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Kinetics of nonsymmetrical impurity segregation at thin film boundaries

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Abstract: Theoretical and numerical analysis is presented for kinetics of impurity segregation at the boundaries of a thin layer of substance dividing two different materials. Time dependences of boundary impurity concentrations and concentration profiles within the film have been obtained. Depending on the energy of impurity interaction with the boundaries and the temperature, some criteria were established to predict probable realization of segregation process. The time of exhausting of areas adjusting segregation layers and the width of the exhausted zone near the boundaries was evaluated.

Keywords: Thin Film; Impurity Segregation; Kinetics; Phase Diagram.

1. Introduction

Peculiarities of impurity segregation from unlimited and limited bulk of material were considered earlier both in theoretical and experimental works [1–8]. It was often noted that the linear size of an impurity-containing grain or a thin film did not always affect the result of segregation. In most cases, when considering grain boundary segregation, a simpler model of impurity redistribution toward a boundary of a half-infinite medium can be used.

Nevertheless, impurity redistribution in a limited bulk of material subject to the specific form of impurity-containing material has been considered in a number of papers. Mostly it was supposed that the environment of an impurity-containing grain or a film is the same in all directions that was not always present in practice. Of course, it can be true for impurity segregation at grain boundaries in bulk metals where the grain can be considered as a sphere or a cylinder, depending on individual peculiarities of alloy. Nowadays, a great interest is attracted by film structures where a solid solution layer is several micrometers thick and different materials are located astride the layer. The simplest example is a film limited by a substrate and a free surface. More often, the samples are of multi-layer structure and the process of impurity redistribution at the interfaces obtains new characteristics.

The processes of mass transfer in thin metal films, particularly, gold and cooper ones, are of considerable interest due to wide use of these films in microelectronic industry. Impurity segregation at film boundaries can determine mechanical and resistive properties of these objects. Particularly, segregation of impurity of chromium or copper at the boundary between the gold film and the substrate improves film adhesion and raises its technological qualities.

2. Basic relations

Now we shall consider impurity segregation at the boundaries of a thin film dividing two different materials (Fig. 1). Because the conditions outside the layer are different, impurity motion toward the left boundary and the right one is not the same, being determined by the energy characteristics of the impurity within the layer and at the boundaries. Generally, the energy characteristics include not only energy difference of impurity atom in the material and at segregation layers of each of the boundaries, but also the interaction energy between impurity atoms within respective segregation layers.

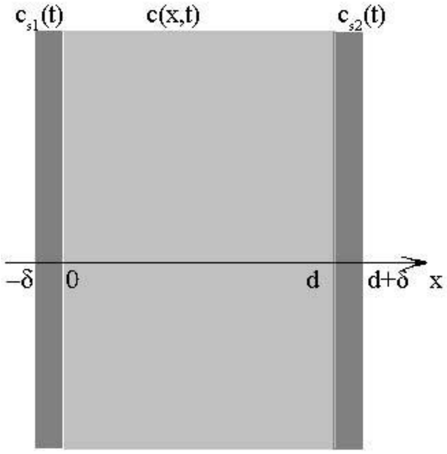

Figure 1: The scheme of an impurity-containing layer located between two different materials.

Boundary enrichment level and the kinetics of segregation at each of the boundaries as well as impurity redistribution in the specimen in whole depend on the type of interaction (attractive or repulsive). Then, it is necessary to take into account the fact that the number of sites within segregation layer, which can be occupied by impurity atoms, can be limited. Site competition is characterized by “capacity” of the segregation layer, i.e. by the maximum number of sites within the boundary accessible for impurity atoms. Evidently, if materials outside the layer are different, boundaries will differ in interaction energies and site numbers with great probability.

Now we go over to the direct consideration of impurity motion in the system described above. It is supposed that the thickness of impurity-containing layer is d, and segregation layers of δ thickness are formed at film’s boundaries. For simplicity, we suppose the thickness of segregation layer to be of the order of interatomic distance and, respectively, $d>>\delta$.

The origin of coordinates we placed at the left boundary. We consider one-dimensional problem of impurity motion in the direction perpendicular to the layer boundaries.

