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Kinetic and Geometric Characteristics of Martensite Conversion in an Iron-Nickel-Manganic Alloy

by

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In a previously published report [1] have been discussed the causes, explaining why the rate of growth of Martensite crystals in iron alloys does not depend upon temperature, while the rate of germination in general case should be described by a curve with a maximum. However up until now no experimental data have been obtained regarding the temperature dependence of the rate of germination during martensite conversion in iron alloys. In report [2] was proposed a method of calculating the activation energy in case, if the volume of martensite crystals does not depend upon the degree of conversion. It was then shown, that the adopted mathematical equation of isothermal conversion does not correspond with basic experimental data [3] because in ratio to the development of martensite conversion the dimensions of the crystals decrease by many times [4].

We have investigated the influence of temperature and degree of conversion on the rate of germination of centers and dimensions of martensite crystals in iron alloys in conditions of pure isothermal conversion, eliminating the possibility for the formation of athermal martensite. On the basis of the investigated dependences were determined the thermodynamic characteristics of the process: magnitude of activation energy and function of formation of martensite crystal nuclei. The obtained data confirm the dislocating nature of martensite conversion.

To determine the rate of germination of centers at any given cases of phase conversions, first of all, it is necessary to calculate the number of particles, which formed over the given area within a specific time period, and then establish the number of particles, formed in a unit of volume per unit of time, i.e. to change over to the magnitude of the rate of germination. The universal method is connected with the necessity of clearly dividing the individual crystalline formations. For the case of martensite conversions in iron alloys this is possible in carbon containing alloys, when all or a considerable number of martensite is formed upon a change in temperature. In the case of purely isothermal conversion calculation of the number of crystals in the plane of the slide appears to be practically impossible in connection with the inaccurate separation of formations, their fusion and imposition. In fig.1 is shown a typical structure of isothermal martensite in an iron-nickel-manganese alloy.

By studying the structure it becomes evident, that quantitatively it is possible to accurately determine the thickness a of martensite crystals. Furthermore, by the method of casual secants in the volume [5] it is possible to determine the surface of martensite crystals in unit of volume S $\frac{\text{mm}^2}{\text{mm}^3}$. It is also possible by the magnetometric method to determine the relative volume V of the ferromagnetic component - martensite.

If the martensite crystal has the form of a flat parallelepiped[1] with sides a,b,b fo a volume of 1 mm^3, then it can be expressed by the following ratios:

$$V \frac{\text{мм}^3}{\text{мм}^3} = N \cdot a \cdot b^2, \qquad (1)$$

$$S \frac{\text{мм}^2}{\text{мм}^3} = 2N(2ab + b^2), \qquad (2)$$

where N - number of crystals, formed within the given time interval.

Having substituted the values b in equation (2), we will obtain

$$N \frac{1}{\text{мм}^3} = \left(\frac{S \cdot a - 2V}{4a\sqrt{aV}} \right)^2. \qquad (3)$$

The thickness of martensite crystals is determined as a mean from 400 measurements a' [6] :

$$a = \frac{a'}{2}. \qquad (4)$$

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[1] It is possible to give any given form of the particle, e.g. form of a lens, flat cylinder etc, which principally does not change the method of investigating.

According to [5] for a degree of reliability, equalling 0.7, at 400 intersections is maximum possible a relative error of determination of a equalling about 5%.

The surface of martensite crystals S was determined for 400 intersections, i.e. at the very same degree of reliability. The absolute error in determining the volume of martensite phase was equal to 1.2 - 1.4% [3].

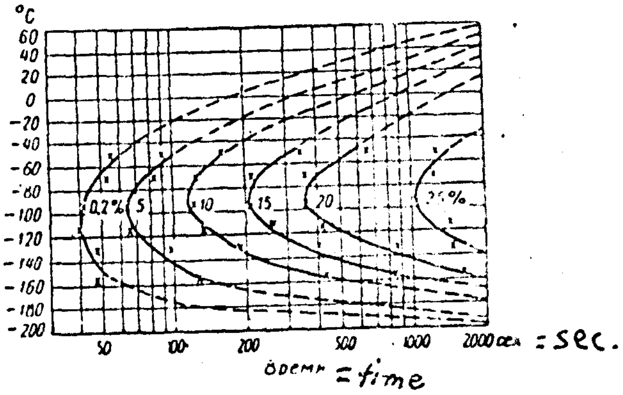

Fig.2. Diagram of isothermal martensite conversion in iron-nickel-manganic steel.

