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Using the Principles of Nonequilibrium Thermodynamics for the Analysis of Phase Transformations in Iron-Carbon Alloys

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Abstract

Using the principles of nonequilibrium thermodynamics, a technique has been developed for calculating diffusion flows during phase transformations in iron-carbon alloys. Expressions for the calculation of cross coefficients, driving forces, and flows in Onsager equations for the model thermodynamic system are given; examples of the use of the developed technique are given for the processes of graphitization and the formation of carbides in chromium steel during tempering. The nonequilibrium thermodynamics analysis of the eutectoid transformation is executed into carbon steel. Onsager's equations of motion are built for the model thermodynamics system describing eutectoid transformation. The basic kinetic parameters of process are growth rate of perlite and between inter-plates distance for the stationary process of eutectoid transformation. We founded dependencies of basic kinetic parameters of process from the size of supercooling. A nonequilibrium thermodynamic model of the austenite nondiffusion transformation in iron and alloys based on it is developed, taking into account internal stresses in the system. Onsager motion equations are found for a model thermodynamic system describing a nondiffusion transformation and kinetic equations for changing deformations and growth rates of the α -phase. A scheme of austenitic nondiffusion transformations is constructed, including normal and martensitic transformations, as limiting cases.

Keywords: nonequilibrium thermodynamics, the iron-based alloys, transformation of austenite, diffusion, equations of motion, nondiffusion transformation

1. Introduction

The study of phase transformations is one of the most important problems in the physics of metals [1–3]. Phase transformations are divided into diffusion and nondiffusion [1]. If the kinetics of phase transformation in steels and cast irons is determined by the diffusion of carbon, this allows them to be attributed to conversions controlled by diffusion [1–4]. Such transformations in iron-carbon alloys include pearlitic transformation of austenite, and transformations occurring during

tempering, graphitization of undoped cementite, separation of carbides in alloyed steels, and others [4–6].

When the rate of transformation of austenite is determined by the rate at which the interface separates, differing only in its crystalline structure, the transformation is called nondiffusion [1]. Kinetically, the normal polymorphic and martensitic transformations of austenite are distinguished. When the temperature of the normal transformation decreases, its velocity first increases and then decreases. The kinetics of the martensitic transformation is characterized by a very high rate of growth of individual crystals and the maximum space velocity at the initial moment of transformation under isothermal conditions.

In addition to martensite, at least two other structural components are known, which are formed with a shear (“martensitic”) morphology of crystal formation—ferrite side-plates and acicular ferrite. They can also be attributed, with some simplifying assumptions, to the products of the nondiffusion transformation of austenite. In addition, in some alloys martensitic and normal transformations occur at the same temperature [1]. The consistent theory of nondiffusion transformations should explain this phenomenon. Thus, the theoretical description of the processes of phase transformations in iron-carbon alloys is a complex and urgent task of modern metal physics.

Nonequilibrium thermodynamics provides the necessary apparatus for analyzing the processes of phase transformations in iron-carbon alloys [7–9]. In the general case, the thermodynamic equations of motion have the form [7]:

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

where J_i are flows, X_k are the thermodynamic forces, $L_{ik} = L_{ki}$ are the Onsager kinetic coefficients [9], and i, k are the charge numbers (transfer substrates).

The main driving forces of phase transformations in nonequilibrium thermodynamics are gradients of the chemical potentials of their components [6–9]. When discontinuous systems are considered, the finite differences of chemical potentials ($-\Delta\mu_i$) as the transition from a metastable state to a stable state are used as thermodynamic forces [10, 11]. Equations of nonequilibrium thermodynamics were first used in the physics of metals to describe the process of graphitization of nonalloyed iron-carbon alloys [6, 11].

As is known, unalloyed cementite in iron-carbon alloys at normal pressure is a metastable phase, its activity in phases with it in equilibrium exceeds the solubility of graphite, a stable phase [11]. Therefore, at a sufficiently high temperature, graphitization of such alloys takes place, that is, phase transition from metastable to stable equilibrium. Despite the seeming simplicity of this process, its theoretical description is a complex task.

If two values are used as charges of the graphitization process—carbon and iron concentrations, then, according to (1), the equations of motion take the form:

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (2)$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \quad (3)$$

where J_1 is the carbon flow characterizing the rate of the graphitization process, J_2 is the flow of iron, and $X_1 = (-\Delta\mu_{Fe})$ and $X_2 = (-\Delta\mu_C)$ are the thermodynamic forces of iron and carbon. The potential drop has a “+” sign as it increases, and the flow is directed toward a decrease in the potential, so the expressions for the forces contain the sign “−.”

The main question that must be solved when using the Onsager Eqs. (1)–(3) is the values of the cross coefficients.

In [5], for the first time on the basis of a special variational procedure, an expression for the cross coefficients in the Onsager equations was proposed in the form:

$$L_{21} = L_{12} = -\sqrt{L_{11} \times L_{22}}, \quad (4)$$

and the sign-before the root is chosen on the basis that the observed flux of iron with respect to the flow of carbon had a negative sign.

As shown in [6, 11], in the complex process with two flows, an increase in the potential of one of the charges is observed, that is, one process is “leading,” and the other is “driven.” The “driven” process in itself, i.e., in isolation from the “lead,” is not possible, since thermodynamically not beneficial. In the system of Eqs. (2) and (3), 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.

Thus, the graphitization process must be accompanied by a very intensive transfer of a solid solution (mainly iron), which makes it possible for the phase with a low-density graphite to grow in it. The authors of [6, 11] assumed that the factor contributing to graphitization is the pressure that arises in the austenite matrix under the action of graphite inclusions that expand it. However, in [12], considering the mechanism of graphitization of cast irons during thermocyclic treatment, K.P. Bunin with A.A. Baranov came to the conclusion that the absolute value of the contact pressures is an order of magnitude less than the necessary for the dislocation creep mechanism under the influence of contact pressure. Since graphite films in pores cannot possess super strong properties, the evacuation of matrix atoms is apparently carried out by another mechanism.

In [5], using nonequilibrium thermodynamic methods, it was shown that under the conditions of the system’s striving for dynamic equilibrium, the concentration of vacancies in graphite inclusion becomes less than the vacancy concentration at the γ -phase-graphite boundary. This can occur as a result of approaching the γ -phase boundary—graphite of austenitic vacancies. In this case, the thermodynamic force ($-\Delta\mu_{0v}$) prevents the graphitization, and the reduced graphitization force ($-\Delta\mu^*C$) decreases to zero and can even take a negative value.

Thus, the goal of this paper is to show how the methods of nonequilibrium thermodynamics can be used fruitfully to solve the theoretical problems of metal physics, namely, the analysis of phase transformations. Let us further consider the application of the principles of nonequilibrium thermodynamics to the analysis of specific cases of phase transformations in iron-carbon alloys.

