# SURFACE SEGREGATION AT THE (111) AND (100) CRYSTAL FACES IN THIN FILMS OF METAL BINARY ALLOYS $A_{1-x}B_x$

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The effect of multi-layer surface segregation in thin films of metal binary alloys $A_{1-x}B_x$ has been studied in the framework of the regular solid solution model. The segregation composition profiles at their (111) and (100) crystal faces contacting with vacuum were calculated for finite-thickness slabs, with two outmost atomic layers being taken into account. The segregation composition profiles were established to differ substantially for the solutions ordered, perfect, and prone to the decay. A special attention was given to studying the depth concentration profiles in a slab, which arise within the temperature range below some critical temperature of decay or ordering. The internal interface between two phases with the excess of either A or B component, respectively, has been shown to emerge in the slabs of decaying solid solutions. In the ordering solid solutions, the effect of alternating-sign segregation is observed, when all the odd layers of the slab have an excess of one component, and all the even ones of the other. It has been found that, for the slabs with the outer surfaces with the (100) orientation, the effect of alternating-sign segregation transforms into the effect of atomic ordering, and, in the temperature range below the ordering temperature, there appear the non-damping depth oscillation concentration profiles into the slab.

## 1. Introduction

The effect of surface segregation, which constitutes the phenomenon, where the compositions of the outer atomic layers and the bulk of the film differ, is an object of researches of a great number of both theoretical and experimental works [1, 2]. Nowadays, in order to develop effective heterogeneous catalysts with tailored properties, the films of metal binary alloys, where one component is a transition metal, and the other a noble one, are widely studied [3–6]. They are also of interest for the development of new magnetic recording devices; in particular, such alloys as Ni–Pt and Co–Pt. Therefore, a special attention is drawn to studying the effects of multi-layer surface segregation, which can affect on the physical and chemical properties of films made up of such alloys [7–9].

Nevertheless, there are a lot of works [10–14], where the single-layer approximation is used to explain the effect of surface enrichment with one of the components of a binary alloy A–B. In so doing, the surface concentration of the alloy is calculated by minimizing a variation of the free energy of system, which corresponds to the exchange between atom B at the surface and atom A in the bulk. The enthalpy of the surface segregation takes into account the contributions of three factors: a difference between the surface tension or the sublimation energy of pure components, a existence of the mixing energies of alloys, and a mismatch elastic energy of the crystal lattices in bulk. Then, the total effect is characterized by the energy gain (or loss) obtained when atoms B and A are exchanged between the surface and the bulk of the alloy.

The contribution of elastic energy for the lattices to the segregation enthalpy is induced by a mismatch between the atomic radii of components. It is known [10–12] that the elastic driving force of the segregation behaves asymmetrically and, according to Friedel, has different signs at the opposite ends of the phase diagram of the binary system A–B. In the crystalline lattices of solid solutions of the atoms with different radii, there emerge local strains, and interatomic distances become distorted; they relax when an impurity segregate from the bulk onto the surface. However, a differences between the surface tensions or the sublimation energies of components should be considered as the basic driving force of segregation [11].

In this connection, there are interesting works [15–18], where the theory of multi-layer surface segregation in finite-thickness films has been proposed. The theory takes into account only the first two contributions to the driving force of the surface segregation. In those works, the molecular-statistical approach was used, which allowed the authors to derive equilibrium equations for a binary system in the mean-field approximation; the energies of pairwise interaction between atoms at the first coordination sphere were considered identical for all layers. A similar theory which proposed in works [15–18] was developed in [19–21], but only for semi-infinite samples with a free surface. For example, an

opportunity to enhance the pairwise interaction energies for the atoms of the top layer was taken into account additionally in [19], the interaction of atoms at the next coordination spheres in [20], while work [21] also allowance for the elastic driving force of segregation.

The aim of this work is carrying on the further researches of the effect of surface segregation in the framework of single- and multi-layer models, using a mean-field approximation. We are going to consider various forms of equilibrium depth segregation profiles at the thin binary films, and to compare them with those obtained using the Monte Carlo (MC) simulation [22, 23]. It is of interest, because the method of MC-simulation, contrary to the mean-field approximation, allows the influence of concentration fluctuations on the thermodynamic equilibrium state of a binary system to be taken into account [24].

