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Non-equilibrium analysis of the graphitization process in cast irons

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A diffusion-vacancy mechanism has been developed that describes the process of graphitization of cast iron, and does not use the pressure of graphite on the matrix to explain the diffusion of iron. The values of thermodynamic forces and kinetic coefficients were calculated for the case of graphitization of a binary alloy of the Fe–C system with 2.5% C at 1100°C. It was established that under the conditions of a stationary flow of vacancies during the graphitization of cast iron in the solid phase, the concentration of vacancies at the γ-phase – graphite boundary is approximately 0.97723 times less than the concentration of vacancies in the γ-phase. An assessment was made of the influence of alloying elements, using the example of chromium and silicon, on the graphitization of cast iron with 2.5% C. A thermodynamic parameter of graphitization was proposed that takes into account the influence of all alloying elements and characterizes the degree of stability of graphite under these conditions.

Keywords: thermodynamics, graphitization, cast iron, alloying elements, vacancies, diffusion.

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Introduction

As is known, under certain temperature-time parameters, the process of formation of graphite is observed in iron-carbon alloys - some steels and cast irons, i.e. graphitization of such alloys occurs [1,2]. Despite the apparent simplicity of this process, its theoretical description is a complex task.

In Fig. 1 double phase diagram of Fe – C [2], giving a general idea of the graphitization process. Graphite can be released directly from a liquid below the C'D' line in temperature, by eutectic (combined with austenite) crystallization below the E'C'F' line, from austenite upon subsequent cooling to the S'K' line, or due to decomposition preformed cementite below line S'E'. Below the SE and ECF lines, the graphitization process competes with the process of cementite formation.

From the point of view of thermodynamics, the graphitization process is explained by an increase in the activity of carbon with a decrease in the temperature of cast iron [3-5].

To theoretically describe the flows of the graphitization process in the solid phase, one can use the concepts of thermodynamics of nonequilibrium thermodynamics [8-11].

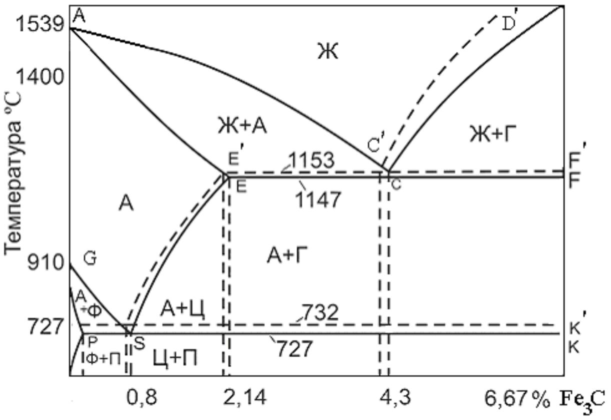

Fig. 1. Double iron-carbon phase diagram.

In the general case, the thermodynamic equations of motion have the form [5, 9]:

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

where J_i are flows; $X_k = \nabla\mu_k$ – thermodynamic forces; $L_{ik} = L_{ki}$ are the Onsager kinetic coefficients [5]; *i,k* are the numbers of charges (transfer substrates).

The main driving forces of phase transformations in nonequilibrium thermodynamics are the gradients of the chemical potentials of their components $\nabla\mu_k$ [5]. When considering discontinuous systems, another technique is used, in which thermodynamic forces are finite drops in chemical potentials ($\Delta\mu_{Fe}$, $\Delta\mu_C$) during the transition from a metastable state to a stable one [3, 5, 9-11]. If two quantities are used as charges for the graphitization process - the concentrations of carbon and iron, then, according to (1), the equations of motion take the form:

$$J_1 = -L_{11}\Delta\mu_{Fe} - L_{12}\Delta\mu_c \quad (2.1)$$

$$J_2 = -L_{21}\Delta\mu_{Fe} - L_{22}\Delta\mu_c \quad (2.2)$$

where J_1 is the carbon flow characterizing the rate of the graphitization process; J_2 – iron flow.

As shown in [10, 11], in a complex process with two flows, an increase in the potential of one of the charges is observed, i.e. one process is the "leading" and the other is the "slave". The "slave" process itself, i.e. in isolation from the "leading", is impossible, since it is thermodynamically unfavorable. In the system of equations (2), the thermodynamic force ($-\ \Delta\mu_{Fe}$) is negative and inhibits the process as a whole, the diffusion of iron is a forced process, and the leading one is the diffusion of carbon.

