

ening;  $t_0^*$ , the induction period in the isothermal process;  $\bar{t}^*$ , the dimensionless induction period;  $\bar{t}$ , dimensionless time;  $\bar{T}$ , dimensionless temperature;  $\bar{U}$ , dimensionless activation energy;  $\alpha$ , the rate of temperature rise;  $\tau$ , the shearing stress;  $\dot{\gamma}$ , the shear rate;  $c$ , heat capacity;  $\rho$ , density;  $K$ , reaction rate;  $\beta$ , rate of conversion;  $k_0$ , initial reaction rate at the temperature  $T_0$ ;  $\bar{k}_0$ , the dimensionless initial reaction rate at the temperature  $T_0$ ;  $\bar{q}$ , dimensionless characteristic of the thermal effect;  $Q$ , the thermal effect of the reaction.

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#### THE MACROKINETICS OF DIFFUSION CONVERSIONS IN METALS

#### WITH A DISPERSION PHASE

Yu. A. Buevich and S. L. Komarinskii

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The evolution of solid dispersions under isothermal conditions has been investigated for the situation in which the exchange of the mass of discrete inclusions with the matrix in which they are embedded is limited by the diffusion into that matrix. Expressions have been derived for the quantities which describe the kinetics of conversion and a comparison with experimental data is carried out.

When heterogeneous metals and certain other types of solid materials are subjected to processes of chemical or heat treatment, their thermodynamic stability is disrupted. If the resulting level of metastability is sufficiently small, the consequent transition of the solid dispersion into a new stable state is not associated with the fluctuating formation of the nuclei of a new phase, but comes about as a result of the growth or dissolution of the initial inclusions. The speed with which this conversion takes place is determined not only by the kinetics of the interphase exchange, but also by the rates of impurity diffusion transport within the heterogeneous system being examined. Therefore, the evolution of the inclusions and the "transit" mass transfer to solid dispersion whose properties vary with the change in the dimensions and diffusion displacement of the inclusions must be taken into consideration simultaneously with consideration of the diffusion interaction of the inclusions and the effect exerted by proximity on the transport of the impurity through the spaces between the inclusions.

A system of nonlinear equations has been formulated in [1] to describe the isothermal processes of diffusion conversion in solid local-monodisperse systems characterized by a uniform numerical concentration of spherical inclusions. This system determines the average concentration of the diffusing impurity in each of the phases, as well as the volumetric concentration of the inclusions in the dispersion, and it also contains a number of quantities which characterize the kinetics of the conversion and which, in rather complex fashion, depend on the physicochemical parameters of the dispersion. This relationship is examined in considerable detail in the following for the case in which the exchange of impurities between the surfaces of the inclusions and the solid solution within the matrix is limited by the diffusion within the matrix, which is most important from the standpoint of application [2, 3].

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The effective coefficient of diffusion  $D$  in the solid dispersion is introduced in conventional fashion as a proportionality factor between the average rate of impurity flow and the gradient of its average concentration  $c_0$  within the matrix, but with opposite sign. The effective coefficient of interphase mass exchange  $K$  is defined as the proportionality factor between the density of the impurity flow when the inclusions to the matrix and the moving thermodynamic force  $c_{*0} - c_0$ , where  $c_{*0}$  functions in the role of equilibrium concentration in the matrix. If we introduce the unknowns  $x$  and  $y$  by means of the equalities

$$D = xD_0, K = y^2(D/a^2) = xy^2(D_0/a^2), \quad (1)$$

from [1] we can obtain for these a system of transcendental equations

$$\frac{1-\rho}{x} = 1-\rho \frac{1+\xi}{1+\beta_1} \left( 3 + \frac{y^2}{1+y} \right) \left\{ \frac{1}{\alpha} - \frac{\xi}{1+\beta_1} \left[ \left( 2 + \frac{y^2}{1+y} \right) x + \beta_0 \right] \right\}^{-1}, \quad (2)$$