## 2. Multi-layer Model of Surface Segregation

A binary solid solution $A_{1-x}B_x$ with the concentration $x$ of component B is considered in the form of a slab consisting of $m$ planar infinite atomic layers. In this case, two layers, the first and the $m$-th ones, border vacuum. The outer layers of the slab are considered in the framework of the broken-bond model, by introducing the surface ($Z_s$), interlayer ($Z_\perp$), and bulk ($Z_0$) coordination numbers which are connected with each other by the relationship $Z_0 = Z_s + 2Z_\perp$. The concentration of component B in each $i$-th layer is designated by $x_i = x + c_i$, where $c_i$ is the deviation concentration at the $i$-th layer with respect to the initial value. Let us suppose that the subsurface regions near the outer layers of the slab have multi-layer structure, and its thickness determine by the condition $|c_i| < \varepsilon_0$, where $\varepsilon_0$ is a small given parameter. Assuming that the thermodynamic system is described by the Maxwell—Boltzmann distribution, let us calculate the statistical sum $Z$ of a binary solid solution in the framework of the independent atomic pair approximation, taking into account only their chemical interaction between the nearest neighbors (the interaction parameter $U_{\beta\beta'}$; here, $(\beta, \beta' = \overline{A, B})$). Further, let us define the free energy of the system: $F = -RT \ln Z$, where $R$ is the molar gas constant and $T$ the absolute temperature.

Then, the values of $c_i$ that correspond to the minimum of the change of system free energy per one site of the surface lattice, $\Delta f$, when the concentration in each layer changes from $x$ to $x_i$, have to be determined from the conditions

$$\frac{\partial \Delta f}{\partial c_i} - \lambda \frac{\partial \Psi}{\partial c_i} = 0, \tag{1}$$

where $\lambda$ is the Lagrange multiplier, which takes into account the mass balance condition $\Psi = \sum\limits_{i=1}^{m} c_i = 0$. This leads us to the following equilibrium equations:

$$\left(-2z_s U_0 c_1 - z_\perp \left[4U_0\Delta + 2U_0 c_2\right] + \right.$$

$$\left. + RT \ln \frac{x + c_1}{1 - x - c_1}\right) - \lambda = 0, \quad i = 1; \tag{2}$$

$$\left(-2z_s U_0 c_i - 2z_\perp U_0 (c_{i+1} + c_{i-1}) + \right.$$

$$\left. + RT \ln \frac{x + c_i}{1 - x - c_i}\right) - \lambda = 0, \quad i \neq 1, \quad i \neq m; \tag{3}$$

$$\left(-2z_s U_0 c_m - z_\perp \left[4U_0\Delta + 2U_0 c_{m-1}\right] + \right.$$

$$\left. + RT \ln \frac{x + c_m}{1 - x - c_m}\right) - \lambda = 0, \quad i = m; \tag{4}$$

where $U_0 = U_{AB} - \frac{1}{2}(U_{AA} + U_{BB})$ is the mixing energy of the binary alloy,

$$\Delta = \frac{1}{4}\left(\frac{Q}{U_0} + (1 - 2x)\right),$$

and

$$Q = \frac{1}{2}(U_{BB} - U_{AA}).$$

The quantities $U_0$ and $Q$ can be expressed in terms of the alloy mixing heat and the difference between the surface tensions or the sublimation energies of pure components, respectively [11,15]. In order to exclude $\lambda$, let us sum up all the equilibrium equations. Then, having taken into account that $\sum\limits_{i=1}^{m} c_i = 0$, we find

$$\lambda = \frac{1}{m}\left[2z_\perp U_0 (c_1 + c_m - 4\Delta) + RT \sum_{i=1}^{m} \ln \frac{x + c_i}{1 - x - c_i}\right].$$

## 3. Limit Cases of Weak and Strong Segregation

The system of equilibrium equations similar to Eqs. (2)—(4) was derived in work [15] and solved there analytically in two limit cases of weak and strong segregation of the components. In the case of weak segregation at high temperatures, the values of $c_i$ are small: $|c_i| \ll x$ and $|c_i| \ll 1-x$. Then, the analytical solution of the system of equations (2)—(4) ultimately takes the form

$$c_i = 2\Delta\left[\frac{y-1}{y^m-1}\frac{1}{y}(y^i + y^{m+1-i}) - \frac{2}{m}\right]\Big/$$

$$\Big/\left[\frac{y-1}{y^m-1}(1-y^{m-1}) + \frac{(y-1)^2}{y} - \frac{2}{m}\right], \qquad (5)$$

