ISSN 1561-8358 (Print)
ISSN 2524-244X (Online)

МАТЕРИАЛОВЕДЕНИЕ, МЕТАЛЛУРГИЯ

MATERIALS ENGINEERING, METALLURGY

UDC 669.12+669.784:539.219.3
https://doi.org/10.29235/1561-8358-2021-66-1-28-36

Received 07.12.2020
Поступила в редакцию 07.12.2020

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NON-EQUILIBRIUM THERMODYNAMICS MODEL FOR CALCULATING DIFFUSION FLUXES UNDER PHASE TRANSFORMATIONS IN ALLOY STEELS

Abstract. The phase transformations in alloyed iron-carbon alloys is largely related to diffusion of components, foremost to the carbon. For the analysis of diffusive processes in alloy steels, it is possible to use the mathematical methods of non-equilibrium thermodynamics. The equation for the diffusive fluxes of the system contains unknown in general case of coefficients activity of elements and vacancies, and their derivatives for to the concentrations, that extraordinarily makes it difficult being of values of cross coefficients. In the article a non-equilibrium thermodynamics methodology of calculation of diffusive fluxes at presence of two phases in alloy steels is described. It allows one to calculate both direct- and cross coefficients in the Onsager equations. Formulas for calculation of thermodynamics forces in the alloy steel – for iron, alloying element of substitution – chrome, of element of introduction – carbon and vacancies, are presented. Common expressions are suggested for calculation of cross-factors, motive forces and fluxes in the Onsager's equations for a multicomponent thermodynamic system. The example of using the developed model to find changes in concentrations and diffusion fluxes over time is given. For the model system used, it was established that at the stage of predominant diffusion of carbon in the alloy steel, cementite inclusions with a size of about 18 nm are formed rather quickly (within ~ 200 s). The technique developed in the article allows one to perform diffusion kinetics calculations in multicomponent thermodynamic systems, which are also iron-carbon alloys and to control the size of the phases formed, for example, of carbide nanoparticles.

Keywords: non-equilibrium thermodynamics, phase transformations, diffusion fluxes, motive forces, cross-factors, alloy steels, nanoparticle

For citation: Bobyr S. V. Non-equilibrium thermodynamics model for calculating diffusion fluxes under phase transformations in alloy steels. *Vestsi Natsyyanal'nai akademii navuk Belarusi. Seryya fizika-technichnych navuk = Proceedings of the National Academy of Sciences of Belarus. Physical-technical series*, 2021, vol. 66, no. 1, pp. 28–36 (in Russian). https://doi.org/10.29235/1561-8358-2021-66-1-28-36

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НЕРАВНОВЕСНАЯ ТЕРМОДИНАМИЧЕСКАЯ МОДЕЛЬ ДЛЯ РАСЧЕТА ДИФФУЗИОННЫХ ПОТОКОВ ПРИ ФАЗОВЫХ ПРЕВРАЩЕНИЯХ В ЛЕГИРОВАННЫХ СТАЛЯХ

Аннотация. Фазовые превращения в легированных сплавах железа с углеродом в значительной степени связаны с диффузией компонентов, в первую очередь с углеродом. Для анализа диффузионных процессов в легированных сталях можно использовать математические методы неравновесной термодинамики. Уравнения для диффузионных потоков системы содержит неизвестные в общем случае коэффициенты активности элементов и вакансий и их производные по концентрациям, что чрезвычайно затрудняет определение значений перекрестных коэффициентов. В статье разработана неравновесная термодинамическая методика расчета диффузионных потоков при наличии двух фаз в легированных сталях. Она позволяет рассчитать в уравнениях Онзагера как прямые, так и перекрестные коэффициенты. Приведены формулы расчета термодинамических сил для легированной стали – железа, легирующего элемента замещения – хрома, элемента введения – углерода и вакансий. Предложены общие выражения для расчета перекрестных коэффициентов, движущих сил и потоков в уравнениях Онзагера для многокомпонентной

термодинамической системы. Приведен пример использования разработанной модели для поиска изменений концентраций и диффузионных потоков во времени. Для используемой модельной системы установлено, что на стадии преимущественной диффузии углерода в легированной стали включения цементита размером около 18 нм образуются довольно быстро (в течение ~ 200 с). Разработанная в статье методика позволяет проводить расчеты диффузионной кинетики в многокомпонентных термодинамических системах, которыми также являются сплавы железо-углерод, и контролировать размер образующихся фаз, например наночастиц карбидов.

