

THEORY
OF METALS

On the Theory of Interdiffusion in Ternary Alloys: Concentration Dependences of Kinetics-Related Coefficients

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Abstract—Calculated concentration dependences of interdiffusion coefficients and coefficients determining contributions of initial and boundary conditions for various alloy components into distribution of concentrations in the diffusion zone are illustrated. The analysis of these dependences shows that kinetics of component redistribution is determined by the component that diffuses slowly, which distinguishes the results of this approach from that of the generalized theories of the Darken approach.

Keywords: interdiffusion, multicomponent alloys, theory, interdiffusion coefficients, “sluggish” diffusion

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INTRODUCTION

The majority of alloys for industrial applications have multicomponent composition and multiphase microstructure. To predict a structure and its degradation upon the production of items from alloys and under the operation condition, respectively, it is necessary to understand and describe diffusion processes in these systems [1–6]. However, peculiarities of the diffusion in multicomponent alloys require clarifying, because their origin is not always known [7–9]. In particular, this is true for the “sluggish” diffusion in high-entropy alloys [9].

In [10], the approach that has been earlier developed for the case of binary systems [11–19] is generalized to ternary alloys. Its mathematical apparatus has been developed, and the expressions for the interdiffusion coefficients that determine contributions of initial and boundary conditions into the distribution of concentrations in the diffusion zone have been derived.

In this work, the concentration dependences of the aforementioned coefficients are calculated and the plots that illustrate these dependences are given; on this basis, the peculiarities of interdiffusion in ternary alloys and possible causes for its retardation are analyzed.

SOLUTION OF SYSTEM OF DIFFUSION EQUATIONS FOR THREE COMPONENTS AND VACANCIES

In [10], basic equations for flows of vacancies and atoms in three-component system were derived by the Gurov hole gas method [3, 4]. After substitution of the

expressions for flows in the continuity equations, we get the system of four nonlinear interrelated equations, which is linearized as it has been done in the case of the interdiffusion in binary systems [13]. In this case, the concentration gradients were considered to be small, because the flow equations were derived for the same conditions [3, 4], the concentrations are represented as a sum of two terms:

$$\begin{aligned}c^i(x + \xi, t + \tau) &= c_i(x, t) + u^i(x, t, \xi, \tau), \\c_v(x + \xi, t + \tau) &= c(x, t) + v(x, t, \xi, \tau),\end{aligned}\quad (1)$$

where c_v is the vacancy concentration and c_i is the component concentration $i = 1, 2, 3$, $0 \leq \xi \leq l$, $\tau < t_i$.

The system of linearized equation for u^i and v (see (5) in [10]) was solved using the Green’s functions for parabolic equations [20], which allowed describing the functions as series (for details see [13]):

$$u^i = \sum_{n=1}^{\infty} \varphi_n^i(\tau) \sin(\lambda_n \xi); \quad v = \sum_{n=1}^{\infty} \varphi_n(\tau) \sin(\lambda_n \xi), \quad (2)$$

where $\lambda_n = \pi n/l$.

Taking into account the orthogonality of $\sin(\lambda_n \xi)$, the system of diffusion equations in [10] was transformed into a system of integral equations for $\varphi_n^i(\tau)$ and $\varphi_n(\tau)$. This system of equations was solved using the Laplace transformation. The characteristic equation ((9) in [10]) has eigenvalues that determine temporal dependence of concentrations of alloy components and vacancies. In this case, the distribution of components concentration in the diffusion zone is

determined by two interdiffusion coefficients with an accuracy up to the vacancy concentration terms of the higher order. These coefficients are roots of the quadratic equation with the following coefficients:

$$B_q = -\frac{(c_2D_2 + c_3D_3)D_1 + (c_1D_1 + c_3D_3)D_2}{(c_1D_1 + c_2D_2 + c_3D_3)} - \frac{(c_1D_1 + c_2D_2)D_3}{(c_1D_1 + c_2D_2 + c_3D_3)}, \quad (3)$$