Consequently, the process of graphitization in the solid phase must be accompanied by a very intense transfer of a solid solution (mainly iron), which allows the growth of a low-density phase, graphite, in it. The authors of [6, 7] believe that the factor causing the flow of iron from the graphite inclusion to the matrix is the pressure that arises in the austenite matrix under the influence of graphite inclusions pushing it apart. However in [11], considering the mechanism of graphitization of cast irons during thermal cycling, K.P. Bunin with A.A. Baranov came to the conclusion that the absolute value of contact pressures is an order of magnitude less than that required for the mechanism of dislocation creep under the influence of contact pressure. Since graphite films in pores cannot have super-strong properties, the evacuation of matrix atoms is apparently carried out by a different mechanism [11]. Similar phenomena also occur in the diffusion processes of graphite grinding during heat treatment [12].

In accordance with the results of [11, 14], the iron flow can be directed in the direction opposite to the thermodynamic force ($-\Delta\mu_{Fe}$) due to the cross coefficient L_{21} and the large value of the thermodynamic force ($-\Delta\mu_C$) in equations (3). However, the mechanism of carbon diffusion against the concentration gradient (drop) from N_C in the alloy to a concentration of ~1.0 in the graphite inclusion remains open. The thermodynamic description of this fact through the activity coefficient of carbon in the alloy is formal and does not explain the diffusion mechanism.

Of significant interest is also the theoretical assessment of the values of forces and flows during the graphitization of cast iron in the γ-phase.

Consequently, the question remains open about the mechanism of the graphitization process of cast iron in the solid phase and about the values of flows and forces for this process.

The purpose of this work is to analyze the graphitization process in high-carbon iron-carbon alloys - cast irons to determine the possibilities of controlling this process.

I. Research results

1.1. Description of the graphitization process in the γ-phase of iron

As an example, let us first take a binary alloy of the Fe–C system with 2.5% C, in which graphitization occurs at 1100°C.

When hypoeutectic cast iron is cooled from a liquid state below temperature AC', a significant amount of austenite is formed, and the composition of the liquid changes to the concentration of point C'. With a subsequent temperature change below Tevt (1153°C), eutectic crystallization of cast iron begins: $Fe_L(C) \rightarrow Fe(C) + Gr$, where $Fe_L(C)$ is a liquid solution of carbon in iron. Holding cast iron at a temperature slightly below the evectic temperature, or slow cooling in the temperature range Tevt → Tmevt (1147°C), where Tmevt is the temperature at which the metastable cementite eutectic begins to form, leads to the formation of a stable Fe(C)-Gr eutectic in an amount of approximately 16 % and reducing the carbon concentration in austenite to a value approximately equal to the value at point E'.

The formation of eutectics occurs due to the diffusion of carbon and iron in the liquid phase and proceeds at a high speed, forming eutectic colonies of large size.

With a subsequent decrease in the temperature of cast iron to 1100°C, the process of graphitization occurs in the γ-phase Fe. Bunin and his colleagues believe that secondary graphite, released during cooling, layers on the eutectic, promoting its growth [12]. However, in this case there should be a flow of carbon from austenite towards graphite (concentration C is close to 1.0) and a flow of iron from the graphite inclusion to the matrix, in the direction of increasing its concentration.

To theoretically describe graphitization in the solid phase, we apply the concepts of nonequilibrium thermodynamics [9-11], also evaluating various possible mechanisms of this process.

It is well known that diffusion processes of metals in alloys occur by the vacancy mechanism, and of carbon by interstices [9, 13]. Therefore, we will use three quantities as charges - the concentrations of carbon, iron and vacancies. In this system there are two phases: a γ-solid solution of carbon in iron Fe and graphite Gr, as well as vacancies and their possible accumulations in the form of pores P and other structural defects of the alloy with a certain low concentration $N_{V0}(\gamma)$ (Fig. 2).