Ключевые слова: неравновесная термодинамика, фазовые превращения, диффузионные потоки, движущие силы, перекрестные коэффициенты, легированные стали, наночастицы

Для цитирования: Бобырь С. В. Неравновесная термодинамическая модель для расчета диффузионных потоков при фазовых превращениях в легированных сталях / С. В. Бобырь // Вес. Нац. акад. навук Беларусі. Сер. фіз.-тэхн. навук. – 2021. – Т. 66, № 1. – С. 28–36. https://doi.org/10.29235/1561-8358-2021-66-1-28-36

Introduction. The phase transformations in the alloyed iron-carbon alloys is largely related to diffusion of components, foremost to the carbon [1, 2]. For the analysis of diffusive processes in alloy steels [3–5] it is possible to use the mathematical methods of non-equilibrium thermodynamics. In general case, thermodynamics equations of motion look like [3]:

$$J_i = \sum_{k=1}^{N} L_{ik} X_k \, (i = 1,.., N), \tag{1}$$

where J_i are fluxes; X_k is thermodynamics forces; $L_{ik} = L_{ki}$ is kinetic Onsager's coefficients [5]; *i, k* are numbers of charges (substrate of transfer). Basic motive forces of the phase transformations in non-equilibrium thermodynamics are gradients of chemical potentials μ_i for components of the system [3–5]:

$$Xi = -\nabla \mu_i . \tag{2}$$

The theory of diffusion in metallic alloys with the vacancy mechanism of migration of atoms was developed by Darken [6]. Basic limitations of this theory are related to the necessity of diagonal matrix of Onsager and condition of equilibrium of concentration of vacancies [7]. In work [8] the considered kinetics of diffusion is in the bimetallic system, taking into account the non-diagonal coefficients of Onsager's matrix. Thermodynamics potentials in this work are presented in a kind:

$$\mu_i = \mu_i^0 = RT \ln(\gamma_i c_i), \tag{3}$$

where c_i – concentration of element *i*; γ_i – coefficient of activity of element *i*, what is considered as dependency upon one concentration of c_i.

Equation for the diffusive fluxes of the system contains coefficients of activity of elements and vacancies, unknown in general case, and their derivatives for the concentrations, that extraordinarily makes it a difficult being of values of lines and cross coefficients. In work [8] expressions of cross coefficients are found for an ideal solid solution.

Using this method for calculation of fluxes at presence of formation of phases in the system is a very difficult task. Therefore, at consideration of the interrupted systems, I mean systems, that contain a few phases, the fluxes of elements and vacancies pass between that as thermodynamics forces, it is possible to use the eventual finite differences of chemical potentials ($-\Delta\mu_i$) [9, 10]. If, for example, we use two sizes – concentrations of carbon and iron, as degrees of process of graphitization, concordantly (1), equations of motion look like:

$$J_1 = L_{11} X_1 + L_{12} X_2 , \tag{4.1}$$

$$J_2 = L_{21} X_1 + L_{22} X_2 , \tag{4.2}$$

where J_1 is a flux of carbon that characterizes speed of process of graphitization; J_2 is a flux of iron; $X_1 = (-\Delta\mu_{Fe})$, $X_2 = (-\Delta\mu_C)$ are thermodynamics forces of iron and carbon. The finite difference of potential between two phases has a sign "+" at its increase, and the flux is directed towards the reduction of potential, so the expression for the forces has a sign "–".

In works [10, 11] it is shown that in the complex process with two fluxes of charges, an increase of one potential takes place, which means one process "conducts", and the other is a "derivative". The "derivative" process itself, which is separated from the "leading", is impossible, since thermodynamically it is not expedient.

In the system of equations (2) thermodynamics force ($-\Delta\mu_{\mathrm{Fe}}$) is negative and it slows down the process overall. The diffusion of iron is induced in a process, and diffusion of carbon is leading.

Thus, process of formation of phase (to the carbide, intermetallic) in the triple system Fe–C–X (alloying element), by analogy with the process of graphitization [10, 12], must be accompanied by the intensive enough transfer of solid solution (alloyed iron). That provides the possibility of growing a phase with a lower density – carbide or intermetallic in it. This condition can be executed as a result of iron flux growing due to cross kinetic coefficient of L_{21} [10].

At presence of alloying element in the triple system, for example, chrome, the equation of motion must contain additional components that characterize diffusion of this element [13].

The non-equilibrium thermodynamic theory of multicomponent systems continues to develop successfully, see, for example [14, 15]. However, obtaining direct kinetic equations for the concentrations and fluxes of system elements is difficult, because of unknown values of cross coefficients. Therefore, the problem of successive theoretical description of diffusive phase-to-phase fluxes in the alloy steels remains.

The aim of work is development of non-equilibrium thermodynamics methodology of calculation over time of diffusive fluxes, kinetic coefficients and thermodynamics forces in the multicomponent alloy steels.

Formulation of the problem and basic ratios. Will consider the process of phase formation in the alloy steel. From the point of view of thermodynamics such a process is a transition from metastable to the stable state with formation of a new phase K. We take into account that in the system Fe–C–X (alloying element) there are two phases – alloyed α-phase (F) and formed phase (K), the fluxes of carbon (J_{C}), iron (J_{Fe}), alloying element (J_X) and vacancies (J_V) (Figure 1). The flux of vacancies in a formed phase will be considered equal to the flux of vacancies in a ferrite.