where

$$y = \frac{\alpha}{2} + \sqrt{\frac{\alpha^2}{4}-1}, \quad \alpha = 2\left[\theta + \left(\frac{z_s}{2z_\perp}\right)(\theta-1)\right],$$

and

$$\theta = \frac{kT}{2z_0U_0x(1-x)}.$$

We note that only the values $|\theta| > 1$, i.e. $|y| > 1$, correspond to the disordered solid solution. At $U_0 > 0$ and $y < 1$, there must be a separation of the solid solution into two phases. But, at $U_0 < 0$, $\theta < 0$, and $-1 < y < 0$, it has to become ordered. If the slab is macroscopic, the number of layers is very big ($m$ is about $10^8$), and formula (5) becomes simpler to give

$$c_i \cong 2\Delta(y^{-i} + y^{i-m-1}). \qquad (6)$$

In the vicinity of each outer surface of the slab ($i \to 1$ or $i \to m$), practically,

$$c_i \approx 2\Delta y^{-i} = 2\Delta\exp(-i\ln y). \qquad (7)$$

That is, the concentration of the segregate falls down towards the slab depth by the exponential law. It also follows from expressions (5)—(7) that the segregate in a binary system $A_{1-x}B_x$ is determined by the sign of the parameter $\Delta$. For example, if $\Delta > 0$, the surface of the alloy will be enriched by the component B, and, on the contrary, if $\Delta < 0$, by the component A. Therefore, the crossover segregation is possible at the concentration

$$x_c = \frac{1}{2} - \frac{U_{AA}-U_{BB}}{4U_0}, \qquad (8)$$

provided the calculated value satisfies the inequality $0 < x_c < 1$.

A strong segregation arises at $|\Delta| \gg 1$. In this case, the concentration of one of the alloy components at the surface, provided low temperatures, has to approach either 0 or 1, depending on the sign of $\Delta$. At the same time, in the vicinity of either slab surface ($i \to 1$ or $i \to m$), practically,

$$c_i \approx c_1 y^{-i+1}. \qquad (9)$$

At high temperatures, when $c_1 \cong 2\Delta/y$, the solution obtained precisely coincides with Eq. (7). On the other hand, if temperatures are low, $c_1$ differs from the corresponding value in the case of weak segregation.

Different shapes of segregation profiles are predicted for binary systems, which decay ($U_0 > 0$) or become ordered ($U_0 < 0$). Really, one can see from expressions (7) and (9) that the shape of the segregation profile is determined by the sign of the parameter $y$. For decaying alloys, the profile will be monotonous at temperatures $\theta > 1$, because $y > 1$. As the ordinal number of a layer increases, the concentration smoothly changes and reaches the bulk value. While approaching the critical point $\theta = 1$, the segregation effect involves more and more layers in the near-surface region and transforms into the effect of separation at temperatures $\theta < 1$ [1,18]. Hereafter, the separation means a layered decay in a binary alloy. At temperatures $|\theta| > 1$, the profile in the ordering alloys will be oscillating, with the amplitude of oscillations decaying into the slab depth, because $-1 < y < 0$. All even layers in the near-surface region are an excess one component, and all odd layers enriched by the other. The oscillating behavior of the segregation profile at a temperature $|\theta| \to 1$ transforms into the ordering effect, becoming non-damping for the singular (100) crystal face [1].

In the case of perfect binary solutions, $U_0 = 0$, so that the segregation is observed only within two outer layers of the slab.

## 4. Single-layer Model of Surface Segregation and the Fowler Equation

Now, let us proceed in Eqs. (2)—(4) to the limit semi-infinite sample with a free surface, i.e. $m \to \infty$, and also suggest that only the content of the upper surface layer can differ from the bulk one: $x_1 \neq x$, whereas $x_2 = x_3 = \ldots = x$. In this case, the following equilibrium

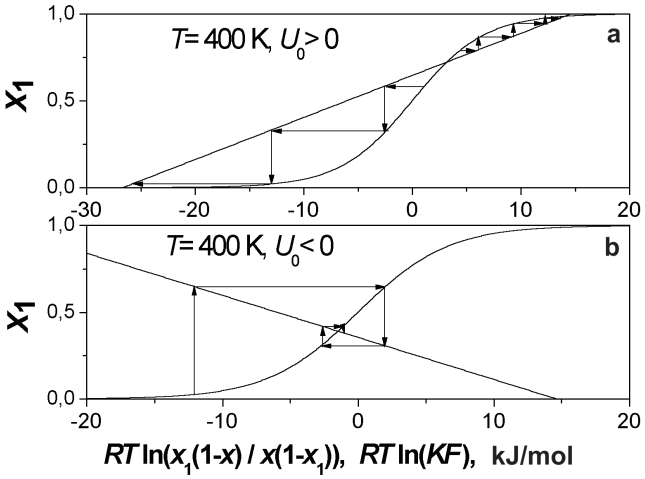


Fig. 1. Convergence of iterative processes for the Fowler equation in the case of the fcc alloy $A_{0.5}B_{0.5}$ (111) crystal face: decaying ($a$) and ordering ($b$) cases