$$\frac{y^2}{1+y} = \frac{3\rho\beta_0}{\beta_0 - x(1+y)\omega}.$$

In this case, for the rate of change in the radius of the inclusions and the velocities of their diffusive motion the following representations are valid [1]:

$$\frac{da}{dt} = \frac{x(1+y)\beta_0}{\beta_0 - x(1+y)\omega} \frac{D_0}{a} \frac{c_{*0} - c_0}{c_{*0} - c_{*1}}, \quad (3)$$

$$\omega = -x \left( 3 + \frac{y^2}{1+y} \right) \left\{ c_{*0} - \frac{\xi}{1+\beta_1} \left[ \left( 2 + \frac{y^2}{1+y} \right) x + \beta_0 \right] c_{*1} \right\}^{-1} D_0 \nabla c_0.$$

We have used the following notation in (2) and (3):

$$\omega = \frac{c_{*1}}{c_{*0} - c_{*1}} = \frac{\alpha}{1-\alpha}, \quad \alpha = \frac{c_{*1}}{c_{*0}}, \quad (4)$$

$$\beta_i = \frac{ak_i}{D_i}, \quad c_{*i} = \frac{k_{si}}{k_i} \Gamma (i=0,1), \quad \xi = \frac{\beta_1}{\beta_0}.$$

$\beta_i \gg 1$  corresponds to the diffusion regime of conversion as it pertains to the  $i$ -th phase, when the exchange between the surface of the inclusion and the solution within the volume of this phase is limited by diffusion;  $\beta_i \ll 1$  corresponds to the kinetic regime in which this exchange is limited by the reactions of sorption-desorption.

It should be stressed that formulas (2) and (3) have been derived under a number of simplifying assumptions whose validity in each specific case must be checked. First of all, these formulas correspond to a continual model of a moderately concentrated dispersion, which, in principle, imposes limitations on the concentration interval over which they are approximately valid. These limitations may be established by comparison with experimental data or with the more general theory, which has not yet been constructed. Second, the indicated formulas have been derived within the framework of a hypothesis of quasisteadiness according to which the time scale of change is assumed to be considerably greater than any of the relaxation times for the exchange processes occurring at the surfaces of the inclusions, with magnitudes on the order of  $a^2/D_0$ ,  $a^2/D_1$ ,  $a/k_0$ , and  $a/k_1$ . Third, it is assumed that in the corresponding surface layers local thermodynamic equilibrium is established, i.e., the surface concentration  $\Gamma$  may be regarded as some characteristic of dispersion that is a function both of temperature and pressure. The quantities  $\Gamma$  and  $c_{*i}$ , introduced in (4), may additionally depend on  $a$ . For macroscopic inclusions it is permissible to neglect this relationship, as well as the volume of the surface layers in comparison to the volume of the phases, which is precisely what was done in formulas (2) and (3).

Assuming that  $\beta_0 \gg 1$ , we can represent  $x$  and  $y$  in the form of the series