Let us consider that the volume of the system can change in general case, which is the reason that the condition of complete equality of streams to 0 is not executed:

$$J_{\mathrm{Fe}} + J_X + J_{\mathrm{C}} + J_V \neq 0.$$

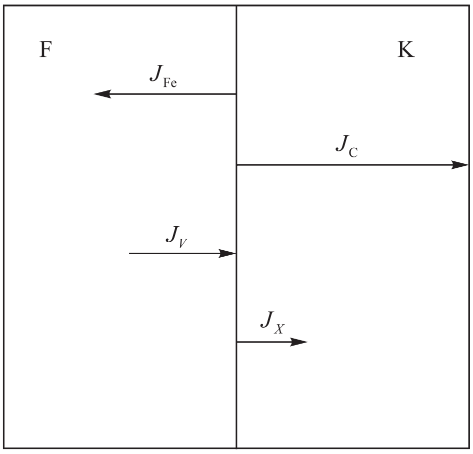

Fig. 1. Scheme of the phase formation (K – carbide) in the alloy steel

According to (1), the thermodynamic equations for the fluxes take the form:

$$J_{\mathrm{Fe}} = -L_{11}\Delta\mu_{\mathrm{Fe}} - L_{12}\Delta\mu_{\mathrm{C}} - L_{13}\Delta\mu_X - L_{14}\Delta\mu_V, \tag{5.1}$$

$$J_{\mathrm{C}} = -L_{21}\Delta\mu_{\mathrm{Fe}} - L_{22}\Delta\mu_{\mathrm{C}} - L_{23}\Delta\mu_X - L_{24}\Delta\mu_V, \tag{5.2}$$

$$J_X = -L_{31}\Delta\mu_{\mathrm{Fe}} - L_{32}\Delta\mu_{\mathrm{C}} - L_{33}\Delta\mu_X - L_{34}\Delta\mu_V, \tag{5.3}$$

$$J_V = -L_{41}\Delta\mu_V - L_{42}\Delta\mu_{\mathrm{C}} - L_{43}\Delta\mu_X - L_{44}\Delta\mu_V, \tag{5.4}$$

where J_{Fe}, J_{C}, J_X, J_V – fluxes of iron, carbon, alloying element and vacancies accordingly. O the base of generals of non-equilibrium thermodynamics, it is possible to find the value of kinetic coefficients, the same as it was executed in process [13]. In the conditions of complete equilibrium

$$\Delta\mu_{\mathrm{Fe}} = 0,\ \Delta\mu_{\mathrm{C}} = 0,\ \Delta\mu_X = 0 \text{ and } \Delta\mu_V = 0.$$

However, for the linear thermodynamics system there is also a possibility of dynamic equilibrium, at that all fluxes are equal 0, but some thermodynamics forces in the system do not equal to zero (there are their variations) [4, 13]. For the first time such an opportunity is considered by the author in the work [12] for the double system, and then for the triple system [13]. Will consider this possibility for the 4-component thermodynamics system. From equations (5) follows, that near-by an equilibrium, at presence of variations of thermodynamics forces, next terms must be executed:

$$J_{\mathrm{Fe}} = 0 \Rightarrow L_{11}\delta\mu_{\mathrm{Fe}} + L_{12}\delta\mu_{\mathrm{C}} + L_{13}\delta\mu_{\mathrm{Cr}} + L_{14}\delta\mu_{V} = 0, \tag{6.1}$$

$$J_{\mathrm{C}} = 0 \Rightarrow L_{21}\delta\mu_{\mathrm{Fe}} + L_{22}\delta\mu_{\mathrm{C}} + L_{23}\delta\mu_{X} + L_{24}\delta\mu_{V} = 0, \tag{6.2}$$

$$J_{X} = 0 \Rightarrow L_{31}\delta\mu_{\mathrm{Fe}} + L_{32}\delta\mu_{\mathrm{C}} + L_{33}\delta\mu_{X} + L_{34}\delta\mu_{V} = 0, \tag{6.3}$$

$$J_{V} = 0 \Rightarrow L_{41}\delta\mu_{\mathrm{Fe}} + L_{42}\delta\mu_{\mathrm{C}} + L_{43}\delta\mu_{X} + L_{44}\delta\mu_{V} = 0, \tag{6.4}$$

where the variations of thermodynamics forces that provide the dynamic equilibrium of the system are marked by an index $\delta\mu_i$.

