

Theoretical principles of kinetics of diffusion saturation of iron-based composite materials

Subhan N. Namazov · Vurgun F. Gahramanov

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Abstract. *In the paper, kinetics of processes that occur in diffusion saturation of composites are analyzed and justified. It is determined that in multi-component composite systems, the analytic solution of diffusion saturation equations is obtained from the assumption that the diffusion coefficients are constant.*

Keywords. sinter · porous · phase · alloy · diffusion

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1 Introduction.

Kinetics of formation of diffusion coatings of powder compositions substantially depends on their structure, phase compositions and properties. Porosity of sintered powder compositions have decisive influence on the character of diffusion coatings formation. Therefore, in the paper, the kinetics of diffusion coatings of iron-based composite materials are considered.

It is known that closed pores may both increase and decrease the diffusion flow-Ratio between surface and volume diffusion are determined by the sizes of pores. In the R radius of the pore, decrease of volume flow is compensated by surface diffusion and is calculated as follows [2]:

$$R = \frac{2\delta D_S}{D_0}. \quad (1.1)$$

Here δ is the thickness of the layer participating in the surface diffusion D_S and D_0 are the coefficients of the surface and volume diffusions, respectively. Here the critical size of pores are estimated by the value about 10^{-3} mm. The ratio D_S/D_0 increases as the temperature decreases. This shows that the critical size of the pore should increase [2,4].

The sizes of granulars of cooked composite materials are determined by their manufacturing technology. They are: pressing, sintered, chemical composition, etc. But in sinter materials, taking into account small inclination and significant compacting pressure it is expected that after ordinary sinter modes the powder compositions do not remain constant.

If we compare the characteristics of compact and sintered materials of the same composition and with the same initial granular, we can affirm that in the sintered material during chemical-thermal treatment process the size of the granular is growing less. The third reason of diffusion velocity increase in powder composites is distortion of the crystal cell and its imperfect structure.

The sintered materials have a great number of vacancy sources-pores. In any case, concentration of vacancies near the pores are significantly high in the equilibrium state. The informations in [2] affirm the influence of the above listed factors.

It should be noted that in the case under consideration the diffusion is not entirely volumetric, the diffusion is the result of flow: surface, boundary and volumetric. Such a variant of diffusion transfer is realized only at great power of the diffusion source. Depending on its decrease (for example, getting away the boundaries), the surface and boundary diffusion dominates over volume diffusion.

The influence of soluble additives on the results of diffusion saturation and the diffusion coefficients of alloy elements (saturation) are less clear compared with influence of other factors. This is stipulated by considerable complexity of the case. Because, in this it is necessary to consider the diffusion not in the binary but in the multi-component system.

2 Problem statement

In multi-component systems, the most part of analytic solution were obtained from the assumption that diffusion coefficients are constant. But as was shown in [7,9], such an approach does not give the accepted results. In this connection, it is necessary to calculate the dependencies of diffusion coefficients, in particular, concentration dependencies of non-diagonal coefficients. But in this case, diffusion equations are nonlinear and it is impossible to get their solution in the closed form. In multi-component systems the numerical method is the most convenient method for calculation of diffusion processes. In [5,6], the problems describing diffusion processes in multi-component solid solutions are considered.

Usually, the system's composition is determined by the number of every type atoms in the share of their general amount: $\bar{C}_i = \frac{n_i}{\sum_{i=1}^n n_i}$, here n_i is the density of the i compact atoms (the i index belongs to the atoms of the matrix).

But it is convenient to pass to appropriate concentrations that create substitution solid solutions and with alloy elements to describe diffusion in solid solution, i.e. $(R - r)$ to $C_i = \frac{n_i}{n_0}$ (here n_0 is the density of the node of crystal cells). \bar{C}_i concentrations and the concentrations with included \bar{C}_i have the following ratio:

$$\bar{C}_i = \frac{C_i}{1 + \sum_{i=r+1}^r C_i}, \quad (2.1)$$

Then we simplicity we assume that in the deformation process the crystal cell is not deformed, i.e. $n_0 = const$. Ignoring Onzager's non-diagonal coefficients, at $i = j$, for density of diffusion flow of the i component we get

$$\vec{I}_C = \frac{1}{V} (C, \vec{v} - L_{ii} \nabla \mu_i), \quad (2.2)$$

here $V = i_{n_0}$ is the volume per each node of the crystal cell; μ_i^m is the chemical potential of the i component, \vec{v} is the velocity of plastic yield of the substance in the diffusion area.

