Hybrid approach to computer design “self-healing” ferritic steels: quantum mechanical calculations, statistical and physico-empirical models, thermodynamic optimization and forecasting

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Abstract. The analysis of experimental data on neutron-structural studies of the sigma - phase of the alloys of the Fe-Cr system, obtained by Yakel, was carried out, which made it possible to introduce the concept of coordination spheres with an average radius around atoms located on all five sublattices of the crystal structure of sigma - phase. This analysis made it possible to develop a simplified statistical three-sub-lattice model for the sigma-phase in order to calculate the structural and thermodynamic properties taking into account its homogeneity region in Fe-(Cr, V, Mo) systems. The functional of the free mixing energy of the sigma - phase is written down as a function of the pair energies of the atoms of the components located on different sublattices of the sigma - phase, as well as the configurational entropy in the Gorsky-Bragg-Williams approximation. A system of equations of state is obtained by minimizing the free energy functional over different configurations. The independent energy parameters of the model are calculated by “linking” to the results of quantum mechanical calculations of the total energy and mixing energy of the sigma - phase of stoichiometric compositions for the ground state relative to sigma - phases of pure components. The solution of the system of equations of state allows one to calculate the distribution of atoms of both components over all sublattices of the sigma - phase, thermodynamic properties depending on the composition and temperature. In order to take into account the effect of temperature on the magnetic component of the free energy of mixing for the sigma phase, within the framework of the Inden-Hillert-Jarl model, estimates of the mean magnetic moment and Curie temperature are made for both the sigma phase of the Fe and the concentration dependences in the Fe-V system.
1. Introduction
Developed over the past three decades, ferritic steels (FS), as well as ferritic steels with hardening dispersed oxide particles, in order to use them as structural materials for a new generation of fast-neutron nuclear reactors, have significant advantages over austenitic steels. Taking into account that FS should be used in the temperature range 650-700°C for 50-60 years, the use of only experimental methods to find the optimal chemical composition for FS with the required mechanical properties and significant resistance to high-temperature creep can be extremely time-consuming. Therefore, it is rational to use the methods of thermodynamic design of high-temperature stable FS and to predict their physical and mechanical properties.

In [1], a model was proposed that takes into account the anisotropy of spin density, short-range order, and size factor for bcc solutions in Fe-(Cr, V, Mo) systems. Analysis of the results of quantum mechanical calculations (QMC) of the total energy and average magnetic moment for bcc-ferromagnetic (FM) Fe, depending on the volume for the ground state, made it possible to introduce the concept of partial magnetic moments of Fe atoms located on 1 - 4 coordination spheres (CS), and calculate their values. Based on the introduced concepts of the partial magnetic moments of Fe atoms, a three-sub-lattice model (3PM) was formulated in [1] for binary FM bcc alloys of the Fe - M systems (where M is the alloying component in the paramagnetic state). Free energy functional for 16 atomic cell is constructed. The size factor was taken into account in a self-consistent manner by expanding the energies of pair interaction between different atoms of both components located at different CSs in terms of the degrees of static displacements of atoms relative to the sites of an ideal crystal lattice. Within the framework of the 3SLM, taking into account the size factor, a system of equations of state for FM bcc alloys for binary systems rich in Fe was obtained in the approximation 1 - 3 CS. The estimates show that it is the anisotropy of the distribution of magnetic moments in the bcc lattice of Fe that is responsible for the appearance of short-range order in bcc-ferromagnetic Fe-rich alloys of the Fe–(Cr, V, Mo) systems [1].

Taking into account the dimensional factor and analyzing the results of an increase in static displacements of matrix atoms located around an impurity atom in different coordination spheres made it possible to formulate a fundamental conclusion about the possibility of creating “self-healing” ternary alloys Fe- (8-9) at.% Cr- (0.75—0.8) at.% Mo (W) by blocking structural vacancies arising due to neutron irradiation through relaxation of static displacements of Fe and Cr atoms located around the formed vacancy. Test X-ray studies [2-3] obtained the relative deviations of the values of the inter-planar distances of the bcc - lattices of alloys of Fe- (Cr, V, Mo) systems relative to their values for the crystal lattice parameters of pure Fe, measured at different reciprocal lattice sites (310) and ( 220). Thus, the conclusion was confirmed that the static displacements of the matrix atoms increase with an increase in the number of coordination spheres relative to the impurity atom and with an increase in the dimensional factor.