equation is obtained to determine the content $x_1$ at the surface:

$$RT \ln \frac{x_1}{1-x_1} \frac{1-x}{x} = Z_\perp (P - 2U_0 x) + Z_s 2U_0 (x_1 - x), \tag{10}$$

where $P = Q + U_0$. This equation can be written down in the form similar to the Fowler adsorption equation [1, 25]:

$$\frac{x_1}{1-x_1} = \frac{x}{1-x} KF, \tag{11}$$

where $K = \exp[Z_\perp Q/RT]$ is the coefficient of surface segregation, and $F = \exp[(Z_\perp U_0(1-2x) + Z_s 2U_0 \times \times (x_1 - x))/RT]$ the Fowler function.

In work [26], the same equilibrium equation was derived in a somewhat different way, namely, by minimizing the surface free energy of binary alloy $A_{1-x}B_x$

$$\Delta f_s = RT\left[x_1 \ln \frac{x_1}{x} + (1-x_1) \ln \frac{1-x_1}{1-x}\right] +$$

$$+ Z_s U_0 (x_1^2 - x^2) + [Z_\perp (P - 2U_0 x) - Z_s 2U_0 x] (x_1 - x) \tag{12}$$

in the monolayer approximation. This expression will be applied below to select the stable thermodynamic solutions of the Fowler equation. Using the conditions

$$\partial \Delta f_s / \partial x_1 = 0, \quad \partial^2 \Delta f_s / \partial^2 x_1 > 0, \tag{13}$$

which are necessary and sufficient for the free energy (12) to be minimal, we obtain an expression for the critical temperature of the separation of atoms at the surface:

$$T_{C1} = \frac{Z_s 2U_0}{R} x(1-x). \tag{14}$$

Let us find the solution of the Fowler equation (11) graphically, at a given values for the parameters of interaction, the coordination numbers, the temperature, and the alloy bulk concentration. The pair interaction energies of atoms A—A and B—B are assumed to be $U_{AA} = -299$ kJ/mol and $U_{BB} = -295$ kJ/mol. The mixing energy for an ordering binary system is given $U_0 = 3.44$ kJ/mol, while, in the case of a decaying binary system, we shall only change the sign of this parameter, so that this parameter is $U_0 = -3.44$ kJ/mol. The bulk coordination number $Z_0 = 12$ for fcc solid solutions. The surface and interlayer coordination numbers are $Z_s = 6$ and $Z_\perp = 3$ for the singular (111) crystal face, and $Z_s = 4$ and $Z_\perp = 4$ for the (100) one.

An example of the graphic solution of the Fowler equation is exposed in Fig. 1 for decaying ($a$) and ordering ($b$) binary systems. From this figure, one can see that there are three solutions of the Fowler equation in the former case, with one of them corresponding to an unstable thermodynamic state, and a single solution in the latter case. The arrows illustrate the convergence of iterative processes, when the solutions of the Fowler equation are found numerically [27]. One can also see that the convergence of iterative processes to two solutions, stable and metastable, is monotonous for a decaying alloy and is spiral for an ordering one. Therefore, more complex are the decaying binary systems, which we study in more detail below.

Fig. 2 depicts the Fowler isotherms for the decaying binary system $A_{1-x}B_x$ (111). From this figure, one can see that, at temperatures below some critical one, $T < Z_s U_0/2R$, the curves becomes $S$-shaped, and the segregation is discontinuous and stick-slip. Ultimately, the state with a high surface content of component B has lower free energy, according to Eq. (12), as compared to the case of a low B content. Moreover, at a given interaction parameters, the crossover segregation is observed at the concentration $x_c = 0.2094$.