Taking into account the accumulation of vacancies and pores leads to the fact that in their presence there is a gradient (difference) in the carbon concentration from N_C in the alloy to 0 in the pore. Therefore, carbon, which also has greater activity in the γ-phase, will diffuse towards the pore (shown in Fig. 2). The vacancies will have a reverse concentration difference from the pore to the metal, and the flow of vacancies at this moment will be directed from the pore to the matrix (not shown in the figure). Despite the acceleration of the process of iron self-diffusion (vacancy flow) at this stage due to the cross coefficient, carbon diffusion occurs much faster than iron and carbon completely fills the pore, forming a graphite inclusion. This stage of the general process of graphitization in the solid phase is characterized by significant nonequilibrium and rapidity and the formation of compact graphite inclusions.

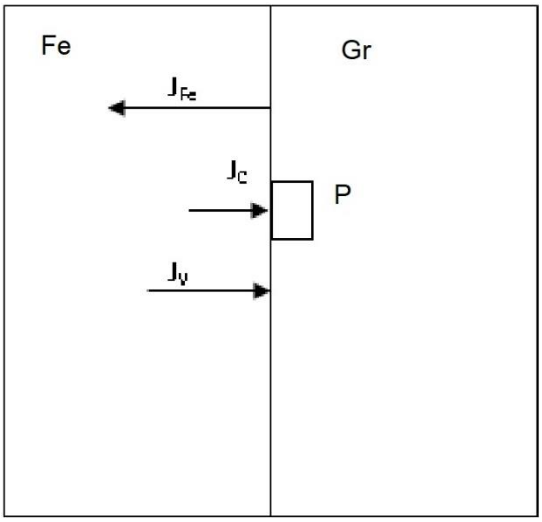

Fig. 2. Scheme of the graphitization process in the Fe(C) – Gr – V system.

After the pore is completely filled with carbon, the number of vacancies at the metal-graphite interface decreases to a value below the equilibrium value in the $N_V(\gamma)$ alloy. The iron content in a graphite inclusion changes to a very low value of its solubility in graphite at a given temperature N_{Fe}(Gr), and the concentration of iron vacancies changes to an even lower concentration N_V(Gr). Therefore, in the system there is a difference in the concentration of vacancies from the alloy towards the graphite inclusions, a nonequilibrium distribution of vacancies from the bulk of the alloy to the graphite surface and a flow of vacancies in this direction (shown in Fig. 2).

At the alloy-graphite interface we have a sink of vacancies, since a vacancy in the metal, reaching the Fe(C)-Gr interface, is filled with carbon, i.e. its annihilation occurs. Therefore, the concentration of vacancies decreases both at the alloy-graphite interface and in the bulk of the metal.

In the alloy, the vacancy concentration is replenished to equilibrium due to vacancy sources at other interfaces. Consequently, a distribution of vacancies arises from the bulk of the alloy to the graphite surface and a stationary flow of vacancies in this direction. The diffusion flow of carbon at this stage of graphitization is consistent with the flow of vacancies, i.e. enough carbon is supplied to fill the vacancies at the iron-graphite interface. The flow of iron in this stationary graphitization process has the opposite sign, towards an increase in the concentration of iron in the matrix. Note that at this stage carbon diffusion in the γ-phase can be expressed at the micro-level due to the gradient of its concentration from the γ-phase to the concentration at the iron-graphite interface.

Let us further evaluate the thermodynamic forces and flows arising in the model system.

1.2. Calculation of thermodynamic forces and kinetic coefficients in the Fe(C) – Gr system

According to (1) data in Fig. 2, the graphitization equations for our cast iron can be written as:

$$J_{Fe} = -L_{11}\Delta\mu_{Fe} - L_{12}\Delta\mu_c - L_{13}\Delta\mu_v \quad (3.1)$$

$$J_C = -L_{21}\Delta\mu_{Fe} - L_{22}\Delta\mu_c - L_{23}\Delta\mu_v \quad (3.2)$$

$$J_v = -L_{31}\Delta\mu_{Fe} - L_{32}\Delta\mu_c - L_{33}\Delta\mu_v \quad (3.3)$$

where J_{Fe}, J_C, J_v are the fluxes of iron, carbon and vacancies, respectively.

