

# THE THEORY OF DIRECT MARTENSITIC TRANSFORMATIONS OF STEELS

## ТЕОРИЯ ПРЯМЫХ МАРТЕНСИТНЫХ ПРЕВРАЩЕНИЙ СТАЛЕЙ

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**Abstract:** A theory of martensitic transformations of carbon steels based on the principle of detailed balance is proposed. This theory supplements the theory of Landau phase transitions in crystalline media, as well as the theory of crystallization of Kolmogorov's and Avrami's substance. In the proposed theory the martensitic transformations are described by the equations of induced transitions between two energy levels, which correspond to the number of particles of the initial phase with low energy (austenite) and the number of particles of the transformed phase with higher energy (martensite). The source of the transformations is the particles of the third kind - phonons, the number of which is associated with the induced transitions of particles between the energy levels and depends on the transformation temperature. The conclusions of the proposed theory correspond quantitatively to the experimental data.

**Keywords:** MARTENSITIC TRANSFORMATION, CARBON STEELS, ATHERMAL DIRECT MARTENSITIC TRANSITION, ISOTHERMAL DIRECT MARTENSITIC TRANSITION, TWO-LEVEL SYSTEM

### 1. Introduction

During cooling of carbon steel being in  $\gamma$ -phase and characterized as austenite (phase A) its structural transformation occurs, which is associated with a change of the crystalline lattice symmetry. FCC symmetry of  $\gamma$ -phase transits to a new, more solid  $\alpha$ -phase with BCC symmetry called martensite (phase M).

Phase transitions, in which the processes of diffusion and self-diffusion carry slowly, are direct martensitic transformations (DMT). DMT results in a large number of crystals  $M$  formed in each predefined grain of the initial phase A, which have the form of a plate with a thin by an order of magnitude smaller than its sizes in orthogonal directions to it. The size of crystals  $M$  depends on the initial state of grains A: homogeneous and perfect crystal structure A gives large crystals  $M$  and inhomogeneous, imperfect structure gives crystals of small sizes.

For DMT description in Landau theory [1] the expansion of Gibbs free energy is realized according to degrees of strain shear. But in some cases such an expansion does not describe experimental results [2-4]

Another approach consists in rigorous solution of the problem of substance crystallization [5, 6].

However, as practice shows, calculations of phase transformation kinetics using the Avrami equation do not always lead to correct results.

The discrepancies between the theoretical description of DMT and experimental data require further search for theories describing phase transformations in metals and alloys.

### 2. Physical model of phase transformations in crystalline media

Phase transformations in crystalline media according to their specific features can be described using a two-level system (TLS), the foundations of which have been formulated by Einstein A. [7].

Structural transformation of A-phase steel into M-phase steel can be characterized in TLS as spontaneous and induced transitions from stable state A to metastable state M and vice versa with probabilities corresponding to these transitions.

Schematic diagram of such transitions is presented in Fig. 1. In this figure the stable state is characterized by energy  $\varepsilon_A$  and temperature  $T_A$  and the metastable state is characterized by  $\varepsilon_M$ ,  $T_M$ , at that  $\varepsilon_A < \varepsilon_M$ ,  $T_A > T_M$ . The arrows in Fig. 1 denote:  $\mu_{MA}$  - the probability of spontaneous transition from level M to level A;  $w_{MA}$  and  $w_{AM}$  - the probability of the induced transitions of the level M to the level A and vice versa respectively.

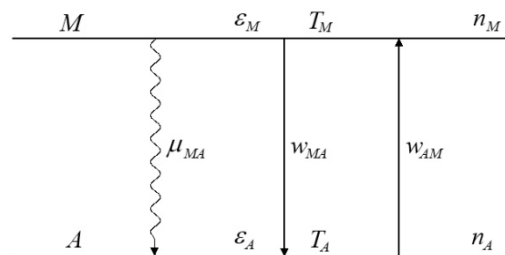


Fig. 1. AM two-level system:  $n_A$  - number of elementary cells of phase A;

$n_M$  - number of elementary cells of phase M

### 3. Equation system for description of DMT in carbon steel

When describing DMT in carbon steel the following requirement must be met: the increase in the number of elementary cells of phase A is equal to the decrease in the number of elementary cells of phase M, provided that the total number of cells is constant.