The temperature dependence of the surface concentration $x_1$ at $x = 0.5$ is shown in Fig. 3. Here,

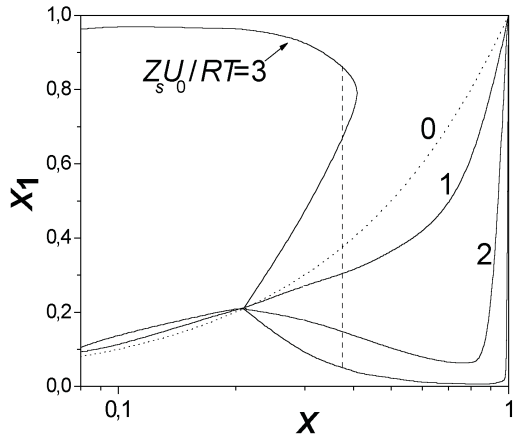


Fig. 2. Fowler isotherms for the fcc alloy $A_{1-x}B_x$ face(111)

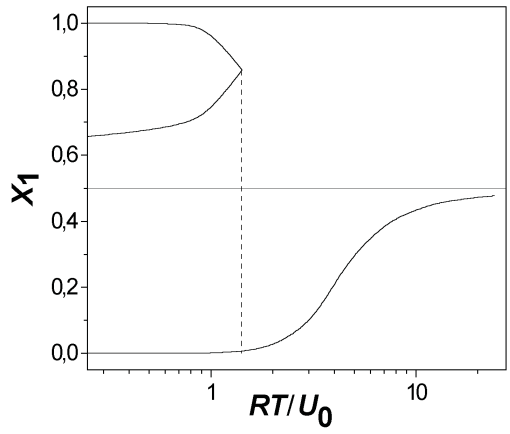


Fig. 3. Temperature dependences of the surface concentration for the alloy $A_{0.5}B_{0.5}$ face (111)

the discontinuous and stick-slip behavior of segregation is also observed. The upper part of the horseshoe-like curve corresponds to the stable solutions of the Fowler equation, and its lower part to the unstable ones. As the temperature grows, the state with a low content of component B now becomes stable. In addition, the surface content tends to the bulk value if $T \to \infty$.

A discontinuous and stick-slip behavior of segregation described in this work can be used for manufacturing the materials with tailored properties. In the granulated materials, for example, doping the granules of component A with a superficially active component B may substantially affects on the composition of their surface region, and, thus, a number of their properties in general.

## 5. Numerical Results and Their Discussion

Consider a film which is composed of 21 planar atomic layers. Let us numerically solve the system of equilibrium equations (2)—(4) for the given coordination numbers $Z_s$ and $Z_\perp$, the concentration $x$, and the temperature $T$, provided the same interaction parameters $Q = 2$ kJ/mol and $U_0 = \pm 3.44$ kJ/mol.Let us write down the equations as

$$c_i = \frac{1}{1 + \exp\left(-(\zeta_i + \lambda)/RT\right)} - x, \tag{15}$$

and find their solutions by the iterative method [27]. The explicit expressions for the quantities $\zeta_i$ are obvious from Eqs. (2)—(4).

Fig. 4 displays the concentration profiles for a binary film which is separated depending on the concentration

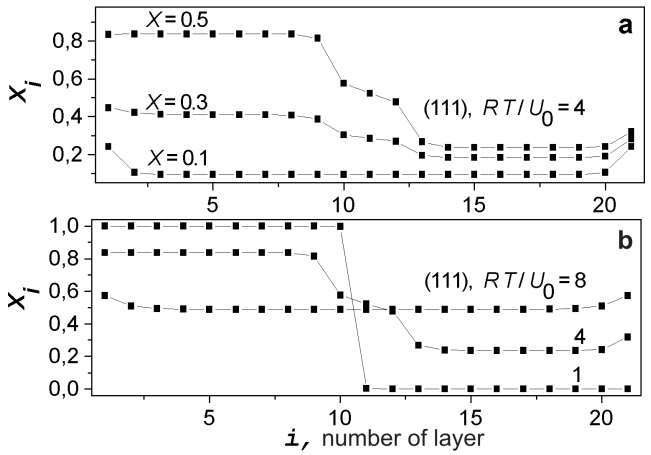


Fig. 4. Dependences of the depth segregation concentration profiles for decaying binary alloy on ($a$) the concentration $x$ and ($b$) the temperature at $x = 0.5$ ($b$)

$x$ ($a$) or the temperature $T$ ($b$). The figure demonstrates that two essentially different shapes of concentration profiles emerge in a separating film: symmetric and asymmetric ones with respect to the central layer. The symmetric shape of the profile is monotonous and such that both the free surfaces of the film become enriched with one of the components. In our case, it is component B. The asymmetric shape appears if the average concentration of component B increases (Fig. 4,$a$) or the temperature becomes lower than the separation point (Fig. 4,$b$). In this case, the internal interface between components A and B is formed in the slab. Separation means that one of the near-surface regions of the film is enriched with component A, while the other with component B.