There is an additional condition in approximation of local quasi-equilibrium distribution for concentrations of substitution components [3]

$$\sum_{i=1}^r C_i = 1.$$

The equations of continuity of flows for each substitution components yield the following expression

$$\nabla = \left(\sum_{i=1}^r I_i \right) = 0.$$

which admits to determine the flow velocity

$$\vec{V} = \sum_{i=1}^r L_{jj} \nabla \mu_j. \quad (2.3)$$

From equations (2.2) and (2.3) we choose C_i , $i = 2 - R$ and taking into account the Gibbs - Dyugon ratio for the density of components

$$\sum_{i=1}^R C_i \delta \mu_i = 0,$$

of flow and mutual diffusion coefficients we get the expression

$$\bar{I}_C = -\frac{1}{V} \sum_{j=2}^R \bar{D}_{ij} \nabla C_i \quad (2.4)$$

$$\tilde{D}_{ij} = \frac{C_i}{RT} \left[D_i^* \frac{d\mu}{dc} + \sum_{\alpha=2}^R C_\alpha (D_i^* - \xi_\alpha D_\alpha^*) \frac{d\mu_\alpha}{dc_j} \right], \quad (2.4')$$

here $D_i^* = L_{ii} RT / C_i$ are the diffusion coefficients of the i element in the matrix

$$\xi_i = \begin{cases} 1, & i \leq r, \\ 0, & i > r. \end{cases}$$

The expressions (2.4) and (2.4') is the generalized form of the results obtained in [3] for a three-component system.

As is seen from the results it is necessary to know the character of concentration values of chemical potentials for solving three-component diffusion problems. The existing methods for calculating the mentioned dependencies [1,10], are based on the use of different approximation models in accordance with specific systems. This essentially complicates their application for numerical solution of diffusion problems. Taking this into account, depending on strong statistic theory, the character of concentration dependencies of chemical potentials in multi-component solutions were analyzed based on pure solvents. In this case, the great canonic ensemble method suggested by Mayer and McMillan [13] and based on distribution function apparatus [11] was used. Being restricted by the first and second row coefficients, we get

$$\mu_i (i > 1) = \psi_i + RT \ln \left(\bar{C}_i + \sum_{j=2}^R A_{ij} \bar{C}_i \bar{C} \right),$$

$$\mu_i = \mu_i^* RT \ln \left(\bar{C}_i + \sum_{2 \leq i \leq j}^R A_{ij}^{(1)} \bar{C}_i \bar{C}_j \right),$$

$$A_{ij} = A_{ji} = -A_{ij}^{(1)} = n_0 \left(\sum_{ij} - \sum_{ij} - \sum_{ij} \right), \quad i \neq j \quad (2.5)$$

$$A_{ij} = -2A_{ij}^{(1)} = -2n_0 \sum_{ij} - \sum_{ij} = \mathbf{b}_{2bi} + \mathbf{b}_{2\delta i} - b_{\delta i + \delta i}.$$

The group integrals contained in the coefficients of formula (2.5) are written as follows:

$$\vec{b}_{\overline{b_i + \delta_j}} = \frac{1}{V} \int \left[\exp \left(-\frac{W(l_i, l_j)}{RT} \right) - 1 \right] d[l_i] d[l_j],$$

$$\vec{b}_{\overline{b_i + \delta_j}} = \frac{1}{2V} \int \left[\exp \left(-\frac{W(l_i, l_j)}{RT} \right) - 1 \right] d[l_i] d[l_j],$$

here $W(l_i, l_j)$ is the potential of average force. The physical meaning of \sum_{ij} is that they show stability of $i - i$ and $j - j$ pair compared with the pair $i - j$. Taking into account the ratio (2.5) in (2.1), in (2.5') the coefficients of mutual diffusion in multi-component solid solutions are reduced to the following expressions:

$$D_{ij} = D_j^* \left(\delta_{ij} + \frac{a_{ij} C_i}{1 + \sum_{\beta=2}^R a_{i\beta} C_\beta} \right) +$$

$$+ C_i \sum_{\alpha=2}^R (D_i^* - \xi_\alpha D_\alpha^*) \left(\delta_{2j} + \frac{a_{\alpha j}}{1 + \sum_{\beta=2}^R a_{\alpha\beta} C_\beta} \right). \quad (2.6)$$