$$x = \sum_{j>0} x_j \beta_0^{-j}, \quad y = \sum_{j>0} y_j \beta_0^{-j}$$

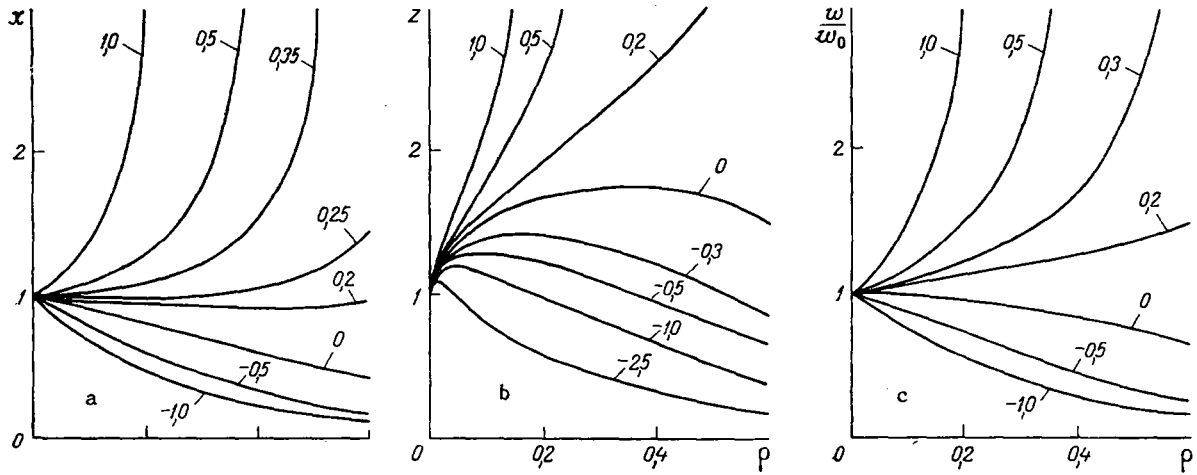


Fig. 1. The relationship between  $\rho$  and the dimensionless effective coefficient of transit diffusion (a), the coefficient of interphase mass exchange and the rate of change in the dimensions of the inclusions (b), and the velocity of diffusive movement on the part of the inclusions (c); the numerals at the curves identify the values of the parameter  $m$ .

and solve Eq. (2) by the small-parameter method. In particular, after performing the calculations for the first two coefficients of these series, we have

$$x_0 = \frac{1-\rho}{1-3\rho(1+\rho)m}, \quad m = \frac{1+\xi}{\eta}, \quad \eta = \frac{1+\beta_1}{\alpha} - \beta_1, \quad (5)$$

$$y_0 = \frac{3\rho}{2} \left( 1 + \sqrt{1 + \frac{4}{3\rho}} \right) = \sqrt{3\rho} \left( \sqrt{1 + \frac{3\rho}{4}} + \frac{3\rho}{2} \right)$$

and subsequently,

$$x_1 = 3\rho \frac{1+\rho}{1-\rho} \frac{x_0^3(1+\xi)}{\eta} \left[ \frac{\rho(1+y_0)\omega}{1+\rho} + \frac{(2+3\rho)\beta_1}{\eta} \right], \quad (6)$$

$$y_1 = \frac{x_0 y_0 (1+y_0)^2}{2+y_0} \omega$$

[the parameter  $\xi$  in (5) and (6) is retained, since it may be of the order of unity even as  $\beta_0 \rightarrow \infty$ , if simultaneously  $\beta_1 \rightarrow \infty$ ].

Let us examine in detail the limit diffusion regime from the standpoint of the continuous phase, assuming formally that  $\beta_0 \rightarrow \infty$ ,  $x \rightarrow x_0$ , and  $y \rightarrow y_0$ . In this case, from (1) and (5) we obtain

$$x = x_0 = \frac{D}{D_0} = \frac{1-\rho}{1-3\rho(1+\rho)m}, \quad (7)$$

$$z = K \frac{a^2}{3\rho D_0} = \frac{1-\rho}{1-3\rho(1+\rho)m} \left[ 1 + \sqrt{3\rho} \left( \sqrt{1 + \frac{3\rho}{4}} + \frac{3\rho}{2} \right) \right],$$

in which case the quantity  $3\rho D_0/a^2$  has the sense of the coefficient of interphase mass exchange, wherein the effects of proximity are neglected.

In this same approximation from formula (3) we have

$$\frac{da}{dt} = x_0(1+y_0) \frac{D_0}{a} \frac{c_{*0} - c_0}{c_{*0} - c_{*1}}, \quad (8)$$

$$\omega = -3(1+\rho)x_0 \frac{D_0 \nabla c_0}{c_{*0} - \zeta c_{*1}}, \quad \zeta = \frac{\beta_1}{1+\beta_1}.$$

Using (3) and (6), it is not difficult also to obtain correction factors for  $da/dt$  and  $w$  on the order of  $1/\beta_0$ .

