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# Kinetics of alloy decomposition taking into account solid-phase wetting of the grain boundary

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Using the Monte Carlo method, the combined influence of grain boundary segregations and the interaction between the grain boundary and the interphase boundary on the equilibrium shape of precipitates and the kinetics of alloy decomposition has been investigated. It has been shown that these mechanisms primarily act in a qualitatively similar manner, leading to partial wetting (coating) of the grain boundary, as well as phase transitions analogous to complete wetting and pre-wetting of the grain boundary with temperature changes. Thus, it has been established that, in general, when quantitatively analyzing the phenomenon of solid-phase wetting of grain boundaries, it is necessary to consider the contribution to the energy responsible for the interaction between the interphase boundary and the grain boundary, which has previously been rarely taken into account in kinetic approaches.

**Keywords:** grain boundary, alloy decomposition, Monte Carlo simulation, solid-phase wetting.

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## 1. Introduction

The state of the grain boundaries (GB) largely determines the properties of materials (strength, ductility, diffusion permeability, electrical resistivity), especially in case of the transition to the nanocrystalline state [1–5]. In particular, the grinding of grains under intense plastic deformation is accompanied by the development of grain boundary (GB) segregation and the formation of phase precipitates at the GB, which has a dramatic effect on the mechanical properties of materials [6–10]. If the grain boundaries are covered with a continuous layer of one of the solid phases co-existing in equilibrium in case of annealing in the two-phase region of the alloy, it is said that the phase transition of solid-phase wetting (enveloping) of the GB is implemented. Currently, this phenomenon is well known in experiments, and a number of reviews are devoted to it [11–14]. GB enveloping is observed, for example, in copper and aluminum alloys [12], in titanium [13] and high-entropy [14] alloys, at triple grain junctions in magnesium alloy EZ33A [15].

In the author's opinion, some uncertainty remains in the theoretical description of the phenomenon of enveloping GB, since the observed pattern may be due to energy causes of various nature.

On the one hand, there are well known Gibbs segregations (grain boundary and surface adsorption) [4,16–18] associated with a change of free energy in case of the transfer of atoms of a certain sort from the volume of the material to the grain boundary or to a free surface. The GB and surface segregation contribute to the formation of a certain configuration of precipitates in case of decomposition of a solid solution [19–22], including complete or partial envelopment of one of the phases [23–26].

On the other hand, there is a qualitative analogy between the enveloping of the GB and the phase transition of the wetting of the GB with the liquid phase [2,14,27], the phenomenological theory of which, based on the principles of equilibrium thermodynamics, was proposed about half a century ago [27–30]. The physical reason for this phenomenon is that in a number of alloys at a certain temperature, the energy of the two interfaces „liquid–solid" turns out to be lower than the energy of the corresponding GB (Gibbs-Smith wetting condition [28,29]). When wetted with the liquid phase, the proportion of wetted GB increases with the increase of the temperature, and the contact angle of the solid and liquid phases decreases to zero, that is, a transition from partial to complete wetting is observed, which was first predicted in Refs. [30,31]. In contrast, the proportion of wetted GB may increase with solid-phase wetting, and the contact angle between phase precipitates may decrease with the decrease of the temperature [32,33].

There is no doubt that the development of GB segregation contributes to a change of the GB energy, leading to a local shift in the conditions of phase equilibrium. However, in the general case, the mechanisms of solid-phase wetting are also caused by local structural changes at the contact of the interfaces [3,27,34–36], which remain insufficiently studied and are not reduced to GB segregation. For example, the segregation of bismuth in copper was correctly described only after the classical Fowler equations for the GB segregations [37] were supplemented by the concepts of the grain boundary wetting [3]. Thus, when describing the enveloping of the GB, free energy should take into account, on the one hand, the mechanism of formation of the GB segregation, and, on the other hand, the interaction of the phase boundary (PB) and the GB.

One of the first theoretical models describing the kinetics of alloy decomposition, taking into account the impact of GB, was proposed in Ref. [21]. The free energy of the alloy is recorded in this paper within the framework of the „phase-field“ phenomenology, without specifying the microscopic meaning of the parameters used, and the impact of the GB on the kinetics of decomposition is attributable to a local change of the volume density of free energy on the GB. This made it possible to observe the formation of regular structures during the development of decomposition in the presence of GB, by analogy with the phenomenon of spinodal decomposition provoked by the free surface [19,20].

Further, a generalization of the regular solid solution model was proposed in Refs. [23–25,38], taking into account the presence of GB. In this approach, the bulk free energy density of a binary alloy contains two energy parameters (coefficients before the linear and quadratic concentration contributions). The role of GB is reduced to the local change of these parameters in the GB area. At the same time, these parameters have a clear physical meaning and they can be found for specific alloys from ab initio or from experimental data. It has been shown that grain boundaries in this model can stimulate the formation of droplet or ribbon microstructures during alloy decomposition, and some effects caused by the movement of GB have been studied as well. The applicability of this model to the description of solid-phase wetting has not been discussed by the authors.

A recent study [26] has significantly developed the approach [21,24]: thermal fluctuations in the composition are consistently taken into account (which makes it possible to describe the formation of precipitates in the metastable region of the phase diagram) and the kinetics of alloy decomposition for polycrystalline samples are modeled, taking into account anisotropic diffusion on the GB and the movement of grain boundaries. As a result, microstructures are qualitatively similar to the partial or complete wetting (enveloping) of grain boundaries observed in experiments. Basically, the totality of the results obtained [21,24,26,38] can be used to draw a conclusion that a consistent physical model has been constructed that provides a fairly complete qualitative description of the phenomenon of solid-phase wetting of GB; further development of this approach involves parameterization and refinement of the type of free energy density for specific alloys.