From the first equalization (6.1) we establish a connection between variations of forces:

$$\delta\mu_{\mathrm{Fe}} = -(L_{12} / L_{11})\delta\mu_{\mathrm{C}} - (L_{13} / L_{11})\delta\mu_{X} - (L_{14} / L_{11})\delta\mu_{V}. \tag{7.1}$$

Substituting (7.1) into equations (6.2)–(6.4), we find:

$$J_{\mathrm{C}} = (L_{22} - L_{21}L_{12} / L_{11})\delta\mu_{\mathrm{C}} + (L_{23} - L_{21}L_{13} / L_{11})\delta\mu_{\mathrm{Cr}} + (L_{24} - L_{21}L_{14} / L_{11})\delta\mu_{V} = 0, \tag{7.2}$$

$$J_{X} = (L_{32} - L_{31}L_{12} / L_{11})\delta\mu_{\mathrm{C}} + (L_{33} - L_{31}L_{13} / L_{11})\delta\mu_{\mathrm{Cr}} + (L_{34} - L_{31}L_{14} / L_{11})\delta\mu_{V} = 0, \tag{7.3}$$

$$J_{V} = (L_{42} - L_{41}L_{12} / L_{11})\delta\mu_{\mathrm{C}} + (L_{43} - L_{41}L_{13} / L_{11})\delta\mu_{\mathrm{Cr}} + (L_{44} - L_{41}L_{14} / L_{11})\delta\mu_{V} = 0. \tag{7.4}$$

At arbitrary variations $\delta\mu_{\mathrm{C},}$ $\delta\mu_X$ and $\delta\mu_V$ the linear system of equations (7.2)–(7.4) is commensurate, if coefficients at $\delta\mu_{\mathrm{C},}$ $\delta\mu_X$ and $\delta\mu_V$ equal 0, from what it is possible to find the partial decision of the system of equations (6) and (7). For the diagonal components of the system of equations (7.2)–(7.4) it is possible to write down:

$$L_{ik}L_{ki} = L_{ii}L_{kk},\ i,\ k = 1\ldots4.$$

Taking into account Onsager's ratio, we find connection between kinetic coefficients:

$$L_{ik} = L_{ki} = \pm\sqrt{L_{ii}L_{kk}},\ i,\ k = 1\ldots4 \tag{8}$$

The sign in front of the root is selected, based on the sign (direction) of the considered fluxes (see Figure 1). It is possible to insure a simple substitution, that undiagonal components of system of equations (7.2)–(7.4) also transform in 0. If we choose the sign of "–" for one of cross kinetic coefficients, then signs of other cross coefficients must be consistent. We found that a partial solution system of equations (6) is the same with unknown cross coefficients. Partial solution (8) of the linear 4-component system of equations (7) it is possible to generalize the component of linear thermodynamics system on N, so as a system of equations (7) has the same kind for the number of components of $n = 2, 3, 4, N$. Therefore, the correlation (8) for cross kinetic coefficients is executed at the number of components of $n = 2, N$.

Such approach allows finding cross coefficients in Onsager's equations since direct kinetic coefficients are expected. Thus, the equation (8) is correct for the systems, not too distant from an equilibrium, and for the real system, it is approximate.

General expressions for thermodynamics forces that operate in the system. We shall find general expressions for thermodynamics forces that operate in our system. For an example we will use steel of the system Fe–C–Cr with 0.15 % C and 5.0 % Cr, that is tempered and annealed at 600 °C with formation of the alloyed carbide [13]. Consider that first there is a chrome with the concentration $C_{\mathrm{Cr}} = 0.05$, carbon with the concentration of $C_{\mathrm{C}} = 0.007$, concentration of iron egale $C_{\mathrm{Fe}} = 0.943$ in solid α-solution of this steel. After annealing during two hours concentration of iron in a solid α-solution rises to $C'_{\mathrm{Fe}} = 0.9574$, the concentration of chrome goes down to $C'_{\mathrm{Cr}} = 0.0425$. In the carbide of cementite there are chrome with mass part ~ 20 % (by the concentration of $C^{K}_{\mathrm{Cr}} = 0.20$) and carbon with the concentration of $C^{K}_{\mathrm{C}} = 0.25$, concentration of iron in the carbide $C'^{K}_{\mathrm{Fe}} = 0{,}55$. Concentration of vacancies Cv in a solid α-solution, is equal to 10^{-4}.

Thermodynamics force for a carbon can be written by the formula [16]

$$-\Delta\mu_C = -RT\ln\frac{a_C^K}{a_C^\alpha}, \tag{9}$$

where R – universal gas constant, T – a temperature of alloy, a_C^K is a size of thermodynamics activity of carbon in cementite, a_C^α is a size of thermodynamics activity of carbon in α-solution.

