0 % (ат.), а титану до 0,5 % (ат.), що узгоджується з експериментальними результатами.

**Ключові слова:** комплексне легування сталі алюмінієм, титаном і азотом; включення; оксиди; нітриди; карбонітриди; ферит, вільна енергія фериту