Let us consider the principle physics of transitions in carbon steel. However, it should be noted that these principle physics are, in our opinion, common for all systems subject to phase transformations.

During quenching the lattice atoms are displaced as a result of thermal vibrations, the concept of a phonon can be used for description of their energy. The phonon is characterized as a quasi-particle with energy  $\varepsilon = \hbar\omega$  and quasi-momentum  $\vec{p} = \hbar\vec{k}$ , where,  $\omega$ ,  $\vec{k}$  - frequency and wavenumber of the wave.

As the carbon steel temperature  $T$  decreases, the phonons acquire energy comparable to the energy barrier of the phase transition and their effect on the crystalline lattice of carbon steel will initiate the transitions of elementary cells from state M to state A and vice versa. Such transitions are induced, because they are caused by an external action associated with a temperature decrease. When interacting with MA two-level system the number of phonons should vary: decrease in the number of elementary cells of phase M leads to increase in phonons (phonon emission) and vice versa, increase in the number of elementary cells of phase M leads to decrease in the number of phonons (phonon absorption).

We consider two DMT modes of carbon steel below: athermal and isothermal.

#### 4. Athermal DMT of carbon steel

Athermal DMT of carbon steel occurs at  $T(t)$  decreasing within the range of  $T_K \leq T(t) \leq T_H^*$ , were  $T_H^*$  - initial temperature of the experiment  $T_K \leq T_H^* \leq T_H$ .

The initial equations of athermal DMT at a sufficiently large number of phonons ( $N \gg n_A, n_M$ ) are as follows:

$$\begin{aligned} \frac{\partial n_M}{\partial t} - \gamma \frac{\partial n_M}{\partial T} &= \mu_{MA}(T)(n_A - n_M)N, \\ \frac{\partial n_A}{\partial t} - \gamma \frac{\partial n_A}{\partial T} &= -\mu_{MA}(T)(n_A - n_M)N, \\ \frac{\partial N}{\partial t} - \gamma \frac{\partial N}{\partial T} &= -\mu_{MA}(T)(n_A - n_M)N, \end{aligned} \quad (1)$$

were,  $T(t) = T_H^* - \gamma t$  - temperature change in course of the time,  $\gamma = (T_H^* - T_K)/t_{AM}$ ,  $\mu_{MA} = w_{MA} = w_{AM}$  - the relation between the transition probabilities, which is valid at all temperatures.

To solve Eqs. (1) we determine the dependence of the probability of the induced transitions  $\mu_{MA}(T)$  upon the temperature in the following form:

$$\mu_{MA}(T) = \mu(T_H^*) \left( 1 - (1 - \beta k \tilde{T}^k) \exp[-\tilde{T}^k] \right), \quad (2)$$

$$\text{were, } \tilde{T}(T) = (T_H^* - T) / (T_H^* - T_K).$$

The representation (2) corresponds to the quenching method in one cooler when metal samples heated to the quenching temperature are immersed in the quench liquid until completely cooled.

As the temperature is decreased the velocity of DMT of phase A to phase M increases to the maximum value and then it decreases to zero, where the DMT velocity can be assumed to be proportional to the transition probability (2).

As the temperature is decreased from the initial  $T = T_H^* \leq T_H$  to  $T = T_K$ , DMT occurs in the alloy steel, as a result of which the elementary lattice cells of phase A almost completely transit to phase M.