Variation of thermodynamics activity of carbon in an alloy at melting its component is possible to find on methodology [16, 17] from equation:

$$\ln(a_C / a_{C_0}) = \beta_i N_i, \tag{10}$$

where a_{C_0} is thermodynamics activity of carbon for an alloy in the standard state, β_i is a coefficient of influence of element on thermodynamics activity of carbon in an alloy, N_i is content of element in an alloy in atomic parts. We will consider that for our steel in the standard state $a_{C_0}^\alpha = a_{C_0}^K = a_{C_0}$, we mean cementite in steel with 0.15 % C is stable and is in an equilibrium with a solid solution at an endurance temperature 600 °C [10]. Using this condition and equation (9) and (10), find:

$$\ln\left(a_C^K / a_C^\alpha\right) = \beta_{Cr}^K N_{Cr}^K - \beta_{Cr}^\alpha N_{Cr}^\alpha. \tag{11}$$

The value of β_i is calculated by the coefficient of the phase distribution of the alloying element $K_i = N_i(K)/N_i(\alpha)$ and the atomic particle of carbon in the N_C alloy in the general form [16, 17]:

$$\beta_i = -\frac{(K_i - 1) + (N_C(K) - K_i N_C(\alpha))}{(K_i - 1)N_C + (N_C(K) - K_i N_C(\alpha))}. \tag{12}$$

With a small error for low-alloy alloys it is possible to accept $N_C(K) = 0.25$, content of carbon in α-phase of steel, taken for the diagram of the state of Fe–C $N_C(\alpha) \approx 0.001$. Using the coefficient K_{Cr} of distribution of chrome between α-phase and the carbide, equal 4, we can find equation for the calculation of coefficients of influence β_{Cr}:

$$\beta_{Cr} = -3.246/(3.0N_C + 0.246), \tag{13}$$

where $\beta_{Cr}^\alpha = -12.16$; $\beta_{Cr}^K = -3.26$.

Then from the expressions (9), (10) and (11) we can find values:

$$\ln\left(a_C^K / a_C^\alpha\right) = -0.6085 + 0.652 = 0.0425 \text{ and } -\Delta\mu_C = 308.47 \text{ J}. \tag{14}$$

The work, executed at diffusion of carbon from α-phase in a carbide, is positive. The difference of thermodynamics potentials at diffusion of alloying element from solid α- solution in the carbide can be estimated after a formula

$$-\Delta\mu_X = -RT\ln\frac{a'_X}{a_X}, \tag{15}$$

where a_X is a size of thermodynamics activity of alloying element in solid α- solution before the beginning of the process, that equals its concentration of C_X^α approximately; a'_X is a size of thermodynamics activity of alloying element in solid α-solution after completion of the process, that equals its concentration of $C_X'^\alpha$ approximately. If an alloying element in our system is a chrome, then $a_{Cr} = C_{Cr}$ and $a'_{Cr} = C'_{Cr}$. The difference of thermodynamics potentials at diffusion of chrome from solid α-solution in a carbide can be found by the formula:

$$-\Delta\mu_{Cr} = -RT\ln\frac{a'_{Cr}}{a_{Cr}} = -7258\ln\frac{0.0425}{0.05} = 1180 \text{ J}. \tag{16}$$

In work [13], the difference of thermodynamics potentials was expected for chromium after its activity at a carbide. The same value of thermodynamics force was got, as well as it is expected after a formula (16). For diffusion of iron, the difference of thermodynamics potentials can be expected from data of change to the concentration of iron from the initial concentration of C_{Fe} (0.943) to the final concentration of C'_{Fe} (stable state) [10]. From experimental data and thermodynamics of process it is known that diffusion of carbon conducts, diffusion of chrome accompanies diffusion of carbon, and diffusion of iron forces, directed towards an increase in iron concentration in ferrite of steel [10]. A final concentration of C'_{Fe} is concentration of iron in steel on completion of process of formation of phase. Then the difference of thermodynamics potentials for iron can be found by a formula:

$$-\Delta\mu_{\mathrm{Fe}} = -RT\ln\frac{C'_{\mathrm{Fe}}}{C_{\mathrm{Fe}}} = -7{,}258\ln\frac{0.9574}{0.943} = -116.7\ \mathrm{J}. \tag{17}$$

And, in the end, for the difference of thermodynamics potentials of vacancies there also a formula, similar to (17) [18]:

$$-\Delta\mu_V = -RT\ln\frac{C'_V}{C_V}, \tag{18}$$

where C'_V is an unknown value of concentration of vacancies for completion of process. In process [12] it values for the process of graphitization are found from additional physical suppositions for the process of diffusion of vacancies – its stationary or equilibrium thermodynamic forces. The value of thermodynamics force for vacancies in our case will be expected below from additional physical supposition about invariability of volume of alloy on the initial stage.

General expressions for kinetic coefficients and fluxes. Taking into account the obtained correlations, one can find the value of kinetic coefficients in Onsager's equations. As known from [8, 19], direct kinetic coefficients of L_{ii} are related to the diffusion coefficients D_i by correlation:

$$L_{ii} = C_i D_i / RT, \tag{19}$$

where C_1 is a concentration of iron in an alloy (0.943); C_2 is a concentration of carbon in an alloy (0.007); C_3 is a concentration of chrome in an alloy (0.05).