The concentration region of stability of the bcc phase is limited by the presence of embrittlement phases, for example, in the Fe - (Cr, V, Mo, W) σ –, μ – or Laves (λ) – systems. Modeling the structural and thermodynamic properties of the σ – phase for binary systems, taking into account its homogeneity region for quantum mechanical calculations, presents significant difficulties, which is due to the presence of a large number of atoms in a crystal cell (30 atoms in its crystal structure containing 5 sublattices) with different coordination environment, Experimental determination of thermodynamic properties for intermetallic compounds, depending on the composition and temperature, also presents significant difficulties, due to sluggish diffusion processes to establish equilibrium. The use of statistical models is also difficult due to the presence in the structure of σ –, μ – or Laves – phases of a large number of sublattices and, as a consequence of the large number of energy parameters of pair interatomic interactions of atoms of components, equal to $5^2 = 25$. Therefore, the use of a hybrid approach, combining, on the one hand, the use of quantum mechanical calculations of the energies of formation of intermetallic compounds of stoichiometric compositions, and on the other hand, the use of statistical models makes it possible to simulate the structural and
thermodynamic properties of chemical compounds with homogeneity regions, which is the main subject of description in this work.

2. Analysis of neutron structure data for the sigma phase.

Table 1 presents in a compact form the results of the analysis of neutron-structural data obtained in the work of Yakel [2]. In the header of Table 1, the identifiers of the sublattices of the Sigma phase structure are indicated, on which atoms with different environments (with the environment of atoms) are located, the number of which corresponds to the coordination number.

| A4(CN=12) | B2(CN=15) | C8(CN=14) |
|-----------|-----------|-----------|
| M(A)-M(D) | 2.367     | 4         | M(B)-M(C) | 2.421     | 2         | M(C)-M(C) | 2.397     | 1         |
| M(A)-M(E) | 2.546     | 4         | M(B)-M(B) | 2.519     | 1         | M(C)-M(B) | 2.42     | 1         |
| M(A)-M(B) | 2.605     | 4         | M(B)-M(A) | 2.605     | 2         | M(C)-M(D) | 2.484     | 2         |
|           |           |           | (M(B)-M(D) | 2.685     | 4         | M(C)-M(D) | 2.489     | 1         |
|           |           |           | M(B)-M(E) | 2.835     | 4         | M(C)-M(D) | 2.492     | 1         |
|           |           |           | M(B)-M(E) | 2.922     | 2         | M(C)-M(E) | 2.761     | 2         |
|           |           |           |           |           |           | M(C)-M(E) | 2.771     | 2         |
|           |           |           |           |           |           |           | M(C)-M(C) | 2.841     | 4         |
| <R(A)>   | 2.506     | <R(B)>   | 2.7023    | <R(C)>    | 2.657     |
| ε₁₂=δR/<R(A)> | 0.0555 | ε₁₅=δR/<R(B)> | 0.1041 | ε₁₄=δR/<R(C)> | 0.0979 |

D8(CN=12) E8(CN=14)

| M(D)-M(A) | 2.366     | 1         | M(E)-M(E) | 2.265     | 1         |
| M(D)-M(D) | 2.422     | 1         | M(E)-M(E) | 2.295     | 1         |
| M(D)-M(C) | 2.484     | 2         | M(E)-M(D) | 2.532     | 1         |
| M(D)-M(C) | 2.489     | 1         | M(E)-M(A) | 2.547     | 2         |
| M(D)-M(C) | 2.492     | 1         | M(E)-M(D) | 2.565     | 1         |
| M(D)-M(E) | 2.532     | 2         | M(E)-M(C) | 2.761     | 2         |
| M(D)-M(E) | 2.565     | 2         | M(E)-M(C) | 2.771     | 2         |
| M(D)-M(B) | 2.695     | 2         | M(E)-M(B) | 2.835     | 2         |
|           |           |           |           | M(E)-M(B) | 2.922     | 2         |
| <R(D)>   | 2.527     | <R(E)>   | 2.64      |
| ε₁₂=δR/<R(D)> | 0.0637 | ε₁₄=δR/<R(E)> | 0.142 |

An analysis of the data presented in Table 1 shows, first, that the average radii of the surface of the coordination environment of atoms <R>, as centers located on sublattices A and D, as well as on sublattices C and E, are approximately equal to each other in pairs <R(A)>₁₂≈<R(D)>₁₂=2.53 and <R(C)>₁₄≈<R(E)>₁₄=2.64, respectively.