The length of martensite crystals b is established by substituting the values a, N, V or S in equation (1) or (2).

Isothermal martensite conversion was investigated on an iron alloy with 23.02% Ni and 3.35% Mn, similar to alloys used by [7,8]*. When quenching in the air from 1200° the martensite point lies at 10°. Subsequent quenching in liquid nitrogen leads to the formation of 72% martensite. To assure purely isothermal conversion in a wide range of temperatures the samples, soldered in in quartz ampoules were cooled together with the furnace from 1200° to room temperature within a period of 3 hrs. As result of stabilizing the austenite there was a drop in temperature of conversion, followed by a reduction in the degree of final conversion (approximately to 25% martensite).

Kinematic Characteristics of martensite Conversion

The diagram of isothermal martensite conversion is shown in fig.2. The temperature range of active process lies between - 50 and -155°. In conformity with this the investigation was conducted at -55, -68, -94, -114, -129 and -155°. The results of determining the value N for degrees of conversion 5,10,15,20 and 25% are given in table 1.

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* The law formulated by the authors is valid for the given alloy, because only in this alloy have the researchers succeeded in obtaining isothermal martensite conversions in pure form. The obtained laws cannot be disseminated to other iron alloys, especially to steel, in which an isothermal martensite conversion has not been practically observed. (Editor's remark).

According to data, given in fig.2 and in table 1, were calculated the values of martensite crystal germination rate.

Table 1. Effect of temperature and degree of conversion on the number of crystals in

$1\ mm^3\ N \cdot 10^{-6},\ \frac{1}{mm^3}$

Degree of conversion in %	Temperature of isothermal conversion in °C					
5	0,0[illegible]7	0,108	0,098	0,091	0,092	0,099
10	0,302	0,328	0,297	0,289	0,280	0,307
15	0,625	0,683	0,667	0,647	0,574	0,607
20	1,170	1,146	1,177	1,127	1,054	1,179
25	1,980	2,086	2,147	1,952	1,849	—

The temperature dependence of the germination rate at martensite conversions coincides qualitatively with analogous dependences, investigated previously for crystallization type processes (fig.3). The principally important thing here is the dependence n upon the degree of conversion in isothermal conditions (fig.4).

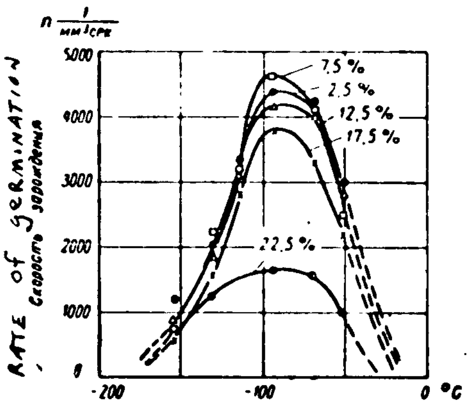

Fig.3. Temperature dependence of the rate of germination of martensite crystals.

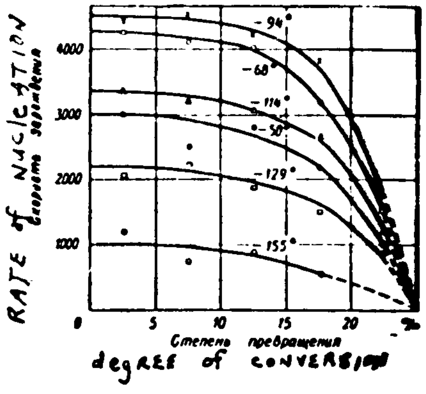

Fig.4. Effect of the degree of conversion on the rate of nucleation of martensite crystals.