The coefficient of transit diffusion depends not only on  $\rho$ , but also on the parameters  $\xi$  and  $\eta$ , and consequently, on the nature of the regime in which exchange takes place between the surface layer and the solution within the inclusions, as well as on the coefficient  $\alpha$ . If  $m < 0$  [ $\alpha > (1 + \beta_1)\beta_1^{-1}$ ],  $x$  and  $D$  diminish with increasing  $\rho$  all the more rapidly, the larger the value of  $\alpha$ . If  $m > 1/3$  [ $(1 + \beta_1)\beta_1^{-1} > \alpha > (1 + \beta_1)[\beta_1 + 3(1 + \xi)]^{-1}$ ],  $x$  and  $D$  increase monotonically. When  $0 < m < 1/3$  [ $\alpha < (1 + \beta_1)[\beta_1 + 3(1 + \xi)]^{-1}$ ] both of the indicated functions diminish within the region of small  $\rho$ , attaining a minimum, and then increasing. Characteristic relationships between  $x$  and  $\rho$  are presented for various  $m$  in Fig. 1a. In the limit diffusion regime relative to the dispersion phase ( $\beta_1 \rightarrow \infty$ ), from (7) we have  $D = (1 - \rho)D_0$ , which coincides with the result for diffusion in the dispersion medium of absorbing or emitting impurity particles which retain their dimensions in this case [4, 5]. In the limit kinetic regime ( $\beta_1 \rightarrow 0$ ) we obtain

$$D = \frac{1 - \rho}{1 - 3\rho(1 + \rho)\alpha} D_0,$$

i.e., when  $\alpha > 1/3$  the coefficient of diffusion increases monotonically with  $\rho$ , while in the case of  $\alpha < 1/3$ , it increases with the minimum. The possibility of increasing the effective coefficient of transit diffusion in a heterogeneous medium in comparison with the coefficient of diffusion in a uniform matrix is a new and somewhat unexpected result. The divergence of  $D$  as  $\rho$  seeks to attain some critical value, possible with  $\alpha$  not small, is apparently associated with the disruption of the conditions of applicability for the continual theory.

The relationship between the coefficient of interphase mass exchange and  $\rho$  is determined by the function  $z(\rho)$  from (7); this relationship is shown in Fig. 1b. The diverse nature of the effect of proximity on the transit diffusion and the diffusion to individual inclusions had been noted earlier in [4, 5].

It follows from (8) that as  $\rho \rightarrow 0$

$$\frac{da}{dt} \rightarrow \left( \frac{da}{dt} \right)_0 = \frac{D_0}{a} \frac{c_{*0} - c_0}{c_{*0} - c_{*1}}, \quad w \rightarrow w_0 = -3 \frac{D_0 \nabla c_0}{c_{*0} - \zeta c_{*1}}.$$

The first of these formulas, describing the evolution of a single inclusion in an unbounded matrix is well known [2, 3]. The second formula also coincides with the known result [6, 7] for the case in which  $\zeta = 1$ , i.e., for diffusion regimes which pertain to both phases. The ratio  $da/dt$  as a function of  $(da/dt)_0$  is also defined by the function  $z(\rho)$  (see Fig. 1b). The relationships of  $w/w_0$  to  $\rho$  for various  $m$  are shown in Fig. 1c.

Separately, we will stress the influence of the nature of the conversion regime which pertains to the dispersion phase on the direction of the diffusive movement of the inclusions. In the diffusion regime ( $\beta_1 \rightarrow \infty$ ,  $\zeta \rightarrow 1$ ) the inclusions move in or opposite to the direction of the concentration gradient, depending on whether the inclusions have been enriched with or deprived of the impurity, relative to the matrix. With departure from the diffusion regime, the critical value  $\alpha = 1/\zeta$  of the distribution factor differs from unity; a pronounced change in the nature of the influence exerted by proximity on transit diffusion corresponds to this same value.

Let us note that with consideration of (8) the conditions of quasisteadiness can be presented in the form

$$\left| \frac{c_{*0} - c_0}{c_{*0} - c_{*1}} \right| \ll \min \{1, \kappa, \beta_0, \kappa\beta_1\}, \quad \kappa = \frac{D_1}{D_0},$$

from which we see that satisfaction of these conditions is facilitated for the diffusion regimes, whereas it is quite problematic in the case of the kinetic regimes. In order for the theory from [1] to be valid, it is required that  $w$  be small, which imposes an upper bound on  $|\nabla c_0|$ .

