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Kinetics of Formation of Martensitic Crystals in Iron-Based Alloys

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From energy considerations, the critical parameters of martensitic crystals and kinetic equations for their growth rate are found. As revealed, the growth rate of martensite crystal thickness depends on the stresses acting in austenite and decreases exponentially with time. It is theoretically substantiated that for the formation of martensite crystals a certain level of the difference between the free energies of the phases and the stresses in austenite are necessary.

Key words: non-equilibrium thermodynamics, martensitic transformation, equations of motion, iron-based alloys, austenite.

З енергетичних міркувань знайдено критичні параметри мартенситних кристалів і кінетичні рівняння для швидкості їх зростання. Встановлено, що швидкість росту кристалу мартенситу по товщині залежить від діючих в аустеніті напружень і експоненційно зменшується в часі. Теоретично обґрунтовано, що для утворення кристалів мартенситу необхідний певний рівень різниці між вільними енергіями фаз і напружень в аустеніті.

Ключові слова: нерівноважна термодинаміка, мартенситне перетворення, рівняння руху, стопи на основі заліза, аустеніт.

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1. INTRODUCTION

Martensite is the basis of hardened steel; therefore, the study of the mechanism and kinetics of its transformation is still of extreme interest for the theory and practice of heat treatment [1].

The kinetics of martensitic transformation has a number of characteristic features that distinguish it from other types of phase transformations [2–4].

The martensitic transformation occurs in a wide temperature range, characterized by the temperatures of the beginning (M_n) and end (M_k) of the martensitic transformation. When the temperature drops below the martensitic point M_n , only part of the austenite transforms into martensite. The phase transformation process during isothermal delay, as a rule, quickly dies out [1]. For its resumption, a further decrease in temperature is required. The beginning of transformation cannot be delayed by any available cooling rates; martensite crystals grow at an appreciable rate even near absolute zero [5, 6].

A consistent theory of martensitic transformations should explain these phenomena. In the works of G. V. Kurdymov *et al.*, the martensitic transformation is considered as an ordinary phase transformation in a one-component system, further complicated by the influence of strong interatomic interaction, which leads to the development of significant stresses in the martensite crystal and matrix [2, 3].

According to an alternative mechanism, the martensitic transformation occurs with the help of an instantaneous shear of atomic planes, which does not require thermal activation and is not associated with thermodynamic stimuli of the transformation [1, 4]. In this case, the factor that initiates the transformation is assumed to be the stresses arising during abrupt cooling of the sample (quenching) [7].

Considering the martensitic transformation as a thermally activated process, B. Ya. Lyubov to describe its kinetics used the equations of normal transformation [1].

However, B. Ya. Lyubov in his theory did not take into account the role of internal stresses that can be induced in austenite and arise during the $\gamma \rightarrow \alpha$ transformation.

The theory of martensitic transformations continues to develop in recent years, see *e.g.* works [7–10], however, the effect of internal stresses on the kinetics of the formation of martensite crystals has not been sufficiently studied. Consequently, the issues of describing the martensitic transformation of austenite taking into account the effect of internal stresses are relevant.

The aim of this work is to construct kinetic equations for the formation of martensite crystals in iron-based alloys, taking into account the effect of internal stresses and to find the main kinetic parameters of the process.

2. EQUATIONS FOR MARTENSITIC TRANSFORMATION

To describe the kinetics of the martensitic transformation, B. Ya. Lyubov used the equations of non-equilibrium thermodynamics [1]. Changes in a complex or composite system under constant external conditions can be described as a process of increasing entropy. The rate of increase in entropy σ can be represented by the sum of the products of fluxes and corresponding forces for all transfer substrates in the amount N [11–14]:

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

In general, fluxes can be represented in the form [12, 13]:

$$J_i = \sum_{k=1}^N L_{ik} X_k \quad (i, k = 1, \dots, N), \quad (2)$$

where J_i —fluxes, X_k —thermodynamic forces, $L_{ik} = L_{ki}$ —Onsager kinetic coefficients [14], i, k —charge numbers (transfer substrates).