As is evident from the figure, with the increase in the degree of martensite conversion at all temperatures the rate of nucleation decreases continuously and tends to zero at a maximum degree of conversion of about 25%.

The given value - ratio of rate of nucleation at given degree of conversion at the inital moment n_0 for all isotherms in dependence upon the degree of conversion (ratio V to maximum V_{max} at given isotherm) leads to a perfectly satisfactory description of data in fig.4 of a single curve (fig.5). This dependence is described by equation:

$$n_\tau = n_0 \left[1 - \left(\frac{V}{V_{max}}\right)^3\right]. \qquad (5)$$

The results of calculating by equation (5) are indicated by dotted line in fig.5. The obtained temperature dependences of the rate of nucleatin of martensite crystals (fig.3) enabled to calculate the thermodynamic characteristics of this process. For this was used equation

$$n = K \cdot e^{-\frac{U}{RT}} \cdot e^{-\frac{A_3}{kT}}. \qquad (6)$$

where U - activation energy; A_3-job of forming nucleus; K - PREEXPONENTIAL factor, the physical sense of which for the given case will be shown below. During the

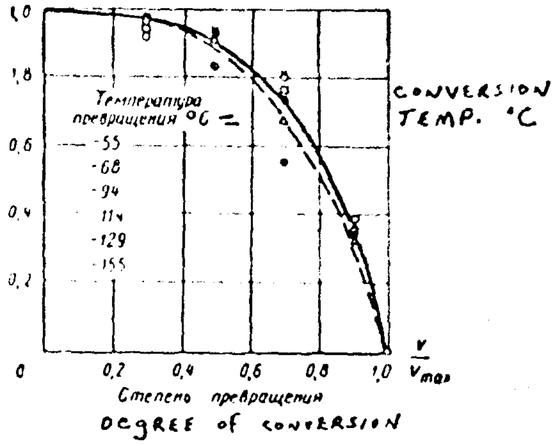

Fig.5.Effect of the degree of conversion on the rate of nucleation of martensite crystals.Combined are points $\frac{n_\tau}{n_0}$ for six conversion temperatures,dotted line indicates curve calculated by equation (5)

Table 2.Thermodynamic Characteristics of the nucleation of crystals during isothermal martensite conversion

Degree of conversion in %	$K \cdot 10^{-9}$ $\frac{1}{мм^3/сек}$ mm³ sec	H $\frac{ккал}{г\text{-}ат}$ U, $\frac{k}{M}$	A_3 $\frac{cal}{g.atm}$ at various temperatures in °C and degrees of conversion					
			−50	−68	−91	−114	−129	−155
2,5	1,14	920	4745	4150	3465	3055	2785	2405
7,5	1,11	932	4780	4180	3490	3080	2800	2420
12,5	1,0	934	4710	4120	3440	3030	2770	2390
17,5	0,755	911	4710	4120	3440	3030	2770	2390
22,5	0,309	967	4570	4000	3350	2940	2680	2320

calculation the index of the second exponent $\frac{A_3}{RT}$ was substituted by the value $\frac{B\sigma^3}{T(\Delta T)^2} = \frac{C}{T(\Delta T)^2}$. To determine the value ΔT it is necessary to know the temperature T_0 above which plastic deformation does not lead to martensite conversion. For the given alloy $T_0 = 210°$.

The results of the calculation are given in table 2.

By examining the data in table 2 we find, that the activation energy of the nucleation process of martensite crystals, does not depend upon temperature not upon the degree of conversion and constitutes 911-967 cal/g.atm (each value I in table 2 was calculated in accordance with 12 determinations at six conversion temperatures). The job of forming the nucleus decreases almost in half at a reduction in conversion temperature: from 4570 - 4780 cal/g-atm at -50° to 2320 - 2420 cal/g.atm at -155°. The preexponential factor K decreases continuously from $1.14 \cdot 10^9$ (at an average degree of conversion of 2.5%) to $0.309 \cdot 10^9$ (at 22.5%). At 25% nuclear conversions have not been revealed.

The effect of temperature and degree of conversion on the values U, A_3, K is shown in fig.6 (for constant degrees of conversion) and fig.7 (for constant conversion temperature).