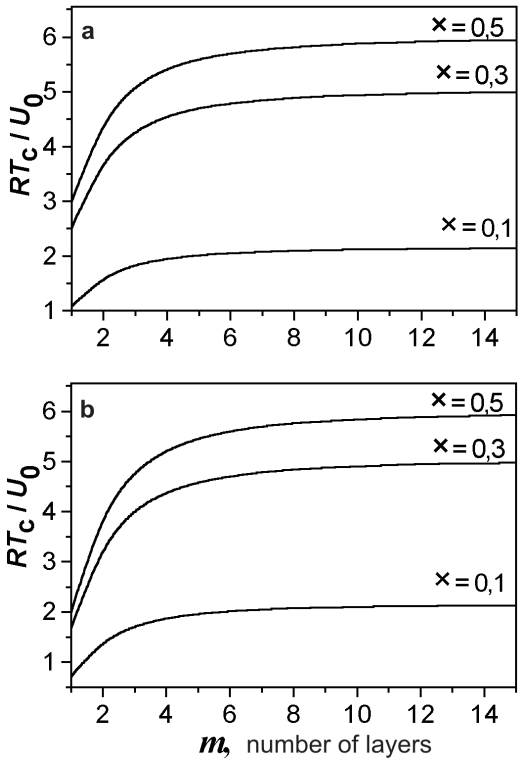


Fig. 5. Dependences of the separation temperature on the number of layers $m$ in a slab for three different concentrations $x$ of binary fcc alloy faces (111) ($a$) and (100) ( $b$)

The separation temperature is coupled with a singularity in the Jacobi matrix of the system of equilibrium equations (2)—(4), which assumes the fulfillment of the equality

$$\det \left|\partial^2 \Delta f / \partial x_i \partial x_j\right| = 0. \tag{16}$$

The analysis of this singularity, according to work [28], allows us to obtain the following expressions for the critical temperature of the separation for a binary alloy film which is composed of $m$ layers and initial concentration $x$:

$$\frac{RT_C(m)}{U_0} = Z_s 2x(1-x)\left[1+\cos\left(\frac{\pi}{m+1}\right)\right] \tag{17}$$

for the face (111) and

$$\frac{RT_C(m)}{U_0} = Z_s 2x(1-x)\left[1+2\cos\left(\frac{\pi}{m+1}\right)\right] \tag{18}$$

for the face (100). The dependences of the separation temperature on the number of layers in the slab $m$ for

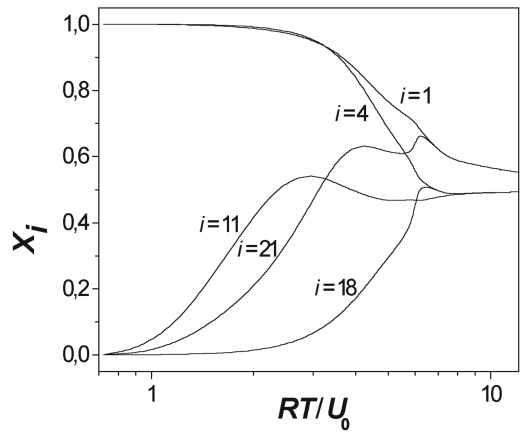


Fig. 6. Temperature dependences of the concentration $x_i$ at the $i$-th slab layers for a decaying alloy $A_{0.5}B_{0.5}$ face (100)

various concentrations $x$ are shown in Fig. 5, $a$ and $b$ for the (111) and (100) crystal faces, respectively. From the figure, one can see that the separation temperature for face (111) is always higher than that for face (100). The relevant bulk value of the separation temperature is attained at film thicknesses of more than 5—7 layers.

The temperature dependences of the concentration $x_i$ in the slab layers with $i = 1$, 4, 11, 18, and 21 are presented in Fig. 6. From this figure, one can see that, at temperatures below the separation point, the concentrations of component B in layers 1 and 21 , as well as in layers 4 and 18, become different. However, the temperature dependences of the concentration $x_i$ in all slab layers remain smooth, though they are nonmonotonic for layers 11, 18, and 21. Thus,atomic separation for the slabs is a second-order phase transition rather than of the first-order one, as it is in the case of semi-infinite samples with a free surface (see Figs. 2 and 3).

