KINETICS OF BINARY MELT – CRYSTAL PHASE TRANSFORMATIONS

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A number of investigations on the mechanism of metallic-type binary crystal growth has recently been performed by the method of statistical modeling on an electronic computer [1, 2]. The purpose of this paper is the analytical description of the kinetics of multicomponent alloy crystallization.

Let us examine the lattice model of a two-phase binary melt–crystal system. The lattice symmetry is assumed cubic. Atoms of the species α or β are situated at its sites and can be liquid or solid. Let us limit ourselves to the consideration of interaction between nearest neighbors so that particle interaction in the system is characterized by the binding energies of the solid particles $\varphi_{11}^{\alpha\alpha}$, $\varphi_{11}^{\alpha\beta}$, $\varphi_{11}^{\beta\beta}$, the solid with the liquid particles $\varphi_{10}^{\alpha\alpha}, \varphi_{10}^{\alpha\beta}, \varphi_{10}^{\beta\alpha}, \varphi_{10}^{\beta\beta}$, and the liquid particles $\varphi_{00}^{\alpha\alpha}, \varphi_{10}^{\alpha\beta}$, $\varphi_{10}^{\beta\beta}$ (the subscript 0 denotes belonging to the liquid phase and 1 to the solid phase). We will describe the configuration of the atom distribution in the system by the set of parameters $g=\begin{Bmatrix}\eta_j\\ \xi_j\end{Bmatrix}$. Here $\eta_j=1$, if there is a solid particle at the j-th site of the lattice and $\eta_j=0$ if there is a liquid particle; ξ_j determines the species of particle at this site ($\xi_j=\alpha, \beta$). We represent the Hamiltonian averaged with respect to the degrees of freedom but not associated with the order parameters characterizing the phase transition in the form H = U + K

$$U=\frac{1}{2}\sum_{i,j\in i}\Big\{\eta_i\eta_j\left[\delta_{\xi_i\alpha}\delta_{\xi_j\alpha}\varphi_{11}^{\alpha\alpha}+\left(\delta_{\xi_i\alpha}\delta_{\xi_j\beta}+\delta_{\xi_i\beta}\delta_{\xi_j\alpha}\right)\varphi_{11}^{\alpha\beta}+\delta_{\xi_i\beta}\delta_{\xi_j\beta}\varphi_{11}^{\beta\beta}\right]+$$
$$+[(1-\eta_i)\eta_j+\eta_i(1-\eta_j)]\left(\delta_{\xi_i\alpha}\delta_{\xi_j\alpha}\varphi_{10}^{\alpha\alpha}+\delta_{\xi_i\beta}\delta_{\xi_j\beta}\varphi_{10}^{\beta\beta}\right)+\Big[(1-\eta_i)\eta_j\delta_{\xi_i\alpha}\times$$
$$\times\delta_{\xi_j\beta}+\eta_i(1-\eta_j)\delta_{\xi_i\beta}\delta_{\xi_j\alpha}\Big]\varphi_{10}^{\beta\alpha}+\Big[\eta_i(1-\eta_j)\delta_{\xi_i\alpha}\delta_{\xi_j\beta}+$$
$$+(1-\eta_i)\eta_j\delta_{\xi_i\beta}\delta_{\xi_j\alpha}\Big]\varphi_{10}^{\alpha\beta}+(1-\eta_i)(1-\eta_j)\left[\delta_{\xi_i\alpha}\delta_{\xi_j\alpha}\varphi_{00}^{\alpha\alpha}+\left(\delta_{\xi_i\alpha}\delta_{\xi_j\beta}+\delta_{\xi_i\beta}\delta_{\xi_j\alpha}\right)\varphi_{00}^{\alpha\beta}+\delta_{\xi_i\beta}\delta_{\xi_j\beta}\varphi_{00}^{\beta\beta}\right]\Big\},$$

$$K=\sum_{i,j\in i}\left[\eta_i\left(\delta_{\xi_i\alpha}\theta_1^{\alpha}+\delta_{\xi_i\beta}\theta_1^{\beta}\right)+(1-\eta_i)\left(\delta_{\xi_i\alpha}\theta_0^{\alpha}+\delta_{\xi_i\beta}\theta_0^{\beta}\right)\right]kT.$$

The summation here is over the neighbors closest to the site i($j\in i$), and over all lattice sites i($1\le i\le N$, N is the number of particles in the system). The term K describes the contribution of the internal degrees of freedom, with respect to which the average is taken, to the Hamiltonian. The liquid phase is assumed homogeneous so that among the liquid neighbors nearest to the site **i, part is of the** species α(c_f^{α}) and part of the species β (c_f^{β}):

$$\sum_{j\in i}(1-\eta_j)\delta_{\xi_j\alpha}=\sum_{j\in i}(1-\eta_j)c_f^{\alpha}\left(\delta_{\xi_j\alpha}+\delta_{\xi_j\beta}\right),$$
$$\sum_{j\in i}(1-\eta_j)\delta_{\xi_j\beta}=\sum_{j\in i}(1-\eta_j)c_f^{\beta}\left(\delta_{\xi_j\alpha}+\delta_{\xi_j\beta}\right), \tag{1}$$