2. Formation of carbides in chrome steel during tempering

Consider the process of separation of carbides in a low-carbon steel system of iron-carbon-chromium with 0.15% carbon and about 5% chromium at 600°C. In this model system, there are two phases—the doped α -phase (F) and carbides (K), in which carbon, iron, chromium, and vacancies flows (**Figure 1**). As charges, we will use four quantities—the concentrations of carbon, iron, chromium, and vacancies. The flow of vacancies in the carbide phase will be assumed to be equal to the flow of vacancies in the ferrite.

In the absence of a change in the volume of the system, for flows in the doped α phase, condition [13] is fulfilled:

$$J_{Fe} + J_{Cr} + J_v = 0, \quad (5)$$

so one of the threads (in our case— J_v) is a dependent quantity. According to (1), the thermodynamic equations for flows in the carbide phase take the form:

$$J_{Fe} = -L_{11}\Delta\mu_{Fe} - L_{12}\Delta\mu_c - L_{13}\Delta\mu_{Cr} \quad (6)$$

$$J_C = -L_{21}\Delta\mu_{Fe} - L_{22}\Delta\mu_c - L_{23}\Delta\mu_{Cr} \quad (7)$$

$$J_{Cr} = -L_{31}\Delta\mu_{Fe} - L_{32}\Delta\mu_c - L_{33}\Delta\mu_{Cr}, \quad (8)$$

where J_{Fe} , J_C and J_{Cr} are the flows of iron, carbon, and chromium, respectively.

Based on the general principles of nonequilibrium thermodynamics, we can find the values of the thermodynamic forces $-\Delta\mu_{Fe}$, $\Delta\mu_{Cr}$, and $-\Delta\mu_C$, as well as the values of the kinetic coefficients L_{12} , L_{13} , and L_{23} , as it was previously performed in [5] for a system with two flows. In the conditions of complete equilibrium, $\Delta\mu_{Fe} = 0$, $\Delta\mu_C = 0$, and $\Delta\mu_{Cr} = 0$. However, for a linear thermodynamic system, there is also the possibility of dynamic equilibrium, in which all the flows are 0, but some thermodynamic forces in the system are not equal to zero (there are their variations) [5, 7].

Let us consider this possibility for a triple thermodynamic system. From Eqs. (6)–(8), it follows that near equilibrium, in the presence of variations of thermodynamic forces, the following conditions must be fulfilled:

$$J_{Fe} = 0 \Rightarrow L_{11}\delta\mu_{Fe} + L_{12}\delta\mu_C + L_{13}\delta\mu_{Cr} = 0, \quad (9)$$

$$J_C = 0 \Rightarrow L_{21}\delta\mu_{Fe} + L_{22}\delta\mu_C + L_{23}\delta\mu_{Cr} = 0, \quad (10)$$

$$J_{Cr} = 0 \Rightarrow L_{31}\delta\mu_{Fe} + L_{32}\delta\mu_C + L_{33}\delta\mu_{Cr} = 0, \quad (11)$$

where the index $\delta\mu$ denotes the coordinated variations of the thermodynamic forces that ensure the dynamic equilibrium of the system. It follows from the system of Eqs. (9)–(11) that the expressions for the flows of iron, chromium, and carbon are connected: the cross rates L_{12} , L_{13} , and L_{23} in expressions for the flows must have values such that the determinant of the matrix A composed of the coefficients of this system was equal to 0. In this case, the values of the flows of iron and chromium can significantly increase due to cross-kinetic coefficients in comparison with the independent diffusion of these elements [7, 16].

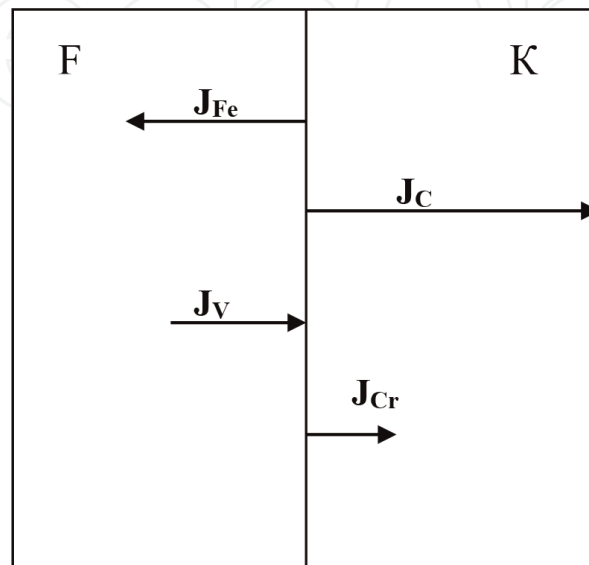


Figure 1.
Scheme of the process of carbides formation in chromium steel.

Let us find the expressions for the cross coefficients, which make it possible to obtain a nontrivial solution of the system of Eqs. (9)–(11). From the first Eq. (9), we establish a connection between the variations of forces:

$$\delta\mu_{Fe} = -(L_{12}/L_{11})\delta\mu_C - (L_{13}/L_{11})\delta\mu_{Cr}. \quad (12)$$

Substituting (12) into Eqs. (10) and (11), we find

$$J_C = (L_{22} - L_{12}^2/L_{11})\delta\mu_C + (L_{23} - L_{12}L_{13}/L_{11})\delta\mu_{Cr} = 0, \quad (13)$$

$$J_{Cr} = (L_{32} - L_{13}L_{12}/L_{11})\delta\mu_C + (L_{33} - L_{13}^2/L_{11})\delta\mu_{Cr} = 0, \quad (14)$$

For independent variations $\delta\mu_C$ and $\delta\mu_{Cr}$, the linear system of Eqs. (13) and (14) is compatible if the coefficients of $\delta\mu_C$ and $\delta\mu_{Cr}$ are equal to 0, from which we immediately find the relation between Onsager's kinetic coefficients:

$$L_{ik} = L_{ki} = \pm\sqrt{L_{ii} \times L_{kk}}, \quad i, k = 1...3 \quad (15)$$

and the sign before the root is selected based on the sign (direction) of the flows under consideration (see **Figure 1**). The considered procedure of variation allows us to find cross rates in the Onsager equations after the direct kinetic coefficients are calculated. In this case, the established connection (15) is satisfied for systems not very far from equilibrium and for the real system is approximate.

3. Calculation of thermodynamic forces and kinetic coefficients

Let us find the values of the thermodynamic forces and kinetic coefficients for the steel of the Fe-C-Cr system with 0.15% C at 600°C. We will assume that in a solid α -solution, there is chromium with a concentration of $C_{Cr} = 0.05$ and a carbon with a concentration of $C_C = 0.007$, an iron concentration of $C_{Fe} = 0.943$. In cementite-type carbide, chromium is found with a mass fraction of $\sim 20\%$ (with a concentration of $C_{Cr} = 0.2$) and carbon with a carbon concentration of 0.25, an iron concentration in the carbide $C'_{Fe} = 0.55$.

