

***Ab-initio* modeling of the short range order in Fe–N and Fe–C austenitic alloys**

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In the present paper, we have studied atomic structure of Fe–N and Fe–C austenitic alloys. High precision *ab-initio* calculation was utilized for calculation of the pair potentials of interatomic interactions N–N and C–C in the FCC Fe lattice. These potentials were used for Monte Carlo modeling of the short range order in Fe–N and Fe–C systems. It was discovered that in the FCC Fe lattice, nitrogen atoms might be partially ordered. In this case, atomic structure of nitrogenous austenite is characterized by availability of Fe₆N phase with the short range order over N atoms located in the third coordination sphere. The calculations have shown that, contrary to nitrogen, carbon atoms in iron FCC lattice repulse and settle at maximum possible distances from each other.

В работе теоретически исследовано атомное строение азотистого и углеродистого аустенитов. Высокоточным *ab-initio* методом FLAPW рассчитаны парные потенциалы межатомного взаимодействия азот-азот и углерод-углерод в ГЦК решетке железа. Эти потенциалы использованы для Монте-Карло моделирования ближнего порядка в системах Fe–N и Fe–C. Установлено, что в ГЦК решетке железа атомы азота могут быть частично упорядочены. В этом случае атомная структура азотистого аустенита характеризуется наличием фазы Fe₆N с ближним порядком по атомам азота, который располагается в третьей координационной сфере. Расчеты показали, что в отличие от азота атомы углерода в ГЦК решетке железа отталкиваются и располагаются на максимально возможных расстояниях друг от друга.

1. Introduction

Most of the researchers attribute the unique physical properties of Fe–N austenite to peculiarities of the short range order in this alloy. It is presumed that short range order in Fe–N and Fe–C austenitic alloys is essentially different, and, in its own turn, it defines the difference in important physical properties like strength, plasticity and others. To describe the short range order and obtain statistical and thermodynamic characteristics of Fe–N and Fe–C austenite, it is necessary to obtain N–N and C–C interaction energies. In the pioneering papers, dedicated to such studies, the semi-phenomenological approaches

based upon experimental data (for instance, temperature-concentration dependence of thermodynamic activity of the austenite interstitials [1]) were used. The undertaken investigations [2 – 4] employed first order quasi-chemical approximation. First coordination sphere interactions evaluated lead to a conclusion that C–C interaction has repulsion with energy of $w_1 = 0.083$ eV [2] or $w_1 = 0.04$ eV [3] for Fe–C alloy. Similar estimations for N–N interaction energies were obtained for Fe–N alloy — $w_1 = 0.04$ eV [4] or $w_1 = 0.02$ eV [3]. It is possible to see that interaction energies absolute values differ significantly according to different authors. Obviously, this difference leads to different distribution of interstitials in the