$$C_q = \frac{D_1D_2D_3}{(c_1D_1 + c_2D_2 + c_3D_3)S_D}.$$

Then, formulas for these roots are calculated as follows:

$$p_3 = -\lambda_n^2 D^+, \quad D^+ = \frac{-B_q}{2} + \left[\left(\frac{B_q}{2} \right)^2 - C_q \right]^{\frac{1}{2}}; \quad (4)$$

$$p_4 = -\lambda_n^2 D^-, \quad D^- = \frac{-B_q}{2} - \left[\left(\frac{B_q}{2} \right)^2 - C_q \right]^{\frac{1}{2}}, \quad (5)$$

where D_1, D_2, D_3 are the self-diffusion coefficients, and $\Phi_n^1(p)$ is determined by the following expression:

$$\begin{aligned} \Phi_n^1(p) = & \Phi_n^1(p) \left[M_1^{1+} \frac{1}{p + \lambda_n^2 D^+} + M_1^{1-} \frac{1}{p + \lambda_n^2 D^-} \right] \\ & + \Phi_n^2(p) \left[M_2^{1+} \frac{1}{p + \lambda_n^2 D^+} + M_2^{1-} \frac{1}{p + \lambda_n^2 D^-} \right] \\ & + \Phi_n^3(p) \left[M_3^{1+} \frac{1}{p + \lambda_n^2 D^+} + M_3^{1-} \frac{1}{p + \lambda_n^2 D^-} \right], \end{aligned} \quad (6)$$

where

$$M_1^{1+} = -\frac{D_1 z_1 c_1 (D^+ - D_2)(D^+ - D_3)}{D^+ (\hat{D} - D^+) (D^+ - D^-) (D^+ - D_1)},$$

$$M_1^{1-} = \frac{D_1 z_1 c_1 (D^- - D_2)(D^- - D_3)}{D^- (\hat{D} - D^-) (D^+ - D^-) (D^- - D_1)},$$

$$M_2^{1+} = -\frac{D_2 z_1 c_1 (D^+ - D_3)}{D^+ (\hat{D} - D^+) (D^+ - D^-)},$$

$$M_2^{1-} = \frac{D_2 z_1 c_1 (D^- - D_3)}{D^- (\hat{D} - D^-) (D^+ - D^-)},$$

$$M_3^{1+} = -\frac{D_3 z_1 c_1 (D^+ - D_2)}{D^+ (\hat{D} - D^+) (D^+ - D^-)},$$

$$M_3^{1-} = \frac{D_3 z_1 c_1 (D^- - D_2)}{D^- (\hat{D} - D^-) (D^+ - D^-)},$$

$$\Phi_n^i(p) = \Phi_n^i(0) + \frac{2\pi n D_i}{l^2} u_{0l}^i(p),$$

$u_{0l}^i(p)$ is the Laplace image of function

$$u_{0l}^i(\tau) = u^i(0, \tau) - (-1)^n u^i(l, \tau),$$

which determines contributions of the first-order boundary conditions set at the boundaries of interval l in the solution of the diffusion equation for component i .

To derive expression for $\Phi_n^2(p)$, in $\Phi_n^1(p)$, it is suffice to change indices $1 \rightarrow 2$; $2 \rightarrow 3$; $3 \rightarrow 1$; and for $\Phi_n^3(p)$, $1 \rightarrow 3$; $3 \rightarrow 2$; $2 \rightarrow 1$.

Thus, temporal change in the concentration of alloy components is determined by two coefficients D^+ and D^- . Besides, the form of the concentration profiles depends not only on the coefficients, but also on six remaining matrix elements of **M1** (see (6)).

CONCENTRATION DEPENDENCES OF COEFFICIENTS D^+ AND D^- AND MATRIX ELEMENTS **M1**

Coefficients D^+ and D^- as well as matrix elements of **M1** (6) demonstrate a complex dependence on the concentration of alloy elements. Therefore, for illustration, such dependences are calculated and plotted for some coefficients D_i , which were considered independent on concentration (often used in theoretical works). So, Figs. 1 and 2 demonstrate dependences of D^+ and D^- for various proportions of coefficients D_1, D_2, D_3 .