It is known from the experimental data that carbon is removed very rapidly (approximately 1 minute) from the α -solution of alloyed steel at a temperature of 550–650°C and, consequently, the formation of carbide inclusions is primarily due to carbon diffusion [14].

The thermodynamic force for carbon can be calculated from the formula [11]:

$$-\Delta\mu_C = -RT \ln \frac{a_C^K}{a_C^\alpha}, \quad (16)$$

where a_C^α is the thermodynamic activity of carbon in α -solution, a_C^K is the thermodynamic activity of carbon in cementite, R is the universal gas constant, and T is the temperature of the alloy.

The change in the thermodynamic activity of carbon in the alloy upon doping with component i can be found by the method of [15, 16] from the equation:

$$\ln(a_C/a_{C0}) = \beta_i Ni, \quad (17)$$

where β_i is the coefficient of the element's influence on the thermodynamic activity of carbon in the alloy, Ni is the content of the element in the alloy in atomic fractions, and a_{C0} is the thermodynamic activity of carbon for the alloy in the standard state.

We will assume that for our steel in the standard state $a_{C0}^{\alpha} = a_{C0}^K = a_{C0}$, i.e., unalloyed cementite in steel with 0.15% C is stable and in equilibrium with the solid solution at a tempering temperature of 600°C [13]. Using this condition and Eqs. (16) and (17), we find:

$$\ln (a_C^K/a_C^{\alpha}) = \beta_{Cr}^K N_{Cr}^K - \beta_{Cr}^{\alpha} N_{Cr}^{\alpha} \quad (18)$$

The value of β_i is calculated through the interfacial distribution coefficient of the alloying element $K_i = N_i(K)/N_i(\alpha)$ and the atomic fraction of carbon in the alloy N_C [15, 16]:

$$\beta_i = -\frac{(K_i - 1) + (N_C(K) - K_i N_C(\alpha))}{(K_i - 1)N_C + (N_C(K) - K_i N_C(\alpha))}. \quad (19)$$

With a slight error for low-alloyed alloys, we can take $N_C(K) = 0.25$, $N_C(\alpha) \approx 0.001$ —the carbon content in the undoped phases of steel, taken from the Fe-C state diagram.

Using the coefficient of chromium distribution between the α -phase and the carbide K_{Cr} , equal to 4, we find the equations for calculating the coefficients of influence β_{Cr} :

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

whence $\beta_{Cr}^{\alpha} = -12.16$ and $\beta_{Cr}^K = -3.26$.

Then from expressions (16)–(18), one can find the values.

$$\ln (a_C^K/a_C^{\alpha}) = -0.6085 + 0.652 = -0.0425 \text{ and } -\Delta_{\mu C} = 308.47 \text{ Joule}. \quad (21)$$

The work done in the diffusion of carbon from the α -phase to cementite is positive. For the diffusion of iron, it is not possible to calculate the difference of thermodynamic potentials, since the coefficient of iron activity in carbide is unknown. However, from the experimental data and the thermodynamics of the process, it is known that diffusion of carbon is the leading one, the diffusion of chromium accompanies the diffusion of carbon, and the diffusion of iron is forced, since it is directed toward increasing the concentration of iron.

With this in mind, we find the values of the kinetic coefficients L_{ii} in the Onsager equations.

As is known [8, 13], the kinetic coefficients L_{ii} are related to the diffusion coefficients D_i by the relation:

$$L_{ii} = C_i D_i / RT, \quad (22)$$

where C_1 is the concentration of iron in the alloy (0.943), C_2 is the concentration of carbon in the alloy (0.007), and C_3 is the concentration of chromium in the alloy (0.05).

Dependences of the diffusion coefficients of chromium and carbon in doped chromium ferrite on the temperature have the form [14, 17]:

$$D_C^{\alpha} = 0,177 \exp \left[\frac{-88230}{RT} \right] \text{ cm}^2/\text{сек}, \quad (23)$$

$$D_{Fe}^{\alpha} = 2,910^{-4} \exp \left[\frac{-251000}{RT} \right] \text{ cm}^2/\text{сек}, \quad (24)$$

$$D_{Cr}^{\alpha} = 3,05 \exp \left[\frac{-358000}{RT} \right] \text{cm}^2/\text{cek}. \quad (25)$$

At a temperature of 600° C:
 $D_1 = D_{Fe}^{\alpha} \approx 3.03 \cdot 10^{-19} \text{ cm}^2/\text{s}$, $D_2 = D_C^{\alpha} \approx 1.02 \cdot 10^{-6} \text{ cm}^2/\text{s}$, and $D_3 = D_{Cr}^{\alpha} \approx 1.38 \cdot 10^{-21} \text{ cm}^2/\text{s}$.

Using relations (23)–(25) and (15), we find the values of the kinetic coefficients for our system:

$L_{11} = 0.394 \times 10^{-22}$, $L_{22} = 0.984 \times 10^{-13}$, $L_{12} = -1.97 \times 10^{-17}$, $L_{33} = 0.95 \times 10^{-26}$, $L_{13} = -0.611 \times 10^{-24}$, and $L_{23} = 0.306 \times 10^{-19}$. Consequently, the system of Eqs. (6)–(8) takes the form:

$$J_{Fe} = 0.394 \times 10^{-22}(-\Delta\mu_{Fe}) - 1.97 \times 10^{-17}(-\Delta\mu_C) - 0.611 \times 10^{-24}(-\Delta\mu_{Cr}), \quad (26)$$

$$J_C = -1.97 \times 10^{-17}(-\Delta\mu_{Fe}) + 0.984 \times 10^{-13}(-\Delta\mu_C) + 0.306 \times 10^{-19}(-\Delta\mu_{Cr}), \quad (27)$$

$$J_{Cr} = -0.611 \times 10^{-24}(-\Delta\mu_{Fe}) + 0.306 \times 10^{-19}(-\Delta\mu_C) + 0.95 \times 10^{-26}(-\Delta\mu_{Cr}). \quad (28)$$

It follows from Eqs. (26)–(28) that the values of iron and chromium fluxes increase substantially due to the cross-ratios L_{12} and L_{32} of a significant thermodynamic force $(-\Delta\mu_C)$. The value of the carbon flux having a positive sign is determined mainly by the intrinsic coefficient L_{22} . The thermodynamic forces of iron and chromium make an insignificant contribution to the fluxes, because of the small value of the kinetic coefficients and their influence can be neglected. Then, as direct calculations show:

$$J_{Fe} = -6.08 \times 10^{-15}, J_C = 3.04 \times 10^{-11}, J_{Cr} = 0.94 \times 10^{-17}, \text{ and } J_V = 6.07 \times 10^{-15} \text{ cm}^2/\text{s}.$$

It was established in [18] that during the tempering period, a certain amount of nanoparticles of special chromium carbide with a size of $\sim 100 \text{ nm}$ can be formed in the steel, which were detected experimentally.