Here $a_{ij} = A_{ij} - 1 + \xi_j$. Analyze this ratio. In linear approximation, formulas (2.6) are essentially simplified. The expression (2.7) is obtained under the condition that the j -element creates substitution solid solution, (2.7'), the inclusion solid solution

$$\vec{D}_{ij} \approx D_i^* \delta_{ij} + C_i D_i^* \left(A_{ij} + \frac{D_i^* - D_j^*}{D_i^*} \right) \quad (2.7)$$

$$\vec{D}_{ij} \approx D_i^* \delta_{ij} + C_i D_i^* \left(A_{ij} + \frac{D_i^* - D_j^*}{D_i^*} \right). \quad (2.7')$$

As we see from expressions (2.7) and (2.7') the diffusion flow of the j -component into i depends not on their thermodynamic interactive parameters, but also on the ratio of the matrix and the diffusion coefficients of atoms of these elements. But if the j -element creates substitution, i creates inclusion solution, then we can ignore the last expression D_i^* , $D_j^* \leq D_i^*$.

Because in this case (2.4) and (2.4') and the expressions of natural diffusion coefficients found for flow density enable to compose the system of equations that determines distribution of concentration of diffusive elements in multi-component solid solutions. Let us

consider only one-dimensional diffusion. In this case the system equations takes the following form:

$$\frac{dC_i}{d_i} = \frac{d}{d_x} \left(\sum_{j=2}^R D_{ij} \frac{\vec{d}C_i}{d_x} \right), \quad i = 2, 3, 4, \dots, R. \quad (2.8)$$

We write the boundary conditions in diffusion saturation of alloys in the form:

$$\sum_{j=2}^R D_{ij} \frac{dC_i}{d_x} \Big|_{x=2} = \sum_{j=2}^R \vec{V}_{ij} \left(\vec{C}_j^n - C_j \right) \Big|_{x=0}; \quad (2.9)$$

$$C_i|_{x \rightarrow \infty} - C_i^\infty, \quad C_i|_{i=0} - C_i''(x), \quad (2.10)$$

here the coefficients $\vec{V}_{ij}(t)$ take into account interaction of the atoms of different elements in the saturated surface (in [8] the necessity of the same consideration was shown). C_i is concentration of the i component in the matrix. C_i^H is the limit surface concentration of the j component. C_i^H is initial distribution of the i -component in (x)-diffusion area.

For solving problem (2.8) and (2.10) as $t \rightarrow 0$ it is required to fulfill the following equalities that determine the functions $\vec{V}_{ij}(t)$.

$$-\sum_{j=2}^R \vec{D}_{ij} \frac{dC_i}{d_x} \Big|_{x=2} = \sum_{j=2}^R \vec{V}_{ij}(0) \left(C_j'' - C_j'' \right) \Big|_{x=0}, \quad C_i^H|_{x \rightarrow \infty}$$

Let us pass to equations (2.8) and (2.10) and pure variables

$$\tau = \frac{t}{t_0}, \quad z = \frac{x}{L}, \quad D_{ij} = \frac{\vec{D}_{ij}}{D_0}, \quad V_{ij} = \frac{\vec{V}_{ij}}{V_0},$$

here $D_0 = L^2/t$, $V_0 = L/t$, L is a measure exceeding the length of diffusion area. Having substituted and closing the unlimited area by the boundary at L distance, we get

$$\frac{\vec{d}C}{d_\tau} = \frac{d}{d_z} \left(D \frac{\vec{d}C}{d_z} \right)$$

$$D \frac{\vec{d}C}{d_\tau} \Big|_{z=0} = V \left(\vec{C}^n - \vec{C} \right) \Big|_{z=0}; \quad \vec{C} \Big|_{z=0} = \vec{C}^\infty; \quad \vec{C}^- \Big|_{t=0} = C^H. \quad (2.11)$$

Here, we included the following matrices: $C = (C_i)$, $D = (D_{ij})$, $V = (V_{ij})$. For numerical solution of problem (1.12) we used the net $\omega = \omega_z + \omega_\tau$ with respect to z and τ .

$$\omega_z = (Z_s, S = 0, 1 \dots N; z_0 = 0, z_N = 1, h_s = z_s - z_{s-1}),$$

$$\omega_\tau = (\tau_j, j = 0, 1 \dots r_i, \tau_0 = 0, \tau_1 = 1, \Delta\tau_j = \tau_{j+1} - \tau_j).$$