The flows in equations (3.1-3.3) are not independent: in the absence of a change in the volume of the system (which is quite accurately carried out in a stationary process), the sum of the flows of iron and vacancies is equal to zero:

$$J_{Fe} + J_y = 0 \quad (4)$$

This leads to the following relationships for kinetic coefficients [9, 13]:

$$L_{11} + L_{31} = 0 \quad (5.1)$$

$$L_{12} + L_{32} = 0 \quad (5.2)$$

$$L_{13} + L_{33} = 0 \quad (5.3)$$

Taking into account relations (5), we obtain the following equations of motion with three independent coefficients L_{11}, L_{12} и L_{22}:

$$J_{Fe} = -L_{11}\Delta\mu^*_{Fe} - L_{12}\Delta\mu_c, \quad (6.1)$$

$$J_C = -L_{21}\Delta\mu^*_{Fe} - L_{22}\Delta\mu_c, \quad (6.2)$$

where $\Delta\mu^*_{Fe} = \Delta\mu_{Fe} - \Delta\mu_v$ – reduced thermodynamic force.

The relationship between the kinetic coefficients, sufficient for our calculations near equilibrium, was established in [9, 14]:

$$L_{21} = L_{12} = -\sqrt{L_{11} \times L_{22}}, \quad (7)$$

and the sign in front of the root was chosen based on the fact that the observed iron flow in relation to the carbon flow has a negative sign.

Let us find the values of thermodynamic forces and kinetic coefficients for the case of a binary alloy of the Fe–C system with 2.5% C at 1100°C. Taking into account the results of work [7], we obtain:

$$\Delta\mu_{Fe} = -RTln\frac{C'_{Fe}}{C_{Fe}} = -11415ln\frac{0.914}{0.908} = -75 \cdot J, \quad (8)$$

where C_{Fe} is the concentration of iron in the γ-phase at point E' (~1-0.092) (Fig. 2);

C'_{Fe} is the iron concentration at stable equilibrium (~1-0.086);

R is universal gas constant; T is alloy temperature.

Corresponding thermodynamic force of graphitization:

$$\Delta\mu_C = -RTln\frac{\alpha_C^G}{\alpha_C^\gamma} = -11415ln\frac{1.0}{1.15} = 1587\cdot J, \qquad (9)$$

where a^{γ}_C =1.15 is the value of the thermodynamic activity of carbon in the γ-phase with a concentration E’ and a temperature of 1100 °C, when choosing graphite as the standard state of carbon, a^G_C =1.00 (Fig. 3).

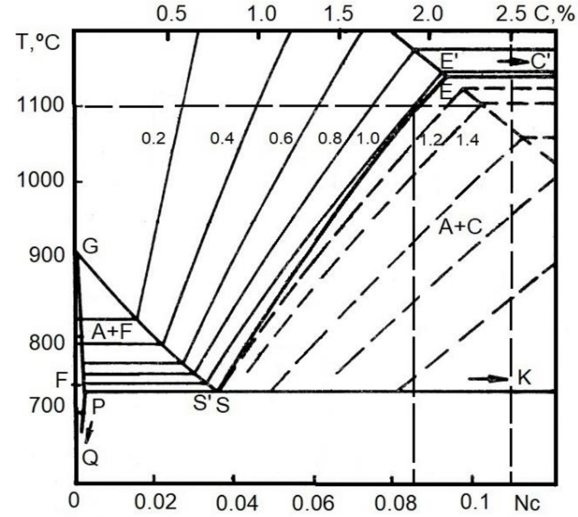

Fig. 3. Part of the double state diagram of Fe – C with carbon isoactivity lines plotted (according to the data of [11]).

As is known [9,13], the kinetic coefficients Lii are related to the diffusion coefficients Di by the relation:

$$L_{ii} = C_iD_i/RT, \qquad (10)$$

where C_1 is the concentration of iron in the γ-phase at point E’ (0.908);

C_2 is carbon concentration in cast iron at point E’ (0.092).

The dependences of the self-diffusion coefficients of iron and carbon diffusion in austenite on temperature have the form [15]:

$$D_{Fe}^{\gamma} = 5.4\times10^{-4}exp\left[\frac{-230120}{RT}\right]m^2/s, \qquad (11)$$

$$D_C^{\gamma} = 39.4\times10^{-8}exp\left[\frac{-91516}{RT}\right]m^2/s, \qquad (12)$$

At a temperature of 1100°C:

$$D_1 = D_{Fe}^{\gamma} \approx 2.84\cdot10^{-11}\ m^2/s;$$

$$D_2 = D_C^{\gamma} \approx 3.32\cdot10^{-8}\ m^2/s.$$

Using expressions (8) – (12), we find the values of the kinetic coefficients for our system: L_{11} = 2,19×10^{-14}; L_{22}= 3,42×10^{-12}; L_{12} = 2,74×10^{-13} (m^2/(J×s)).