alloy. The possibility to study in more detail the parameters of the interatomic interaction is provided by Mossbauer spectroscopy [5–9]. Interatomic interaction energies C–C and N–N in the two coordination spheres were estimated with help of Monte-Carlo modeling [6–9]. Monte-Carlo modeling allows obtaining the distribution of the interstitial atoms detected by Mossbauer spectroscopy. The disadvantage of this approach is that, as a rule, it is possible to obtain the interaction only for two coordination spheres. Authors of the most papers dedicated to the short range order study in nitrogenous austenite [5, 6, 8] concluded that nitrogen atoms are distributed according to Fe_4N non-stoichiometric composition. Recently [10], the energies of formation for C–C and C–V (V-vacancy) pairs were obtained from the thermodynamic activity data analysis with the use of quasi-chemical approximation (QCA) of the statistical mechanics. The values of these energies were used in further Monte-Carlo modeling of the different Fe–C austenite concentrations. Obtained distributions of the atoms C and vacancies V were compared with known decompositions of Mossbauer spectra. Modeling results are in a good agreement with $\text{Fe}_8\text{C}_{1-x}$ model proposed in [7]. Three types of iron atoms are distinguished in the frame of this model: Fe_{10} — iron atom with one carbon atom as a closest neighbor in the first coordination sphere, Fe_{0n} — iron atom with n carbon atoms only in the second coordination sphere and Fe_{00} — iron atom, which does not contain carbon atoms in the two primary coordination spheres. It will be shown later, that our results are in a good correspondence with $\text{Fe}_8\text{C}_{1-x}$ model. N–N atoms interaction was described in [11] with the help of Lennard-Jones pair potential with parameters obtained in the frame of quasi-harmonic approximation. Disadvantage of this approach is related to the supposition about an adequacy of the harmonic approximation and difficulties with obtaining the information about electrochemical interaction potentials. Still, the values of the pair interaction energies were obtained for six coordination spheres ($w_1 = 0.11$, $w_2 = 0.07$, $w_3 = -0.06$, $w_4 = 0.01$, $w_5 = 0.03$, $w_6 = 0.02$). As a result, the obtained decomposition up to 7th sphere indicates the formation of non-stoichiometric $\gamma\text{-Fe}_8\text{N}_2$ phase, which is not observed experimentally. Therefore, until now, there is no clear common opinion about the distribution of nitrogen and carbon atoms in FCC iron lat-

tice. Moreover, theoretical *ab-initio* short-range order modeling studies in these alloys are almost non-existent. So, the present paper is dedicated to the cluster decomposition [12] theoretical investigation of Fe–N and Fe–C austenites.

2. Results and discussion

The essence of an approach used in the present investigation is the following. The energy of any atomic configuration in the crystal lattice of the binary alloy, where every site is occupied by A or B atom, is possible to write in the form of the expansion $E = \sum V_\alpha P_\alpha$, where summation is done on all clusters. V_α — effective cluster interactions. P_α — product of the $s_i = (\pm 1)$ values, where index i runs about on the nodes of cluster. Cluster decomposition is the P_α basis expansion and it represents the generalization of the Ising model. V_α — structurally independent parameters, which are needed to be defined. An effectiveness of the cluster decomposition application is based upon the fact that, as a rule, it is possible to do with clusters of small dimension like, for instance, of 2, 3 or 4. In the present paper the pair approximation was used: clusters possess dimension of 2. Energy values for these clusters might be obtained from *ab-initio* calculations of the electronic structure for the set of the model ordered structures. Total energies of such structures together with known parameters give linear set of equations, which the unknown interaction values are found from. To solve this task, the high precision *ab-initio* FLAPW method (Wien2k package [13]) was used in the present paper. Exchange-correlation potential was calculated in the frame of gradient approximation (GGA) in accordance with Purdue-Burke-Ernzerhof model [14]. The number of k -points in the first Brillouin zone is 1000. The number of plane waves per atom in a basic set was equal to 160. This made it possible to ensure the precision for the total energy calculation of 0.001 eV. Calculations of the total energies of the ordered crystal structures were carried out taking into account full structural optimization, which includes lattice parameters and the unit cell atomic positions optimization.

Calculations have shown that in the FCC iron lattice pair potentials for nitrogen-nitrogen (N–N) interatomic interaction depend essentially upon nitrogen concentration. In this work two sets of pair potentials of N–N

Table 1. Coefficients of the set of equations c_i , total energies of the model structures E and pair potentials of atomic interactions of the nitrogen atoms v_i (eV) for Fe_4N nitride

Type of structures	n	A_0	A_1	c_1	c_2	c_3	c_4	E_n	
Fe_8N_2	1	1	0	0	1/2	1	1/2	-35007.361	
	2	1	0	1/2	1/2	0	1/2	-35007.293	
Fe_{48}N_6	3	0	1	0	1/24	0	7/12	-34820.995	
Fe_{32}N_4	4	0	1	0	1/4	0	1/4	-34821.009	
	5	0	1	0	3/16	0	3/8	-34820.992	
	6	0	1	0	0	0	3/4	-34820.998	
	7	0	1	0	0	3/8	0	-34820.995	
	8	0	1	3/16	0	0	0	-34820.963	
	9	0	1	1/16	0	1/8	0	-34820.986	
			E_0	E_1	v_1	v_2	v_3	v_4	
			-35007.368	-34820.998	0.169	-0.022	0.014	0.004	