The main driving forces of phase transformations in nonequilibrium thermodynamics are the gradients of chemical potentials [12, 13]. When considering discontinuous systems, finite differences in chemical potentials ($\Delta\varphi_i$) are used as thermodynamic forces during the transition from one state to another [15, 16]. If, as charges of the process of diffusionless transformation of austenite, we use two quantities—the concentration of particles of the α -phase and the magnitude of deformation, then, according to (2), the equations of motion take the form:

$$J_1 = L_{11}X_1 + L_{12}X_2, \quad (3.1)$$

$$J_2 = L_{21}X_1 + L_{22}X_2, \quad (3.2)$$

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

The system of equations (3) describes the contribution of stresses and strains to the diffusionless transformation of austenite. The solution to the system of equations (3) has the form [17]:

$$J_\alpha = (L_{11}\Delta\varphi + L_{12}\sigma_\gamma)e^{-\frac{v}{L}t}, \quad (4)$$

where v —velocity of microstrain propagation in the sample (~ 1000 m/s) [2], L —the characteristic distance over which the shear microstrain extends (length of martensite laths or plates). At the initial stage of the formation of the shear structure, it has a value of the order

of the austenite grain diameter ($\sim 100 \mu\text{m}$), and then decreases with decreasing temperature [1, 17].

From expression (4), we can conclude that the growth rate of particles of the α -phase depends on the stresses in the γ -phase. The higher the tensile stresses in the γ -phase, the higher the growth rate of ferrite particles. The growth rate of α -phase particles at a constant temperature decreases very rapidly (exponentially) with time, determining the incompleteness of the transformation.

At temperatures below Mn :

$$L_{11}\Delta\varphi \ll L_{12}\sigma_\gamma, \quad (5)$$

Inequality (5) determines the condition for the formation of 'athermal' martensite, when the self-diffusion component does not affect the formation of the shear structure. The L_{11} coefficient is related by a simple expression to the iron self-diffusion coefficient $L_{11} = D_\gamma/RT$ (see [1, 17]). Therefore, the quantity $L_{11}\Delta\varphi$ can be called the self-diffusion component. The $L_{12}\sigma_\gamma$ value, the shear component, has a much larger value at the temperature of the formation of 'athermal' martensite (estimated at 10^{14} times).

Then equation (4) takes the form:

$$J_\alpha = L_{12}\sigma_\gamma e^{-\frac{v}{L}t}. \quad (6)$$

From expression (6), it can be concluded that the main effect on the rate of martensite formation is exerted by thermal stresses in the γ -phase. In this case, the process of the phase transformation of austenite into martensite at a constant temperature rapidly (exponentially) decays in time, which corresponds to the experimental data [1–5]. Thus, a theoretical substantiation of one of the features of the isothermal martensitic transformation has been given.

As shown by direct calculations, the rate of martensitic transformation at $T_0 = 400^\circ\text{C}$ is 10^{14} times higher than the rate of the normal (self-diffusion) component of the transformation. Therefore, it is of interest to assess the effect of stresses on the parameters and kinetics of the formation of martensite crystals.

3. PARAMETERS OF MARTENSITE CRYSTALS

Let us consider the parameters of the formed martensite crystals at the microlevel. Microstructural studies show that the martensite crystal has the shape of a plate with a sharp edge, which is visible in the plane of the microsection as a needle [20]. We will consider the shape of the crystal to be close to a biconvex lens formed by segments of a sphere (Fig. 1).

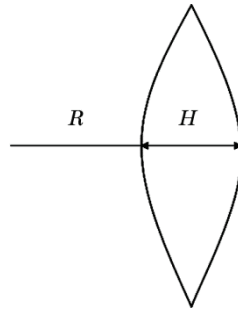


Fig. 1. Geometrical parameters of the martensite crystal.

If the thickness of the lens in its central part is denoted by H and the radius by R , then the volume of the martensite crystal is

$$V = \frac{\pi}{2} H^2 \left(R - \frac{H}{6} \right) \quad (7)$$

and its surface area

$$S_m = 2\pi RH. \quad (8)$$

When a martensite crystal appears in austenite cooled below the martensite point, the following change in the free energy of the system occurs [1].