where $c_f^{\alpha}+c_f^{\beta}=1$. Taking account of (1) and simple manipulations, the expression for the Hamiltonian can be represented to the accuracy of a constant in the form

$$H=-\frac{1}{2}\sum_{i,j\in i}\{\eta_i\eta_j[\delta_{\xi_i\alpha}\delta_{\xi_j\alpha}\Phi_{\alpha\alpha}+\delta_{\xi_i\alpha}\delta_{\xi_j\beta}\Phi_{\alpha\beta}+\delta_{\xi_i\beta}\delta_{\xi_j\beta}\Phi_{\beta\beta}]+$$
$$+\eta_i\delta_{\xi_i\alpha}(\varepsilon_\alpha-\tfrac{1}{3}kT\theta_\alpha)+\eta_i\delta_{\xi_i\beta}(\varepsilon_\beta-\tfrac{1}{3}kT\theta_\beta)+\eta_j\Big[\delta_{\xi_i\alpha}\delta_{\xi_j\alpha}(c_f^{\alpha}\varphi_{00}^{\alpha\alpha}+$$
$$+c_f^{\beta}\varphi_{00}^{\alpha\beta}-\varphi_{10}^{\alpha\alpha})+\delta_{\xi_i\alpha}\delta_{\xi_j\beta}(c_f^{\alpha}\varphi_{00}^{\alpha\alpha}+c_f^{\beta}\varphi_{00}^{\alpha\beta}-\varphi_{10}^{\beta\alpha})+\delta_{\xi_i\beta}\delta_{\xi_j\beta}(c_f^{\beta}\varphi_{00}^{\beta\beta}+c_f^{\alpha}\varphi_{00}^{\alpha\beta}-\varphi_{10}^{\beta\beta})+\delta_{\xi_i\beta}\delta_{\xi_j\alpha}(c_f^{\beta}\varphi_{00}^{\beta\beta}+c_f^{\alpha}\varphi_{00}^{\alpha\beta}-\varphi_{10}^{\alpha\beta})\Big], \tag{2}$$

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where [1, 2]

$$\Phi_{\nu\xi} = \varphi_{01}^{\nu\xi} - \varphi_{11}^{\nu\xi} - \varepsilon_{\nu};$$
$$\varepsilon_{\nu} = \sum_{\xi} \left(\varphi_{00}^{\nu\xi} - \varphi_{10}^{\nu\xi}\right) c_f^{\xi};$$
$$\theta_{\nu} = \theta_0^{\nu} - \theta_1^{\nu} \quad (\nu, \xi = \alpha, \beta).$$

Henceforth, the value of θ_{ν} is assumed independent of the temperature and of the species of the particle neighbor ν.

We determine the chemical potentials of the solid and liquid phase components in terms of the system Hamiltonian

$$\mu_{\nu}^{s} = \left\langle \left(\frac{\partial H}{\partial N_{\nu}^{s}}\right)_{N_{\xi}^{f}, N_{\xi}^{s}, N_{\nu}^{f}, T} \right\rangle,$$
$$\mu_{\nu}^{f} = \left\langle \left(\frac{\partial H}{\partial N_{\nu}^{f}}\right)_{N_{\xi}^{f}, N_{\xi}^{s}, N_{\nu}^{s}, T} \right\rangle. \tag{3}$$

Taking account of (3), we express the difference between the chemical potentials in terms of the mean change in energy in the process of a ν particle in one of the lattice sites going from one aggregate state into another

$$\Delta\mu_{\nu} = \mu_{\nu}^{f} - \mu_{\nu}^{s} = \langle H(N_{\xi}^{f}, N_{\xi}^{s}, N_{\nu}^{f} + 1, N_{\nu}^{s} - 1, T) - H(N_{\xi}^{f}, N_{\xi}^{s}, N_{\nu}^{f}, N_{\nu}^{s}, T)\rangle. \tag{4}$$

From (4) and (2) we obtain

$$\Delta\mu_{\nu} = \sum_{g} \sum_{j \in i} \left[\eta_j \left(\delta_{\xi_j \alpha} \Phi_{\nu\alpha} + \delta_{\xi_j \beta} \Phi_{\nu\beta}\right) + \varepsilon_{\nu} - kT\theta_{\nu}\right] \rho(g), \tag{5}$$

where ρ (g) is the probability of finding the system in the state g and the summation is over all possible sets of the parameters $\binom{\eta_i}{\xi_i}$. Equation (5) sets up a relationship between the differences of the chemical potentials of the liquid and solid phase components and the microscopic characteristics of the system. In the case of growth of stable crystalline faces in the stationary mode, $\Delta\mu_{\nu}$ has the meaning of a difference between the chemical potentials of the volume phases. Indeed, let us represent the potential energy U in the form of a sum of volume U_{vol} and surface U_{surf} parts such that

$$U = U_{\text{vol}} + U_{\text{surf}},$$
$$U_{\text{vol}} = \frac{1}{2} \sum_{\nu,\xi} \left(N_{11}^{\nu\xi} \varphi_{11}^{\nu\xi} + N_{00}^{\nu\xi} \varphi_{00}^{\nu\xi}\right) \quad (\nu, \xi = \alpha, \beta),$$

where $N_{11}^{\nu\xi}$, $N_{00}^{\nu\xi}$ are the numbers of solid–solid and liquid–liquid bonds of particles of the species ν and ξ in the volume phases. In the stationary growth mode, the mean changes in the volume and surface parts of the energy during an elementary act of the particles making the transition from one aggregate state to another will satisfy the relationships

$$\langle \Delta U_{\text{surf}} \rangle = 0, \quad \langle \Delta U \rangle = \langle \Delta U_{\text{vol}} \rangle.$$