Table 2. Coefficients of the set of equations c_i , total energies of the model structures E and pair potentials of atomic interactions of the nitrogen atoms v_i (eV) for $\text{FeA}_{0.0625}$ ($A = \text{N}, \text{C}$) alloys

Type of structures	n	A_0	c_1	c_2	c_3	c_4	c_5	E_n^{N}	E_n^{C}
Fe_{32}A_2	1	1	1/32	0	0	0	2/32	-34727.814	-34699.455
	2	1	0	0	0	0	0	-34727.817	-34699.460
	3	1	0	0	1/16	0	0	-34727.818	-34699.458
	4	1	0	0	0	1/8	0	-34727.813	-34699.453
Fe_{48}A_3	5	1	0	1/48	0	0	0	-34727.810	-34699.453
	6	1	0	0	2/48	2/48	2/48	-34727.817	-34699.457
		E_0	v_1	v_2	v_3	v_4	v_5		
N-N	1	-34727.817	0.131	0.298	-0.013	0.030	-0.024		
C-C	2	-34699.460	0.177	0.338	0.028	0.056	-0.007		

interaction (one, which describes short range order in Fe_4N nitride, and another one — for $\text{FeN}_{0.0625}$ austenite) have been calculated. One set of C-C pair potentials was also calculated for $\text{FeC}_{0.0625}$ austenite.

To define first set of potentials, the total energies of two ordered Fe_8N_2 structures, six Fe_{32}N_4 structures and one Fe_{48}N_6 structure have been calculated. According to Fe-N phase diagram [8] the formation of Fe_4N nitride in FCC iron matrix is possible in 12.5–25 at.% concentration range. Stoichiometry of the chosen model structures corresponds to this concentration interval. All calculations were carried out in spin-polarized ferromagnetic approach in order to describe ordering in the nitride, which is ferromagnetic itself. Calculation results for pair potentials and corresponding coefficients in the total energy equations for all structures

$E = A_0E_0 + A_1E_1 + \sum c_i v_i$ are given in Table 1. To define the set of potentials of the $\text{FeA}_{0.0625}$ ($A = \text{N}, \text{C}$) austenites, total energies of the five ordered Fe_{32}A_2 ($A = \text{N}, \text{C}$) structures and two Fe_{48}A_3 ($A = \text{N}, \text{C}$) ones were calculated. As these austenites are paramagnetic, calculations were carried out in non-spin-polarized approximation. Calculated pair potentials and corresponding coefficients in the total energy equations for all structures $E = A_0E_0 + \sum c_i v_i$ are presented in Table 2. Two sets of pair potentials for nitride and nitrogenous austenite are essentially different. In the case of nitride, nitrogen atoms attraction is observed in the second coordination sphere, while in the case of austenite — in the third one, which must lead to fundamentally different short range order in these materials. Poten-