However, the situation is somewhat more complicated according to the author. It was assumed in all the mentioned models that the impact of GB on the kinetics of alloy decomposition is primarily attributable to a local change of the volume density of free energy on the GB. At the same time, the volumetric density of free energy contains energy parameters, the meaning of which is well defined in Refs. [24,26]. The change of the GB coefficient before the linear concentration contribution to the free energy is the segregation energy, defined as the difference in the energy of the alloy when a single impurity atom is placed at the boundary and in the grain volume, respectively. The change of the coefficient before the quadratic contribution shows how the energy of the interaction of two impurity atoms changes, which determines the tendency for the alloy decomposition. Moreover, the coefficient before the concentration gradient contribution to the free energy functional, which determines surface tension, was either not discussed in these models, or was assumed to be equal (with the opposite sign) to the coefficient before the quadratic contribution to the volumetric energy density, as follows from the analysis for an alloy with an ideal lattice [39]. Hence it can be seen that the interaction of PB and GB, due to a change of the lattice structure when the interface boundaries are aligned, was not taken into account in these approaches, while the analysis of wetting [27,30] considers this contribution to be the main one. The model in Ref. [21] neglects, in particular, the interaction of gradients of order parameters related to concentration and grain structure, which apparently requires appropriate refinements when describing solid-phase wetting. This feature was inherited by subsequent models. Abstract mathematical models were considered in a recent paper [40] that made it possible to observe partial wetting of GB for two characteristic cases: when the GB cuts off the precipitates and when the GB disappears in the area of contact with the precipitates; the latter situation can be considered as a special case of the interaction of PB and GB.

A qualitative analysis of the kinetics of solid solution decomposition is conducted in this paper within the framework of a simple model that simultaneously takes into account the contribution of grain boundary segregation and the interaction of PB and GB. The joint role of these factors in the implementation of GB envelopment is discussed.

## 2. Formulation of the model

Let us consider an AB alloy in which decomposition is possible with the formation of precipitates based on component A, as well as segregation of this component at the grain boundary. Let $\xi(\mathbf{r})$ be a grain boundary shape function that is equal to 0 in the volume of the material, 1 directly at the grain boundary, $0 < \xi < 1$ in a transitional boundary layer with a width of $d$ ($\sim 1\,\mathrm{nm}$). Then the Ginzburg-Landau functional [41] of the free energy of the alloy can be written as:

$$F = \int \big(f^0_{GB}(\xi) - \nu_{AB} c_A c_B + \varepsilon_{segr} c_A \xi(\mathbf{r}) + R^2 \sigma_A (\nabla c_A)^2 + f_{A-GB} - TS_{mix}\big) dV, \qquad (1)$$

where $f^0_{GB}(\xi)$ is the energy density of GB in pure metal, $\nu_{AB}$ is the energy of interaction of atoms of sort A and B,

$\varepsilon_{segr}$ is the energy of segregation of atoms of sort A on GB, $c_{A(B)}$ is the atomic concentration of component A(B), $c_A + c_B = 1$, $R$ is the small parameter of the order of the radius of interatomic interaction, $\sigma_A$ is the energy coefficient determining the surface energy of precipitates, $f_{A-GB}$ is the interaction energy of the interfacial boundary with the grain boundary, $S_{mix}$ is the configuration entropy of mixing components of the AB alloy. The first contribution in the expression (1) does not affect the evolution of concentrations and can be omitted when the GB is stationary. The second contribution corresponds to the enthalpy of a regular solid solution. The third contribution takes into account the energy preference of the placement of component A atoms at the grain boundary and corresponds to traditional approaches to the analysis of GB segregation [16,18]; a local change of the parameters leading to the decomposition of the alloy into GB can be accounted for by the concentration dependence $\varepsilon_{segr}$.

For general reasons, the energy of interaction between the phase boundary and the grain boundary can be represented as the sum of two terms:

$$f_{A-GB} = R^2(\sigma^{(1)}_{A-GB}\xi(\nabla c_A)^2 + \sigma^{(2)}_{A-GB}\nabla c_A \nabla \xi). \qquad (2)$$

The first term takes into account the change in the surface energy of the precipitate upon contact with the GB (isotropic contribution). The second term is the contribution to the energy of interaction between PB and GB, depending on their mutual orientation; a similar contribution, in the form of a product of gradients of order parameters characterizing different phases, was taken into account in the model of wetting of GB with a liquid phase [42], as well as in a model describing the interaction of precipitates of different varieties [39]. In this case, the value of $\xi$ acts as an order parameter characterizing the „grain boundary phase".

Basically, the free energy functional (1) makes it possible to study the kinetics of segregation and decomposition by solving continuum diffusion equations within the framework of the Cahn-Hilliard phenomenological approach [43]. However, we will use the kinetic Monte Carlo method in this paper, by analogy with Ref. [39], instead of solving the equations [44]. Unlike the continuum equations, this approach naturally takes into account the thermal fluctuations of the composition, which largely determine the configuration of the precipitates during decomposition. In addition, the energy of PB and the configuration entropy of atoms are taken into account automatically in Monte Carlo modeling, so that no specification of the corresponding contributions is required. At the same time, the simulation will be conducted on an ideal lattice, so the presence of GB should be taken into account in the form of corresponding coordinate-dependent contributions in the Hamiltonian.