The solution of equation system (1) under condition (2) has the following form:

$$N(\xi) \approx N_{eq}, \quad (3)$$

$$n_M(\xi) \approx \frac{n_{M0} + n_{A0}}{2} \left( 1 - \frac{n_{A0} - n_{M0}}{n_{M0} + n_{A0}} \exp(-2\mu' N_{eq} \xi) \right) \quad (4)$$

$$n_A(\xi) \approx \frac{n_{M0} + n_{A0}}{2} \left( 1 + \frac{n_{A0} - n_{M0}}{n_{M0} + n_{A0}} \exp(-2\mu' N_{eq} \xi) \right). \quad (5)$$

were,  $\xi(t, T) = t + F(T, T_H^*)$ ,  $n_{M0} = n_M(0)$ ,  $n_{A0} = n_A(0)$ ,  $N_0 = N(0)$ ,  $N_{eq} = N_0 - (n_{A0} - n_{M0})/2$ ,  $\mu' = \mu(T_H^*)$ ,  $F(T, T_H^*) = \frac{1}{\gamma} \int_{T_H^*}^T \left\{ 1 - (1 - \beta k (\tilde{T}(x))^k) \exp[-(\tilde{T}(x))^k] \right\} dx$ .

Analysis (3) - (5) shows that the total number of elementary cells that have transited from level A to level M is determined by the following expression:

$$n_{MS} = (n_{A0} + n_{M0}) \left( 1 - \exp(-2\mu' N_{eq} \xi(t, T)) \right). \quad (6)$$

Expression (6) is obtained as a result of summing the phase M for a large number of TLS with a short characteristic transition time

( $\mu' t_{AM} \gg 1$ ) into which the temperature interval is divided. Phase M is formed in each of these TLSs in such a way that the final state of one TLS determines the initial state of the subsequent TLS. The total amount of the transited phase M can be obtained by summing the phase M in each TLS to which the DMT temperature interval is divided.

Thus, it can be concluded from the expression (6) that as the temperature is decreased from the initial temperature  $T = T_H^* \leq T_H$  to  $T = T_K$  then DMT occurs in the alloy steel as a result of which the elementary lattice cells of phase A almost completely transit to phase M.

#### 5. Isothermal DMT of carbon steel in high-temperature range

The high temperature range will be considered as a specified by ratio  $T_K \leq T(t) \leq T_H^*$ . Intense thermal vibrations of the crystalline lattice are observed within this temperature range; it corresponds to availability of a large number of phonons in the system, i.e.  $N_0 \gg n_{A0}, n_{M0} \gg 1$ .

For example, for an isothermic DMT when quenched within heterogeneous temperature range  $Ac_3$  the DMT velocity increases first from zero, reaches a maximum at  $T \sim 700^\circ \text{C}$  then decreases and at  $< 550^\circ \text{C}$  assumes a small value [8].

For analytical description of isothermal DMT of carbon steel a solution for athermal DMT is applicable provided that the characteristic time of athermal DMT -  $t_{AM}$  must be replaced by the characteristic time of isothermal DMT -  $t_{AM}^*$  which is much greater than the first ( $t_{AM}^* \gg t_{AM}$ ). In this case, at a given experiment temperature  $T_H^*$  the expression (6) can be transformed to the following form:

$$\frac{n_{MS}}{(n_{M0} + n_{A0})} = \left( 1 - \exp \left( -2\mu' N_{eq} t \left( 1 - \exp \left( -\beta \left( \frac{t}{t_{AM}^*} \right)^k \right) \right) \right) \right) \quad (7)$$

We used analytical dependence (7) to describe isothermic DMTs of steel ( $Fe + 7\% Cr + 2\% Ni$ ) [2].