In order to obtain simple results which might be compared against the experimental data, let us examine in greater detail the evolution of three-dimensional uniform dispersion as described by the following equations from [1]

$$(1-\rho) \frac{dc_0}{dt} - (c_{*0} - c_{*1}) \frac{d\rho}{dt} = 0, \quad c_1 = \left(1 - \frac{1}{k_1} \frac{da}{dt}\right) c_{*1}, \quad (9)$$

$$\frac{3\rho}{a} \frac{da}{dt} \equiv \frac{d\rho}{dt} = 3\rho z \frac{D_0}{a^2} \frac{c_{*0} - c_0}{c_{*0} - c_{*1}}.$$

These equations were formulated with utilization of the condition of quasisteadiness, and within the limits of accuracy assumed in [1] the first of these equations is equivalent to the equation

$$(d/dt)[(1-\rho)c_0 + \rho c_1] = 0,$$

reflecting the balance of the impurity throughout the dispersion as a whole, and we will make use of this here. Taking into consideration the formula for  $c_1$  from (9), we obtain

$$c_0 = \frac{c^\circ}{1-\rho} - \frac{\rho c_{*1}}{1-\rho} \left(1 - \frac{1}{k_1} \frac{da}{dt}\right),$$

where  $c^\circ = (1-\rho^\circ)c_0^\circ + \rho^\circ c_1^\circ$  is the average concentration of the impurity in the dispersion at some initial instant of time. Using this representation in the formula for  $da/dt$  from (8), we have

$$\frac{da}{dt} \equiv \frac{a}{3\rho} \frac{d\rho}{dt} = \frac{z}{1-\rho} \left(1 + \frac{\rho z}{1-\rho} \frac{\omega}{\kappa \beta_1}\right)^{-1} (\rho_\infty - \rho) \frac{D_0}{a}, \quad (10)$$

$$\rho_\infty = (c_{*0} - c^\circ)(c_{*0} - c_{*1})^{-1}.$$

If  $0 < \rho_\infty < 0.5-0.6$ , then  $\rho_\infty$  represents the volume concentration of the dispersion in a thermodynamic state of equilibrium. When  $\rho_\infty < 0$ , the solid solution in the uniform matrix corresponds to the equilibrium state. When  $\rho_\infty > 1$ , the solid solution in the material of the inclusions which occupies the entire volume corresponds to the equilibrium state.

If the conversion regime is of the diffusion type relative to each of the phases, it then follows from (9) and (10) that

$$\frac{da}{dt} \equiv \frac{a}{3\rho} \frac{d\rho}{dt} = x_0(1+y_0) \frac{\rho_\infty - \rho}{1-\rho} \frac{D_0}{a}, \quad (11)$$

where  $x_0$  and  $y_0$  are determined in (5). It is not difficult also to obtain a correction factor on the order of  $\beta_1^{-1}$  for the quantity in (11). However, derivation of a similar formula for a regime that is kinetic relative to the dispersion phase is pointless, since the conditions of quasisteadiness, such as are required for the validity of (9), demand that  $k_1^{-1} \cdot (da/dt) \ll 1$  and, consequently, it cannot be assumed that  $\beta_1 \ll \omega/\kappa$  in (10).