1. Change in free energy in the volume occupied by the crystal of the α -phase (in the region of the martensitic transformation, the free energy of the α -phase is naturally less than the free energy of austenite).

2. Formation of the interface between the α -phase crystal and surrounding austenite.

3. Change in elastic energy in the bulk of the crystal of the α -phase and in the initial austenite.

To change the elastic energy, we will use the relations obtained by B. Ya. Lyubov [1]. We will assume that the distortions are mainly concentrated in austenite and have a simple shear character. The relative displacement of the boundary layers of atoms in the crystal is proportional to its thickness H with a factor K , which is determined from the crystallographic data. The pure shear strain ε , which transforms the austenite lattice into the martensite lattice, is equal in order of magnitude to $KH/2R$. The density of elastic energy is equal to

$$E_0 = \frac{G\varepsilon^2}{2} = GK^2 \frac{H^2}{8R^2}, \quad (9)$$

where G —austenite shear modulus.

Elastic energy concentrated in the area surrounding the martensite crystal:

$$\Delta F_E = \frac{4}{3} \pi R^3 E_0 = \frac{\pi}{6} GK^2 RH^2 = \pi\gamma RH^2. \quad (10)$$

The complete change in the free energy of the system due to the formation of a martensite crystal:

$$\Delta F = -\frac{\pi}{2} \left(R - \frac{H}{6} \right) H^2 \Delta F_0 + 2\pi\sigma RH + \pi\gamma RH^2. \quad (11)$$

We will assume that the most probable are martensite crystals with parameters H and R , which provide a minimum of ΔF . The differential $d\Delta F$ can be represented as

$$d\Delta F = F_H dH + F_R dR, \quad (12)$$

where

$$F_H = -\pi \left(RH - \frac{1}{4} H^2 \right) \Delta F_0 + 2\pi\sigma R + 2\pi\gamma RH, \quad (13)$$

$$F_R = -\frac{\pi}{2} H^2 \Delta F_0 + 2\pi\sigma H + \pi\gamma H^2. \quad (14)$$

Equating to zero $d\Delta F$ at $R = \text{const}$, *i.e.* $F_H = 0$, from (13) we find the following relationship between the parameters H and R :

$$R = \frac{\Delta F_0 H^2}{4H(\Delta F_0 - 2\gamma) - 8\sigma}. \quad (15)$$

Equating to zero $d\Delta F$ at $H = \text{const}$, *i.e.* $F_R = 0$, from (14) we find the critical value of the parameter H :

$$H_0 = \frac{4\sigma}{\Delta F_0 - 2\gamma}. \quad (16)$$

From (16) it follows that during the formation of a martensite crystal, the value of ΔF_0 must meet the condition:

$$\Delta F_0 \geq \Delta F'_0 = 2\gamma. \quad (17)$$

The thermodynamic condition (17) establishes one more feature of the martensitic transformation and gives an answer to the question why it begins at a certain temperature Mn [22]. It shows that the difference between the free energies of the austenite and ferrite phases,

which increases with decreasing temperature, must be greater than a certain value 2γ , which is calculated through the austenite shear modulus. Therefore, relation (17) is fulfilled when austenite reaches a certain temperature Mn during cooling. With an increase in the degree of alloying of austenite, its shear modulus increases and, accordingly, the steel temperature Mn decreases [22].

At a given value of ΔF_0 , the martensite parameter R should take on well-defined values. Substituting (16) into (15), we find the critical value R :

$$R_0 = \frac{2\sigma\Delta F_0}{(\Delta F_0 - 2\gamma)^2}. \quad (18)$$

And finally, we find an expression for the important ratio $H/2R$, which determines the deformation of pure shear:

$$\frac{H_0}{2R_0} = \frac{\Delta F_0 - 2\gamma}{\Delta F_0}. \quad (19)$$

We will assume that during the growth of a martensite crystal at a constant temperature at any moment of time, a thermodynamically determined relationship between its parameters of the form (19) is fulfilled.