Consequently, we have instead of (5)

$$\Delta\mu_{\nu} = 3\left(c_f^{\alpha} \varphi_{00}^{\nu\alpha} + c_f^{\beta} \varphi_{00}^{\nu\beta} - \varphi_{11}^{\nu\nu}\right) - \frac{1}{2}\left(2\varphi_{11}^{\alpha\beta} - \varphi_{11}^{\alpha\alpha} - \varphi_{11}^{\beta\beta}\right) \gamma_{\nu} - kT\theta_{\nu},$$
$$\gamma_{\nu} = \left\langle \left(\frac{\partial N_{11}^{\alpha\beta}}{\partial N_{\nu}^{s}}\right)_{N_{\xi}^{f}, N_{\xi}^{s}, N_{\nu}^{f}, T} \right\rangle \quad (\xi \neq \nu).$$

In particular, for single-component systems

$$\Delta\mu_{\nu} = 3\left(\varphi_{00}^{\nu\nu} - \varphi_{11}^{\nu\nu}\right) - kT\theta_{\nu} = \frac{3\left(\varphi_{00}^{\nu\nu} - \varphi_{11}^{\nu\nu}\right)}{T_{eq}^{\nu}} \left(T_{eq}^{\nu} - T\right), \tag{6}$$

which permits finding the entropy factor

$$\theta_{\nu} = \frac{3\left(\varphi_{00}^{\nu\nu} - \varphi_{11}^{\nu\nu}\right)}{kT_{eq}^{\nu}},$$

where T_{eq}^{ν} is the equilibrium transition temperature for the pure ν component.

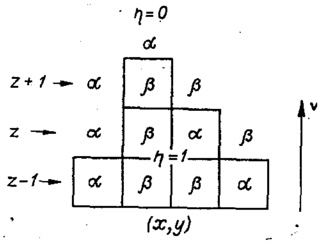

Fig. 1

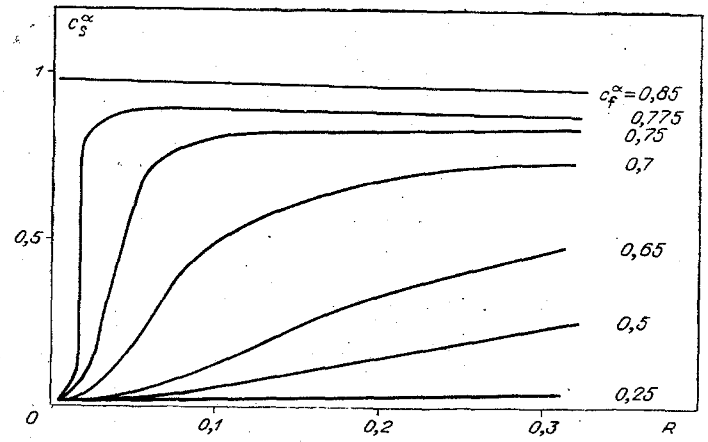

Fig. 2

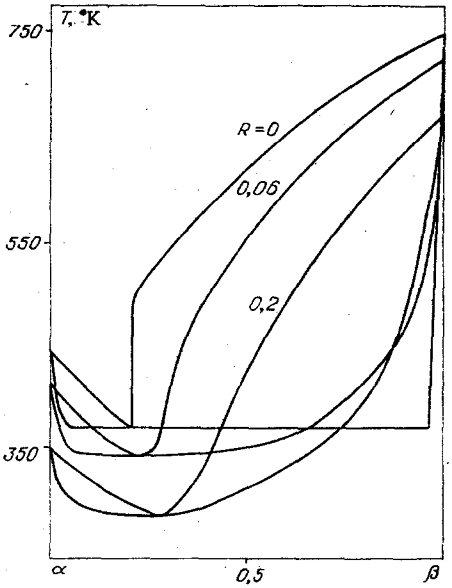

Fig. 3

We represent the crystallization process as a set of sequential terminations of elementary transition events at separate lattice sites on the surface of the growing face for a fixed configuration of the particle distribution at the sites not taking part in the elementary process at this instant. A cut of the binary system in the direction of growth in the neighborhood of the crystal–melt interface is represented in Fig. 1. To simplify the model, we limited ourselves to a consideration of the state of the system corresponding to configurations of the interphasal boundary without an overhang. This means that only one solid atom had a neighbor belonging to the fluid above it in the atomic column in the direction of the growth rate **v**. Such a solid atom and the adjoining liquid atom above it are called surface atoms.