Thus, the interaction Hamiltonian at the node $i$, defined by the occupation numbers $n^{(i)}_\alpha$ on a discrete lattice corresponding to the formula (1), has the form:

$$H^{(i)}_{int} = -\sum_{i' \neq i} \nu^{(i;i')}_{AB} n^{(i)}_A n^{(i')}_B + \varepsilon_{segr} n^{(i)}_A \xi(\mathbf{r}_i)$$
$$+ R^2\big(\sigma^{(1)}_{A-GB}\xi(\nabla c_A)^2 + \sigma^{(2)}_{A-GB}\nabla c_A \nabla \xi\big), \qquad (3)$$

where $n^{(i)}_\alpha = 1$ if the node $i$ contains an atom of the $\alpha$ sort, and $n^{(i)}_\alpha = 0$ in the opposite case; $\nu^{(i;i')}_{AB}$ is the energy of interaction of atoms of varieties A and B on the distance determined by the nodes $i, i'$. We limit ourselves to considering a 2D model with a simple square lattice and periodic boundary conditions like before in the Ref. [39]. Let's assume that the radius of interaction of atoms is 3 coordination spheres (CS), i.e. each atom interacts with 12 neighbors; $\nu^{(k)}_{AB}$ is the energy of interaction of atoms $A$ and $B$ on $k$-th sphere, for simplicity we will consider them the same, $\nu^{(k)}_{AB} = \nu_{AB}/12$. The local concentration $c_A$ is determined by averaging the occupation numbers $n^{(i)}_A$ over two CS. The parameter $R$ is assumed to be equal to twice the distance between neighboring lattice sites, $R = 2a$.

Let the grain boundary be oriented along the axis $x$, and its shape function has the form:

$$\xi(x) = \left[1 + \left(\frac{y - 0.5}{\lambda_0}\right)^4\right]^{-1}, \qquad (4)$$

where $0 < y < 1$ is a dimensionless coordinate, $\lambda_0 = d/L$ is the half-width of the GB divided by the size of the calculated area. Then the gradients in the last term in the formula are (3) are reduced to derivatives along the axis $y$ and calculated using the function values in nodes taken on different sides of the selected node $i$:

$$\nabla_x c_A(\mathbf{r}_i) = \frac{1}{2a}\big(c_A(y_i + a) - c_A(y_i - a)\big), \qquad (5)$$

$$\nabla_x \xi(\mathbf{r}_i) = \frac{1}{2a}\big(\xi(y_i + a) - \xi(y_i - a)\big), \qquad (6)$$

where $a$ is the lattice parameter.

The modeling algorithm should take into account that the values of the grain-boundary diffusion coefficients are usually much higher than the volumetric ones. Therefore, the Metropolis probability should be multiplied by a correction factor $\Omega_i$, depending on the distance of the considered grid node from the GB, which is determined by the formula:

$$\Omega_i = \Omega_0 + (1 - \Omega_0)\xi(y_i), \qquad (7)$$

where $\Omega_0 = \omega_{bulk}/\omega_{GB}$ is the ratio of the diffusion mobilities of an atom of sort A in volume and on GB. $\Omega_i = 1$ follows from the formulas (4), (7) if the atom is located directly on the GB ($y_i = 0.5$). If the atom is located far from the GB, we obtain $\Omega_i = \Omega_0$.

Taking into account this correction, the kinetic Monte Carlo algorithm [39,44] is modified as follows. An atom of sort A located at a certain node $i$ and an adjacent atom are randomly selected. If these are atoms of

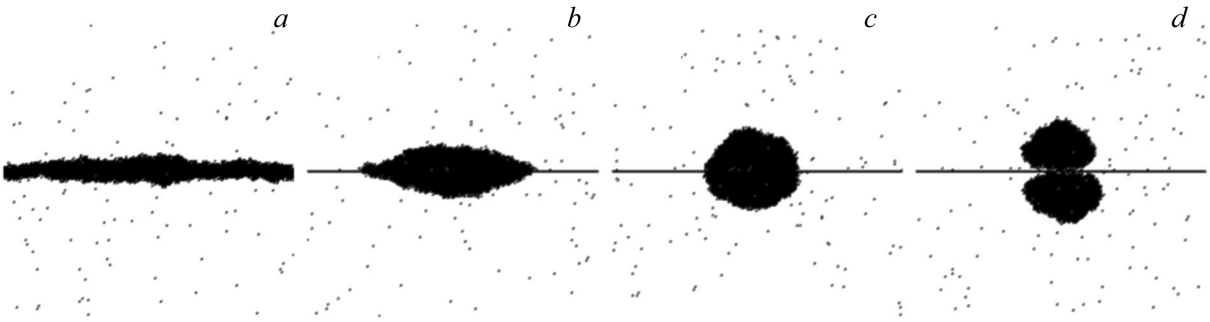

**Figure 1.** Secretion at the grain boundary after prolonged exposure at different segregation energies in the precipitate volume; $-\nu_{AB}/(kT) = 3$, $\sigma^{(1,2)}_{A-GB} = 0$, $\lambda_0 = 0.01$, $\Omega_0 = 1$, $\varepsilon^0_{segr}/\nu_{AB} = 0.83$; $\kappa = 0$ (*a*), 0.5 (*b*), 1 (*c*), 2 (*d*).

different varieties, an attempt is made to swap them. The energies are calculated for this reason using the interaction Hamiltonian (3)

$$E = \frac{1}{2}\sum_j H^{(j)}_{int}$$

for the initial configuration and after rearranging the atoms, $E_1$ and $E_2$. The new configuration is accepted with probability $\Omega_i$ if $E_2 < E_1$; otherwise, it is accepted with probability $P = \Omega_i \exp[(E_1 - E_2)/(kT)]$.