From equation (6) and experimental data in table 2 and fig.7 is evident that in isothermal conditions the rate of nucleation and preexponential factor K are linearly connected (because U and A_3 are constant and consequently the derivative $e^{-\frac{U}{RT}}$ $e^{-\frac{A_3}{RT}}$ also appears to be a constant value).

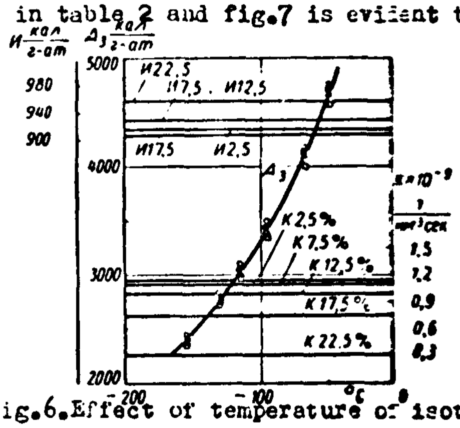

Fig.6. Effect of temperature of isothermal martensite conversion on the magnitude of activation energy I, job of nucleation and preexponential factor

In this way

$$\frac{n_1}{n_2}=\frac{K_1}{K_2}. \qquad (7)$$

Combining equation (7) with equation (5), we obtain the following dependence K upon the degree of conversion:

$$K_\tau = K_0\left[1-\left(\frac{V}{V_{max}}\right)^3\right]. \qquad (8)$$

Substituting in equation (6) instead K the value K_γ from equation (8) we obtain the dependence of the rate of nucleation of martensite crystals upon temperature and degree of conversion (i.e.time)

$$n = K_0\left[1-\left(\frac{V}{V_{max}}\right)^3\right]\cdot e^{-\frac{U}{RT}} \times \times e^{-\frac{A_3}{RT}}. \qquad (9)$$

In equation (6) the product $e^{-\frac{U}{RT}}\cdot e^{-\frac{A_3}{RT}}$ represents the probability of nucleation of new phase crystals. In this case the factor K characterizes the number of particles or volumes, participating in the conversions. And so according to V.I.Danilov[9] $K = 10^{23}-10^{24}$ for the crystallization of the liquid and it corresponds to the number of atoms (molecules) in gram-atom or gram-mole, i.e. to the number of particles, participating in the conversion. In the given case the value $K = 10^9$ differs by many orders from the number of atoms in a gram-atom or 1 mm^3 of austenite.

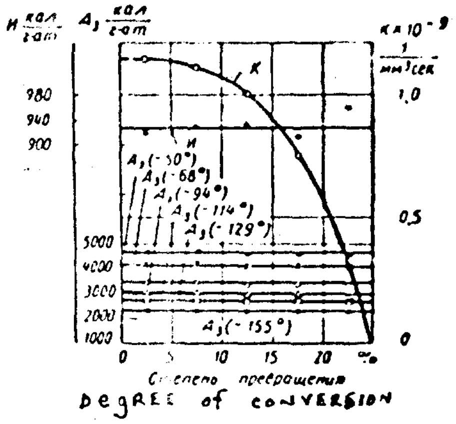

Fig.7. Effect of the degree of conversion on activation energy I, job of nucleation and preexponential factor K

According to[1c] the order 10^9 corresponds to the number of dislocation imperfections in annealed state (10^8-10^9 disl/cm^2) i.e.10^6-10^7 disl/mm^2, hence the number of dislocations in 1 mm^3 equals $(10^6-10^7)^{3/2} = 10^9-10^{10}$ disl.mm^3. A similar coincidence proves directly the heterogeneity of nucleation of martensite crystals with preferential use for same of dislocation imperfections.

Direct proof of the validity of this conclusion was obtained by us as result of the following experiment. After ultrahigh frequency microplastic deformation and subsequent cooling to room temperatures the structure of austenite was fixed. Special etching enabled to reveal the dislocation imperfections in the plabe of the slide (dark lines in fig.8). Subsequent thorough quenching led to martensite conversion, whereby the accicular relief originated preferably in points of previously revealed imperfections (see fig.8).