Consequently, the system of equations (6) takes the form:

$$J_{Fe} = -2.19\times10^{-14}(\Delta\mu_{Fe} - \Delta\mu_v) + 2.74\times10^{-13}\Delta\mu_C, \qquad (13.1)$$

$$J_C = -2.74\times10^{-13}(\Delta\mu_{Fe} - \Delta\mu_v) + 3.42\times10^{-12}\Delta\mu_C, \qquad (13.2)$$

From equations (13) it follows that the iron flow, which has the opposite sign, is significant due to the cross coefficient L_{12} and the significant value of the thermodynamic force $\Delta\mu_C$. The carbon flux, which has a positive sign, increases slightly due to the cross coefficient L_{12}.

Let at the initial moment of time:

$$\Delta\mu_v = -\Delta\mu_{Fe} = 264\cdot J \qquad (14)$$

As direct calculations show, even in this limiting case, the flow of iron depends primarily on the magnitude of the thermodynamic force of graphitization ΔμC and the cross coefficient L_{12}: $J_{Fe} = -0.83\times10^{-9}$, $J_C = 1.05\times10^{-8}$, m^2/s.

In turn, the thermodynamic force $\Delta\mu_v$ is equal to:

$$\Delta\mu_V^0 = -RTln\frac{\alpha_v^{\gamma-Gr}}{\alpha_v^{\gamma}} \approx -11415ln\frac{N_v^{\gamma-Gr}}{N_v^{\gamma}}, \qquad (15)$$

$N_v^{\gamma-Gr}$ here is the concentration of vacancies at the γ-phase – graphite boundary;

N_v^{γ} is the concentration of vacancies in the γ-phase; from where,

$$N_v^{\gamma-Gr} = 0.97723N_v^{\gamma}. \qquad (16)$$

Under conditions of a stationary vacancy flow and equality (14) is satisfied, the concentration of vacancies at the γ-phase–graphite boundary is approximately 0.97723 times less than the concentration of vacancies in the γ-phase. Thus, the development of the diffusion-vacancy mechanism of graphitization of cast iron is given, which does not use elevated pressures to explain the change in the sign of the iron flow.

1.3. Calculation of the influence of alloying elements on the graphitization of cast iron

Let's find the values of thermodynamic forces and kinetic coefficients for steel of the Fe–C–Cr system with 2.5% C and 1% Cr at 1100°C. We will assume that the solid α-solution contains chromium with a concentration of C_{Cr} = 0.01 and carbon with a concentration of C_C = 0.118, and an iron concentration of C_{Fe} = 0.872.

The change in the thermodynamic activity of carbon in cast iron when alloyed with component i can be found using the method [14, 15] from the equation:

$$\ln\,(\alpha^K c/\alpha^K c_0) = \beta i N i, \qquad (17)$$

where βi is the coefficient of influence of the element on the thermodynamic activity of carbon in the alloy (relative to carbide);

Ni is the element content in the alloy in atomic fractions; $a^K{}_{C0}$ is the thermodynamic activity of carbon for cast iron in the standard state.

We will assume that for our cast iron in the standard state (without chromium), the activity of carbon in cementite, taken from the diagram in Fig. 3, $a^K{}_{C0} = 1.02$.

The value βi is calculated through the coefficient of interphase distribution of the alloying element $Ki = Ni(K)/Ni(\gamma)$ and the atomic fraction of carbon in the alloy N_C [17, 18]:

$$\beta i = -\frac{(Ki-1)+\left(Nc(K)-KiNc(\gamma)\right)}{(Ki-1)Nc+\left(Nc(K)-KiNc(\gamma)\right)}. \qquad (18)$$

With a small error for low-alloy alloys, we can accept $Nc(K) = 0.25$, $Nc(\gamma) \approx 0.087$ is the the carbon content in the unalloyed phases of steel at a given temperature, taken from the Fe-C phase diagram.