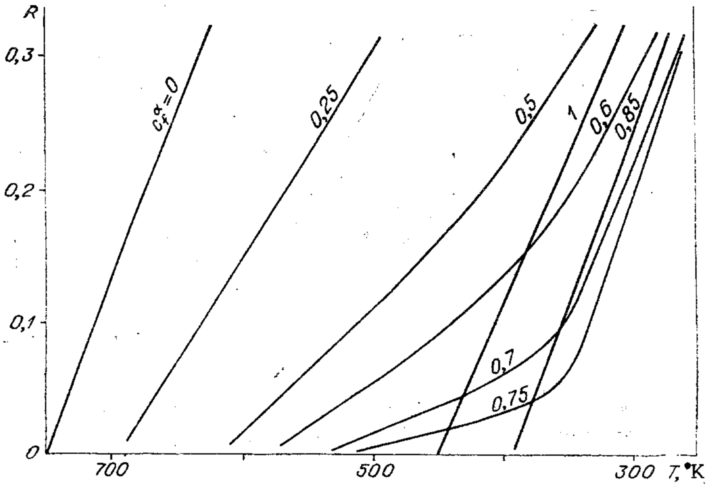

Fig. 4

A liquid surface atom of the species ξ with the frequency W^{ξ}_{10} can become solid, and a solid surface atom with frequency W^{ξ}_{01} can go over into a melt. Let us partition the physical time into intervals of duration τ. The probabilities of transitions in the time τ from the phase state η_j' into η_j at the site j are

$$\widetilde{W}^{\xi_j}_{\eta_j\eta_j'} = \tau W^{\xi_j}_{\eta_j\eta_j'}, \quad \sum_{\eta_j} \widetilde{W}^{\xi_j}_{\eta_j\eta_j'} = 1. \tag{7}$$

The kinetic equation for the distribution function ρ (g, t) in the space **g** can be represented in the form

$$\frac{\partial\rho(\xi_1, \eta_1; \ldots \xi_j, \eta_j; \ldots \xi_N, \eta_N; t)}{\partial t} = \sum_j \Big[W^{\xi_j}_{\eta_j 0} \rho(\xi_1, \eta_1; \ldots \xi_j, \eta_j'; \ldots \xi_N, \eta_N; t)\Big|_{\eta_j'=0} +$$

$$+ W^{\xi_j}_{\eta_j 1} \rho(\xi_1, \eta_1; \ldots \xi_j, \eta_j'; \ldots \xi_N, \eta_N; t)\Big|_{\eta_j'=1} - \left(W^{\xi_j}_{0\eta_j} + W^{\xi_j}_{1\eta_j}\right) \rho(\xi_1, \eta_1; \ldots \xi_j, \eta_j; \ldots \xi_N, \eta_N; t)\Big]. \tag{8}$$

The first two terms in the square brackets denote the transition probabilities of particles at the site j in the state η_j from the liquid and solid phases, respectively. The next two terms are the probabilities of reverse transitions from the state η_j into the liquid and solid states, respectively. The transition frequencies $W^{\xi_j}_{\eta_j\eta_j'}$ are defined so that they are not zero only for lattice sites at which surface atoms are situated. By definition

$$\sum_{\mathbf{g}} \rho(\mathbf{g}, t) = 1.$$

Let us consider the relaxation properties of (8). Let $\rho(\xi_j, \eta_j) = \rho(\xi_1, \eta_1; \ldots \xi_j, \eta_j; \ldots \xi_N, \eta_N; t)$ denote the probability of detecting a system with the configuration **g**, to whose j-th site the parameter $\begin{pmatrix} \xi_j \\ \eta_j \end{pmatrix}$ corresponds. Let us represent the solution of (8) in the form

$$\rho(\xi_j, \eta_j) = f(\xi_j, \eta_j) + \Delta f(\xi_j, \eta_j) \exp(-At), \tag{9}$$

where $f(\xi_j, \eta_j)$ is the equilibrium distribution function, $\Delta f(\xi_j, \eta_j)$ is the deviation of $\rho(\xi_j, \eta_j)$ from its equilibrium value for $t = 0$.

Substituting (9) into (8), and taking account of (7), we obtain an equation to find the eigenvalues $\lambda = 1 - A$ and eigenvectors $\chi(\xi_j, \eta_j)$ in the matrix form

$$\begin{pmatrix} \widetilde{W}^{\xi_1}_{11}\widetilde{W}^{\xi_1}_{10} & & & & & 0 \\ \widetilde{W}^{\xi_1}_{01}\widetilde{W}^{\xi_1}_{00} & & & & & \\ & \widetilde{W}^{\xi_2}_{11}\widetilde{W}^{\xi_2}_{10} & & & & \\ & \widetilde{W}^{\xi_2}_{01}\widetilde{W}^{\xi_2}_{00} & & & & \\ & & \ddots & & & \\ 0 & & & & & \widetilde{W}^{\xi_N}_{11}\widetilde{W}^{\xi_N}_{10} \\ & & & & & \widetilde{W}^{\xi_N}_{01}\widetilde{W}^{\xi_N}_{00} \end{pmatrix} \begin{pmatrix} \chi(\xi_1, \eta_1)\,|_{\eta_1=1} \\ \chi(\xi_1, \eta_1)\,|_{\eta_1=0} \\ \chi(\xi_2, \eta_2)\,|_{\eta_2=1} \\ \chi(\xi_2, \eta_2)\,|_{\eta_2=0} \\ \vdots \\ \chi(\xi_N, \eta_N)\,|_{\eta_N=1} \\ \chi(\xi_N, \eta_N)\,|_{\eta_N=0} \end{pmatrix} = \lambda \begin{pmatrix} \chi(\xi_1, \eta_1)\,|_{\eta_1=1} \\ \chi(\xi_1, \eta_1)\,|_{\eta_1=0} \\ \chi(\xi_2, \eta_2)\,|_{\eta_2=1} \\ \chi(\xi_2, \eta_2)\,|_{\eta_2=0} \\ \vdots \\ \chi(\xi_N, \eta_N)\,|_{\eta_N=1} \\ \chi(\xi_N, \eta_N)\,|_{\eta_N=0} \end{pmatrix}. \tag{10}$$