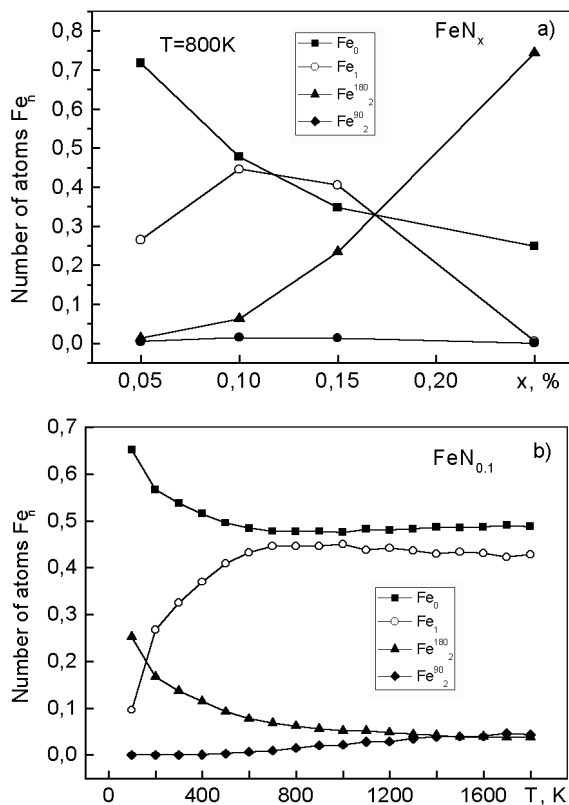


Fig. 1. a) Concentration dependences of the number of different iron atoms in FeN_x ($x = 0.05, 0.1, 0.15$) alloy and Fe_4N nitride; b) Temperature dependences of the number of different iron atoms in $FeN_{0.1}$ alloy.

tials for nitrogenous and carbon austenite are also different. The C-C interaction is characterized by repulsion in the third coordination sphere.

Different thermodynamic characteristics of nitride and austenitic $FeN_{0.0625}$ alloy were calculated in the broad temperature interval by Monte-Carlo method using two sets of the obtained potentials. Changes in nitrogen atomic positions were carried out with the hopping probabilities according to Metropolis. A cell with 24^3 atomic positions was used. Temperature step was 100 K with fixed nitrogen concentration. Short range order calculation was conducted with the decrease of temperature. Equilibrium configuration of the previous calculation was used as a starting one. Phase transformation points were found from the maximum location on the heat capacity versus temperature curve. Short range order modeling in FeN_x alloy with primary set of potentials

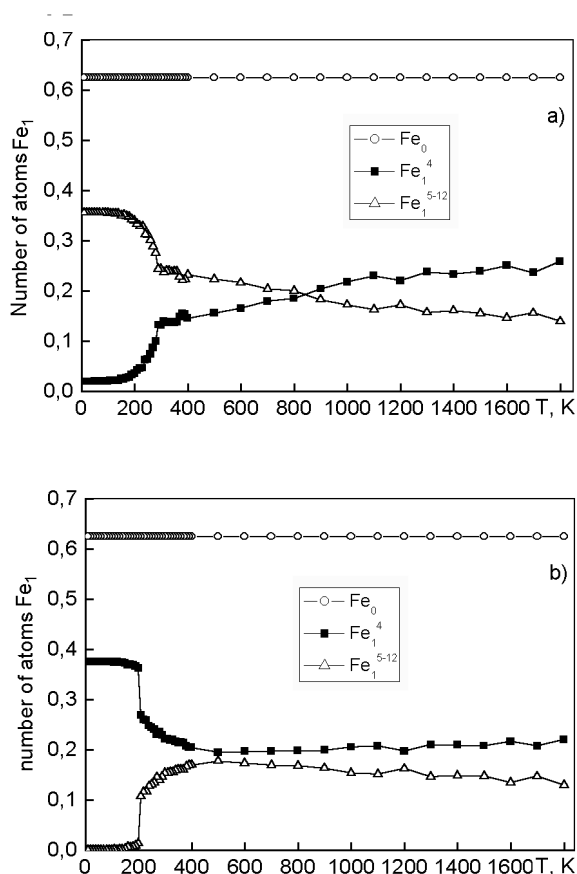


Fig. 2. Temperature dependences of the number of different iron atoms in a) $FeN_{0.0625}$, b) $FeC_{0.0625}$ alloys.