Using the chromium distribution coefficient between the γ-phase and K_{Cr} carbide, equal to 2 [18], we find equations for calculating the influence coefficients β_{Cr}:

$$\beta_{Cr} = -2.9/(3.0N_c - 0.1) = -11.42. \qquad (19)$$

Then from expression (17) you can find the values: ln $(a^K{}_C/a^K{}_{C0}) = -\,0{,}1142$ и $a^K{}_C = 1.02\times0.892 = 0.91$, where

$$-\Delta\mu K_C = 1077\cdot J. \qquad (20)$$

The thermodynamic force of cementation of cast iron becomes greater than the thermodynamic force of graphitization of cast iron by 1077 J, therefore, in cast iron with 1% Cr, the formation of cementite rather than graphite occurs.

Let now in our cast iron instead of 1% Cr, there will be 1% Si. Using the silicon distribution coefficient between the γ-phase and carbide K_{Si}, equal to 0.57 [18], we find equations for calculating the influence coefficient β_{Si}:

$$\beta_{Si} = -0.85/(-0.75N_C - 0.0218) = 7.7. \qquad (21)$$

Then from expression (17) we find: ln $(a^K{}_C/a^K{}_{C0}) = 0{,}077$, $a^K{}_C = 1.02\times1.08 = 1.1$, where

$$-\Delta\mu^K c = -1088\cdot J. \qquad (22)$$

The thermodynamic force of graphitization of cast iron becomes greater than the thermodynamic force of carbide formation of cast iron by 1088 J, and in cast iron with 1% Si, the formation of graphite rather than cementite occurs.

We can also see from our calculations that silicon and chromium are elements that compensate for each other's influence on the graphitization process.

When complex alloying of cast iron, it is possible to introduce a thermodynamic parameter of graphitization T_G, taking into account the influence of all alloying elements (excluding carbon and iron) [19]:

$$T_G = \textstyle\sum_{k=1}^{N} \beta_k N_k, \qquad (23)$$

N is the number of alloying elements taken into account in cast iron.

At a given graphitization temperature, for the formation of graphite rather than cementite in the structure of cast iron, the thermodynamic condition must be met:

$$T_G \geq ln(\alpha^G c/\alpha^K c) \approx \alpha^G c - \alpha^K c. \qquad (24)$$

At $T_G > 0$, the thermodynamic parameter of graphitization characterizes the degree of stability of graphite and can be related to the morphology and size of graphite inclusions. The concentration heterogeneity of cast iron after crystallization determines that the T_G parameter has changing local values over the cross section of the dendritic branches of austenite and the interdendritic spaces. This leads to structural heterogeneity, i.e. the formation of graphite with varying degrees of stability, and therefore size and morphology.

If the local value of the T_G parameter is negative, then cementite will form in these areas of the cast iron, which is very often undesirable in gray cast iron.

Conclusions

1. A diffusion-vacancy mechanism is proposed that describes the process of graphitization of cast iron, and does not use the pressure of graphite on the matrix to explain the diffusion of iron.
2. The values of thermodynamic forces and kinetic coefficients were calculated for the case of graphitization of a binary alloy of the Fe–C system with 2.5% C at 1100°C.
3. It has been established that under conditions of a stationary flow of vacancies during the graphitization of cast iron, the concentration of vacancies at the γ-phase – graphite boundary is approximately 0.97723 times less than the concentration of vacancies in the γ-phase.
4. An assessment was made of the the influence of alloying elements, using chromium and silicon as an example, on the graphitization of cast iron with 2.5% C.
5. A thermodynamic parameter of graphitization T_G has been proposed, taking into account the influence of all alloying elements and characterizing the degree of stability of graphite under given conditions.

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Нерівноважний термодинамічний аналіз процесу графітизації чавунів

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Розвинено дифузійно-вакансіонний механізм, що описує процес графітизації чавуну, і не використовує тиск графіту на матрицю для пояснення дифузії заліза. Розраховано значення термодинамічних сил та кінетичних коефіцієнтів для випадку графітизації бінарного сплаву системи Fe–C з 2,5 % при 1100°C. Встановлено, що в умовах стаціонарного потоку вакансій при графітизації чавуну в твердій фазі, концентрація вакансій на межі γ-фаза – графіт приблизно в 0.97723 рази менша від концентрації вакансій у γ-фазі. Виконано оцінку впливу легуючих елементів, на прикладі хрому та кремнію, на графітизацію чавуну з 2.5% C. Запропоновано термодинамічний параметр графітизації, що враховує вплив усіх легуючих елементів та характеризує ступінь стабільності графіту в даних умовах.

Ключові слова: термодинаміка, графітизація, чавун, легуючі елементи, вакансії, дифузія.