The solution of (10) yields two eigenvalues for each site:

$$\lambda_1^j = 1,\ \lambda_2^j = 1 - \widetilde{W}_{01}^{\xi_j} - \widetilde{W}_{10}^{\xi_j}. \tag{11}$$

For the components of the eigenvector corresponding to the eigenvalue λ_1^j, we have

$$\chi(\xi_j, \eta_j)|_{\eta_j=1} = \frac{\widetilde{W}_{10}^{\xi_j}}{\widetilde{W}_{01}^{\xi_j}} \chi(\xi_j, \eta_j)|_{\eta_j=0}.$$

Expanding $f(\xi_j, \eta_j)$ in terms of $\chi(\xi_j, N_j)$, we obtain

$$\frac{f(\xi_j, \eta_j)|_{\eta_j=1}}{f(\xi_j, \eta_j)|_{\eta_j=0}} = \frac{\widetilde{W}_{10}^{\xi_j}}{\widetilde{W}_{01}^{\xi_j}}. \tag{12}$$

Taking account of (2), the normalized $f(\xi_j, \eta_j)$ have the form

$$f(\xi_j, \eta_j)|_{\eta_j=1} = \sum_\nu \frac{\delta_{\xi_j\nu} \exp\left(\frac{l_{\nu\alpha}\Phi_{\nu\alpha} + l_{\nu\beta}\Phi_{\nu\beta} + 6\varepsilon_\nu}{kT} - \theta_\nu\right)}{1 + \exp\left(\frac{l_{\nu\alpha}\Phi_{\nu\alpha} + l_{\nu\beta}\Phi_{\nu\beta} + 6\varepsilon_\nu}{kT} - \theta_\nu\right)},$$

$$f(\xi_j, \eta_j)|_{\eta_j=0} = \sum_\nu \delta_{\xi_j\nu} \Big[1 + \exp\left(\frac{l_{\nu\alpha}\Phi_{\nu\alpha} + l_{\nu\beta}\Phi_{\nu\beta} + 6\varepsilon_\nu}{kT} - \theta_\nu\right)^{-1} \quad (\nu = \alpha, \beta), \tag{13}$$

where $l_{\nu\xi}$ is the number of nearest solid neighbors of the species ξ with ν particles. Taking account of (12), the second eigenvalue in (11) yields the relationship

$$A^{\xi_j} = \widetilde{W}_{10}^{\xi_j} [f(\xi_j, \eta_j)|_{\eta_j=1}]^{-1}. \tag{14}$$

Starting from the physical meaning of the quantity A^{ξ_j}, we represent it in the form

$$A^{\xi_j} = \tau (\tau_{\text{rel}}^{\xi_j})^{-1}, \tag{15}$$

where $\tau_{\text{rel}}^{\xi_j}$ is the characteristic relaxation time of the system at the j-th site if the configuration at the remaining sites is fixed. From (14) and (15) we find

$$\tau_{\text{rel}}^{\xi_j} = \tau f(\xi_j, \eta_j)|_{\eta_j=1} \left(\widetilde{W}_{10}^{\xi_j}\right)^{-1} = f(\xi_j, \eta_j)|_{\eta_j=1} \left(W_{10}^{\xi_j}\right)^{-1}.$$

Taking account of (13) for the characteristic relaxation time, we obtain

$$\tau_{\text{rel}}^{\xi_j} = \sum_\nu \delta_{\xi_j\nu} \left(W_{10}^{\xi_j}\right)^{-1} \left[1 + \exp\left(-\frac{l_{\nu\alpha}\Phi_{\nu\alpha} + l_{\nu\beta}\Phi_{\nu\beta} + 6\varepsilon_\nu}{kT} + \theta_\nu\right)\right]^{-1} \tag{16}$$

$$(\nu = \alpha, \beta).$$

We select the minimal of the characteristic relaxation times in the model

$$\tau = \min \tau_{\text{rel}}^{\xi_j} \quad (1 \leqslant j \leqslant N) \tag{17}$$

as the time interval τ of the process. To determine τ it is necessary to know $W_{10}^{\xi_j}$. It is ordinarily assumed in kinetic Ising models [3] that the dependence of $W_{10}^{\xi_j}$ on the configuration of the nearest particle neighbors ξ_j has the form

$$W_{10}^{\xi_j} \sim \sum_\nu \delta_{\xi_j\nu} \left[1 + \exp\left(-\frac{l_{\nu\alpha}\Phi_{\nu\alpha} + l_{\nu\beta}\Phi_{\nu\beta} + 6\varepsilon_\nu}{kT} + \theta_\nu\right)\right]^{-1}.$$

Then $\tau_{\text{rel}}^{\xi_j}$ is independent of the species of their neighbors for all lattice sites.