## 3. Modeling results

First, let us consider the enveloping of the grain boundary in the absence of its interaction with the interphase boundary ($\sigma^{(1,2)}_{A-GB} = 0$), i.e. only due to the predominant tendency of segregation at the GB of atoms of a certain sort ($\varepsilon_{segr} \neq 0$). In this case, the shape of the precipitate is determined by the competition of the segregation contribution and surface tension. In this case, the observed pattern depends on how the energy of segregation changes in the boundary section passing through the precipitate. To roughly account for this dependence, we assume that the segregation energy may depend on the local concentration, $\varepsilon_{segr} = \varepsilon^0_{segr}(1 - \kappa c_A)$, and the local concentration $c_A$ is calculated by averaging the occupation numbers over two coordination spheres around the selected node.

Let's place the round shape selection in the center of the calculation area and perform the Monte Carlo procedure with a long exposure (on the order of $10^5$ hops per atom of sort A), up to the transition to the quasi-stationary mode. Figure 1 shows the distributions of atoms in several possible cases (hereafter, the calculation is performed on a square area with size of $200 \times 200$ nodes, atoms of sort A are shown by black color, the position of the GB is shown by a straight line): (1) the value of $\varepsilon_{segr}$ is the same in the matrix and in the volume of precipitate ($\kappa = 0$); (2) the inducement mechanism of GB segregation is weakened in the volume of precipitate ($\kappa = 0.5$); (3) zeroed in the volume of precipitate ($\kappa = 1$); (4) changes the sign in the precipitate volume ($\kappa = 2a$). It can be seen that with an increase of $\kappa$, the pattern changes from a continuous band of component A along the GB (analogy of complete wetting) to two isolated precipitates near the GB (absence of wetting). The case $\kappa = 1$ can be interpreted as the disappearance of GB in the precipitate volume; in this case, the precipitate retains its original shape at $\varepsilon^0_{segr} > \nu_{AB}$ (Figure 1,—it c), and an outflow of substances occurs from the precipitate at GB at $\varepsilon^0_{segr} < \nu_{AB}$.

Figure 2 shows the achieved patterns for the case $\kappa = 0$ at different temperatures. It can be stated that with the increase of the temperature, the precipitate becomes more elongated along the GB, up to the formation of a continuous band. There is a pre-transition state at the GB with even higher $T$ (in the single-phase region of the diagram), which is classified as Gibbs segregation [16,37] (Figure 2, *a*). Thus, the equilibrium distribution of atoms can change qualitatively similar to the wetting of GB with a liquid phase under the impact of the GB segregation mechanism [3,27]. In particular, a transition from partial to complete envelopment of the GB is observed with an increase of $T$, and the phenomenon of pre-wetting corresponds to Gibbsian segregation. At the same time, it should be emphasized that this situation is a rather specific case: the grain boundary passes through the center of the precipitate, and the reason for the segregation is the same both in the matrix and in the volume of precipitate. This formulation of the problem corresponds to the models [21,24,26], however, it significantly differs from the theoretical concepts of wetting [27], according to which, the position of the GB and PB coincide in case of wetting, or there is no GB in the area of contact with the precipitate.

Next, we will consider the interaction of GB and PB in the absence of segregation inducement, i.e. when choosing $\varepsilon_{segr} = 0$. In the general case $\sigma^{(1)}_{A-GB} < 0$, $\sigma^{(2)}_{A-GB} = 0$, the presence of PB at the grain boundary is energetically advantageous, although their mutual orientation can be arbitrary (for example, numerous clusters on the GB are advantageous). Calculations show (Figure 3) that in this case the main effect is „sticking“ of PB to the grain boundary, in other words, partial wetting of the grain. Pre-transition phenomena (clusters) are observed along the entire length of the GB as the temperature increases, and as