If  $\rho_\infty > 0$ , then as  $t \rightarrow \infty$  the solutions of Eqs. (10) or (11) monotonically approach some limit values such that the corresponding  $\rho$  becomes equal to  $\rho_\infty$ . In this regard, they differ significantly from solutions (known to the authors) relating to problems dealing with the growth of grains in the new phase, according to which the radius of the grain increases without bound, usually in proportion to  $\sqrt{t}$ . As an example Fig. 2 shows the dimensionless radius  $a/b = \rho^{1/3}$  as a function of the dimensionless time  $\tau = D_0 b^{-2} t$  ( $b$  is the average distance between the centers of the inclusions), which follows from (11) under the initial condition  $\rho \approx 0$ ; here we also find the relationships which flow out of the cell model, as well as the curves  $a/b = 2\lambda\sqrt{\tau}$ ,  $\lambda = \sqrt{\rho_\infty/2} + \sqrt{\pi\rho_\infty}/4$ , which correspond to the theory from [3, 8]. We see that the theory from [3, 8] leads to a conclusion of an unlimited, nearly parabolic, growth in the inclusions, whereas the values of  $a/b \geq 1$  are entirely devoid of physical meaning. This is apparently associated with the poor convergence of the series in [3, 8] for longer times and with considerable error, which arises when we take into consideration only the first terms.

For low values of  $\tau$ , the curves following from solution (11), pass above the corresponding curves derived from the theory put forward in [3, 8]. This is a consequence of the above-noted intensification of the interphase exchange as the concentration of the dispersion

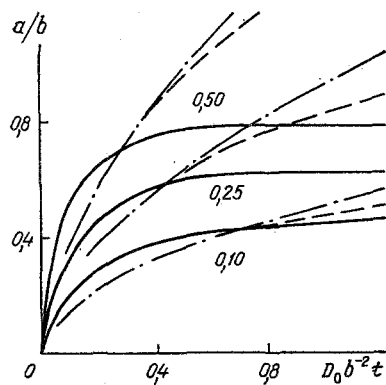


Fig. 2

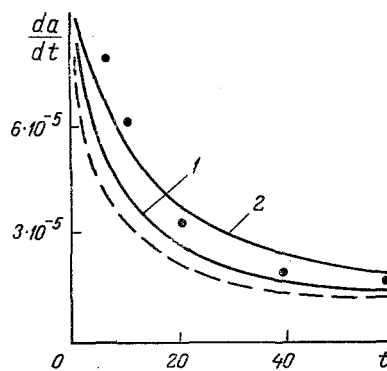


Fig. 3

Fig. 2. The kinetics of the growth of the inclusions in the diffusion regime relative to each of the phases; the solid lines, the dashed lines, and the dot-dash lines pertain, respectively, to Eq. (11), the cell model, and the nonsteady theory without consideration of proximity [3, 8]; the numerals at the curves represent the values of  $\rho_\infty$ .

Fig. 3. Experimental values and the theoretical curve (dashed) for the rate of growth in ferrite grains within austenite, taken from [3]; the solid curves represent the proposed theory [Eq. (11)] when  $n = 10^{11}$  (1) and  $10^{13}$  (2)  $\text{cm}^{-3}$ .  $da/dt$ ,  $\text{cm}/\text{sec}$ ;  $t$ ,  $\text{sec}$ .