Let us assume that the frequency of particle attachment to the crystal in the surface node is

$$W_{10}^{\nu} = \frac{D_\nu}{a^2},$$

if the particle species at the site is fixed, where D_ν is the diffusion coefficient of particles of species ν in the melt, and a is the lattice parameter. The probability of solid particles of species ν making the transition into the liquid phase is determined by (12), and the characteristic time of the process by (16) and (17).

Let us define a two-particle distribution function in the form

$$\rho^{(2)}(\xi_j, \eta_i; \xi_k, \eta_k; t) = \sum_{\ldots\xi_j,\eta_j\ldots} \rho(g, t); \begin{pmatrix} 1 \leqslant j \leqslant N \\ j \neq i, k \end{pmatrix},$$

where the summation is over all possible values of ξ_j, η_j at all lattice sites with the exception of the sites i, k. A one-particle distribution function is

$$\rho^{(1)}(\xi_i, \eta_i; t) = \sum_{\xi_k, \eta_k} \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t).$$

Let us introduce the concentration $c_{ik}^{\nu\gamma}$ of solid–solid bonds of nearest neighbors of the species ν and γ

$$c_{ik}^{\nu\gamma} = \sum_{\xi_i, \eta_i, \xi_k, \eta_k} \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \eta_i \eta_k \rho^{(2)}(\xi_i, \eta_i; \xi_k, \eta_k; t) \equiv \sum_{g} \delta_{\xi_i \nu} \delta_{\xi_k \gamma} \eta_i \eta_k \rho(g, t).$$

Let us multiply the left and right sides of (8) by $\delta_{\xi_i \nu}\delta_{\xi_k \gamma}\eta_i\eta_k$ and let us sum over all possible states g. Upon summing the expression in the square brackets in the right side of (8) over η_j at the site j for j ≠ i, k and taking account of (7), we obtain

$$\rho(\xi_j, \eta_j')\big|_{\eta_j'=0} + \rho(\xi_j, \eta_j')\big|_{\eta_j'=1} - \sum_{\eta_j} \rho(\xi_j, \eta_j) = 0.$$

Therefore, the equation for the two-particle distribution function $c_{ik}^{\nu\gamma}$ is determined by the transition frequencies only at the i, k lattice sites

$$\frac{dc_{ik}^{\nu\gamma}}{dt} = \sum_{g} \delta_{\xi_i \nu}\delta_{\xi_k \gamma}\eta_i\eta_k \Big[W_{\eta_i 0}^{\xi_i}\rho(\xi_i, \eta_i')\big|_{\eta_i'=0} + W_{\eta_i 1}^{\xi_i}\rho(\xi_i, \eta_i')\big|_{\eta_i'=1} +$$
$$+ W_{\eta_k 0}^{\xi_k}\rho(\xi_k, \eta_k')\big|_{\eta_k'=0} + W_{\eta_k 1}^{\xi_k}\rho(\xi_k, \eta_k')\big|_{\eta_k'=1} - \left(W_{0\eta_i}^{\xi_i} + W_{1\eta_i}^{\xi_i}\right)\rho(\xi_i, \eta_i) - \left(W_{0\eta_k}^{\xi_k} + W_{1\eta_k}^{\xi_k}\right)\rho(\xi_k, \eta_k)\Big]. \tag{18}$$

The following identities hold

$$\sum_{\eta_i} \eta_i W_{\eta_i 0}^{\xi_i}\rho(\xi_i, \eta_i')\big|_{\eta_i'=0} = \sum_{\eta_i} (1-\eta_i) W_{1-\eta_i, \eta_i}^{\xi_i}\rho(\xi_i, \eta_i),$$
$$\sum_{\eta_i} \eta_i W_{\eta_i 1}^{\xi_i}\rho(\xi_i, \eta_i')\big|_{\eta_i'=1} = \sum_{\eta_i} \eta_i W_{\eta_i \eta_i}^{\xi_i}\rho(\xi_i, \eta_i). \tag{19}$$

Substituting (19) into (18), we obtain

$$\frac{dc_{ik}^{\nu\gamma}}{dt} \sum_{g} \delta_{\xi_i \nu}\delta_{\xi_k \gamma}\Big\{\Big[\big[(1-\eta_i) W_{1-\eta_i, \eta_i}^{\xi_i} - \eta_i W_{1-\eta_i, \eta_i}^{\xi_i}\Big]\eta_k\rho(\xi_i, \eta_i) +$$
$$+ \Big[(1-\eta_k) W_{1-\eta_k, \eta_k}^{\xi_k} - \eta_k W_{1-\eta_k, \eta_k}^{\xi_k}\Big]\eta_i\rho(\xi_k, \eta_k)\Big\} \equiv$$
$$\equiv \sum_{j\in i} \sum_{\xi_i, \eta_i, \xi_j, \eta_j} \delta_{\xi_i \nu}\delta_{\xi_k \gamma}\Big\{\Big[(1-\eta_i) W_{1-\eta_i, \eta_i}^{\xi_i} - \eta_i W_{1-\eta_i, \eta_i}^{\xi_i}\Big]\eta_k\rho^{(7)}(\xi_i, \eta_i; t) +$$
$$+ \Big[(1-\eta_k) W_{1-\eta_k, \eta_k}^{\xi_k} - \eta_k W_{1-\eta_k, \eta_k}^{\xi_k}\Big]\eta_i\rho^{(7)}(\xi_k, \eta_k; t)\Big\}, \tag{20}$$

where $\rho^{(7)}(\xi_i, \eta_i; t)$ is a seven-particle distribution function with central site i and six nearest neighbors $j \in i$.

