NOTATION

q, heat flux; τ, time of action; λ, wavelength; T, absolute temperature; $\rho_{\lambda n}$, normally hemispherical reflectivity; $\varepsilon_{\lambda n}$, spectral normal radiant emittance; $\varepsilon_{\Sigma n}$, partial integral normal radiant emittance; $I_{\lambda n}$, spectral normal brightness; λ_i, emission line of mercury vapors; $\lambda_j = 0.60$ μm. Superscripts: s, summary proper and reflected radiation; o, specimen; st, standard; blb, blackbody.

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PHASE TRANSITION KINETICS IN IRON AND STEEL DURING HEATING

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Similarity theory is used to analyze phase transformations in iron and steel during heating. A kinetic equation is obtained by assumption of self-similarity of the phase transition. Experimental data are processed and effective kinetic parameters determined. It is concluded from the results obtained that the elementary act of phase transition consists of a cooperate transition into the new phase of regions containing $(1\text{-}2)\cdot 10^2$ atoms.

I. A large number of studies [1-4] have been dedicated to the kinetics of phase transitions in iron and steel. Theoretical studies of hardening have been directed mainly toward a search for some single micromechanism controlling phase transitions, for example, carbon diffusion [1, 5]. However critical analysis of the results of [2, 6-8] does not permit the conclusion that such an approach is universal.

The complexity of theoretical description of phase transition kinetics is the result of simultaneous occurrence of a number of subprocesses (lattice readjustment, dopant redistribution, formation, movement, and annihilation of defects, etc.), among which it is difficult to establish valid quantitative cause—effect relationships. Therefore it is of interest to use the methods of similarity theory to analyze phase transition kinetics. In fact, analysis shows that simplification of the process is possible only in the case of self-similar occurrence of the phase transition, i.e., in the case of similarity of all subprocesses [3, 9, 10]. In [9] the criterion for quasistatic occurrence of the process was introduced

$$Q = \exp(-\Delta G/RT), \tag{1}$$

where ΔG is the motive force and T is temperature. Here $Q \simeq 1$ corresponds to thermodynamic equilibrium, and $Q \simeq 0$ to self-similar behavior. As was shown in [9], at $Q \simeq 0$ all internal

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parameters having dimensions of length are insignificant. In fact, this implies transition to a macro-description, in which averaging occurs over portions larger than the characteristic dimension of the kinetic quantities. All system parameters are then defined in terms of the thermodynamic potential, which has the property of additiveness. Change in any parameter Δp during phase transition is related only to change in the system thermodynamic potential ΔG:

$$\Delta G = C(1 - \Delta p), \tag{2}$$

where C is a coefficient, and Δp = ξ is the degree of conversion. Thus, the kinetics are determined only by the state of the system, and not its "thermal trajectory". Under conditions of self-similar occurrence of the phase transition the most general kinetic equation has the form [3, 4]

$$\frac{d\Delta p}{d\tau^*} = C_1 (1 - \Delta p)^{C_2} \tau^{*C_3 - 1}, \tag{3}$$

where C_1, C_2, C_3 are parameters; $\tau^* = t/\tau$ is the reduced time; t is time; τ, relaxation time:

$$\tau = \tau_0 \exp(U/RT)/2\,\mathrm{sh}(\Delta G/RT), \tag{4}$$

where $1/\tau_0$ is the atomic frequency and U is the activation energy. For subsequent comparison with experiment we choose for the quantity Δp the degree of conversion ξ. Then in the cases ξ ≃ 0 and ξ ≃ 1 the result does not depend on C_2.

In studying conversions during heating, it will be convenient to transform to the new variable T = tv (where v is the heating rate). The degree of conversion is then

$$\xi = C_1 \int_0^T \frac{dT}{T} (T/\tau_0 v)^{C_3} [2\,\mathrm{sh}(\Delta G/RT) \exp(-U/RT)]^{-C_3}. \tag{5}$$

In view of self-similarity 2sh(ΔG/RT) ≃ exp(ΔG/RT), and thus, the value of the integral is determined by its upper limit with integration extended to zero. We take ΔG in the form:

$$\Delta G = n \Delta S \Delta T, \tag{6}$$

where n is a coefficient, ΔS is the entropy of the phase transition, ΔT is the superheat above the phase equilibrium point T_0. We can then introduce the effective activation energy

$$W = U + n \Delta S T_0. \tag{7}$$

As a result, the effective relaxation time can be expressed as

$$\tau = \tau_0 \exp(-n\Delta S/R) \exp(W/RT). \tag{8}$$

Expanding the integral of Eq. (5) in an asymptotic series by the Laplace method [11] and performing transformations analogous to those of [12], we obtain:

$$T = (W/RA)(1 + \ln v/A), \tag{9}$$

$$A = -n\Delta S/R - \ln \tau_0 + \ln(RTC_1/WC_3\xi)/C_3 + \ln T. \tag{10}$$

The quantity A is essentially defined by the first two terms. Here T is the temperature to which heating is carried out at the rate v for a specified small degree of conversion ξ. We note that Eq. (9) is also valid for the case ξ ≃ 1.