Results shown in Figs. 1, 2 suggest that for different concentrations D^+ varies in the range between average and maximum values of self-diffusion coefficients; D^- varies in the range between minimal and average values of self-diffusion coefficients. This means that terms of the second column of equation (6) change slowly with time. In addition, these coefficients are essentially lower than in any cases of linearly dependent diagonal coefficients, e.g., in the generalized theories of the Darken approach for three-component alloys [4]. Besides, these deviations are maximal for the equiatomic alloy composition.

To enhance analysis, the concentration dependences of the coefficients D^+ and D^- were calculated for constant concentration of one of the components. Results are demonstrated in Fig. 3.

All expressions $\Phi_n^i(p)$ have the same structure as in the case of the two-component system (see [13]). However, coefficients of functions dependent on p , which determine time dependence, have a more complicated form, and it is difficult to express them conveniently in terms of D_i, D_ν . Therefore, Figs. 4–7 demonstrate plots of concentration dependences of matrix elements of **M1** for the above-described rela-

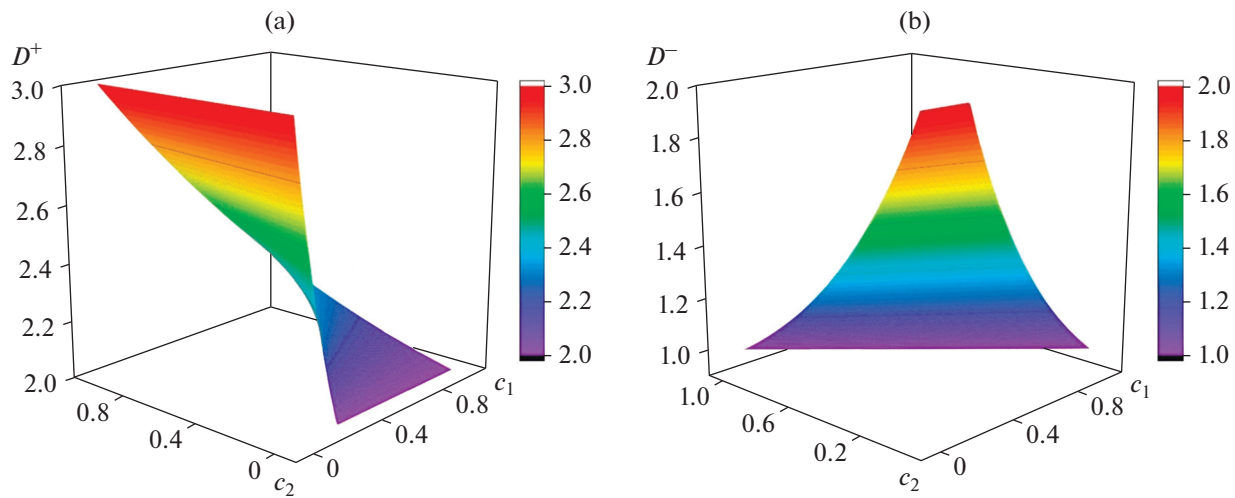


Fig. 1. Concentration dependence of coefficients D^+ (a) and D^- (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 3 : 2 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$), $D^+ = 2.434$, $D^- = 1.232$.