4. The nonequilibrium thermodynamics analysis of the eutectoid transformation

In [19], a generalization of the equations characterizing the growth of the pearlite colony is proposed, based on the application of nonequilibrium thermodynamic methods.

To this end, Eq. (19) from [20], which characterizes the growth rate of a pearlite colony, is represented as:

$$\frac{dX}{dt} = D_x \left[\left(C'_{\phi} - C'_{\text{u}} \right) / \left(C'_{\phi} - C_{\phi} \right) + \left(C'_{\phi} - C'_{\text{u}} \right) / \left(C_{\text{u}} - C'_{\text{u}} \right) \right] / \Delta = (D_x / \Delta)(-\Delta\varphi), \quad (29)$$

where D_x is the carbon diffusion coefficient in austenite along the x axis at a given temperature T , Δ is the thickness of a layer of austenite with different concentration of carbon, C'_{ϕ} and C'_y is the carbon concentration in the austenite near the ferrite and cementite plates, respectively, at a temperature T (**Figure 2**), C_y is the carbon content in cementite ($\sim 6.67\%$), C_{ϕ} is the carbon content in the ferrite at a given temperature T , and $-\Delta\varphi$ is the thermodynamic force of pearlite lateral growth. It is determined by the carbon concentrations in ferrite and cementite and has a dimensionless value.

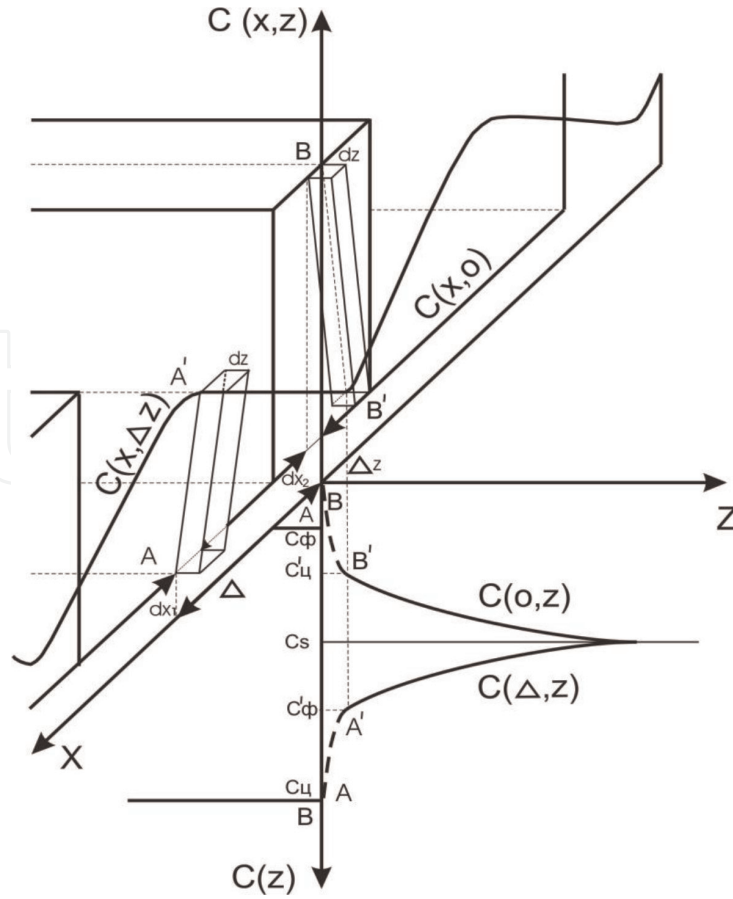


Figure 2.
Carbon distribution in the austenite-perlite system [20].

The second equation characterizing our system—the heat balance Eqs. (23)–(25) from [20]—is written in the form:

$$C\gamma dT/dt = \alpha \Delta T - (q\gamma/\Delta) dX/dt \quad (30)$$

where α is the heat transfer coefficient, C is the specific heat, ΔT is the temperature difference between the sample (T) and the cooling medium, q is the specific amount of heat released during the formation of perlite, and γ is the density of steel.

If two quantities are used as charges for the eutectoid transformation of austenite—the temperature of the sample T and the thickness of the plates of perlite X , then, according to (4), the Onsager motion equations must have symmetric forms (2) and (3),

where $J_1 = -dX/dt$ is the flow of the pearlitic layer (with increasing absolute value of the thermodynamic growth force of perlite, the flow increases in absolute value), and $J_2 = -C\gamma dT/dt$ is the heat flow in the sample (with a drop in sample temperature, the flow is positive), $X_1 = (-\Delta\phi)$, $X_2 = (-\Delta T/T)$ is the thermodynamic forces of perlite growth and temperature [14].

In order for Eq. (29) to correspond to Eq. (2), it must contain an additional term $L_{12}(-\Delta T/T)$; with the value of the coefficient $L_{11} = (D_x/\Delta)$:

$$J_1 = (D_x/\Delta)(-\Delta\phi) + L_{12}(-\Delta T/T) \quad (31)$$

where L_{12} is a cross ratio whose value is not yet known. Thus, we introduce (we assume) an additional dependence of the growth rate of the perlite layer not only on the carbon concentrations in the phases but also on the temperature.

Substituting expression (34) into the energy balance Eq. (33), we find the expression for the heat flow J_2 :

$$\begin{aligned} J_2 &= (q\gamma/\Delta)((D_x/\Delta)(-\Delta\varphi) + L_{12}(-\Delta T/T)) - \alpha T(-\Delta T/T) \\ &= (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q\gamma L_{12}/\Delta - \alpha T)(-\Delta T/T) \end{aligned} \quad (32)$$

Relating Eqs. (3) and (32) to each other, we obtain:

$$L_{21} = q\gamma D_x/\Delta^2 \quad (33)$$

Using for the kinetic coefficients, the Onsager reciprocity relations $L_{ik} = L_{ki}$ [9], we find that

$$L_{12} = L_{21} = q\gamma D_x/\Delta^2, \quad (34)$$

whereas

$$L_{22} = q^2\gamma^2 D_x/\Delta^3 - \alpha T. \quad (35)$$

The system of Eqs. (31) and (32) takes the form:

$$J_1 = (D_x/\Delta)(-\Delta\varphi) + q\gamma D_x/\Delta^2(-\Delta T/T) \quad (36)$$

$$J_2 = (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q^2\gamma^2 D_x/\Delta^3 - \alpha T)(-\Delta T/T). \quad (37)$$

In accordance with (36), the perlite growth rate is affected not only by the concentration thermodynamic force, but also by the temperature difference between the sample and the environment. Let us further consider the phase transformation of austenite under special conditions of steady growth of the pearlite colony, when it can be assumed that $\Delta T \approx \text{const}$, $dT/dt \approx 0$. In this case, Eq. (37) takes the following form:

$$J_2 = (q\gamma D_x/\Delta^2)(-\Delta\varphi) + (q^2\gamma^2 D_x/\Delta^3 - \alpha T)(-\Delta T/T) = 0. \quad (38)$$

For small ΔT , we can write approximately, as was done in [20]:

$$\Delta\varphi = \kappa\Delta T/T, \quad (39)$$

where κ is the proportionality coefficient.