In [12] a functional dependence in the form of Eq. (9) was obtained commencing from a first order relaxation equation. However the more general analysis performed herein on the basis of similarity theory shows that first, self-similarity, and thus the possibility of using a relaxation equation, sets in only at some deviation from the equilibrium position, and second, the phase transition activation energy is an effective value. Moreover, since use of the self-similar equation near the phase equilibrium point is incorrect, one cannot identify $T^* = W/RA$ with T_0. By not considering these facts [13, 14] arrived at parameter values far from experimental ones. We will note that the agreement of calculation results with experiment in those studies is the result of numerical errors.

In the present treatment we have also refined the expressions for τ and A.

II. We will use Eqs. (7)-(10) to analyze the following phase transitions: martensite and austenite decay in steel and formation of the γ-phase in iron upon heating. It was

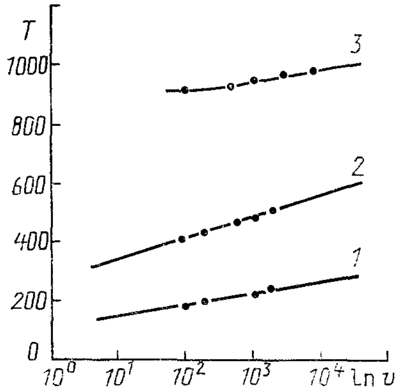

Fig. 1. Temperature T, °C, for beginning of martensite (1) and austenite (2) conversions in U12 steel and temperature T for beginning of α–γ-transition ($\xi = 0.05$) in iron (3) vs logarithm of heating rate v, deg/sec. Points are experimental data from [1].

shown earlier [12] that Eq. (9) satisfactorily describes martensite decay upon rapid heating. Then

$$\tau = \tau_0 \exp(U_C/RT), \tag{11}$$

where U_C is the activation energy of carbon diffusion. The transformation has a purely kinetic character and is described by a relaxation equation. The absence of a phase transition temperature is characteristic.

Description of austenite decomposition is possible only on the basis of Eqs. (7)-(10). Analysis of the experimental data of [1] on austenite decomposition in U12 steel, shown in Fig. 1, yields a value of $W \simeq 70$-85 kJ/mol, while taking ΔS as the entropy of the α–γ-conversion we obtain $n \simeq 100$. Similar processing of experimental data from [1] on formation of the γ-phase in iron at a low ($\xi = 0.05$) degree of α–γ-conversion leads to values of $W \simeq 530$ kJ/mol, $n \simeq 200$.

In accordance with the definition of ΔG as the motive force n has the meaning of the effective number of atoms participating in the elementary phase transition act. It is evident that beginning at a superheat of some tens of degrees (in the self-similarity region), the osmotic stress begins to exceed the yield limit σ:

$$\Delta G/V > \sigma, \tag{12}$$

where V is the molar volume.

As was shown in [15], lattice readjustment into the new phase then occurs. However in contrast to the martensite conversion no global loss of lattice stability occurs, since the process requires significant activation, Eq. (8). The elementary phase transition act is then transit into the new phase of a region containing $(1\text{-}2)\cdot 10^2$ atoms.

To summarize the results obtained, we make the following conclusions:

1. Phase transitions during heating of iron and steel have been analyzed from the positions of similarity theory. It has been shown that a universal description is possible only under self-similarity conditions.

2. An equation has been obtained which relates the logarithm of the heating rate to the temperature to which heating must be extended for a constant degree of conversion. Effective kinetic parameters were determined by analyzing the experimental results of [1].

3. From analysis of effective phase transition kinetic parameters it has been concluded that the elementary phase transition act is cooperative transformation into the new phase of regions containing $(1\text{-}2)\cdot 10^2$ atoms.

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THERMAL REGIMES OF CHEMICAL GAS-PHASE DEPOSITION OF CONDENSED PRODUCTS ON A MOVING SUBSTRATE HEATED WITH AN ELECTRIC CURRENT

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A nonstationary model is constructed for gas-phase formation of coatings on a moving fiber heated with an electric current.

Setups in which zonal electric heating of a moving substrate wire in a chemically active medium is realized are now widely employed for producing fibers from inorganic substances by the method of chemical gas-phase deposition. In the ohmic-heating zone deposition of condensed product on a substrate, as a result of which the transverse cross section of the substrate changes, occurs as a result of heterogeneous chemical transformations. The change in the transverse cross section of the substrate wire affects, through the electric resistance, both the electric power released in a given cross section of the specimen and the conditions of heat transfer. Thus, the case at hand the heating and deposition of condensed product on the substrate are determined by a collection of interrelated factors: chemical reactions, electric heating, and heat emission into the surrounding medium.

In this paper we give a mathematical description of this process for the purpose of constructing an algorithm for controlling the condensation regimes when preparing continuous fibers by the method of chemical gas-phase deposition.

1. Mathematical Model of the Deposition Process. A substrate filament with radius r_0 is heated on the section $X = 0-\ell$ with a stable electric current ($I = \text{const}$); the current is stabilized with the help of tracking devices. The filament moves with velocity U in the laboratory coordinate system. In the heating zone heterogeneous chemical condensation occurs on the surface of the filament; this changes the transverse size of the specimen as a

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