Let us separate the crystal–melt system into atomic layers parallel to the phase interface. Let us characterize each layer by concentrations c_z^{ν} with solid atoms of the species ν (z is the layer number), concentrations of solid–solid bonds $c_z^{\nu\gamma}$ of the nearest neighbors of all species in the xy plane, and $c_{z,z-1}^{\nu\gamma}$ in the growth direction, respectively, where $z \to \infty$ corresponds to the liquid phase completely, and $z \to -\infty$ to the solid phase completely. Let xyz be integer coordinates governing the position of the lattice site in the layer; $\eta_{xyz} = 1$, if there is a solid particle at the site with coordinates xy of the layer z, and $\eta_{xyz} = 0$, if there is a liquid particle. Taking account of the condition of no overhang configuration of the interphasal boundary, the frequency of particle attachment to the crystal is

$$W_{10}^{\nu} = \frac{D_\nu}{a^2}\eta_{xy,z-1}(1-\eta_{xyz}), \tag{21}$$

if the particle species is determined.

Let us introduce the two-particle approximation $\rho^{(7)}(\xi_{xyz}, \eta_{xyz}; t)$

$$\rho^{(7)}(\xi_i, \eta_i; t) = \rho^{(1)}(\xi_i, \eta_i; t)\prod_{j=1}^{6}\frac{\rho^{(2)}(\xi_i, \eta_i; \xi_j, \eta_j; t)}{\rho^{(1)}(\xi_i, \eta_i; t)}, \tag{22}$$

where j are the coordinates of the six nearest neighbors to the site i = (x y z). Substituting (22) into (20), taking account of (12) and (21), and summing over all possible system configurations, we obtain

$$\frac{dc^{\nu\nu}_{z,z-1}}{dt} = c^{f\nu}_{z,z-1} W^{\nu}_{10} c^{\nu}_{f} - \frac{c^{f\nu}_{z+1,z} c^{\nu\nu}_{z,z-1}}{c^{\nu}_{z}} Q^{4}_{\nu} W^{\nu}_{10} \exp\left(-\frac{\Phi_{\nu\nu}+6\varepsilon_{\nu}}{k\,T}+\theta_{\nu}\right) \tag{23}$$

$$(\nu = \alpha,\ \beta),$$

where

$$Q_{\nu} = \frac{c^{\nu\nu}_{z}}{c^{\nu}_{z}} \exp\left(-\frac{\Phi_{\nu\nu}}{kT}\right) + \frac{c^{\alpha\beta}_{z}}{2c^{\nu}_{z}} \exp\left(-\frac{\Phi_{\alpha\beta}}{kT}\right) + \frac{c^{\nu f}_{z}}{2c^{\nu}_{z}}.$$

Moreover, the condition of mixing of the liquid phases

$$(1-\eta_i)\,\delta_{\xi_i\nu}\rho(\xi_i,\ \eta_i) = (1-\eta_i)\,c^{\nu}_{f}\,(\delta_{\xi_i\alpha}+\delta_{\xi_i\beta})\,\rho(\xi_i,\ \eta_i)$$

has been introduced in the averaging so that $c^{f\nu}_{z,z-1}$, $c^{f\nu}_{z}$ are the concentrations of the bonds of solid particles of species ν with the nearest liquid neighbors between the z and z − 1 layers and in the xy plane, respectively. Introduction of the superscript f means that the concentration of particle bonds belonging to different phases is considered.

An equation for two-particle distribution functions in the xy plane of the layer z can be obtained analogously to (23)

$$\frac{dc^{\nu\nu}_{z}}{dt} = \frac{c^{f\nu}_{z}}{\left(1-c^{\alpha}_{z}-c^{\beta}_{z}\right)} \left(c^{f\alpha}_{z,z-1}+c^{f\beta}_{z,z-1}\right) W^{\nu}_{10} c^{\nu}_{f} - \frac{2c^{f\nu}_{z+1,z} c^{\nu\nu}_{z}}{\left(c^{\nu}_{z}\right)^{2}} Q^{3}_{\nu} W^{\nu}_{10} \times$$

$$\times \exp\left(-\frac{\Phi_{\nu\nu}+6\varepsilon_{\nu}}{kT}+\theta_{\nu}\right)\left[c^{\nu\alpha}_{z,z-1}\exp\left(-\frac{\Phi_{\nu\alpha}}{kT}\right)+c^{\nu\beta}_{z,z-1}\exp\left(-\frac{\Phi_{\nu\beta}}{kT}\right)\right],$$