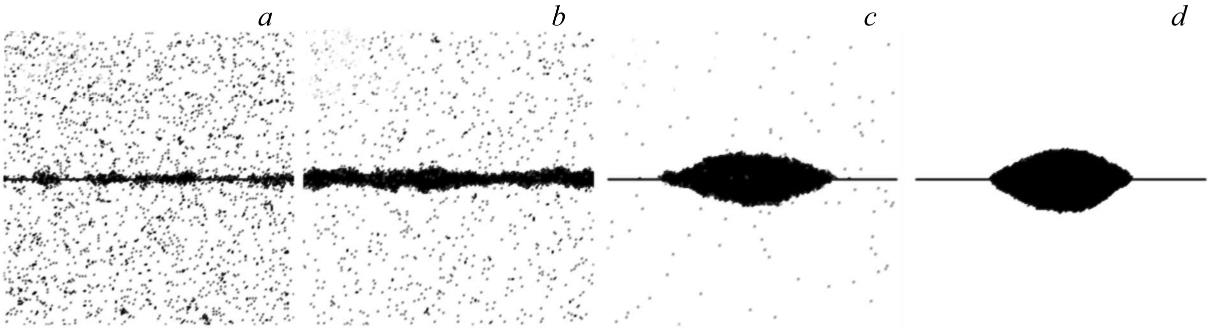

**Figure 2.** Secretion at the grain boundary after prolonged exposure at different temperatures; $-\nu_{AB}/(kT) = 1.6$ (*a*), 2 (*b*), 3 (*c*), 4 (*d*); $\sigma^{(1,2)}_{A-GB}/\nu_{AB} = 0$, $\lambda_0 = 0.01$, $\Omega_0 = 1$, $R = 2a$, $\varepsilon^0_{segr}/\nu_A B = 0.42$, $\kappa = 0$.

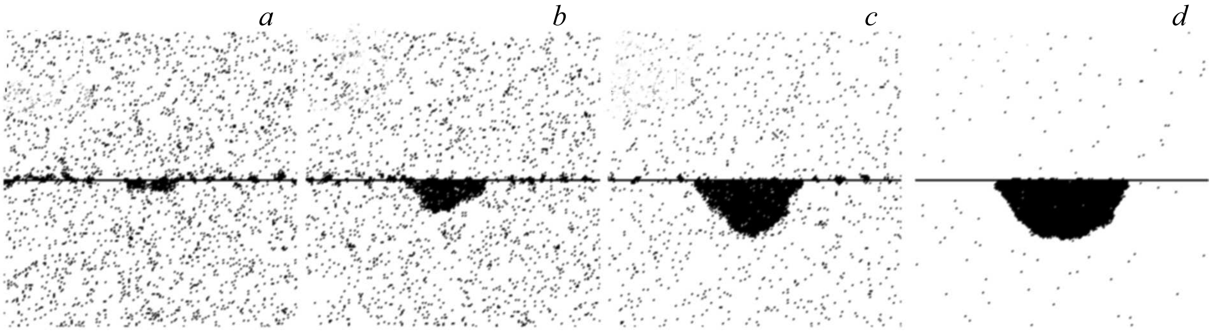

**Figure 3.** Secretion at the grain boundary after prolonged exposure at different temperatures; $-\nu_{AB}/(kT) = 1.6$ (*a*), 1.7 (*b*), 2 (*c*), 3 (*d*); $\sigma^{(1)}_{A-GB}/\nu_{AB} = 1.25$, $\sigma^{(2)}_{A-GB} = 0$, $\varepsilon_{segr} = 0$, $\lambda_0 = 0.01$, $\Omega_0 = 1$, $R = 2a$.

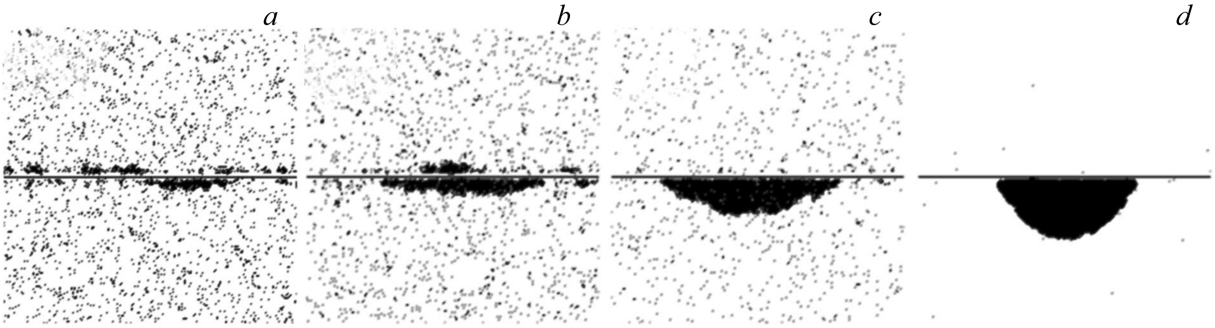

**Figure 4.** Secretion at the grain boundary after prolonged exposure at different temperatures; $-\nu_{AB}/(kT) = 1.6$ (*a*), 1.7 (*b*), 2 (*c*), 4 (*d*); $\sigma^{(2)}_{A-GB}/\nu_{AB} = -1.6$, $\sigma^{(1)}_{A-GB} = 0$, $\varepsilon_{segr} = 0$, $\lambda_0 = 0.01$, $\Omega_0 = 1$, $R = 2a$.

the ratio $\sigma^{(1)}_{A-GB}/\nu_{AB}$ increases, the contact angle between the PB and the GB decreases. However, the wetting phase transition (coating of the GB with a solid strip of component A) was not realized in these calculations.