Dependencies of coefficients of diffusion of chrome and carbon in the ferrit, alloyed by a chrome, from a temperature look like [19]:

$$D^{\alpha}_{\mathrm{Fe}} = 2.910^{-4}\exp\left[\frac{-251{,}000}{RT}\right]\mathrm{cm}^2/\mathrm{s}, \tag{20.1}$$

$$D^{\alpha}_{\mathrm{C}} = 0.177\exp\left[\frac{-88{,}230}{RT}\right]\mathrm{cm}^2/\mathrm{s}, \tag{20.2}$$

$$D^{\alpha}_{\mathrm{Cr}} = 3.05\exp\left[\frac{-358{,}000}{RT}\right]\mathrm{cm}^2/\mathrm{s}. \tag{20.3}$$

At a temperature of 600 °C:

$$D_1 = D^{\alpha}_{\mathrm{Fe}} \approx 3.03\cdot10^{-19}\ \mathrm{cm}^2/\mathrm{s};\ D_2 = D^{\alpha}_{\mathrm{C}} \approx 1.02\cdot10^{-6}\ \mathrm{cm}^2/\mathrm{s};\ D_3 = D^{\alpha}_{\mathrm{Cr}} \approx 1.38\cdot10^{-21}\ \mathrm{cm}^2/\mathrm{s}.$$

The value of direct kinetic coefficient for vacancies with the sufficient degree of accuracy can be found based on the next considerations. We'll consider fluxes in α-phase in ideal case – to formation of additional phase and their cooperation. The volume of the system here is unchanging, which is why for fluxes in α-phase the equation is correct:

$$J_{\mathrm{Fe}} + J_{\mathrm{Cr}} + J_V = 0. \tag{21}$$

So as equation (21) is correct at the arbitrary values of thermodynamics forces of iron and chrome, then the ratio can be obtained by direct coefficients:

$$L_{44} = -L_{11}\mathrm{sign}(-\Delta\mu_{\mathrm{Fe}}) - L_{33}\mathrm{sign}(-\Delta\mu_{\mathrm{Cr}}), \tag{22}$$

where sign of $(-\Delta\mu_{\mathrm{Fe}})$ and sign of $(-\Delta\mu_{\mathrm{Cr}})$ are signs of corresponding thermodynamic forces.

Using correlation (8), (19) and (22), we can find the expressions of cross kinetic coefficients for our system:

$$L_{ik} = L_{ki} = \pm\frac{\sqrt{C_i D_i \cdot C_k D_k}}{RT}, \tag{23}$$

where the concentrations of the elements C_i and the Onsager coefficients change in time.

Using correlation (19), (22) and (23), the calculated valus of kinetic coefficients for our system at the initial moment of time are:

$$L_{11} = 0.394 \cdot 10^{-22};\ L_{22} = 0.984 \cdot 10^{-13};\ L_{12} = -1{,}97 \cdot 10^{-17},\ L_{33} = 0.95 \cdot 10^{-26};\ L_{13} = -0.611 \cdot 10^{-24},$$

$$L_{23} = 0.306 \cdot 10^{-19},\ L_{44} = 0.393 \cdot 10^{-22},\ L_{14} = -0.3935 \cdot 10^{-22};\ L_{24} = 1.97 \cdot 10^{-17};\ L_{34} = 0.611 \cdot 10^{-24}.$$

Equation (21) allows us to find the value of thermodynamics force for vacancies, if thermodynamics forces of iron (17) and alloying element are known (16). The simple substitution of values of thermodynamics forces and kinetic coefficients:

$$-\Delta\mu_V = (-L_{11}(-\Delta\mu_{\mathrm{Fe}}) - L_{33}(-\Delta\mu_{\mathrm{Cr}}))/L_{44} = 116.71\ \mathrm{J}. \tag{24}$$

The value of thermodynamics force for vacancies almost equals the value of thermodynamics force of iron with the sign of "–", because contribution of chrome is a few orders below, than compatible diffusion of iron. Thus, the system of equations (5) can be obtained:

$$J_{\mathrm{Fe}} = 0.394 \cdot 10^{-22}(-\Delta\mu_{\mathrm{Fe}}) - 1.97 \cdot 10^{-17}(-\Delta\mu_{\mathrm{C}}) - 0.611 \cdot 10^{-24}(-\Delta\mu_{\mathrm{Cr}}) - 0.3935 \cdot 10^{-22}(-\Delta\mu_V), \tag{25.1}$$

$$J_{\mathrm{C}} = -1.97 \cdot 10^{-17}(-\Delta\mu_{\mathrm{Fe}}) + 0.984 \cdot 10^{-13}(-\Delta\mu_{\mathrm{C}}) + 0.306 \cdot 10^{-19}(-\Delta\mu_{\mathrm{Cr}}) + 1.97 \cdot 10^{-17}(-\Delta\mu_V), \tag{25.2}$$

$$J_{\mathrm{Cr}} = -0.611 \cdot 10^{-24}(-\Delta\mu_{\mathrm{Fe}}) + 0.306 \cdot 10^{-19}(-\Delta\mu_{\mathrm{C}}) + 0.95 \cdot 10^{-26}(-\Delta\mu_{\mathrm{Cr}}) + 0.611 \cdot 10^{-24}(-\Delta\mu_V), \tag{25.3}$$

$$J_V = -0.3935 \cdot 10^{-22}(-\Delta\mu_{\mathrm{Fe}}) + 1.97 \cdot 10^{-17}(-\Delta\mu_{\mathrm{C}}) + 0.611 \cdot 10^{-24}(-\Delta\mu_{\mathrm{Cr}}) + 0.393 \cdot 10^{-22}(-\Delta\mu_V). \tag{25.4}$$