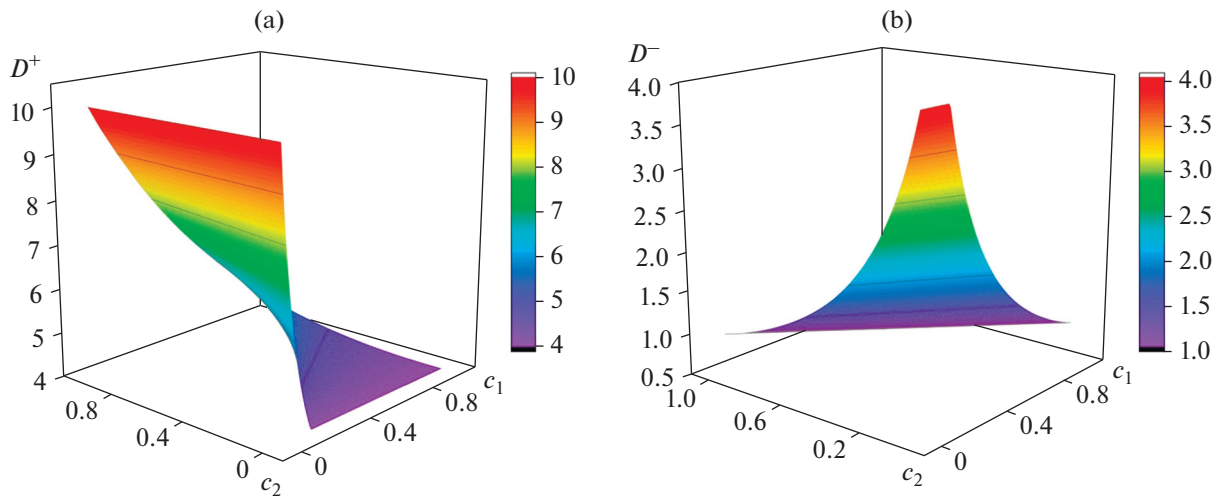


Fig. 2. Concentration dependence of coefficients D^+ (a) and D^- (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 10 : 4 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$), $D^+ = 5.827$, $D^- = 1.373$.

tionships of self-diffusion coefficients. Besides, the plots only represent matrix elements with higher order of vacancy concentration. First, Figs. 4 and 6 show plots for matrix elements of $\mathbf{M1}$ (6), which determine contributions of the terms controlled by initial and boundary conditions for the first (see Eq. (6)) and then for the second (Figs. 5, 7) components into the dependence of the first-component concentration in diffusion zone on coordinate and time.

It is necessary to note that coefficients have the same order of magnitude. Besides, in a certain concentration range, elements of the right column of matrix $\mathbf{M1}$ (6), which determine contributions of

slowly changing terms (D^- dependent), have higher values than those of the matrix middle column (D^+ dependent). This means that in this concentration region the slow time-dependent variation of the component concentration prevails.

Figures 6 and 7 show dependences of the same matrix elements for another relationship between the self-diffusion coefficients.

The data presented demonstrate that they have similar behavior and only somewhat differ in value. Additionally, D^+ and D^- are calculated for two relationships of self-diffusion coefficients, presuming that their average values are the same (Figs. 8 and 9).