The equilibrium depth concentration profiles, which take place in finite-thickness films, are represented in Fig. 7. As was already marked, if the mixing energy is negative, the alloy becomes ordered in the temperature range below the critical point. Higher the ordering temperature, the damping depth segregation profile of the concentration, are formed. In this case, all odd or even layers of the film possess, respectively, an excess of one component or the other (Fig. 7,$a$). As the critical point is approached, the effect of alternative-sign segregation transforms into the effect of ordering for the singular (100) crystal face. On the contrary, in the case of the densely packed (111) crystal face, the ordering suppresses the effect of

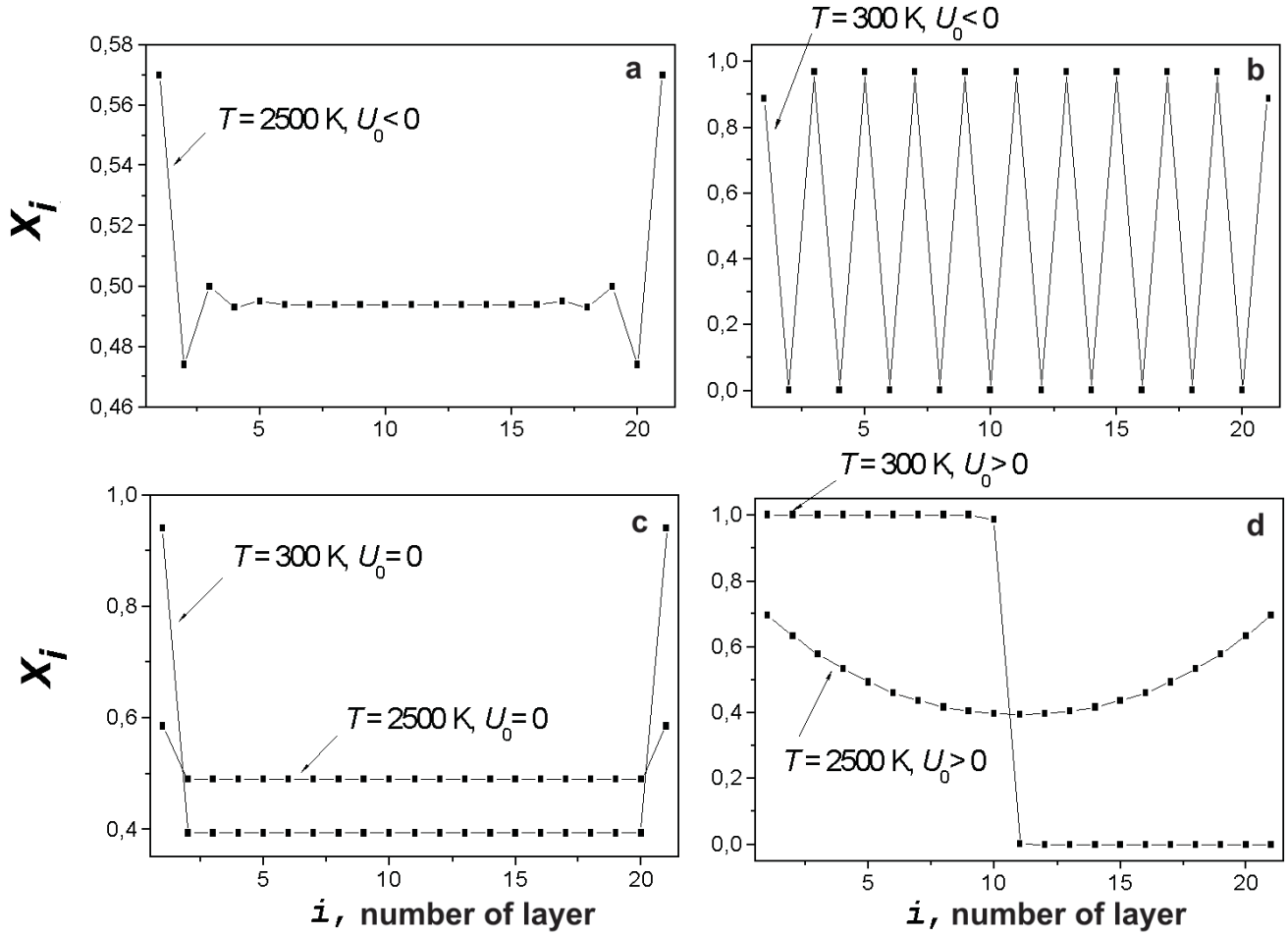


Fig. 7. Equilibrium depth concentration profiles for a 21-layers film of the alloy $A_{0.5}B_{0.5}$ face (100) at two various temperatures $T = 2500$ and 300 K: *a*, *b* — $U_0 = -3.44$ kJ/mol, *c* — $U_0 = 0$, *d* — $U_0 = 3.44$ kJ/mol