Comparison of the theoretical dependence (7) with experimental data [2] is carried out by transforming (7) to the percentage of the amount of the transformed phase A upon the time:

$$\frac{n_{AS}}{n_{A0}} = A \cdot 100 \cdot \left( 1 - \exp \left( -Bt \left( 1 - \exp(-Ct^k) \right) \right) \right), \quad (8)$$

$$\text{were, } A = 1 + n_{M0}/n_{A0}, \quad B = 2\mu' N_{eq}, \quad C = (t_{AM}^*)^{-k}.$$

Digitized experimental curves [2] (points) and analytical solutions (8) (solid lines) are shown in Fig. 2 a), b).

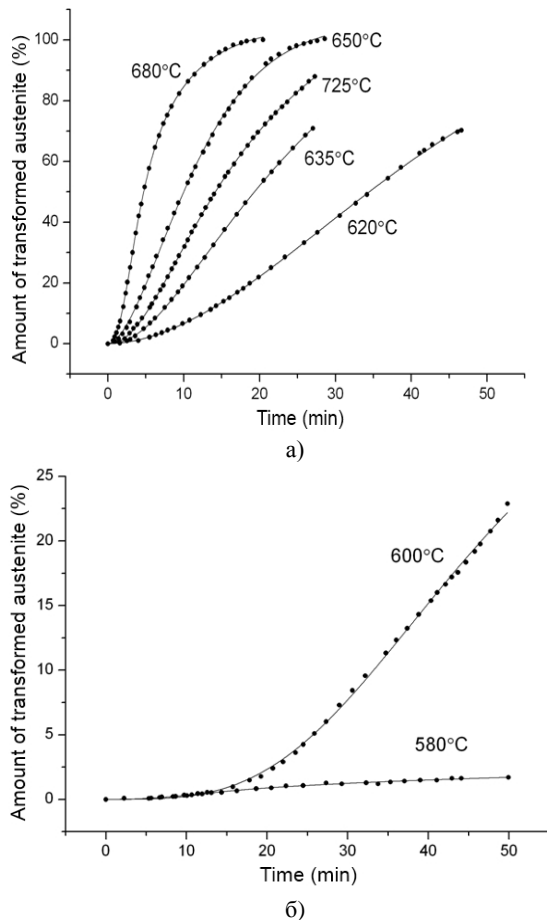
Comparison of the analytical dependencies describing the isothermal DMT of one of the alloy steel types with experimental data (Fig. 2) shows their good quantitative agreement. This agreement indicates the possibility of describing DMT processes on the basis of the detailed balance principle formulated for elementary cells of phase A (austenite) and phase M (martensite) - the main participants of DMT kinetics.

The values of  $A, B, C, k$  coefficients obtained as a result of approximating the experimental data by the analytical dependence (8) are presented in Table 1.

#### 6. Isothermal DMT of carbon steel in low-temperature range

As the temperature of martensitic transformations decreases, when  $T_{K0M} \leq T(t) \leq T_H^* \leq T_K$ , the intensity of vibrations of the

crystalline lattice also decreases, which leads to decreasing the phonon number, i.e. to the relations  $N_0 > (n_{A0} - n_{M0})/2 \gg 1$ .



**Fig. 2.** Comparison of digitized experimental data (points) with analytical solutions (8) (solid lines) for different temperatures of isothermal DMT of steel Fe+7%Cr+2%Ni

- a) Amount of transformed austenite (%);  
b) Time (min)

**Table 1.** The values of  $A, B, C, k$  coefficients and characteristic time  $t_{AM}^*$  of isothermal DMT for different quench temperature

	Quench temperature, $T_H^*$ (°C)						
	580*	600*	620*	635	650	680	725
$A$	2.51	525.61	104.41	167.51	106.07	104.3	130.94
$B$	0.02	9.3E-4	0.45	0.02	0.15	0.17	4.1E-2
$C$	0.02	1.53E-4	2E-3	0.05	8.8E-3	0.16	6.8E-2
$k$	1.73	2.53	0.87	1.21	0.81	1.545	1.21
$t_{AM}^*$	10.60	33.6	1.3·10 <sup>3</sup>	11.51	20.18	3.3	9.2

\* The experimental data are insufficient for approximation.