was conducted for concentrations $x = 0.05, 0.10, 0.15, 0.25$. Fig. 1 shows concentration dependencies of the number of different type iron atoms in alloy at temperature $T = 800$ K. As it can be seen at $x = 0.25$ nitrogen concentration (Fe_4N nitride), only atoms Fe_{2-180} (Fe_2 atom possesses nitrogen atoms, which are under the angle 180°) and atoms Fe_0 exist. It is an evidence of Fe_4N nitride phase formation. Calculations have shown that this phase forms at 800 K, which correlates with the experimental value of the nitride formation temperature (923 K). Further, Monte-Carlo modeling of the short range order in austenitic alloys with smaller nitrogen concentrations was carried out with the help of the same interaction pair potentials. Calculations have also shown that at 800 K iron atoms of different kinds exist in these alloys. For instance, there are two kinds atoms: atom Fe_1 , which possesses one nitrogen atom, and atom Fe_2 , which possesses two nitrogen atoms under the angle 90° . However, during

the modeling for alloys of all $x = 0.05$, 0.10, 0.15 concentrations starting from certain temperature, which decreases with the decrease of nitrogen concentration, the ordering takes place, which is characteristic for nitride formation. It contradicts the experimental data, as it is well-known that in the austenitic alloys no nitride formation is observed at such nitrogen concentrations. Thus, the set of potentials given in Table 1 does not describe the short range order in austenite alloy correctly.

For Monte-Carlo modeling of the short range order in nitrogenous and carbon austenites the pair potentials were used. The potentials were obtained with the help of model structures Fe_{32}A_2 and Fe_{48}A_3 ($\text{A}=\text{N}, \text{C}$), which are actually modeling $\text{FeA}_{0.0625}$ ($\text{A} = \text{N}, \text{C}$) alloys. Calculations have shown that in the case of nitrogenous austenite no Fe_4N nitride formation is observed at the temperature decrease. Fig. 2 shows the results of the short range order modeling in $\text{FeA}_{0.0625}$ ($\text{A} = \text{N}, \text{C}$) alloys. The temperature dependence of the number of iron atoms of different type (Fe_1^4 , Fe_1^{5-12} and Fe_0) was calculated too. Fe_1^4 atoms possess one impurity atom and 4 iron atoms in the first coordination sphere. Correspondingly, Fe_1^{5-12} atoms possess from 5 to 12 iron atoms of Fe_1 type. For the $\text{FeN}_{0.0625}$ nitrogenous austenite the increase in number of Fe_1^{5-12} atoms with the decrease of temperature (Fig. 2a) is an evidence of the partial ordering of the nitrogen atoms in the FCC iron lattice. For $\text{FeC}_{0.0625}$ carbon austenite (Fig. 2b), starting from 400 K the sharp decrease of the amount of Fe_1^{5-12} atoms is observed, that is an evidence of carbon atoms disordering in the FCC iron lattice. Analysis of the results has shown that nitrogen atoms are situated mainly in the third coordination sphere in respect to each other, while carbon atoms — in the 5th and 6th coordination spheres. It means that, in the case of nitrogenous austenite with the temperature decrease, Fe_6N octahedra, consisting of Fe_1 atoms, unite but do not possess common iron atoms. In the case of carbon austenite the carbon atoms are distributed at the maximal distance from each other. Actually, the phase of Fe_6N stoichiometry with the short range order of the nitrogen atoms in the third coordination sphere is formed in the FCC iron lattice of the nitrogenous austenite. The obtained results lead to the conclusion that in this case it is impossible to form the long range order over nitrogen atoms. Fe_1^4 atoms are situ-