alternative-sign segregation in atomic layers. Since the linear problem was considered, the ordering is observed only in one direction – perpendicularly to the layers. In the temperature range below the critical point for the (100) crystal face, the non-damping depth oscillating concentration profiles are formed (Fig. 7,*b*) .

For perfect binary alloys, $U_0 = 0$, and the segregation is observed only in the outermost layers of the film (Fig. 7,*c*). The decay alloy, at the temperatures higher than separation critical point, have a monotonous depth concentration profiles, which are symmetric with respect to the central layer of the film. As the temperature lower than the critical point, the depth concentration profiles become asymmetric. Segregation spread over more and more film layers and transform into the separation effect. As a result, the internal interface between components A and B is formed (Fig. 7,*d*).

In works [22, 23], the method of Monte Carlo (MC) simulation was used to obtain the damping oscillating and monotonous depth concentration profile into the decaying and ordering alloys Ni—Pt and Ni—Cu, respectively. A good agreement was achieved between the results of calculations carried out in the mean-field approximation and those of MC-simulation in the temperature range above the critical point, $|\theta| > 1$. However, the concentration fluctuations, which have been taken into account at MC-simulation, disorder the thermodynamic system and reduce the calculated critical temperature found in the mean-field approximation by a factor of 0.57 for the (100) crystal face [1].

## 6. Conclusions

1. The calculations of the surface segregation in thin films and semi-infinite samples with a free surface have been carried out in the multi- and single-layer approximations, using the equilibrium equation obtained in the mean-field approximation.

2. Two limit cases of weak and strong segregation have been studied analytically. It has been shown that, in the case of weak segregation, there can be three shapes of concentration profiles in the film at high temperatures: monotonous – for decaying binary systems ($U_0 > 0$), single-layer – for perfect ones ($U_0 = 0$), and damping oscillating – for ordering ones ($U_0 < 0$).

3. Segregation in semi-infinite samples with a free surface is discontinuously and in a stick-slip manner at a temperature equal to some critical point of separation has been found.

4. The formation of the asymmetric depth concentration profiles into the film of binary alloy at the temperatures below the critical point of separation has been found. Ultimately, the separation results in formation of an internal surface into the film, which separates components A and B.

5. We have predicted the appearance of non-damping depth oscillating concentration profiles into the films of the ordered binary alloys with the orientation of external surfaces (100).

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ПОВЕРХНЕВА СЕГРЕГАЦІЯ В ТОНКИХ ПЛІВКАХ МЕТАЛЕВИХ БІНАРНИХ СПЛАВІВ $A_{1-x}B_x$ З ГРАНЯМИ (111) І (100)

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Р е з ю м е

Досліджено ефект багатошарової поверхневої сегрегації в тонких плівках бінарних сплавів $A_{1-x}B_x$ в рамках моделі регулярного твердого розчину. Сегрегаційні профілі складу розраховано для пластин скінченної товщини, в яких з вакуумом межують два зовнішніх атомних шари з орієнтацією (111)

або (100). Установлено, що сегрегаційні профілі складу істотно відрізняються для впорядкованих, ідеальних та схильних до розпаду твердих розчинів. Особливу увагу приділено вивченню концентраційних профілів по глибині пластин, що виникають в області температур, нижчих за деяку критичну температуру розпаду або впорядкування. Показано, що в пластинах твердих розчинів, які розпадаються, формується внутрішня поверхня поділу двох фаз із надлишком компонента A та B відповідно. У твердих розчинах, що упорядковуються, виникає ефект знакозмінної сегрегації, коли всі непарні шари пластин мають надлишок одного компонента, а всі парні — іншого. Виявлено, що для пластин з орієнтацією (100) ефект знакозмінної сегрегації переходить в ефект упорядкування атомів та виникають незатухаючі з глибиною осцилюючі концентраційні профілі в області температур, нижчих за температуру упорядкування.