By analogy with the previously obtained solutions [21], we introduce the following notation:

$$\Delta_0 = \sqrt{\kappa q\gamma D_x/\alpha T}; \quad (40)$$

$$\text{where } \Delta_l = q\gamma/\kappa \text{ is the characteristic parameter of the system.} \quad (41)$$

Eq. (38) can now be represented in the form:

$$\Delta^3 - \Delta_0^2\Delta - \Delta_0^2\Delta_l = 0 \quad (42)$$

For $\Delta_l = 0$, as expected, the solution of Eq. (31) $\Delta = \Delta_0$. We obtain a well-known solution for the pearlite transformation of austenite [20]. In the real domain, there is one solution of Eq. (44). For small Δ_l (< 0.5), the root Xk is in the region close to 1 ($Xk \rightarrow D_0$), with increasing Δ_l (in units of D_0), the root value increases. For large values of Δ_l , the root of Xk is approximately equal to

$$Xk \approx \sqrt[3]{\Delta_l/\Delta_0}. \quad (43)$$

The between interplate distance of perlite for a stationary growth process is found from the formula:

$$S_0 = 2X\kappa \times \Delta_0 = 2\kappa Xk\sqrt{\Delta l D_x / \alpha T}. \quad (44)$$

Using Eqs. (36) and (43), (44), we also find an improved expression for the perlite growth rate for an isothermal transformation

$$\frac{dX}{dt} = \frac{kDx}{S_0} \frac{\Delta T}{T} \left(1 + \frac{2\Delta l}{S_0}\right) \quad (45)$$

The formula (45) is a more precise expression for determining the growth rate of perlite in the eutectoid transformation, than the expression obtained earlier by the authors of [20].

We use the well-known dependence of the diffusion coefficient on temperature [17]:

$$D = A \exp.(-Q/RT),$$

где Q is the activation energy, ($Q \approx 134$ кJ/mol), and R is a constant ($R = 8314$ J/(mol·K)).

After substituting the known values of the steel parameters and taking into account that to 2.0, we find the calculated dependence of the perlite growth rate on the supercooling value of the alloy (**Figure 3**). In this figure, the dependence of the perlite growth rate on the supercooling value, calculated according to Zener's formula (1) [22, 23], is given for comparison.

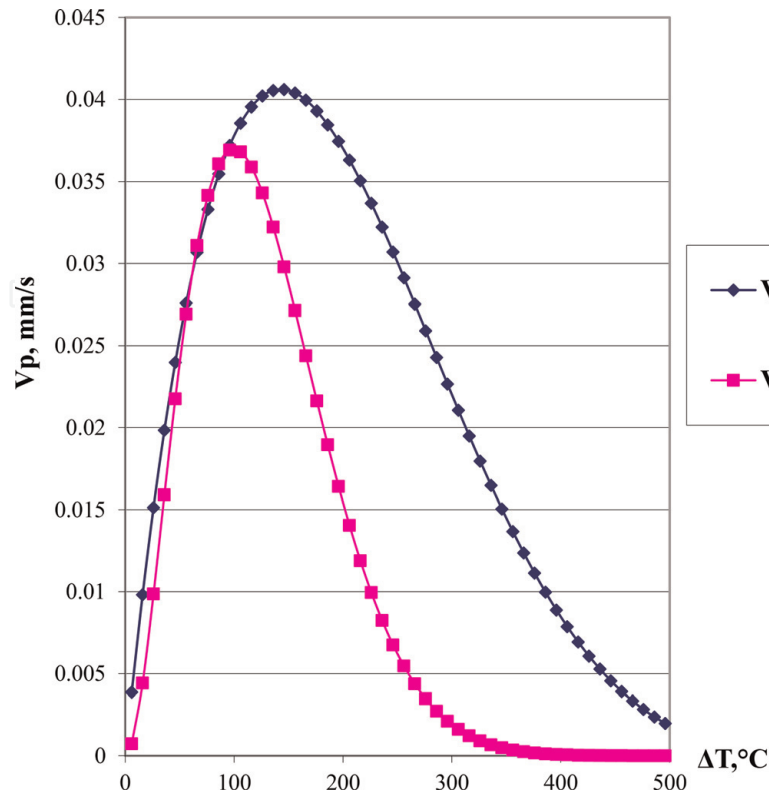


Figure 3.

Dependence of the perlite growth rate on the supercooling value, calculated from formula (47) of the present work (Vp1) and Zener's formula (1) [22, 23] (Vp2).

According to the constructed model, the perlite growth rate in the direction of the X axis has a maximum value at supercooling $\Delta T = 140.0^\circ\text{C}$. The perlite growth rate calculated according to Zener's formula has a theoretical maximum value at overcooling $\Delta T = 96.0^\circ\text{C}$. Consequently, the theoretical expressions (31) and (32) make it possible to describe with greater accuracy the maximum and the course of the experimental curve for the perlite formation rate presented in [3, 24] for high-purity eutectoid steel.

The expression for perlite growth rate obtained in this section has a significant value at supercooling of $300\text{--}400^\circ\text{C}$, thereby determining the possibility of perlite formation in this temperature range. Indeed, the formation of perlite in carbon steels in the temperature range $375\text{--}325^\circ\text{C}$ was revealed in [24].

The calculated dependence of the between interplate distance of perlite by formula (46) on the magnitude of the supercooling of steel is shown in **Figure 4**. The same figure shows the experimental points from [24].

A fairly good agreement of the calculated dependence with the results of the latest experiments is observed, which indicates the adequacy of the proposed model.

5. Application of the positions of nonequilibrium thermodynamics to the analysis of the nondiffusion transformation of austenite

Martensite is the basis of hardened steel, so studying the mechanism and kinetics of its transformation is still of extreme interest for the theory and practice of heat treatment.

In the works of G.V. Kurdymov and coworkers, the martensitic transformation is considered as the usual phase transformation in a one-component system, further complicated by the influence of a strong interatomic interaction, which leads to the development of significant stresses in the martensite crystal and matrix [25].

In accordance with the alternative mechanism, the martensitic transformation takes place by means of an instantaneous shift of atomic planes that does not require thermal activation and is not associated with thermodynamic transformation stimuli [1], [26]. In this case, the stress initiating the transformation is believed to be the stresses arising from the sharp cooling of the sample (quenching) [26].