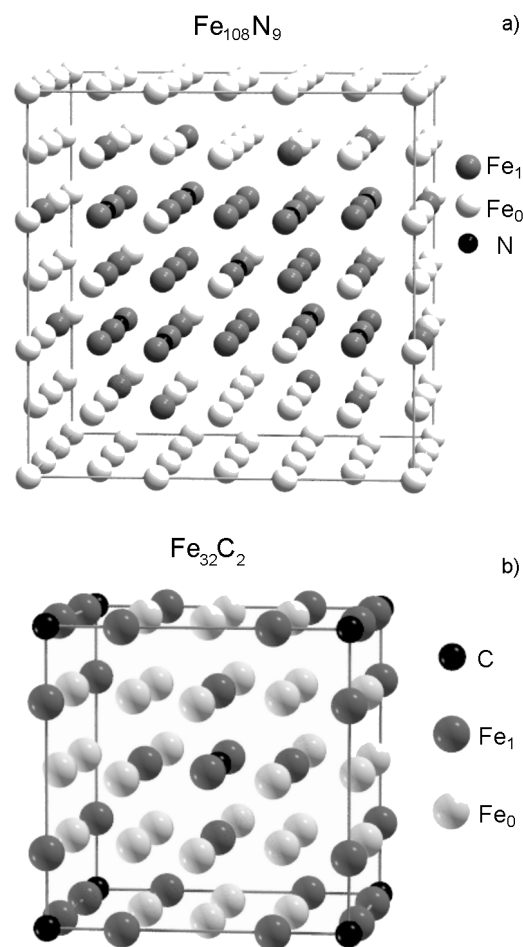


Fig. 3. a) Structure $\text{Fe}_{108}\text{N}_9$, simulating the nitrogen atoms distribution in the third coordination sphere of FCC iron lattice. b) Structure Fe_{32}C_2 , simulating the nitrogen atoms distribution in the sixth coordination sphere of FCC iron lattice.

ated on the surface of this phase. As it can be seen in Fig. 2a, the number of these atoms decreases sharply starting at the temperature of formation of the short range order over nitrogen and formation of the phase with Fe_6N stoichiometry. For the carbon austenite with the temperature decrease, the number of Fe_1^4 iron atoms increases (Fig. 2b), which might help to explain smaller solubility of carbon atoms (9 at. %) comparing to nitrogen (10.5 at. %) in the FCC iron matrix. It has to be noted that the number of Fe_0 atoms does not depend upon temperature.

The results of this Monte-Carlo modeling allow singling out the fragment of FCC lattice, which demonstrates the distribution of nitrogen atoms in the third coordination sphere. Fig. 3a represents the scheme of

$\text{Fe}_{108}\text{N}_9$ structure, which might be a good model for the nitrogenous austenite. Fe_1 atoms are marked with the dark color around each nitrogen atom. These atoms form Fe_6N octahedra in the the FCC lattice. Fig. 3b shows Fe_{32}C_2 structure, which appeared to be energy favorable amongst all calculated structures. In this structure carbon atoms are situated in the 6th coordination sphere. It corresponds to $\text{Fe}_8\text{C}_{1-x}$ model proposed in [7] and might be a good model for the calculation of the hyperfine interactions.

3. Conclusions

In current study it was revealed that nitrogen atoms in the nitrogenous austenite can be partially ordered. In this case, its atomic structure is characterized by the presence of Fe_6N phase with the short range order over the atoms of nitrogen, which are located in the third coordination sphere.

The calculations have shown that, contrary to nitrogen, carbon atoms in iron FCC lattice repulse and settle at maximum possible distances from each other.

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***Ab-initio* моделювання ближнього порядку в аустенітних сплавах Fe–N і Fe–C**

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У роботі теоретично досліджено атомну будову азотистого та вуглецевого аустенітів. Високоточним *ab-initio* методом FLAPW розраховано парні потенціали міжатомної взаємодії азот-азот і вуглець-вуглець в ГЦК гратці заліза. Ці потенціали використано для Монте-Карло моделювання ближнього порядку у системі Fe–N та Fe–C. Встановлено, що в ГЦК гратці заліза атоми азоту можуть бути частково впорядковані. У цьому випадку атомна структура азотистого аустеніту характеризується наявністю фази Fe_6N з ближнім порядком за атомами азоту, який розташовується у третій координаційній сфері. Розрахунки показали, що на відміну від азоту атоми вуглецю в ГЦК гратці заліза відштовхуються і розташовуються на максимально можливих відстанях один від одного.