4. KINETIC EQUATIONS FOR THE GROWTH OF MARTENSITIC CRYSTALS

Knowing the values of the fluxes that characterize the kinetics of the formation of martensite crystals, it is possible to calculate the rate of change in their sizes. We will assume that the growth of martensite particles occurs due to the flux of the α -phase through the surface of the crystal S . During the time dt , the change in the amount of substance of the martensite crystal is equal to

$$dM = \rho dV = \frac{3\pi\rho}{2} H^2 \left(K_0 - \frac{1}{6} \right) dH, \quad (20)$$

where ρ —density of the formed particle (mol/cm^3).

In expression (20), formula (7) is used for the volume of a martensite crystal, where

$$K_0 = \frac{R}{H} = \frac{\Delta F_0}{2(\Delta F_0 - 2\gamma)}. \quad (21)$$

But the change in the amount of the α -phase during the same time can be determined in accordance with the continuity equation [15, 19]:

$$dM = J_\alpha S dt = 4\pi K_0 H^2 J_\alpha dt, \quad (22)$$

where the particle flux J_α is mol/cm²·s.

Comparing equations (20) and (22), we find

$$\frac{3\left(K_0 - \frac{1}{6}\right)\rho}{8K_0} dH = J_\alpha dt, \quad (23)$$

from where

$$\frac{dH}{dt} = \frac{8K_0}{3\left(K_0 - \frac{1}{6}\right)\rho} L_{12}\sigma_\gamma e^{-\frac{\nu}{L}t} = \frac{4\Delta F_0}{\rho(\Delta F_0 + \gamma)} L_{12}\sigma_\gamma e^{-\frac{\nu}{L}t}. \quad (24)$$

Thus, the growth rate of a martensite crystal over thickness depends on the stresses σ_γ acting in austenite and decreases exponentially with time. Substituting K_0 from (21) and integrating over time, we find the thickness of the martensite crystal formed during the isothermal transformation of austenite:

$$H = \frac{4}{\rho} \frac{\Delta F_0}{(\Delta F_0 + \gamma)} L_{12}\sigma_\gamma \frac{L}{\nu}. \quad (25)$$

The crystal thickness is directly proportional to the stresses acting in the austenite and the characteristic transformation time (L/ν). Naturally, only those crystals whose thickness meets the condition: $H \geq H_0$ can be stable. At $H < H_0$, the α -phase formed by a shift by the value of H is unstable and does not lead to the formation of martensite crystals with a certain radius.

From expression (25) we find the radius R_s of martensite crystals formed by stresses σ_γ acting in austenite:

$$R_s = \frac{2}{\rho} \frac{\Delta F_0^2}{(\Delta F_0 + \gamma)(\Delta F_0 - 2\gamma)} L_{12}\sigma_\gamma \frac{L}{\nu}. \quad (26)$$

As expected, at $\Delta F_0 \leq 2\gamma$, the formation of martensite crystals does not occur. Thus, the condition $\Delta F_0 = 2\gamma$ determines the point of the onset of the formation of Mn martensite on the temperature axis. At a temperature higher than Mn , the shear of atomic planes in austenite is energetically unfavourable. With an increase in $\Delta F_0 \geq \Delta F_0'$, the resulting crystals of martensite have a radius R_s quite determined by the transformation parameters and stresses in austenite. If the radius of the formed particles is $R_s \leq R_0$, then the formation of such crystals of the α -phase is also energetically unfavourable and it again transforms into austenite. For the condition $R_s > R_0$ to be satisfied at a given value

of ΔF_0 , a certain level of stresses in the γ -phase $\sigma_\gamma > \sigma_{\gamma 0}$ is also required.

Thus, for the formation of a martensite crystal, several conditions must be met—thermodynamic $\Delta F_0 \geq \Delta F_0'$ and a certain stress level in the γ -phase $\sigma_\gamma > \sigma_{\gamma 0}$.