In equations (25) well-known values of all thermodynamics forces that operate in the system are presented. From the system of equations (25) follows, that the values of fluxes of iron, chrome and vacancies substantially grow through the large values of cross coefficients of L_{12}, L_{32}, L_{42} and considerable size of thermodynamics force ($-\Delta\mu_{\mathrm{C}}$). Size of carbon flux, that has a positive sign, determined, mainly, by the own coefficient of L_{22}. Direct calculations allow us to find the value of diffusive fluxes on the initial stage of formation of additional phase at the initial moment of time:

$$J_{\mathrm{Fe}} = -6.08 \cdot 10^{-15}\ \mathrm{cm^2/s};\ J_{\mathrm{C}} = 3.04 \cdot 10^{-11}\ \mathrm{cm^2/s};\ J_{\mathrm{Cr}} = 0.94 \cdot 10^{-17}\ \mathrm{cm^2/s};\ J_V = 6.07 \cdot 10^{-15}\ \mathrm{cm^2/s}.$$

As possible to see, in the case of cooperation of fluxes, equation (21) is also true. So as a flux of chrome has a considerably less value, than flux of iron, then the flux of vacancies has the same value as flux of iron practically, with the sign of "–".

Kinetic equations for calculation of concentration and fluxes in the system. As already shown, the proposed equations for the calculation of diffusion fluxes depend on the concentrations of alloying elements, and those, in turn, vary over time. For a complete calculation of the kinetics of a multiphase thermodynamic system, a system of first-order differential equations should be used, in the form of continuity equations for each element of the system under consideration [19]:

$$\begin{gathered} \frac{\partial K_1}{\partial t} = J_1 S, \ldots, \\ \frac{\partial K_i}{\partial t} = J_i S, \ldots, \\ \frac{\partial K_N}{\partial t} = J_N S,\ i=1,\ldots,N. \end{gathered} \tag{26}$$

where K_i is the amount of each element in the system ($dK_i = dC_i\Delta V$).

The system of differential equations (26) allows us to find the change in concentrations and fluxes of a multicomponent system over time. For the particular case of our system represented by fluxes (25), the following relations and simplifications can be introduced at the stage of determining carbon diffusion.

At the stage of carbon diffusion, which has a very high diffusion coefficient, the thermodynamic force for carbon will be decisive.

Its expression can be found from relations (9) and (13):

$$-\Delta\mu_{\mathrm{C}} = -RT\left(\beta^{K}_{\mathrm{Cr}} N^{K}_{\mathrm{Cr}} - \beta^{\alpha}_{\mathrm{Cr}} N^{\alpha}_{\mathrm{Cr}}\right) = -RT\left(-0.652 + \frac{3.246 C_{\mathrm{Cr}}}{3C_{\mathrm{C}} + 0.246}\right). \tag{27}$$

Thermodynamic force (27) is the difference of thermodynamic potentials for carbon in α-phase and carbide. For calculations using the system of equations (26), we must calculate the flux expressed through the gradient of the thermodynamic potential:

$$-\nabla\mu_{\mathrm{C}} = -\frac{\Delta\mu_{\mathrm{C}}}{a}, \tag{28}$$

where a is the distance that carbon diffuses. Usually, this distance is assumed to be equal to the interplanar distance between the atoms in the alloy ($a \sim 3\cdot10^{-8}$ cm) [19].

The expressions for the carbon and chromium fluxes at this stage in the first approach are:

$$J_{\mathrm{C}} = C_{\mathrm{C}} D_{\mathrm{C}}^{\alpha}(-\nabla\mu_{\mathrm{C}}) / RT, \tag{29.1}$$

$$J_{\mathrm{Cr}} = \frac{(-\nabla\mu_{\mathrm{C}})\sqrt{C_{\mathrm{C}} D_{\mathrm{C}}^{\alpha}\cdot C_{\mathrm{Cr}} D_{\mathrm{Cr}}^{\alpha}}}{RT}. \tag{29.2}$$

Also, in the expressions for the fluxes, we used element concentrations expressed in atomic or volume fractions, because of which the dimension of the flux previously had the dimension of diffusion coefficients cm^2/s and in expression (29) it had the dimension cm/s. To recalculate fluxes to commonly used units (mol/cm$^2\cdot$s) [15], flows should be multiplied by a constant conversion factor:

$$J_i^0 = \frac{\rho}{N_i} J_i\left(\frac{\mathrm{mol}}{\mathrm{cm}^2\cdot\mathrm{s}}\right), \tag{30}$$

where N_i is the atomic number of the diffusing element (g$\cdot$mol^{-1}); ρ is the alloy density (g$\cdot$cm^{-3}).