The alignment of PB and GB is energetically beneficial in case $\sigma^{(2)}_{A-GB} \neq 0$, $\sigma^{(1)}_{A-GB} = 0$. If $\sigma^{(2)}_{A-GB} > 0$, the grain boundary protrudes like a low-permeable substrate over which precipitate „spreads“ (Figure 4). In this case, the qualitative difference from the previous case (Figure 3) is that component A does not penetrate into the GB, so if the precipitates of component A are present on both sides of the GB (Figure 4, *b*), they are separated by a thin layer of substance on the GB in this model and this layer does not contain component A. With an increase of temperature or with an increase of the ratio $|(\sigma^{(2)}_{A-GB}/\nu_{AB}|$, the contact angle between the PB and the GB decreases, up to the realization of complete wetting of the GB (with a sufficient amount of component A). In the opposite case ($\sigma^{(2)}_{A-GB} < 0$), a thin layer of the GB is occupied with component A, but the GB is isolated from the main precipitate. Thus, in the case of a nonzero gradient contribution $\nabla c_A \nabla \xi$, qualitatively new possibilities arise when the boundary layer is wetted

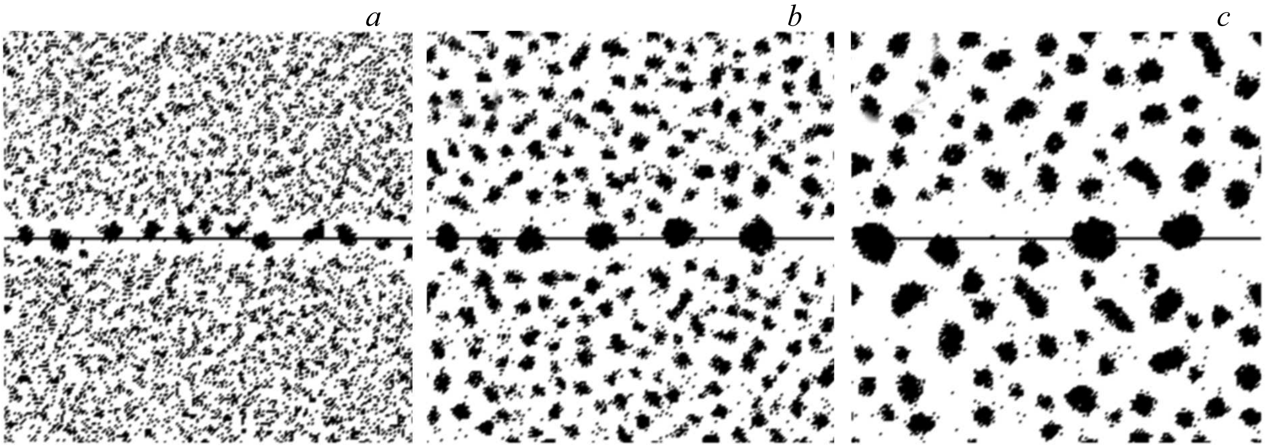

**Figure 5.** Kinetics of alloy decomposition in the absence of activation of segregation and wetting, $\varepsilon_{segr} = 0$, $\sigma^{(1,2)}_{A-GB} = 0$, at time points corresponding to 40, 400, 6000 hops per atom of sort A. Average concentration $c^0_A = 0.2$; interaction energy $-\nu_{AB}/(kT) = 3$; $\lambda_0 = 0.01$; $\Omega_0 = 0.001$, $R = 2a$.

in the presence of a low-permeable GB „core“ or vice versa.

Above, the equilibrium distributions of atoms were considered with a different choice of mechanisms of GB segregation and the interaction of PB and GB. Now let's discuss the specifics of the kinetics of the transition to these states.

Figure 5 shows the kinetics of alloy decomposition in the absence of segregation and wetting mechanisms, i. e. at $\varepsilon_{segr} = 0$, $\sigma^{(1,2)}_{A-GB} = 0$. In this case, the main factor determining the effect of the GB on the kinetics of decomposition is the increased (compared with the volume value) diffusion mobility of atoms at the GB. Therefore, a chain of equidistantly located precipitates on the GB is observed at the early stages (Figure 5, *a*), while the precipitates in the volume of the material have not yet had time to form. Secretions are formed in volume in case of a prolonged exposure (Figure 5, *b, c*), however, precipitates that previously appeared on the GB have an advantage in growth, because large precipitates grow at the expense of small ones in the late stages of decomposition. Thus, the grain boundary largely determines the configuration of the precipitates during decomposition, even in the absence of interaction of GB with single atoms or boundaries of precipitates.

Figures 6–8 shows the kinetics of alloy decomposition with different energy parameters $\varepsilon_{segr}$, $\sigma^{(1,2)}_{A-GB}$. When $\varepsilon_{segr} < 0$, $\sigma^{(1,2)}_{A-GB} = 0$ is chosen (Figure 6), the precipitates are stretched along the GB as a result of the activation of segregation. In the case when both energies $\varepsilon_{segr}$, $\sigma^{(1)}_{A-GB}$ differ from zero and are negative, the tendency of enveloping the GB increases, so that a continuous band of a new phase quickly forms at the GB (Figure 7). It can be shown that the effect of these factors is compensated in case of a different sign of the energies $\varepsilon_{segr}$, $\sigma^{(1)}_{A-GB}$. When $\sigma^{(2)}_{A-GB} > 0$ is chosen, wetting is realized on each side of the GB, while the GB itself acts as a low-permeable substrate (Figure 8). It can be shown that when $\sigma^{(2)}_{A-GB} < 0$ is chosen, a solid band of component A at the GB is implemented, the width of which is determined by the width of the GB. Thus, despite the different nature of the energies $\varepsilon_{segr}$, $\sigma^{(1,2)}_{A-GB}$, the impact of these contributions on the kinetics of decomposition and on the final state of the alloy as a whole turns out to be qualitatively similar, adds up or is compensated. The greatest qualitative difference is related to the bilateral wetting of the GB (Figure 8), which was not previously discussed in the theory of wetting.