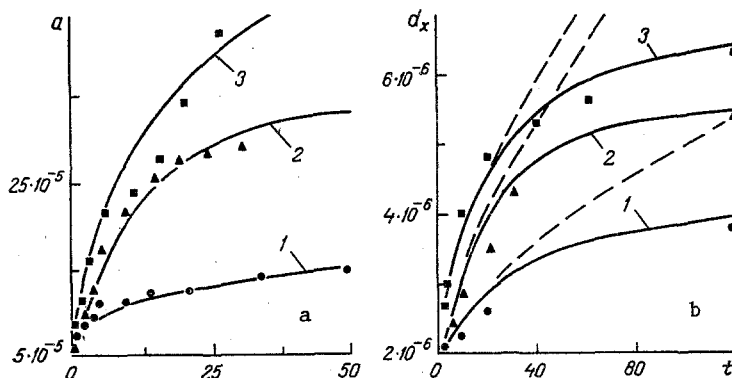


Fig. 4. Isothermal growth in cementite particles within the ferrite; the points denote the experimental data from [9] (a) and [10, 11] (b); a. 1-3)  $T = 720, 750, 800^\circ\text{C}$ ;  $10^7 \rho_\infty = 0.9, 2.2, 0.75$ ;  $10^6 D_0 = 0.942, 2.61, 13.6 \text{ cm}^2/\text{sec}$ ;  $10^{-4} n = 0.60, 0.12, 0.15 \text{ cm}^{-3}$ . b. 1-3)  $T = 450, 500, 550^\circ\text{C}$ ;  $10^7 \rho_\infty = 0.59, 0.75, 0.75$ ;  $10^8 D_0 = 0.91, 1.7, 4.0 \text{ cm}^2/\text{sec}$ ;  $10^{-9} n = 1.45, 0.48, 0.23 \text{ cm}^{-3}$ ,  $H = 1.82, 2.24, 2.69$ , the form factor  $H$  determines the dimensions of the crystals  $d_x = \sqrt{2\pi/H}$  (a) in the direction of one of the axes; the solid curves represent solutions for Eq. (11), the dashed curves (b) represent the nonsteady theory in which proximity is neglected, as taken from [3, 8]. a,  $d_x$ ,  $\text{cm}$ ;  $t$ ,  $\text{h}$ ,  $\text{min}$ .

phase increases. It becomes clear from (11) that the diffusion constriction leads, on the one hand, to the indicated intensification of mass exchange which, in turn, promotes acceleration of the growth of the inclusions and, on the other hand, to an accelerated approximation of the concentration within the bounded volumes of the matrix to its equilibrium value, which brings about the subsequent reduction in the rate of growth. Obviously, it is the former effect that predominates in the early stage. The increase in the rate of new-phase grain growth relative to the theoretical values has been repeatedly observed experimentally, but no satisfactory explanation for this phenomenon has been proposed. As an example, Fig. 3 shows the experimental values for the rate of grain growth for ferrite in austenite and the

curve  $da/dt = \lambda(D_0/t)^{1/2}$ , taken from [3]. Here we also find the theoretical relationships which follow from (11) in the assumption that numerous grains undergo simultaneous growth, rather than just a single grain. We see that the concepts being discussed here may, in actual fact, be utilized to explain the indicated divergence between theory and experiment.

The theoretical relationships which follow from Eq. (11) are in rather good agreement with many experimental data from various authors, thus offering the needed basis for a general conclusion as to the adequacy of the theory developed here for purposes of describing diffusion conversion regimes. Figure 4a shows some of the experimental results collected in [9] on the growth of globular cementite in a ferrite matrix (pure carbon steels). Figure 4b shows similar data from [10, 11], obtained under conditions of isothermal tempering. Here we also find the theoretical curves which follow from (11), and we have taken the numerical concentration  $n$  of the inclusions as the single running parameter. In the experiments shown in Fig. 4b the shape of the carbide crystals differs significantly from the spherical and the shape factor has been determined in the usual manner, from the condition of equality between the surface areas of actual crystals and the various dimensions along the principal axes of the cementite lattice and the equivalent sphere [10, 11]. For purposes of comparison, Fig. 4b also shows the curves which follow from the nonsteady theory of inclusion diffusion growth, taken from [3, 8], wherein the effect of proximity constrictions are neglected.

As we can see from Figs. 3 and 4, the agreement of the theory developed in [1] and in this paper with the experimental data is quite satisfactory. This enables us to speak of the adequacy of this theory for purposes of describing the diffusion conversion regimes. However, generally speaking, this does not apply to regimes that differ significantly from diffusion regimes. From the results obtained above it becomes clear that the change in the conversion regime must lead to extremely nontrivial changes in the nature of the relationships between the macrokinetic quantities and both the physical and regime parameters. Therefore, in extending the theory to the phase-conversion regimes that are nearly kinetic, we can consider one of the primary problems in the subsequent investigations.

In conclusion, let us note that certain of the attempts to formulate both a system of equations to control the processes of conversion and those of transit mass transport in solid dispersions, as well as the relationships between the quantities contained in these equations and the dispersion concentrations, as well as other parameters, are clearly phenomenological in nature (see, for example, [12-14]). In this case, the resulting equations differ significantly from those formulated in [1] and utilized above. There is therefore no doubt that the traditional approaches to the description of phase conversions in heterogeneous metals are in need of considerable correction, if not total reexamination.