The indefinite difference scheme (balance method) constructed by means of the integro-interpolation method in the net ω is as follows [1, 10]

$$\frac{\vec{C}_S^{j+1} - \vec{C}_S^j}{\Delta\tau_j} = \frac{2}{h_S + h_{S+1}} \left(\frac{D_{S+1}}{2} \frac{\vec{C}_{S+1}^{i+1} - \vec{C}_S^j}{h_{S+1}} - D_{S-1/2} \frac{\vec{C}_{S+1}^{iH} - \vec{C}_S^{j+1}}{h_S} \right)$$

$$D_{1/2} \vec{C}_1^{iH} - \vec{C}_0^{j+1} = V^{j+1/2} \left(\vec{C}_0^{j+H} - \vec{C}^H \right) + \left(\vec{C}_0^{jH} - \vec{C}_0^j \right) \frac{h_1}{2\Delta\tau_1} \quad (2.12)$$

$$\vec{C}_N^{jH} = \vec{C}^\infty, \quad \vec{C}_S^0 = \vec{C}_S^H.$$

Here C_S^j is concentration of components in time interval τ_j at the point z_s

$$D_{S+1/2} = D \left[\frac{1}{2} \left(\vec{C}_{S+1}^{j+1} + \vec{C}_S^{j+1} \right) \right].$$

The error of this scheme approximation is $(\Delta\tau_{\max} + \Delta\tau_{\max}^2)$ [12]. For solving nonlinear system (2.12) we usually use iteration method [12]. In equations (2.12) the iteration process is structured by the following three changes

$$\vec{C}_S^{j+1} \rightarrow \vec{C}_S^{j+1,\alpha}, \quad D_{S+1/2} \rightarrow D_{S+1/2}^{\alpha-1} = D \left[\frac{1}{2} \left(\vec{C}_S^{j+1} + \vec{C}_S^{j+1,\alpha+1} \right) \right].$$

In the ratio C_S^{j+1} , $S = 0, 1, \dots, N$ the numerical difference scheme is linear. For the initial iteration the distribution concentration of the previous value of time is taken. For $\vec{C}_S^{j+1,0} = C_S^{j+1} C_S^{j+1,\alpha}$ the numerical scheme is three-point. Reducing this scheme to calculations we get

$$\begin{aligned} D_{S+H}^{\alpha-1} \vec{C}_S^{j+1} - \left(D_{S+1/2}^{\alpha-1} + D_{S-1/2}^{\alpha-1} W_S + \delta_S E \right) \vec{C}_S^{j+1,\alpha} + D_{S-1/2}^{\alpha+1} W_S \vec{C}_S^{j+1,\alpha} &= -\delta_S \vec{C}_S^j \\ D_{1/2}^{\alpha-1,jH,\alpha} - \left(D_{1/2}^{\alpha-1} + h_1 V^{jH/2} + \frac{h_1}{2\Delta\tau_1 E} \right) C_0^{jH,\alpha} &= - \left(h_1 V^{jH/2} C^R + \frac{h_1^2}{2\Delta\tau_1 \vec{C}_0^j} \right), \\ \vec{C}_N^{jH} = \vec{C}^\infty, \quad \vec{C}^0 = \vec{C}^H \end{aligned}$$

here E is a unit matrix, $W_S = h_{S+1}/h_{S+1}$, $\sigma_S = (h_S + h_{S+1})/2\Delta\tau_j$. This problem is solved by the sweeping method [10]

$$\vec{C}_{S-1}^{j+1,\sigma} = x \vec{C}_S^{j+1,\sigma} + z_S, \quad S = 1, 2, 3, \dots, N \quad (2.13)$$

here x_S and z_S matrices are calculated from recurrent ratios for $S = 1, 2, \dots, N - 1$

$$x_1 = \left(D_{1/2}^{\alpha-1} + h_1 V^{j+1/2} + \frac{h_1^2}{2\Delta\tau_1 E} \right)^{-1} D_{1/2}^{\alpha-1}, \quad (2.14)$$

$$\begin{aligned} z_1 &= \left(D_{1/2}^{\alpha-1} + h_1 V h_1 V^{j+1/2} + \frac{h_1^2}{2\Delta\tau_1 E} \right)^{-1} \left(h_1 V^{j+1/2} C^n + \frac{h_1^2}{2\Delta\tau_1 \vec{C}_0^j} \right), \\ X_{SH} &= \left(D_{1/2}^{\alpha-1} + D_{S-1/2}^{\alpha-1} W_S + \delta_S E - D_{S-1/2}^{\alpha-1} W_S X_S \right) D_{S+1/2}^{\alpha-1}, \\ X_{S+1} &= \left(D_{S-1/2}^{\alpha-1} + D_{S-1/2}^{\alpha-1} W_S + \delta_S E - D_{S-1/2}^{\alpha-1} W_S X_S \right)^{-1} \times \\ &\quad \times \left(D_{S-1/2}^{\alpha-1} W_S Z_S + \delta_S \vec{C}_S^j \right). \end{aligned} \quad (2.14')$$