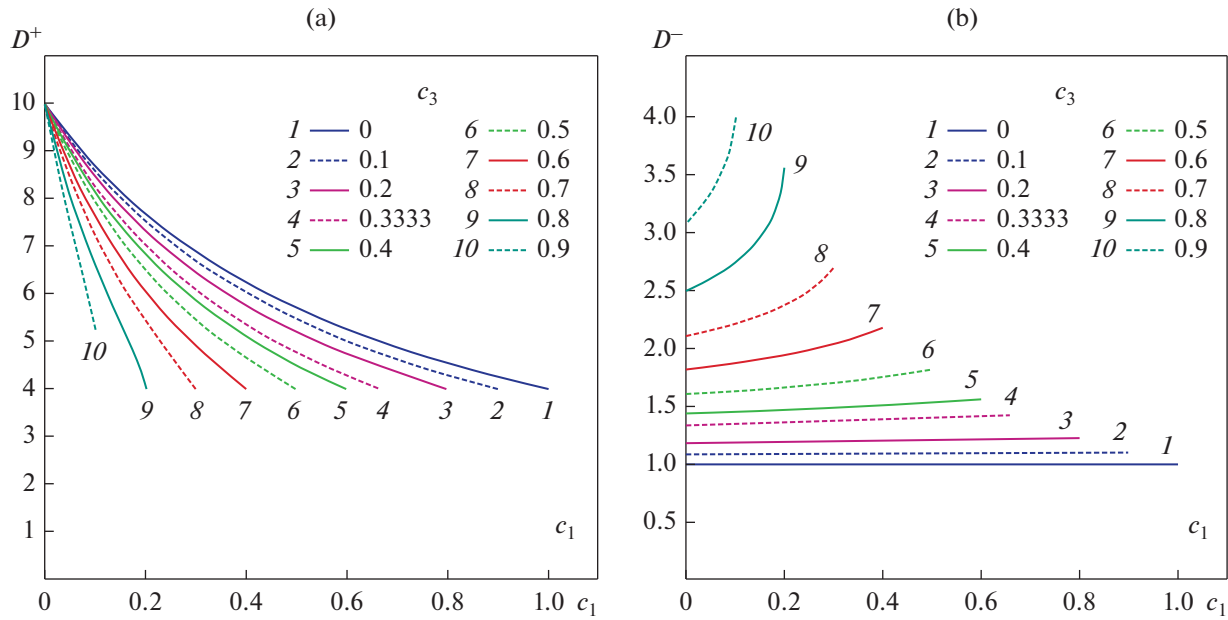


Fig. 3. Concentration dependence of coefficients D^+ (a) and D^- (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 10 : 4 : 1 for different values of component c_3 .

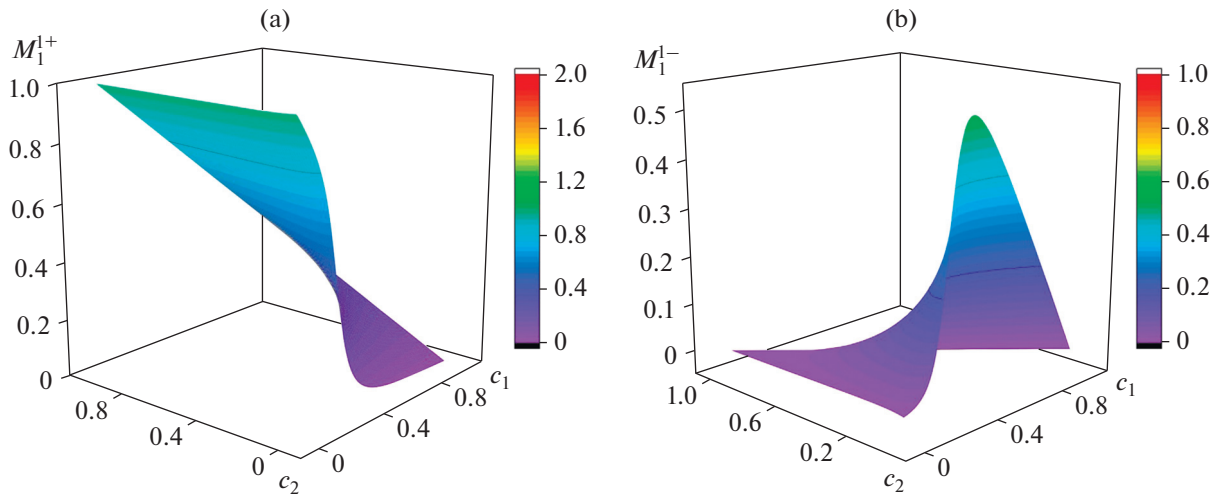


Fig. 4. Concentration dependence of coefficients M_1^{1+} (a) and M_1^{1-} (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 3 : 2 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$), $M_1^{1+} = 0.564$, $M_1^{1-} = 0.102$.

Analysis of the results shown in these figures demonstrates that the higher the difference in the self-diffusion coefficients in an alloy (for the same average value), the less the D^- coefficient and the more pronounced retardation of the interdiffusion in equiatomic and some other alloys. In addition, under these conditions the contribution of such terms is also higher, which originates from the \mathbf{M} matrix components.