## 4. Discussion

Thus, according to the author, the GB envelopment observed in experiments for many alloys can generally be due to a combination of factors, including kinetic (differences in the diffusion mobility of atoms in the volume and at grain boundaries) and thermodynamic (grain boundary segregation and interaction between PB and GB). Although the mechanisms of GB segregation and the interaction between PB and GB are described by different contributions to the energy of the alloy, it follows from the above calculations that their effect on the kinetics of decomposition can be qualitatively similar, it can add up or can be compensated. The latter circumstance should be taken into account when quantifying the phenomenon. Currently, the energy of segregation $\varepsilon_{segr}$ at different types of GB is reliably determined in *ab initio* calculations [45] as the energy difference of an alloy containing an impurity atom placed on the GB and in the grain volume, respectively. The change of the energy of interaction of atoms, which determines the tendency to alloy decomposition, can also be taken into account. At the same time, methods for determining the energies $\sigma^{(1,2)}_{A-GB}$ have not been sufficiently developed.

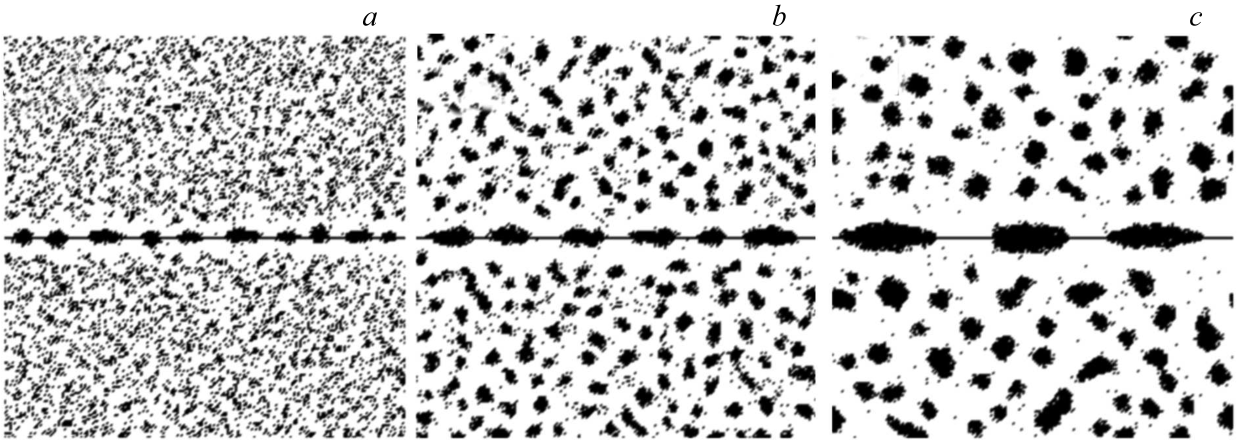

**Figure 6.** The kinetics of alloy decomposition at different values of energy parameters at time points corresponding to 40, 400, 6000 hops per atom of sort A; $\varepsilon_{segr}/\nu_{AB} = 0.42$, the values of the remaining parameters are similar to Figure 5.

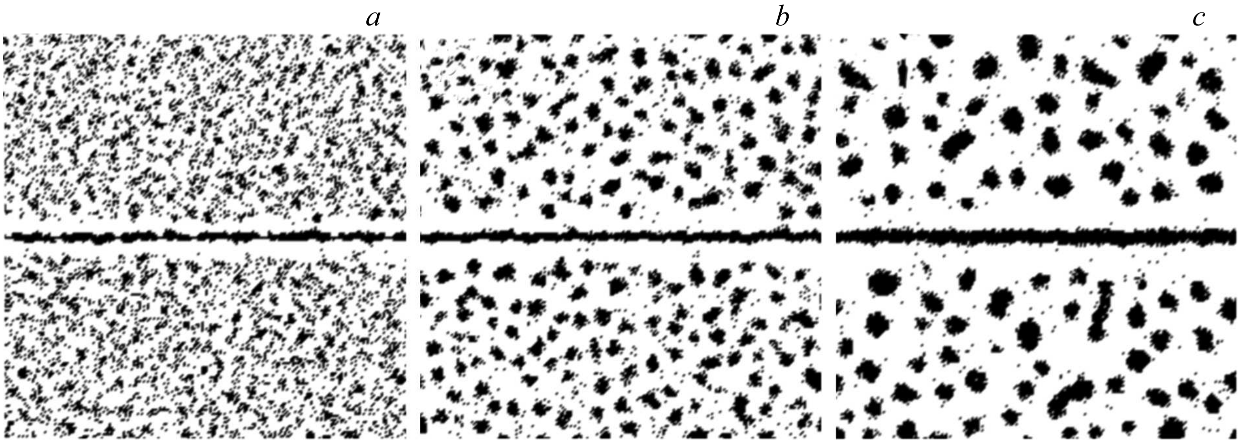

**Figure 7.** The kinetics of alloy decomposition at different values of energy parameters at time points corresponding to 40, 400, 6000 hops per atom of sort A; $\sigma^{(1)}_{A-GB}/\nu_{AB} = 1.25$, $\varepsilon_{segr}/\nu_{AB} = 0.42$. The values of the other parameters are similar to Figure 5.