At first, by formulas (2.14) and (2.14') we calculate the matrices x_S and z_S for $S = 1, \dots, N - 1$. Then, we take into account that by means of the ratio $\vec{C}_N^{j+1} = \vec{C}^\infty$ (2.14) the concentration $C_S^{j+1,\alpha}$ is determined in all the nodes of the cell. Iterations are successively calculated until the following inequality is obtained

$$E \geq \max_{R,S} \left| C_{R,S}^{j+1,\alpha} - C_{R,S}^{j+1,\alpha-1} \right|. \quad (2.15)$$

As the diffusion coefficients of elements differ several times, for saving time we can apply unequal cracks with respect to z and τ . To this end, to M simultaneously WM and mM whose elements $W_S = W_R$ give the amount of $W_h = h_{S+1}/h_S$. In this case the following relations are fulfilled:

$$\frac{h_{\max}}{h_{\min}} \sim \left(\frac{D_{i,\max}^*}{D_{i,\min}^*} \right)^{\frac{1}{2}}, \quad \sum_{R=1}^m = N - 1.$$

Here N is the number of node of space cell. $D_{i,\max}^*$ ($D_{i,\min}^*$) is the greatest and least coefficient of the h_{\max} (h_{\min}) diffusion is the greatest (the least) step of the space cell. By the time $\Delta\tau_j$ the step increases according to linear law

$$\Delta\tau_{j+1} = \Delta\tau_j + \Delta\tau, \quad \Delta\tau = \frac{h_{\min}^2}{\lambda}, \quad \lambda = 1.$$

So the suggested expressions enable to calculate different diffusion processes in multi-parameter solid solutions.

3 Conclusions

1. Kinetic of processes that occur in diffusion saturation of compositions are analyzed and justified. It was determined that kinetics of multi-component diffusion depends on the character of concentration of chemical potentials.

2. A significant part of analytic solution of diffusion saturation equations in multi-component systems is obtained from the assumption that diffusion coefficients are constant. But in this case diffusion equations are obtained as nonlinear and it is impossible to solve them in the closed form. Therefore, it is the most suitable method is to the numerical method.

3. The higher the open porosity of the press-billet of the saturation medium penetrates the deeper layers of the product.

References

1. Borerskii, I.B., etc.: Mutual diffusion processes in alloy, *M. Nauka*, 325 (1993).
2. Finkelstein, T.V.: *Cementation and nitrocarburization of steel powder products*, In: Thermal and chemical-thermal treatment in powder metallurgy. Kiev, Naukova Dumka (Russian) 53-65 (1999).
3. Geguzin, Ya.E.: Essays on diffusion in crystals, *II edition. M.. Nauka*, 128 (1984).
4. Krishtal, M.A., Zakharev, P.N., Mokrov, A.P.: *Mutual diffusion in multi-component system*, FMM, Issue 4 (3), 752-758 (1992).
5. Lyakhovich, L.S., Voroshnin, L.G., Husid, B.M.: *Metallurgy, issue 8, Minsk, BPI*, 452 (1996).
6. Lyakhovich, L.S., Voroshnin, L.G., Husid, B.M.: *Vesti of AN BSSR, sci. phys. energy*, 3, 253-258 (1986).
7. Minkevich, A.N.: Chemical-thermal treatment of metals and alloys, *M. Mashinostroenie*, 458 (1988).
8. Mitchell, E., Dawes, C.: *Metal treatm. and Drop. Forging*, 31 (230), 137-145 (2004).
9. Namazov, S.N., Jafarova, A.A., Gahramanov V.F.: *Structural characteristics of iron graphite and powder gelatin graphite with subsequent oxidation*, Innovational technologies in machine-building / Collection of papers of the VII International scientific practical conference. May 19-21, 2016, Yurga 91-94.

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10. Samarskiy, A.A.: *Introduction to theory of difference systems*, M. Nauka, 343 (2001).
 11. Samsonov, G.V., Zhunkovskiy, G.L.: *Protective coatings in metals*, issue 7, Kiev, Naukova Dumka, 230 (1983).
 12. Tsikh, S.G., Lisitskii, V.N., Glebova, Ya. A.: *Modern technologies of chemco-thermal treatment in machine-building*, Moscow, N.E. Baumann MSTU **1** (64), (2010).
 13. Vagner, K.: Thermodynamics of alloys, *M. Metallurgia*, 502 (1997).