CONCLUSIONS

Thus, in this work, concentration dependences of diffusion coefficients that determine the redistribution of the alloy components in the diffusion zone and the kinetics of the diffusion transformations are studied. The derived equations and presented figures demonstrate that these coefficients depend nonlinearly on concentration and self-diffusion coefficients. In this case, the largest of these coefficients falls in the range

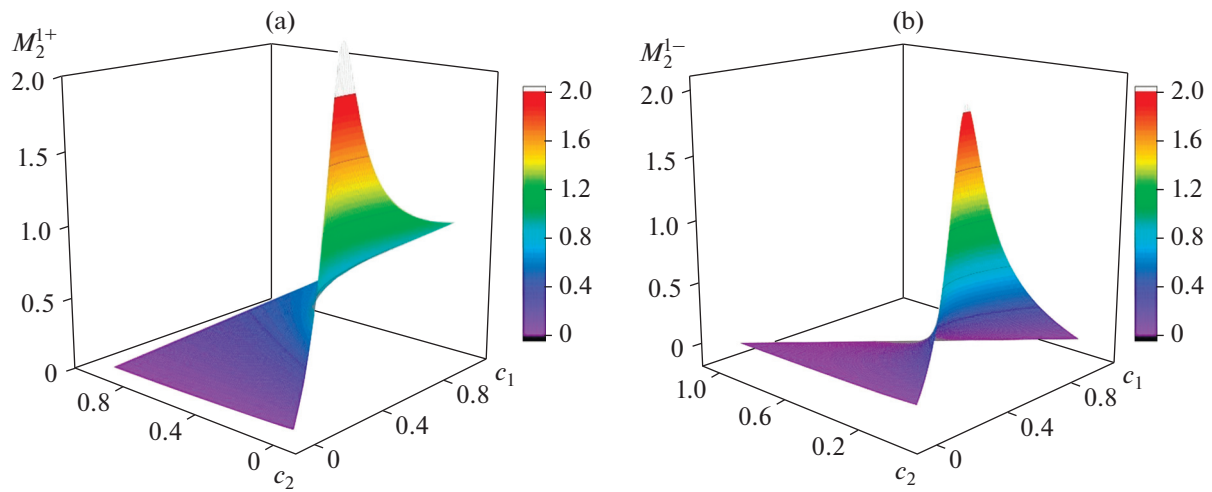


Fig. 5. Concentration dependence of coefficients M_2^{1+} (a) and M_2^{1-} (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 3 : 2 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$) $M_2^{1+} = 0.490$, $M_2^{1-} = 0.156$.