The first pair is fcc - similar, and the second pair of bcc - similar, judging by the coordination numbers of their environment. Secondly, the calculated relative linear deviations of the arrangements of atoms from the surface of a sphere with an average radius, which are surrounded by atoms that are the center and located on the sublattices A and D (C and E) demonstrate that they are ε₁₂(A)=δR/<R(A)>=0.056 ≈ ε₁₂(D)=δR/<R(D)>=0.064 are also approximately equal and (ε₁₄(C)=δR/<R(C)>=0.098 ≈ε₁₄(E)=δR/<R(E)>=0.142) are also approximately equal, taking into account that the atoms in the bcc lattice located in the 1st coordination sphere are at a relative distance...
\[ R_{111} / a = \sqrt{3}/2 \approx 0.866 \] (where \( a \) is the lattice parameter), and the atoms located in the 2nd coordination sphere are at a distance equal to \( R_{100} / a = 1 \).

Thus, the difference in the relative distances of atoms located on the 1st and 2nd coordination spheres is 0.134. This value is approximately equal to the average value \([\varepsilon_{14}(C)+\varepsilon_{14}(E)]/2 = 0.12\) of the relative deviation of atoms from the surface of the surrounding sphere, drawn relative to the central atoms located on the sublattices of the C and E sigma-phase. The above arguments allow us to simplify and replace real 5 sigma sublattices - phase by model with 3 sublattices on which atoms having a coordination environment of atoms of both components equal to 12, 14, and 15 can be located, which can be schematically represented by formula (1)

\[
(Fe,M)_{y_1}^{12} (Fe,M)_{y_2}^{12} (Fe,M)_{y_3}^{15} (Fe,M)_{y_4}^{15} (Fe,M)_{y_5}^{14} \Rightarrow (Fe,M)_{y_1}^{12} (Fe,M)_{y_2}^{12} (Fe,M)_{y_3}^{12} (Fe,M)_{y_4}^{15} (Fe,M)_{y_5}^{14}
\]

In formula (1) \( M = Cr, Mo, V, W \), i.e. the atoms of the components Cr, Mo, W or V can be placed as atoms of the second component. To give a quantitative form to relation (1), it is advisable to present the right side of formula (1) in expanded form

\[
(Fe,M)_{y_1}^{12} (Fe,M)_{y_2}^{12} (Fe,M)_{y_3}^{14} (Fe,M)_{y_4}^{14} \Rightarrow (Fe,M)_{y_1}^{12} (Fe,M)_{y_2}^{12} (Fe,M)_{y_3}^{12} (Fe,M)_{y_4}^{15} (Fe,M)_{y_5}^{14}
\]

In formula (2), the quantities \( y_1^{12}, y_2^{12} \) correspond to the atomic fractions of the 1st and 2nd atom of components located in the model sub-lattice with the coordination environment of atoms equal to 12 for the sigma phase in the Fe-M binary system. This is similarly true for other model sublattices.

### 3. Thermodynamic formulation of a three-sublattice model for the sigma-phase

#### 3.1. Motivation for formulating a three-sub-lattice model for the Sigma phase

Taking into account the application of the three-sub-lattice model for the sigma-phase for Fe- (Cr, V, Mo, W) systems, it becomes necessary to take into account the size factor for both the bcc and sigma-phases. It should be noted that taking into account the presence of a large dimensional linear factor, for example, for bcc lattices \( \varepsilon_{lin} = [a(Mo) - a(Fe)]/ a(Fe) = (3.147-2.8665)/2.8665=0.098 \), which is equivalent to almost 32% of the relative difference volumes of atoms of components, it is very problematic to apply the method of coherent potential for bcc disordered solution of the Fe-Mo system. Whereas a more acceptable approach is to take into account the relaxation of the crystal lattice in the framework of the use of quantum mechanical calculations.

Due to the existence of different values of static displacements of iron and molybdenum atoms relative to the sites of an ideal crystal lattice, due to the presence of:

1) large dimension factor,
2) different masses of atoms, differing from each other by about 2 times, and
3) significantly different values of the bulk modulus of elasticity of the components (\( B(Mo) / B(Fe) = 265 GPa / 167 GPa = 1.59 \)) [3]