#### NOTATION

$a$ ,  $b$ , radius and mean distance between the centers of the inclusions;  $c_0$ ,  $c_1$ , the mean impurity concentrations within the matrix and in the inclusions;  $c_{*0}$ ,  $c_{*1}$ , the respective equilibrium concentrations;  $D$ ,  $D_0$ ,  $D_1$ , the diffusion coefficients in the dispersion as a whole, in the matrix, and in the inclusions, respectively;  $K$ , the coefficient of interphase mass exchange;  $k_0$ ,  $k_1$ , the rate constants of impurity sorption by the surface layer out of the mass of the matrix and the inclusions;  $k_{s0}$ ,  $k_{s1}$ , the rate constants of the corresponding desorption reactions;  $n$ , the numerical concentration of inclusions;  $t$ , time;  $w$ , the velocity of diffusional motion on the part of the inclusions;  $x$ ,  $y$ ,  $z$ , the unknowns introduced into (1) and (7);  $\alpha$ , the distribution factor;  $\beta_i = ak_i/D_i$ ;  $\Gamma$  is the surface concentration;  $\zeta$ ,  $\eta$ ,  $\xi$ , the parameters introduced into (5), (8), and (4);  $\kappa = D_1/D_0$ ;  $\rho$ , the volumetric concentration of the inclusions;  $\rho_\infty$ , a quantity determined in (10);  $\omega$ , a parameter introduced in (5); the exponents indicate the initial values of the quantities.

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APPLICATION OF THE THEORY OF SIMILARITY FOR PURPOSES  
OF GENERALIZING THE THERMAL-DIFFUSION FACTOR FOR  
MIXTURES OF MULTIATOMIC NONPOLAR GASES

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The thermal-diffusion factor of 14 nonpolar-gas mixtures has been generalized on the basis of similarity theory. The theoretical values of  $\alpha_{th}$  obtained on the basis of this generalized relationship are compared with the experimental data.

A great amount of experimental material on the thermal diffusion of mixtures containing multiatomic gases has recently been published in the literature. Nevertheless, the practical application of these data frequently encounters difficulties. Indeterminacy arises in the evaluation of the reliability of these experimental data, obtained by various authors for the corresponding ranges of average temperatures and concentrations, differing from one another by more than 10%. The various semiempirical methods of forecasting thermal-diffusion characteristics are complicated in their application, as for example [1, 2] those which are based on the utilization (in the calculations) of experimental data.

The thermal-diffusion results are presented in the literature, as a rule, in the form of a relationship between the thermal-diffusion factor  $\alpha_{th}$  and the average (characteristic) temperature  $T$  or the concentration  $x$ . In a number of cases, in the place of  $\alpha_{th}$  we are confronted with the values of  $\Delta c_1$  (or  $q$ ) as a function of  $T_1$  and  $T_2$  ( $T_1$  and  $T_2$  denote the temperatures of the vessels in the thermal-diffusion apparatus, in which case  $T_1 > T_2$ ).

Various methods exist for the averaging of the temperature [3], but the most widely used is the Brown formula [4], which determines the mean logarithmic temperature:

$$T = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{T_1}{T_2} \quad (1)$$

Since in accordance with (1) various experimental conditions (i.e., various values of  $T_1$  and  $T_2$ ) may correspond to one and the same average temperature, we are interested in evaluating the changes in the quantity  $\alpha_{th}$  with a change in the values of  $T_1$  and  $T_2$ , but with the mean logarithmic temperature kept constant. The values of  $\alpha_{th}$  were studied in [5] for various temperature values in the upper and lower vessels of the thermal-diffusion apparatus. It was demonstrated (as an example, for the mixture He-N<sub>2</sub>) that with a fixed temperature  $T_2$  for the lower vessel on the order of 290-293 K and with a change in the temperature  $T_1$  in the upper vessel from 400 to 1010 K the quantity  $\alpha_{th}$  undergoes virtually no change.

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