Numerical simulation of the system allows you to find the change in diffusion fluxes and concentrations of elements over time. Calculations were carried out per unit area of 1 cm^2 and unit volume of steel 1 cm^3. The obtained dependencies are shown in Figure 2 and Figure 3. The size calculations of the formed carbides were carried out according to the method described in [13].

The established dependencies and the performed calculations show that at the initial stage the magnitude of the diffusion flux of chromium substantially depends on the thermodynamic force for carbon (see Figure 2). Carbon is very quickly removed from a solid solution of alloy steel, leading to the formation of cementite-type nanoparticles with a size of about 18 nm (see Figure 3).

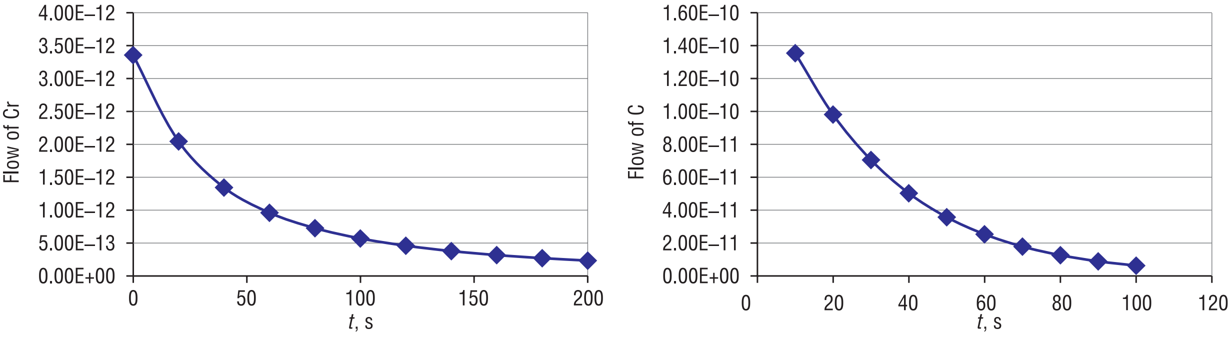

Figure 2. Estimated time-dependent changes in the fluxes of Cr and C (mol/cm$^2\cdot$s)

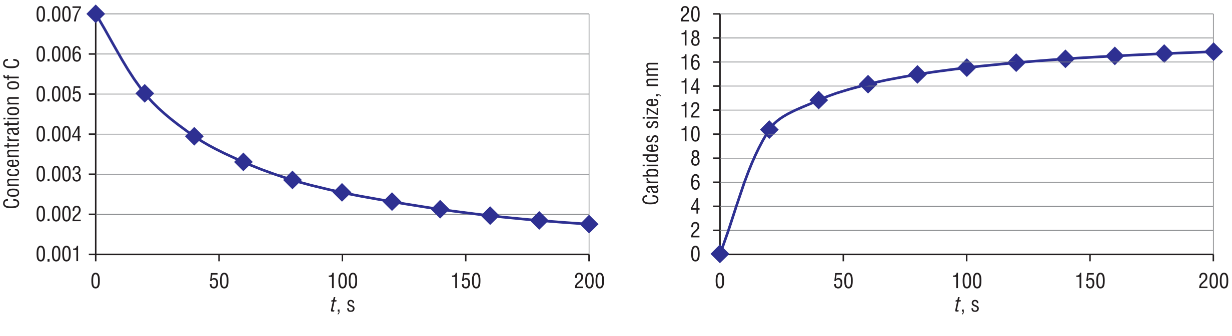

Figure 3. Estimated time-dependent changes of carbon concentration in α-phase and carbides size

Conclusions. The non-equilibrium thermodynamics methodology of calculation of diffusive fluxes is offered at presence of two phases in alloy steels. That allows expecting both line- and cross coefficients in equations. Formulas for calculation of thermodynamics forces are presented for alloy steel – for iron, alloying element of substitution – chrome, for element of introduction – carbon and vacancies. Common expressions are suggested for calculation of cross-factors, motive forces and fluxes in the Onsager's equations for a multicomponent thermodynamic system.

The examples of using the developed method to find changes in concentrations and diffusion fluxes over time are given. For the model system used, it was established that at the stage of predominant diffusion of carbon in the alloy steel, cementite inclusions with a size of about 18 nm are formed rather quickly (within ~ 200 s).

The technique developed in the article allows one to perform diffusion kinetics calculations in multicomponent thermodynamic systems, which are also iron-carbon alloys and to control the size of the phases formed, for example, carbide nanoparticles.

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