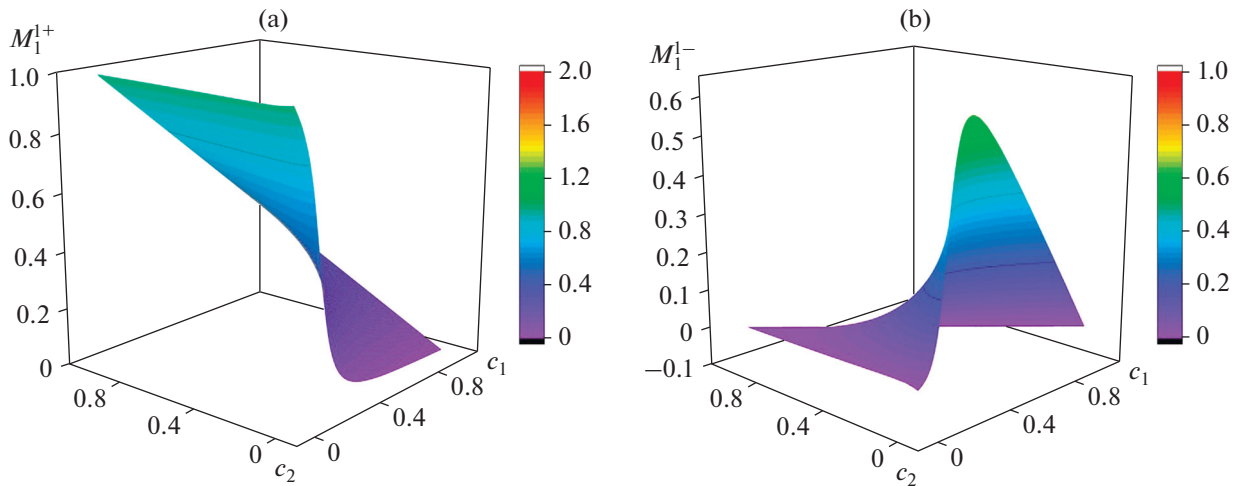


Fig. 6. Concentration dependence of coefficients M_1^{1+} (a) and M_1^{1-} (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 10 : 4 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$) $M_1^{1+} = 0.543$, $M_1^{1-} = 0.124$.

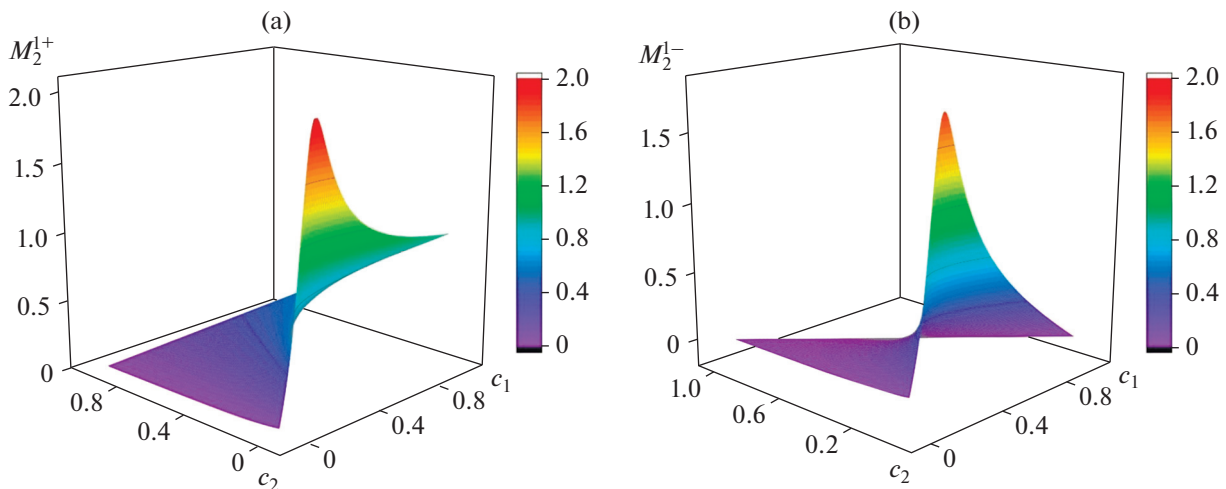


Fig. 7. Concentration dependence of coefficients M_2^{1+} (a) and M_2^{1-} (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 10 : 4 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$) $M_2^{1+} = 0.496$, $M_2^{1-} = 0.163$.