- therefore, the application of the method of variation of clusters seems to be little justified both for a disordered bcc \( Fe_{1-x}Mo_x \) solution and for the structure of the sigma-phase. Due to the fact that the lengths of the “edges” of the clusters will have different lengths (different lengths of the cluster edges - compare the results for the distances between atoms located in different sublattices and, accordingly, in their environments - Table 1), which will lead to an irregular cluster shape; for example, tetrahedrons will differ from the regular tetrahedron shape). In addition, the edge lengths of the clusters will vary with composition. Therefore, the clusters will take an irregular shape, taking into account that the “average” or effective modulus of elasticity of the solution will also change depending on the composition of the alloy. Therefore, the shape and size of the clusters will also depend on the composition, leading to the nonequivalence of such “non-rigid” clusters for different compositions.
3.2. Thermodynamic formulation of the three-sub-lattice model

For a closed system, the material balance conditions follow from the distribution of the atoms of the components over the model sublattices:

\[
\begin{align*}
& a^{12}y_1^{12} + a^{14}y_1^{14} + a^{15}y_1^{15} = 30 \cdot x_1, \\
& a^{12}y_2^{12} + a^{14}y_2^{14} + a^{15}y_2^{15} = 30 \cdot x_2,
\end{align*}
\]

where \( a^{12} = 10; \ a^{14} = 16; \ a^{15} = 4; \ \sum_{i=12,14,15} a^i = 30 \), and the values \( x_1, x_2 \) correspond to the molar fractions of atoms of 1 and 2 components, respectively.

Taking into account that the conditions for the connection between the number of atoms located in different sublattices and the total number of atoms in a cell are obtained per mole, therefore relations (3) will take the form

\[
\begin{align*}
& a^{12}y_1^{12} + a^{14}y_1^{14} + a^{15}y_1^{15} = x_1, \\
& a^{12}y_2^{12} + a^{14}y_2^{14} + a^{15}y_2^{15} = x_2,
\end{align*}
\]

\( a^{12} = a^{12} / 30 = 1 / 3; \ a^{14} = a^{14} / 30 = 7 / 15; \ a^{15} = a^{15} / 30 = 2 / 15. \)

After summing the equations in relations (4), we obtain the normalization conditions for the fractions of the filling of the sublattices with various types of atoms of chemical components:

\[
\begin{align*}
& y_1^{12} + y_2^{12} = 1; \ y_1^{14} + y_2^{14} = 1; \ y_1^{15} + y_2^{15} = 1. \\
& a^{12} + a^{14} + a^{15} = 1
\end{align*}
\]

Then the configurational component of the Gibbs energy functional of mixing for the phase, depending on the composition with respect to the phases of pure components for the ground state, will be written in the following form

\[
\sigma \Delta G_{\text{conf}}^\sigma (x, y_1^{12}, y_2^{15}; T = 0) = y_1^{12} \left( y_2^{12} \cdot \delta E_1^{12} + y_2^{14} \cdot \delta E_1^{14} + y_2^{15} \cdot \delta E_1^{15} \right) + \\
+ y_1^{14} \left( y_2^{14} \cdot \delta E_1^{14} + y_2^{14} \cdot \delta E_1^{14} + y_2^{15} \cdot \delta E_1^{15} \right) + y_1^{15} \left( y_2^{15} \cdot \delta E_1^{15} + y_2^{14} \cdot \delta E_1^{14} + y_2^{15} \cdot \delta E_1^{15} \right) + \\
RT \left\{ a^{12} \ln y_1^{12} + a^{14} \ln y_1^{14} + a^{15} \ln y_1^{15} \right\}
\]

On the left side of equation (7), the composition of the 2nd component is left as independent variables \( y_1^{12}, y_1^{14}, y_1^{15} \), and the general composition of the 2nd component \( x \equiv x_2 \), of the alloy is left as an external variable. Whereas the variable \( y_2^{14} = (x - a^{12} y_1^{12} - a^{15} y_1^{15}) / a^{14} \) is expressed in terms of the selected independent variables and the external variable, and the remaining variables are the proportions of filling the first component by atoms, due to the presence of normalization relations (5), are associated with the selected independent variables. The equation (7) includes 9 energy parameters of the model \( E_1^{12}, E_1^{14}, ..., E_1^{15} \), which can be calculated by “linking” to the results of quantum-mechanical calculations for the ground state at fixed composition values equal to the composition values for the corresponding stoichiometric chemical compounds with the \( \sigma \)-phase structure, as is done in an example of the Fe-Cr system [3]. However, in [3], the results of quantum-mechanical calculations on the mixing energy obtained in [4-5] for the paramagnetic states of chemical compounds with the structure sigma - phases of stoichiometric compositions were used as input data, while in the proposed approach it is advisable to use the results of quantum -mechanical calculations carried out taking into account magnetism in work [6]. The minimization of the functional of the configurational free energy of mixing depending on the temperature, composition of the second component and two independent internal degrees of freedom (7) over independent configurational degrees of freedom, taking into account the constraint equations (4)-(5), makes it possible to obtain a system of transcendental equations, and for the ground state it transforms into a system of linear equations for the energy parameters of the model.
under the conditions of stability

\[
\frac{d^2 \Delta^\sigma G^\sigma (x, T)}{dy_2^{(12)}} = 0 \\
\frac{d^2 \Delta^\sigma G^\sigma (x, T)}{dy_2^{(15)}} = 0
\]  