Let us discuss the possible causes for change in K in dependence upon the degree of conversion.

As is shown in fig. 9 the rise in degree of martensite conversion leads to a substantial rise in stresses of second order and pulverization of coherent diffusion zones.

In this way, the process of martensite conversion is connected with the continuous change in the state of unconverted austenite [11], [12]. The given change in the state of austenite alike cold hardening in connection with the effect of outer forces can lead to blocking of dislocation imperfections . Assuming that the number of blocked dislocations K_γ is proportional to the degree of conversion $\left(\frac{V_{max}}{V}\right)$ we will obtain:

$$K_{\text{б}} = K_0 \left(\frac{V}{V_{max}} \right)^b. \quad (10\,a)$$

Then with the increase in the degree of conversion the number of volumes, capable of martensite conversion K_γ changes in the following manner:

$$K_\gamma = K_0 - K_{\text{б}} = K_0 - K_0 \left(\frac{V}{V_{max}} \right)^b = \\ = K_0 \left[1 - \left(\frac{V}{V_{max}} \right)^b \right]. \quad (10)$$

It should be mentioned, that equation (10) coincides with the empirical equation (8) at b = 3.

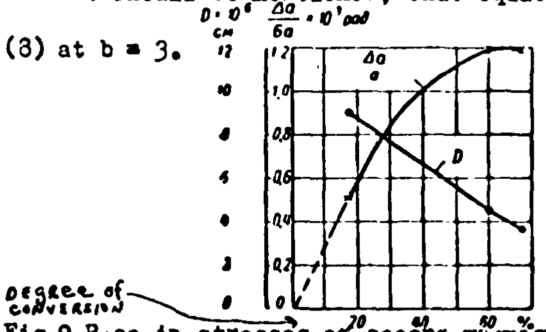

Fig.9. Rise in stresses of second magnitude $\frac{\Delta a}{a}$ and pulverization of block structure in austenite in the process of martensite conversion (0.67% C; 4,27% Ni, 4,86 M_n).

In this way, the reduction in the rate of nucleation of martensite crystals n_γ with the increase in degree of conversion can be connected with the blocking of dislocation imperfections, in connection with the change in the state of the unconverted austenite due to increase in degree of phase cold hardening.

Total blocking leads to cesation of conversion and its restoration in a majority of instances is connected with change in temperature or to the application of stresses.

Geometric Characteristics of Martensite Conversion

In conformity with above described method a direct experiment enabled to determine the true thickness of martensite plates a, their surface S and volume V. Having calculated by these data N (equation (3)), it is possible by equations (1) and (2) to determine the extent of martensite plates b. Results of investigating the values a,b and mean volume of martensite plates V in relation to the degree and conversion temperature are listed in table 3. The characteristics of martensite crystals (thickness a, extent b and volume V) within limits of experimental accuracy do not depend upon temperature at constant degree of conversion. These values are determined exclusively by the degree of conversion (fig.10).

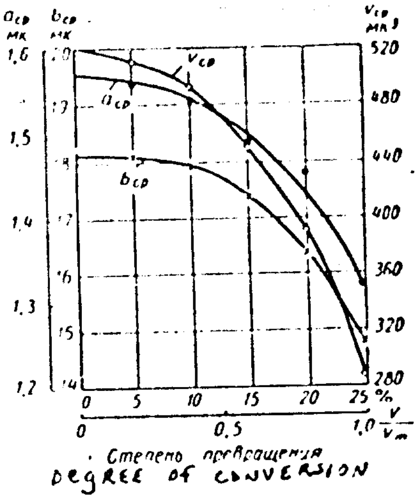

Fig.10. Effect of degree of conversion on the geometric characteristics of martensite crystals (mean values for temperatures of isothermal conversion)

With an increase in degree of conversion the thickness, extent and volume of martensite crystals decrease gradually. Up to the moment of inhibiting the conversion the value a_{mean} changes from 1,56 to 1,32 microns; b_{aver} = 18.2 - 14.8 microns; V_{aver} = 520 - 289 microns^3. Judging by the relatively small change in these characteristics to the moment of total cesation of the process, the determinant factor appears to be the nucleation of martensite crystals, the rate of which tends toward zero, as is shown in fig.4 and 5.