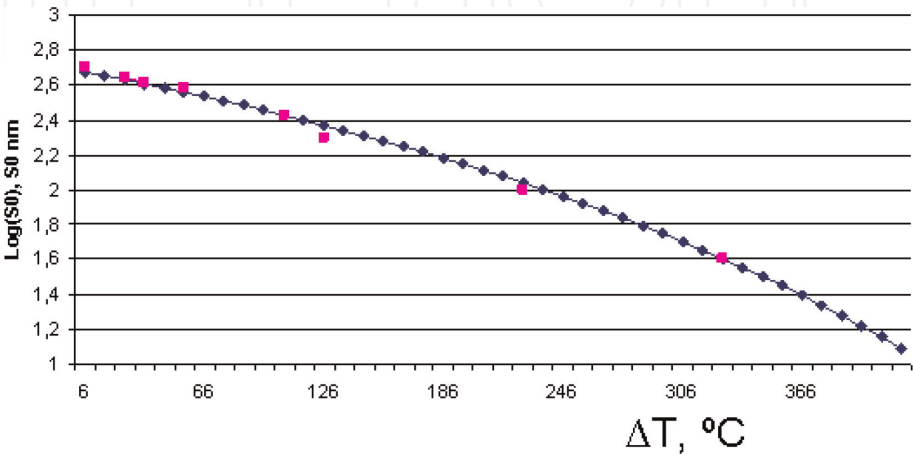


Figure 4.
The calculated dependence of the between interplate distance of perlite on the magnitude of the supercooling of steel (■ — experimental points from [24], p. 122, ■ — calculated points).

Considering the martensitic transformation as a thermally activated process, B.Ya. Lyubov used the equations of normal transformation obtained on the basis of the positions of nonequilibrium thermodynamics to describe his kinetics [3].

Changes in a complex or composite system under constant external conditions can be described as the process of increasing entropy. The rate of increase of entropy σ can be represented as the sum of the flux products and the corresponding forces for all transfer substrates in an amount of N [7–10]:

$$\sigma = \frac{dS}{dt}_{irrev} = \sum_{k=1}^N J_k X_k \quad (k = 1, \dots, N), \quad (47)$$

In the general case, the flows can be represented in the form (1).

The irreversible change in the entropy dS_{irrev} is equal to the sum of entropy changes in the system and the environment:

$$dS_{irrev} = dS + dS_e \quad (48)$$

Under isothermal conditions, when the released heat is absorbed by the environment and the temperature remains constant:

$$\begin{aligned} dS_e &= -dQ/T, \quad dQ = dU + PdV \\ dS_{irrev} &= dS - (dU + PdV)T^{-1} = (TdS - dU - PdV)T^{-1}. \end{aligned} \quad (49)$$

Since $dU + PdV - TdS = dG$, and if we take into account the low compressibility of bodies in the condensed state and relatively small pressures, then.

$$\frac{dS}{dt}_{irrev} = -T^{-1} \frac{dG}{dt} \approx -T^{-1} \frac{dF}{dt}, \quad (50)$$

where F is the free energy of the system.

The change in free energy in a system with a variable number of particles and internal stresses can be represented in the form [3], p. 142:

$$dF = dF_\varepsilon + dFn = \sigma_{ik} d\varepsilon_{ik} + \varphi_l dn_l, \quad (51)$$

where dF_ε is the change in free energy in the system related to internal stresses, dFn is the change in the free energy in the system, determined by the variable number of particles of type l , σ_{ik} is the stress tensor, ε_{ik} is the strain tensor of the system, φ_l is the chemical potential of the l th element of the system, and n_l is the number of particles of the l st element of the system per unit volume, $l = 1, N$.

We now introduce some simplifying assumptions. First, for the nondiffusion transformation of austenite, only one kind of particles, the α -phase of iron n_α , will be taken into account. Approximately, this is also true for alloys of iron with close elements (nickel, chromium, cobalt). Of course, φ is some effective (averaged) chemical potential of the atoms of the alloy.

Secondly, we assume that the deformation of the system is a triaxial compression-expansion, and in the expression for dF_ε , only the diagonal components of stress and strain tensors are taken into account:

$$\sigma_{ik} = \varepsilon_{ik} = 0, \quad i \neq k, \quad \sigma_{ii} = \sigma, \quad \varepsilon_{ii} = \varepsilon \quad (52)$$

The change in internal energy can then be represented as:

$$dF = 3\sigma d\varepsilon + \varphi dn_\alpha \quad (53)$$

but the change in entropy:

$$\frac{dS}{dt}_{irrev} = -T^{-1} \left(3\sigma \frac{d\varepsilon_\alpha}{dt} + \varphi \frac{d\varepsilon_\alpha}{dt} \right). \quad (54)$$

Thus, in our system, in addition to the particle flow from the γ phase to the α -phase of $J_1 = dn_\alpha/dt$, we will also take into account the change in the strain of the sample with time $J_2 = d\varepsilon/dt$. These flows are related to the driving forces by the Eq. (1).

If, as charges of the process of nondiffusion transformation of austenite, the two quantities are the concentration of α -phase particles and the strain value, then, according to (1), the equations of motion take the form:

$$J_1 = L_{11}X_1 + L_{12}X_2 \quad (55)$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \quad (56)$$

where $X_1 = \Delta\varphi$ is the thermodynamic force for iron, the change in the chemical potential at the transition of particles from the γ -phase to the α -phase, and $X_2 = \Delta\sigma$ is the change in the internal stress during the transition from the γ -phase to the α -phase.

The system of Eqs. (55) and (56) describes the contribution of stresses and deformations to the nondiffusion transformation of austenite. However, we do not yet know the coefficients of the equations in it. We now find expressions for the coefficients of the system of Eqs. (55) and (56). The coefficient L_{11} characterizes the normal transformation:

$$J_1 = \frac{dn_\alpha}{dt} = L_{11}(\varphi_\gamma - \varphi_\alpha) \quad (57)$$

In the normal kinetics of the phase transformation, the formation of the center (particle) of the α -phase occurs through separate (independent) acts of detachment of particles from the γ -phase and the attachment of atoms to the ferrite center. If we consider the process of formation of an α -phase close to the process of self-diffusion of iron in the γ -phase, then the coefficient L_{11} has the form [13]:

$$L_{11} = \frac{D_\gamma}{RT} \quad (58)$$

where D_γ is the self-diffusion coefficient of iron in the γ -phase (or the effective coefficient of self-diffusion in the γ -phase of the alloy), T is the transformation temperature, and R is the gas constant [27].

The self-diffusion coefficient of iron is taken in the usual notation [17]:

$$D_\gamma = D_0 e^{-\frac{U}{kT}} = 4.58 \cdot 10^{-4} \exp(-252,000/RT) \quad (59)$$

where D_0 is a multiplier and U is the activation energy of diffusion.