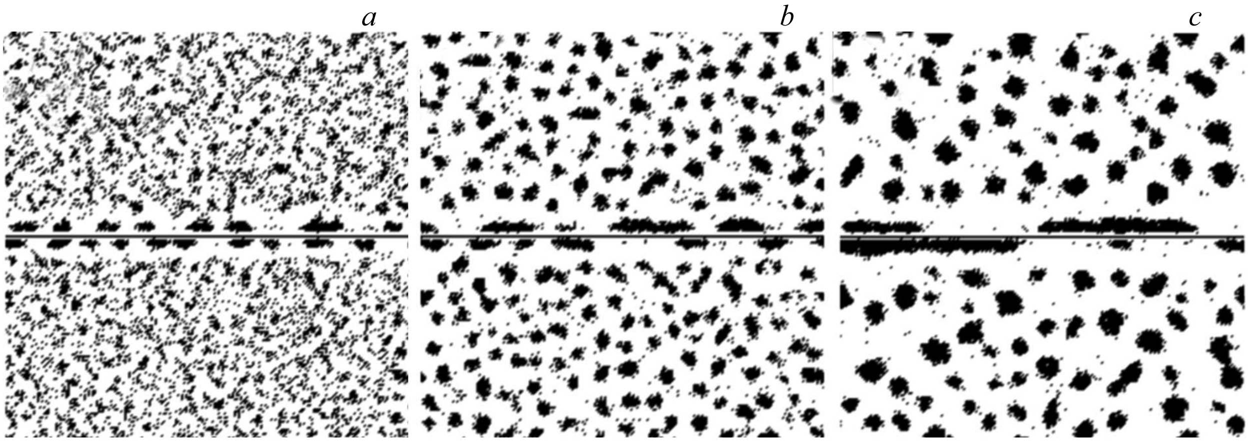

**Figure 8.** The kinetics of alloy decomposition at different values of energy parameters at time points corresponding to 40, 400, 6000 hops per atom of sort A; $\sigma^{(2)}_{A-GB}/\nu_{AB} = -2$, $\varepsilon_{segr}/\nu_{AB} = 0.42$. The values of the other parameters are similar to Figure 5.

It also follows from the analysis that the phenomenon of GB enveloping has some differences from wetting with a liquid phase. When the GB is wetted with a liquid phase on one side of the boundary junction, the GB is replaced by two PB „solid–liquid“, from where the equilibrium condition of the boundary junction has the form $\gamma_{GB} = 2\gamma_A \cos\theta$ [3,27], where $\gamma_{GB}$, $\gamma_A$ is the surface energies of GB and PB, $\theta$ is the equilibrium contact angle of GB and PB (partial wetting is realized under condition $\cos\theta > 0$, and full wetting is realized when condition $\theta = 0$ is reached). Apparently, with solid-phase wetting, the situation is more realistic when the GB remains in the area of contact with the precipitates, either passing along the interphase boundary of the precipitates, or even cutting it, and changing its energy at the same time, which corresponds to the considered model. Therefore, the effects of GB enveloping are attributable not to the disappearance of GB, but to its interaction with impurity atoms in the matrix, with the volume of precipitate and with the interphase boundary of precipitate. For the case when GB acts as a low-permeable substrate for precipitate (Figure 3, 4), the following condition for local equilibrium of the triple junction of the interface can be written:

$$\gamma_{GB} = \gamma_{A-GB} + \gamma_A \cos\theta, \qquad (8)$$

where $\gamma_A$, $\gamma_{GB}$, $\gamma_{A-GB}$ are the surface energies of the PB in the matrix, the GB in the matrix, and the GB coinciding with the PB. In this case, the surface tension coefficient for PB in the absence of GB is expressed in terms of the energies of interatomic interactions, $\sigma_A = -\nu_{AB}$ [39]. Hence, it follows that at a given temperature taking into account the formula (1), the shape of the precipitate located at the GB is determined by the competition between the attraction of atoms of the same sort, the process of grain boundary segregation, and the interaction of PB and GB, i.e., the ratios of parameters $\varepsilon_{segr}/\nu_{AB}$ and $|\sigma^{(1,2)}_{A-GB}/\nu_{AB}|$. A complete envelopment of the GB is realized below the initial decomposition temperature if at least one of the specified ratios is above the critical value.

Despite the above-mentioned differences in the formulation of the problem, the calculations performed generally demonstrate qualitative agreement with the main conclusions of the wetting theory. In particular, it follows from the calculations that a transition from partial to complete envelopment of the GB is possible with a change of temperature, and pre-transition states similar to pre-wetting are realized in the area of homogeneity of the phase diagram [3,27].

## 5. Conclusions

(i) Unlike wetting of the grain boundary with a liquid phase, solid-phase wetting (enveloping) does not necessarily should lead to the disappearance of GB in the area of contact with the precipitate. The precipitate can remain coherent with the matrix, while the GB cuts it or passes along the interphase boundary.

(ii) The enveloping of the grain boundary of one of the phases may be attributable to the combined action of various factors: accelerated diffusion at the GB, segregation of atoms of a certain sort at the GB, interaction of the interphase boundary and the GB.

(iii) The effect of GB segregation processes and the interaction of GB with the interphase boundary on the shape of precipitates may be similar in case of some parameters. In both cases, phase transitions similar to wetting and prewetting of the grain boundary are possible with a change of temperature.

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### Conflict of interest

The author declares that he has no conflict of interest.

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