Besides, it is known from experiments, that as the temperature decreases from martensitic  $T_K$  to room temperature  $T_{Kom}$ , DMT is observed, as a result of which the amount of transformed austenite increases from 5% at  $T_H^* = 450$  °C to 95% at  $T_H^* = 300$  °C [2, 9].

In this case, the DMT characteristic time  $\tilde{t}_{AM}$  is practically the same for the full temperature range and is short in comparison with DMT characteristic time at high temperatures  $t_{AM}^*$  (

$$t_{AM}^* \gg \tilde{t}_{AM} \approx 1 \text{ min.})$$

Under these conditions the expressions for a high-temperature isothermal DMT can be used to describe isothermal DMT at low temperatures, if only in the expression for  $\gamma$  we replace  $T_K$  by  $T_{Kom}$  and  $t_{AM}^*$  by  $\tilde{t}_{AM}$ , the probability of the induced transitions  $\mu'$  by  $\mu''$  which corresponds to the frequencies of induced transitions at low quench temperatures.

At that, because of a small number of phonons, the exponential summands in denominators of accurate solutions of equations (1) can not be omitted.

In view of the fact that the number of phonons is still large compared with the number of elementary cells in phase A and phase M, the athermal DMT process can also be represented as a number of transitions from one TLS to another.

In general, based on solutions for DMT in high-temperature range the expression for total amount of transformed austenite is valid:

$$\frac{n_M^{tot}(t)}{n_{A0}A} \approx \frac{1}{2} \frac{\left(1 - A \frac{(n_{A0} - n_{M0})}{(n_{A0} + n_{M0})} \exp(-2\mu'' N_{eq} t)\right)}{1 - \frac{n_{A0} - n_{M0}}{2N_0} \exp(-2\mu'' N_{eq} t)}, \quad (9)$$

If martensite formed in high-temperature range is excluded in (9), the amount of transformed austenite in low-temperature range will be equal to:

$$\begin{aligned} n_M(t) &= n_M^{tot}(t) - n_{M0} = \\ &= \frac{(n_{A0} - n_{M0})}{2} \frac{(1 - \exp(-2\mu'' N_{eq} t))}{1 - \frac{n_{A0} - n_{M0}}{2N_0} \exp(-2\mu'' N_{eq} t)}. \end{aligned} \quad (10)$$

With a relatively small number of phonons it can be shown that the amount of transformed phase A can be represented with a sufficient degree of accuracy by the sum of two solutions of the form (10).

In dimensionless notation the amount of transformed phase A can be represented as a sum of constant magnitude and two exponents:

$$\frac{n_{MS}(t)}{n_{A0}} = A' - B' \exp(-Bt) - C' \exp(-Dt), \quad (11)$$

$$\text{were, } A' = 100 \left(1 - \frac{n_{M0}}{n_{A0}} - \frac{n'_{M0}}{n_{A0}}\right), \quad B' = 100 \left(1 - \frac{n_{M0}}{n_{A0}}\right) A,$$

$$C' = 100 \left(1 - \frac{n_{M0}}{n_{A0}}\right) C.$$

The theoretical dependence (11) was used to interpret experimental data according to isothermal DMT within low-temperature range [2].

The points obtained by digitizing the experimental data are shown by marks in Fig. 3. Solid lines depict the corresponding curves obtained from (11) at the values of coefficients given in Table 2.

The obtained analytical dependence (11) includes five constant coefficients, the values of which depend on the transformation temperature and are determined by experiment.

Comparison of analytical dependencies describing the isothermal DMT with the experimental data of the same process for one of the types of alloyed steel shows good quantitative agreement. The obtained agreement indicates the possibility of using DMT model based on the principle of detailed balance in alloy steels within a low-temperature range.