A reduction in dimensions of martensite crystals in ratio to the development of conversion, most likely, can be bound with the continuous change in the state of austenite. In this connection a substantial influence ,especially on the development of martensite plates in length, may be produced by the reduction in spaces for free growth in connection with the general increase in volume of martensite phase.

Table 3. Effect of Temperature and Degree of Conversion on the Geometric Characteristics of Martensite Plates (all data given in microns)

Martensite volume in %	Geometr. character.	Temperature of isothermal conversion in degrees						Mean value
		−50	−68	−94	−114	−129	−155	
5	a	1,59	1,49	1,60	1,53	1,60	1,58	$1{,}565^{+0{,}035}_{-0{,}075}$
	b	18,0	17,6	17,8	19,0	18,4	17,9	$18{,}11^{+0{,}89}_{-0{,}5}$
	V	515	462	508	551	540	505	511^{+40}_{-49}
10	a	1,50	1,50	1,59	1,49	1,59	1,56	$1{,}538^{+0{,}052}_{-0{,}048}$
	b	18,0	17,4	17,7	18,4	18,3	17,6	$17{,}9^{+0{,}5}_{-0{,}5}$
	V	487	456	497	504	532	482	492^{+40}_{-36}
15	a	1,56	1,48	1,41	1,45	1,52	1,54	$1{,}49^{+0{,}05}_{-0{,}08}$
	b	17,2	16,9	17,0	17,0	18;3	18,0	$17{,}4^{+0{,}9}_{-0{,}5}$
	V	461	421	407	418	510	497	452^{+58}_{-45}
20	a	1,49	1,49	1,39	1,43	1,49	1,48	$1{,}46^{+0{,}03}_{-0{,}07}$
	b	15,7	17,0	16,8	17,1	16,8	15,4	$16{,}46^{+0{,}64}_{-1{,}06}$
	V	367	431	392	418	418	350	396^{+35}_{-46}
25	a	1,32	1,21	1,34	1,40	1,32		$1{,}318^{+0{,}082}_{-0{,}108}$
	b	15,3	14,8	13,9	14,7	15,4	--	$14{,}82^{+0{,}58}_{-0{,}92}$
	V	309	265	258	303	313	—	289^{+24}_{-31}

Conclusions: 1 A method was developed and the effect of temperature and degree of conversion on the rate of nucleation and dimensions of martensite crystals was investigated.

2. It is shown, that the temperature dependence of the rate of nucleation is characterized by a curve with maximum, and the absolute value of the rate of nucleation n drops continuously and progressively at a rise in the degree of conversion and becomes equal to zero at the moment conversion ends. A similar nature of change n is connected, apparently, with the dislocation nature of martensite conversion (shown directly by value K = 10^9 and direct experiment on the formation of plate relief in dislocations revealed by preliminary etching). Introduced were equations ,binding n and K with the degree of conversion.

3. It is shown, that the activation energy of nucleation of martensite crystals does not depend upon temperature and degree of conversion and equals about 940 cal/g.atm. The job of nucleation of martensite crystals A_3 does not depend upon the degree of conversion, but it decreases almost doubly upon a drop in temperature of the isotherm from 4670 (at - 50°) to 2360 cal/g-atm (at - 155°).

4. The proposed dependence of the rate of nuvleation of martensite crystals upon temperature and degree (time) of conversion

$$n = K_0 \left[1 - \left(\frac{V}{V_{\max}}\right)^3\right] \cdot e^{-\frac{U}{RT}} \times \times e^{-\frac{A_3}{RT}}. \qquad (10b)$$

5. It is shown, that thickness, extent and volume of martensite crystals practically do not depend upon temperature and are determined exclusively by the degree of conversion. Up to the moment of ending the conversion a reduction in thickness and extent of martensite plates reaches 15-18%, which is determined by the change in state and by the reduction in volumes of unconverted austenite.

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