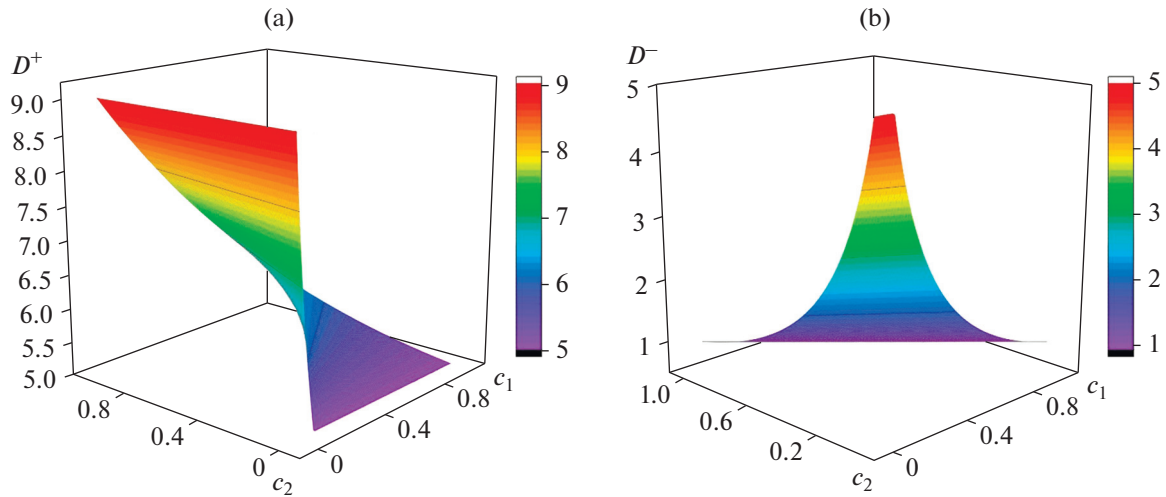


Fig. 8. Concentration dependence of coefficients D^+ (a) and D^- (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 9 : 5 : 1. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$), $D^+ = 6.477$, $D^- = 1.389$.

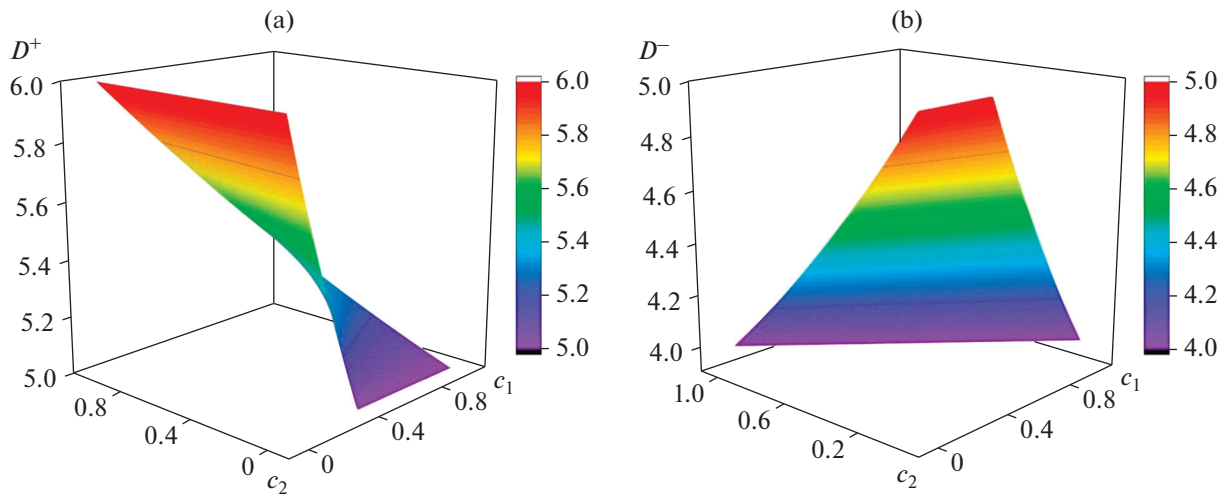


Fig. 9. Concentration dependence of coefficients D^+ (a) and D^- (b) for diffusion coefficients ratio $D_1 : D_2 : D_3$ as 6 : 5 : 4. The case of equiatomic composition ($c_1 = c_2 = c_3 = 1/3$), $D^+ = 5.515$, $D^- = 4.352$.

between average and maximal self-diffusion coefficients; the smallest one, between the minimal and average. Preliminary results show that in the ternary alloy the interdiffusion is slower than predicted by the generalized theories of the Darken approach [4]. This difference is the highest for the equiatomic alloys and for higher deviation in self-diffusion coefficients. In other words, it can be expected that the “sluggish diffusion” will be observed in alloys in which the maximal self-diffusion coefficient is five or more times larger than the minimal one.

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