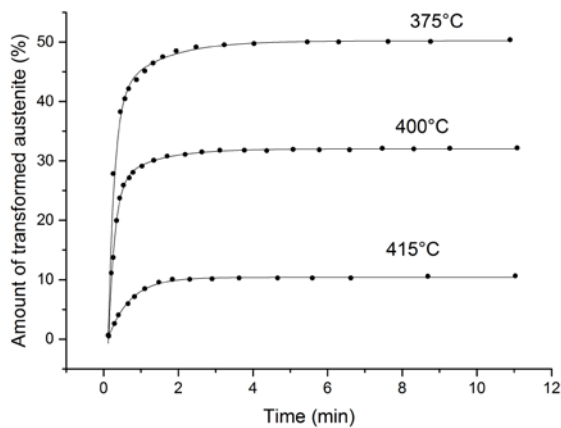


Fig. 3. Isothermal DMT in low-temperature range

a) Amount of transformed austenite (%);  
b) Time (min)

Table 2. The values of coefficients of curves (11) describing the experimental data [2].

°C	$A'$	$B'$	$B$	$C'$	$D$
415	10.39448	12.54669	1.67272	0	0
400	32.02108	6.86054	0.93142	59.43278	6.12407
375	50.19302	85.35374	6.10650	11.05937	0.83587

## 7. Conclusion

The paper analyzes the existing approaches in describing phase transitions in crystalline lattices of solids starting with the phenomenological paper of Landau and ending with publications of Kolmogorov and Avrami on nucleation and growth of a new phase. By the example of phase transformations of carbon and alloy steels it is noted that the proposed theories do not always give theoretical diagrams of austenite decay kinetics that are in good agreement with the experimental data. To eliminate the noted drawbacks in the existing theories it is proposed in this paper to describe the phase transformations of carbon steels on the basis of the principle of detailed balance formulated first by Einstein. On the basis of the approach proposed in this paper a system of equations has been obtained that describes both athermal and isothermal direct martensitic transformations of carbon steels.

In high-temperature range  $T_K \leq T(t) \leq T_H^*$  and at a large number of phonons due to such a temperature the DMT process can be represented in the form of a large number of TLSs with a short transition characteristic time ( $\mu' t_{AM} \gg 1$ ). In each of these TLSs a phase  $M$  is formed in such a way that the final state of one TLS determines the initial state of the next one. The total amount of the transformed phase  $M$  is obtained as a result of summing the phase  $M$  in each TLS to which the temperature interval of the DMT is divided.

The analytical dependences obtained from the initial equations include four constant coefficients, the values of which depend on the transformation temperature and are determined by experiment.

Comparison of analytical dependencies describing the isothermal DMT with experimental data of the same process for one of the types of alloy steel ( $Fe + 7\%Cr + 2\%Ni$ ) shows their good quantitative agreement. Such a quantitative agreement indicates the possibility of using DMT model based on the principle of detailed balance in alloy steels within a high-temperature range.

It was concluded on basis of the obtained analytical solutions that within a high-temperature range DMT occurs in alloy steel with decreasing temperature from initial  $T = T_H^* \leq T_H$  to  $T = T_K$ , as a result of which the elementary lattice cells of phase  $A$  almost completely transit to phase  $M$ .

The analytical dependences of isothermal DMT of alloy steels in a low-temperature range ( $T_{KOM} \leq T(t) \leq T_H^* \leq T_K$ ), when a small number of phonons are realized ( $N_0 > (n_{A0} - n_{M0})/2 \gg 1$ ), can be represented as a sum of three summands: a constant summand and two decreasing in time exponents, each of which has its own constant factor and its characteristic time value. The values of the constant summand, two constant factors and two characteristic times (only five constants) depend on the transformation temperature and are determined by experiment. Comparison of analytical dependencies describing the isothermal DMT of one of the alloy steel types with the experimental data in low-temperature range shows a good quantitative agreement. Such an agreement indicates the possibility of using DMT model of alloy steels based on the principle of detailed balance in a low-temperature range.

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