5. CONCLUSIONS

1. It has been revealed that the main effect on the rate of martensite formation is exerted by thermal stresses in the γ -phase. In this case, the growth rate of a martensite crystal in thickness depends on the stresses acting in austenite and decreases exponentially with time.

2. It was found that at the difference between the free energies of austenite and martensite $\Delta F_0 \leq 2\gamma$, the formation of martensite crystals does not occur. It is assumed that the condition $\Delta F_0 = 2\gamma$ determines the point of the onset of the formation of *Mn* martensite on the temperature axis.

3. Formulas for calculating the radii of the martensite crystal of critical R_0 and current R_s are obtained. It is shown that for the fulfilment of the condition $R_s > R_0$ at a given value of the difference of the free energies of the phases ΔF_0 , a certain level of stresses in the γ -phase is required.

REFERENCES

1. B. Ya. Lyubov, *Kineticheskaya Teoriya Fazovykh Prevrashcheniy* (Moscow: Metallurgiya: 1969) (in Russian).
2. Ya. S. Umanskiy and Yu. A. Skakov, *Fizika Metallov* (Moscow: Atomizdat: 1978) (in Russian).
3. G. V. Kurdyumov, *Yavleniya Zakalki i Otpuska Stali* (Moscow: Metallurgizdat: 1960) (in Russian).
4. G. V. Kurdyumov, L. M. Utevskiy, and R. I. Entin, *Prevrashcheniya v Zheleze i Stali* (Moscow: Nauka: 1977) (in Russian).
5. L. Kaufman and M. Koen, *Uspekhi Fiziki Metallov* (Moscow: Metallurgizdat: 1961) (in Russian).
6. S. A. Kulin and M. Cohen, *J. Metals*, **2**, No. 11: 1139 (1950).
7. S. P. Oshkaderov, *Uspehi Fiziki Metallov*, **12**: 269 (2011).
8. V. A. Lobodyuk, *Uspehi Fiziki Metallov*, **15**: 173 (2014).
9. A. N. Lihachev and Yu. N. Koval, *Uspehi Fiziki Metallov*, **16**: 1 (2015).
10. V. A. Lobodyuk, *Uspehi Fiziki Metallov*, **17**: 89 (2016).
11. L. Onsager, *Phase Transformation in Solid. Conference* (Cornwell: N.Y.C.: 1951).
12. I. Prigozhin, *Vvedenie v Termodinamiku Neobratimyykh Protssessov* (Moscow: IL: 1960) (in Russian).
13. S. de Groot and P. Mazur, *Neravnovesnaya Termodinamika* (Moscow: Mir: 1964) (in Russian).
14. L. Onsager, *Phys. Rev.*, **37**: 405 (1931).

15. A. A. Snezhnoy and R. L. Zhukov, *Diffuzionnye Protsessi v Metallakh* (Kyiv: Naukova Dumka: 1966) (in Russian).
16. M. A. Krishtal, *Termodinamika, Fizicheskaya Kinetika, Strukuroobrazovanie i Svoystva Chuguna i Stali* (Moscow: Metallurgiya: 1971) (in Russian).
17. S. V. Bobyr, *Metallofiz. Noveishie Tekhnol.*, **40**, No. 11: 1437 (2018) (in Russian).
18. K. Dzh. Smitlz, *Metally: Sprav. Izd.* (Moscow: Metallurgiya: 1980) (in Russian).
19. M. V. Belous and M. P. Braun, *Fizika Metallov* (Kyiv: Vyshcha Shkola: 1985) (in Russian).
20. D. F. Kalinovich, I. I. Kovenskiy, and M. D. Smolin, *Ukrayinskyy Fizychnyy Zhurnal*, **14**, No. 2: 515 (1969).
21. S. Z. Bokshiteyn, *Struktura i Mekhanicheskie Svoystva Legirovannoy Stali* (Moscow: Metallurgizdat: 1954) (in Russian).
22. V. I. Prosvirin and S. D. Entin, *Izotermicheskoe Obrazovanie Martensita* (Moscow: GNTI ML: 1953) (in Russian).