$$\frac{dc^{\alpha\beta}_{z}}{dt} = \frac{\left(c^{f\alpha}_{z,z-1}+c^{f\beta}_{z,z-1}\right)}{\left(1-c^{\alpha}_{z}-c^{\beta}_{z}\right)} \left(c^{f\beta}_{z} W^{\alpha}_{10} c^{\alpha}_{f} + c^{f\alpha}_{z} W^{\beta}_{10} c^{\beta}_{f}\right) - \frac{c^{f\alpha}_{z+1,z} c^{\alpha\beta}_{z}}{\left(c^{\alpha}_{z}\right)^{2}} \times$$

$$\times Q^{3}_{\alpha} W^{\alpha}_{10} \exp\left(-\frac{\Phi_{\alpha\beta}+6\varepsilon_{\alpha}}{kT}+\theta_{\alpha}\right)\left[c^{\alpha\alpha}_{z,z-1}\exp\left(-\frac{\Phi_{\alpha\alpha}}{kT}\right)+c^{\alpha\beta}_{z,z-1}\exp\left(-\frac{\Phi_{\alpha\beta}}{kT}\right)\right] -$$

$$- \frac{c^{f\beta}_{z+1,z} c^{\alpha\beta}_{z}}{\left(c^{\beta}_{z}\right)^{2}} Q^{3}_{\beta} W^{\beta}_{10} \exp\left(-\frac{\Phi_{\alpha\beta}+6\varepsilon_{\beta}}{kT}+Q_{\beta}\right)\left[c^{\beta\beta}_{z,z-1}\exp\left(-\frac{\Phi_{\beta\beta}}{kT}\right)+c^{\beta\alpha}_{z,z-1}\exp\left(-\frac{\Phi_{\alpha\beta}}{kT}\right)\right]. \tag{24}$$

The remaining two-particle functions are found from the balance conditions

$$c^{\nu}_{z} = c^{f\nu}_{z+1,z} + c^{\nu\nu}_{z+1,z} + c^{\gamma\nu}_{z+1,z} = c^{\nu\nu}_{z} + \frac{1}{2}\left(c^{\nu\gamma}_{z} + c^{\nu f}_{z}\right) \quad (\gamma \neq \nu). \tag{25}$$

Supplementing (23), (24), (25) by equations for the solid particle concentrations in the layer

$$\frac{dc^{\nu}_{z}}{dt} = \sum_{\gamma} \frac{dc^{\nu\gamma}_{z,z-1}}{dt} (\gamma = \alpha,\ \beta),$$

we have a closed system to find $c^{\nu\gamma}_{z,z-1}$, $c^{\nu\gamma}_{z}$, c^{ν}_{z}. We define the velocity of the interphasal boundary motion in the form

$$R = \sum_{z}\sum_{\nu} \frac{a^{2}}{D_{\alpha}} \frac{dc^{\nu}_{z}}{dt}.$$

Dependences of the solid phase component composition on the dimensionless velocity $R = va/D$ are given in Fig. 2 for different values of the melt concentration c^{α}_{f}.

The results were obtained for a binary $\alpha-\beta$ system with the following values of the parameters: $\varepsilon_{\alpha} = \varepsilon_{\beta} = 0$, $\Phi_{\alpha\alpha} = 300$ cal/mole, $\Phi_{\alpha\beta} = 200$ cal/mole, $\Phi_{\beta\beta} = 1500$ cal/mole, $\theta_{\alpha} = 1$, $\theta_{\beta} = 3$, $D_{\alpha} = D_{\beta}$.

The curves presented disclose an anomalous dependence on R in the range of values $0 < c^{\alpha}_{f} < 0.8$, viz: the concentration of the α component drops sharply in the solid phase as the growth rate of the concentration diminishes. Extrapolation of the results to equilibrium (R = 0) shows that equilibrium compositions of the solid phase close to a pure β component correspond to compositions of the liquid phase $0 < c^{\alpha}_{f} < 0.8$, and close to a pure α component to the values $0.8 \le c^{\alpha}_{f} < 1$. The jump in the liquid and solid phase concentrations diminishes with the increase in the growth rate, and the kinetic diagrams take on the shape of cigars with a point minimum at which the compositions of both phases agree. This regularity is graphically illustrated in Fig. 3 also, where kinetic phase diagrams are given for the values R = 0.06 and 0.2 and also the equilibrium diagram obtained by extrapolation of the results to equilibrium is given. The equilibrium diagram has a eutectic form, where T = 375 K, $c^{\alpha}_{f} = 0.8$ correspond to the eutectic point. The jump in the liquid and solid phase concentrations diminishes with the increase in the growth rate but the kinetic diagrams degenerate into diagrams of the cigar type with a point minimum.

Dependences of the growth rate on the temperature are presented in Fig. 4 for different liquid phase compositions. The linear temperature dependence of the rate of crystallization for the pure α and β components indicates a normal growth mechanism for the alloys studied. At the same time, the nonlinear temperature dependence of the rate for $c_f^\alpha = 0.65-0.7$ denotes the specifics for the appearance of a normal mechanism for multicomponent systems.

Therefore, in the general case the degree of roughness of the growing boundaries can apparently be a criterion for any growth mechanism.

V. F. Kiselev carried out the computation on the electronic computer.

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