The coefficient L_{22} characterizes the direct relationship:

$$J_2 = \frac{d\varepsilon_\alpha}{dt} = L_{22}(\sigma_\gamma - \sigma_\alpha). \quad (60)$$

Let $\sigma_\gamma = 0$. Let us take into account that for triaxial compression stretching [28]: where σ_α is the stress in the α phase and σ_γ is the stress in the γ phase.

Let $\sigma_\gamma = 0$. Let us take into account that for triaxial compression-stretching [28]:

$$\sigma_\alpha = \frac{E}{3(1-2\mu)} \frac{\Delta V}{V} = \frac{E}{1-2\mu} \varepsilon_\alpha, \quad (61)$$

where E is the modulus of elasticity of steel ($\sim 2.17 \cdot 10^5$ MPa) and μ is the Poisson ratio (~ 0.26).

Then, expression (60) can be transformed as follows:

$$\frac{d\varepsilon_\alpha}{dt} = L_{22}\sigma_\alpha = L_{22} \frac{E}{1-2\mu} \varepsilon_\alpha = \frac{v}{L} \varepsilon_\alpha, \quad (62)$$

where the following values are entered:

v is the propagation velocity of the microdeformation in sample (~ 1000 m/c) [3] and L is the characteristic distance over which the microdeformation of the shear is propagated (the size of the martensitic strips or plates). At the initial stage of the formation of the shear structure, it has a magnitude of the order of the diameter of the austenite grain (~ 100 μ m), and then decreases with decreasing temperature [1].

From Eq. (62), we find that the coefficient L_{22} is equal to:

$$L_{22} = \frac{v(1-2\mu)}{LE}. \quad (63)$$

The cross-coefficients $L_{12} = L_{21}$ for a nonequilibrium thermodynamic system are found with sufficient accuracy by the formulas proposed in [5]:

$$L_{12} = \sqrt{L_{11}L_{22}} = \sqrt{\frac{D_\gamma}{RT} \frac{v(1-2\mu)}{LE}} \quad (64)$$

Thus, we obtained simple differential equations for a nonequilibrium thermodynamic system describing the nondiffusion transformation of austenite taking into account the influence of internal stresses.

Let us write the equations of motion of our system in the form:

$$\frac{dn_\alpha}{dt} = L_{11}\Delta\varphi + L_{12}\sigma_\gamma - L_{12}\sigma_\alpha. \quad (65)$$

$$\frac{d\varepsilon_\alpha}{dt} = L_{21}\Delta\varphi + L_{22}\sigma_\gamma - L_{22}\sigma_\alpha. \quad (66)$$

We first transform Eq. (66) taking into account expression (62). We have:

$$\frac{d\varepsilon_\alpha}{dt} + v\varepsilon_\alpha/L = L_{21}\Delta\varphi + L_{22}\sigma_\gamma, \quad (67)$$

where ε_α is the magnitude of deformations of the α -phase. The differential Eq. (66) with constant coefficients (temperature) has a solution:

$$\varepsilon_\alpha = \frac{(L_{21}\Delta\varphi + L_{22}\sigma_\gamma)(1-2\mu)}{L_{22}E} (1 - e^{-\frac{vt}{L}}). \quad (68)$$

This kinetic equation describes the change in the magnitude of the deformation of the α -phase in time. At $t = 0$, $\varepsilon_\alpha = 0$. When the time is counted, a fast ($\sim 10^{-6}$ s) process of transition to deformation occurs:

$$\varepsilon_\alpha = \varepsilon_\gamma + \Delta\varepsilon_\alpha = \varepsilon_\gamma + \frac{L_{21}\Delta\varphi(1-2\mu)}{L_{22}E}. \quad (69)$$

Eq. (69) shows that the residual deformation of the α -phase after the transient process consists of the deformation of the austenite ε_γ and the additional deformation $\Delta\varepsilon_\alpha$. This additional deformation determines the change in the volume of the sample as $\gamma \rightarrow \alpha$ -transformation:

$$\frac{\Delta V_{\gamma \rightarrow \alpha}}{V_\gamma} = 3n_\alpha \Delta\varepsilon_\alpha. \quad (70)$$

Then, substituting expression (53) into Eq. (51.1), we find:

$$\begin{aligned} \frac{dn_\alpha}{dt} &= L_{11}\Delta\varphi + L_{12}\sigma_\gamma - \frac{L_{12}(L_{21}\Delta\varphi + L_{22}\sigma_\gamma)}{L_{22}}(1 - e^{-\frac{v}{L}t}) = L_{11}\Delta\varphi + L_{12}\sigma_\gamma - \\ &(L_{11}\Delta\varphi + L_{12}\sigma_\gamma)(1 - e^{-\frac{v}{L}t}) = (L_{11}\Delta\varphi + L_{12}\sigma_\gamma)e^{-\frac{v}{L}t}. \end{aligned} \quad (71)$$

It can be concluded from expression (71) that the growth rate of α -phase particles depends on the stresses in the γ -phase. The greater the value of tensile stresses in the γ phase, the higher the growth rate of ferrite particles. The rate of growth of the α -phase particles at a constant temperature very rapidly (exponentially) decreases in time, determining the incompleteness of the transformation.

Integration of Eq. (71) with time-independent coefficients L_{11} and L_{12} allows us to obtain the kinetic equation for n_α :

$$n_\alpha = \frac{(L_{11}\Delta\varphi + L_{12}\sigma_\gamma)L}{v}(1 - e^{-\frac{v}{L}t}). \quad (72)$$

In accordance with Eq. (72), the amount of α -phase formed depends not only on the thermodynamic force $\Delta\varphi$, but also on the magnitude of the stresses in the γ -phase.

6. Scheme of the nondiffusion transformation of austenite based on the constructed model.

Before discussing the equations obtained, we introduce some more useful relations characterizing the $\gamma \rightarrow \alpha$ transformation. With the $\gamma \rightarrow \alpha$ transformation, the effective atomic volume of the iron lattice changes in the sample under consideration, characterized by $\Delta V_{\gamma \rightarrow \alpha}$ and the relative volume change $\frac{\Delta V_{\gamma \rightarrow \alpha}}{V_\gamma}$. According to the data of [3]:

$$\Delta V_{\gamma \rightarrow \alpha} = 0.268 - 1.62 \cdot 10^{-4}T, \text{ sm}^3/\text{mol} \quad (73)$$

We will assume that with the formation of the α -phase, the relative change in volume is determined by the additional deformation: $\frac{\Delta V_{\gamma \rightarrow \alpha}}{V_\gamma} = 3\Delta\varepsilon_\alpha$, and the compressive stress arising in the α -phase has the value.

$$\sigma_\alpha = \frac{E}{1-2\mu} \Delta\varepsilon_\alpha. \quad (74)$$

When the alloy sample is cooled by ΔT , a deformation occurs in its surface layer: $\varepsilon_\gamma \sim \alpha\Delta T$ and the tensile stress σ_γ corresponding to this deformation:

$$\sigma_{\gamma} = \frac{E}{1-2\mu} \alpha \Delta T. \tag{75}$$

Comparing the values of thermodynamic forces among themselves, it is possible to classify the types of nondiffusion transformation according to the kinetic criterion. As shown in [1], p. 208, for small deviations of the system from equilibrium, the growth of crystals is more likely, controlled by self-diffusion, at large-cooperative growth. The same phase transition in a single-component system under different external conditions can take place with an independent (or slightly dependent) temperature growth rate (martensitic kinetics) and with a rate that exponentially depends on the temperature at an activation energy close to the activation energy of self-diffusion (normal kinetics). The parameter characterizing the deviation of the system from equilibrium is the supercooling of the alloy $\Delta T = A_{c3} - T$, where A_{c3} is the temperature of the end $\alpha \rightarrow \gamma$ of the conversion upon heating, and T is the transformation temperature. The transformation scheme for the constructed model is shown in **Figure 5**.