(8)

The details of this procedure are described in [3] for the paramagnetic states of the sigma phase.

4. Evaluation of the magnetic properties of the sigma - phase in the Fe - V system

At elevated temperatures, the use of the functional for the Gibbs energy requires the inclusion, in addition to the configurational free energy described by Eq. (7), three more terms: 1) the vibrational component of the free energy, for example, in the framework of the Debye model, 2) the electronic component of the free energy due to the excitation of the electron density in the vicinity of the Fermi surface, measured in the form of electronic heat capacity, 3) the magnetic component of the free energy, for example, in the framework of the empirical Inden-Hillert-Jarl model [8]-[10], often used in the framework of the CALPHAD – method.

The last model requires knowledge of 3 parameters: 1) the difference in magnetic energies between bcc - and Sigma - structures for both pure Fe and alloys, depending on the composition. 2) the average magnetic moment <m> also for sigma - phases of pure Fe and the dependence of <m> for sigma phase alloys on the composition; 3) Curie temperature (Tc) for sigma - phases of pure Fe and its dependence on composition for alloys with a structured sigma phase. In addition, according to the Inden-Hillert-Jarl model, the magnetic component of the free energy for sigma phase alloys can be calculated from two dependences on the composition <m (x)> and Tc (x). From the listed characteristics, the energy difference for the ground state of the pure sigma phase of Fe can be calculated by calculating the difference in total energies for the ferromagnetic and paramagnetic states, respectively, minimized in volume. In view of the great difficulties in calculating the total energies for stoichiometric compositions for chemical compounds with the structure of the Sigma-phase without the possibility of taking into account the arrangement of atoms of both components in its different sublattices, except for the calculation for the Sigma-phase of pure components, therefore, it is necessary to estimate the magnetic characteristics based on the analysis and processing of experimental data. In this section, we have presented such an analysis.

In [7], experimental studies were carried out to measure the partial and average values of the magnetic moment (<m>), depending on the composition, on alloys with the sigma structure - the phase in the Fe-V system. The alloys were preliminarily heat treated at 973K for 25 days. Then they in [7] were investigated using Mössbauer spectroscopy in the range 5 - 427K. These results for <m> depending on the composition are presented in Figure 1. The processing of these data is presented in the form of constructing a linear dependence on the composition and its extrapolation to zero composition values allows us to estimate the value of <m> for the metastable sigma phase of pure Fe, which is 2.165 mB / atom.
A similar processing of the Curie temperature (Tc) values depending on the composition, which is shown in Figure 2, with different dependences of the trend curves on the composition of the linear and cubic leads to different values of the root mean square errors. The result obtained by extrapolation in Fig. 1 is in good agreement with the value of the average magnetic moment calculated in the framework of quantum mechanical calculations [12] for the sigma phase of pure iron \( <m> = 2.273 \text{ m}_B/\text{atom} \).

**Figure 1.** Dependence of the average magnetic moment on the composition for alloys with the sigma structure - the phase of the Fe-V system, obtained on preliminarily heat-treated alloys at 973K using Mössbauer spectroscopy in the range of 5 ÷ 427K according to the results of [7].

**Figure 2.** Concentration dependence of the Curie temperature for the sigma - phase in the Fe-V system, obtained using Mössbauer spectroscopy in [7] on alloys preliminarily heat-treated at 973K for 25 days; measurements were carried out in the temperature range 5 - 427K. Left - the trend line is presented as a linear relationship; on the right - the dependence for the trend curve is plotted as a 3rd degree polynomial.
In the first case, the left side of Figure 2 leads to the $T_C$ value for the Sigma-phase of pure Fe 790K, while in the right-hand fragment of Figure 2, the $T_C$ value for the Sigma-phase of pure Fe gives a value of $T_C \approx 1000K$. In view of the lesser magnitude of the error, it should be preferred.

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