A_{c1} is the temperature of the beginning of $\alpha \rightarrow \gamma$ transformation when the alloy is heated and M_{ni} is the temperature of the onset of the formation of isothermal martensite upon supercooling of the alloy. M_n is the temperature of the onset of athermal martensite formation upon supercooling of the alloy. M_k is the temperature of the end of martensite formation upon supercooling of the alloy.

Thus, for small

$$\Delta T : L_{11}\Delta\varphi > L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}, \tag{76}$$

then the growth of α -phase crystals is determined by self-diffusion by the normal mechanism. However, as follows from Eq. (72), in this case too, the contribution of deformations (and stresses) to the conversion kinetics is very significant. In order that the condition (76) is satisfied, it is necessary that the stress level in the γ - and α -phases be small; for the α -phase, this is possible only in the case of relaxation of internal stresses in the alloy at high temperature by the mechanism of recrystallization.

With increasing supercooling of the alloy, the thermodynamic stimulus and the rate of normal transformation increase.

For a larger

$$\Delta T : L_{11}\Delta\varphi \sim L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma} \tag{77}$$

A_{c3}	
	$L_{11}\Delta\varphi > L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}$, normal transformation, polygonal ferrite
A_{c1}	$L_{11}\Delta\varphi \sim L_{12}\sigma_{\alpha} > L_{12}\sigma_{\gamma}$, shear + normal transformation, ferrite side-plates
M_{ni}	$L_{11}\Delta\varphi < L_{12}\sigma_{\alpha}$, $\sigma_{\alpha} = \sigma_{\gamma}$
M_n	$L_{11}\Delta\varphi < L_{12}\sigma_{\alpha}$, $\sigma_{\alpha} < \sigma_{\gamma}$, shear transformation isothermal martensite, acicular ferrite
M_k	$L_{11}\Delta\varphi \ll L_{12}\sigma_{\gamma}$, shear transformation athermal martensite

Figure 5.
Scheme of nondiffusion transformations from the constructed model.

The existing thermal stresses in the γ phase (75) contribute to the formation of the α -phase by the shear mechanism, and the stresses arising in the α -phase compensate thermal stresses in the γ -phase. With a certain amount of α -phase, the stress equals $\sigma_\alpha = \sigma_\gamma$ arises and the further formation of the α -phase occurs according to the normal mechanism with the relaxation of the arising stresses by recrystallization. Consequently, the condition (77) corresponds to the transformation of the γ -phase by a mixed mechanism, and also to the formation of a ferrite side plates (Widmanstätten), followed by the release of the α -phase by the normal mechanism [1].

With a certain supercooling of ΔT_i , stress compensation occurs only when the γ -phase is completely transformed into ferrite by a shearing mechanism. In this case:

$$L_{11}\Delta\varphi \sim L_{12}\sigma_\alpha, \sigma_\alpha = \sigma_\gamma$$

The temperature corresponding to this supercooling is the starting point for the formation of the isothermal martensite Mni (**Figure 5**). Below the point Mni, the formation of the α -phase occurs by a shearing mechanism. However, the normal component of the process still has a significant value, affecting the morphology of the resulting precipitates. When supercooling a greater ΔT_i , $L_{11}\Delta\varphi < L_{12}\sigma_\alpha$, $\sigma_\alpha < \sigma_\gamma$

At temperatures below Mni, isothermal martensite or acicular ferrite is formed with a “reticular” or acicular morphology of precipitates. Finally, for large ΔT (below Mna):

$$L_{11}\Delta\varphi \ll L_{12}\sigma_\gamma, \quad (78)$$

Inequality (78) determines the condition for the formation of “athermal” martensite, when the normal component does not affect the formation of the shear structure. The main effect on the rate of the $\gamma \rightarrow \alpha$ transformation, in accordance with expression (71), is due to thermal stresses in the γ phase. Thus, the constructed model of the nondiffusion austenite transformations allows us to consider the normal and martensitic transformations, as limiting cases.

7. Conclusions

Based on the possibility of dynamic equilibrium, expressions are found for calculating the cross-kinetic coefficients of a thermodynamic system consisting of two and three components. The values of the thermodynamic force for diffusion of carbon, kinetic coefficients and flows of a thermodynamic system describing the kinetics of carbide precipitation during the tempering of chromium steel are calculated. It has been established that the values of iron and chromium fluxes increase substantially due to the cross ratios and the significant magnitude of the thermodynamic force ($-\Delta\mu_C$).

Analysis of the eutectoid transformation of austenite using the relations of nonequilibrium thermodynamics allowed us to generalize the equations of motion of the system obtained earlier by the authors of [20] and to find more accurate theoretical expressions for the perlite growth rate and its between interplate distance on the magnitude of the supercooling of steel. According to the constructed model, the perlite growth rate in the direction of the X axis has a maximum value at supercooling $\Delta T = 140.0^\circ\text{C}$. The perlite growth rate calculated according to Zener's formula has a theoretical maximum value at overcooling $\Delta T = 96.0^\circ\text{C}$. Consequently, the theoretical expressions (31) and (32) make it possible to describe with greater accuracy the maximum and the course of the experimental curve for the perlite formation for high-purity eutectoid steel.

The application of nonequilibrium thermodynamics to the analysis of the nondiffusion transformation of austenite made it possible to obtain a system of equations for the thermodynamic system and to generalize the results obtained earlier by B.Ya. Lyubov the equations for a normal transformation. The theoretical expression for the growth rate of the α -phase, obtained in this paper, takes into account the influence of stresses on the process of austenite transformation. It is shown that the rate of growth of α -phase particles at a constant temperature very rapidly (exponentially) decreases in time, determining the incompleteness of the transformation. According to the constructed model, a scheme of nondiffusion austenite transformations was developed, including normal and martensitic transformations, as limiting cases.

Thus, the use of the principles of nonequilibrium thermodynamics makes it possible to obtain completely new results in the analysis of phase transformations in iron-carbon alloys.


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