Naturally, we suppose that it is energetically favorable for impurity to leave the bulk of the layer and to concentrate at the boundaries. The impurity motion is described by diffusion equation

$$\frac{\partial c(x,t)}{\partial t}=D\frac{\partial^2 c(x,t)}{\partial x^2}, \tag{1}$$

where $c(x,t)$ is the impurity concentration within the layer, D is the diffusion coefficient. Then at the boundaries, the following relations are satisfied due to the law of conservation of the number of impurity atoms in the system of bulk and segregation layers:

$$\frac{dc_{s1}(t)}{dt}=\frac{D}{\delta}\frac{\partial c(x,t)}{\partial x}\bigg|_{x=0}, \tag{2}$$

$$\frac{dc_{s2}(t)}{dt}=\frac{D}{\delta}\frac{\partial c(x,t)}{\partial x}\bigg|_{x=d}, \tag{3}$$

where $c_{s1}(t)$, $c_{s2}(t)$ are the impurity concentrations within segregation layers at $x=0$ and $x=d$, respectively.

The initial and boundary conditions are formulated as follows. We assume that initially, the impurities are uniformly distributed in the bulk with the concentration of c_0, and the impurity concentrations within boundaries are zero. Fowler isotherm accounting for the site competition and interaction between impurity atoms within segregation layer is often used as boundary condition [5-7]:

$$c(0,t)=\frac{c_{s1}(t)}{1-c_{s1}(t)}\frac{1}{K_1(T)}\exp\left(-\frac{z|u_{s1}|}{T}c_{s1}(t)\right), \tag{4}$$

$$c(d,t)=\frac{c_{s2}(t)}{1-c_{s2}(t)}\frac{1}{K_2(T)}\exp\left(-\frac{z|u_{s2}|}{T}c_{s2}(t)\right), \tag{5}$$

where z is the coordination number of the interface lattice, $K_1(T)$, $K_2(T)$ are the enrichment factors determined by the values of energy of interaction of an impurity atom with boundaries:

$$K_1(T)=\exp\left(|u_1|/T\right),\ K_2(T)=\exp\left(|u_2|/T\right), \tag{6}$$

u_1, u_2 are the differences of impurity atom energies in the depth of the bulk and within segregation layer at one of the boundaries, u_{s1}, u_{s2} are the energies of lateral interaction between impurity atoms within the respective segregation layers.

To obtain quantitative results, we can limit by using the linear Henry's law instead of Fowler isotherm, when impurity concentration within segregation layer is proportional to the concentration in the adjacent layer of material.

$$c(0,t)=c_{s1}(t)/K_1(T), \quad c(d,t)=c_{s2}(t)/K_2(T) \tag{7}$$

In [7], a number of Fowler isotherms calculated at varied temperature were presented. It was stated that in a layer of finite thickness, a linear term should be added to the traditional Fowler isotherm, so the form of the curve approaches the linear one in a large part of the initial concentration range. So, the use of linear boundary condition allows describing the most of systems where segregation at the boundaries of a limited layer occurs.

As noted in [5-7], the impurity concentration within segregation layers can be described by the integral equations

$$c_{s1}(t)=\frac{1}{\delta}\sqrt{\frac{D}{\pi}}\int_0^t \frac{c_m(\tau)-c(0,\tau)}{\sqrt{t-\tau}}d\tau, \tag{8}$$

$$c_{s2}(t)=\frac{1}{\delta}\sqrt{\frac{D}{\pi}}\int_0^t \frac{c_m(\tau)-c(d,\tau)}{\sqrt{t-\tau}}d\tau, \tag{9}$$

where

$$c_m(t)=c_0-\frac{\delta}{d}\left(c_{s1}(t)+c_{s2}(t)\right) \tag{10}$$

is the average impurity concentration in the material at the moment.

The above-listed equations and relations enable us to analyze the process of impurity redistribution in this system. We can obtain preliminary features of segregation kinetics before the solution of differential equation system in partial derivatives.

To the moment of t, $c_{s1}(t)\delta$ impurity atoms have migrated to the left boundary. The adjacent to the boundary region of material of $c_{s1}(t)\delta/c_0$ thickness is depleted. Similar situation takes place at the right boundary. At some moment t^*, the depleted regions merge, but it doesn't mean that the segregation process is over. The concentrations $c_{s1}(t^*)$, $c_{s2}(t^*)$ can differ from the equilibrium values c^e_{s1}, c^e_{s2} determined by the following system of equations

$$\begin{cases} \delta\left(c_{s1}^e + c_{s2}^e\right) + dc_m^e = c_0\left(d + 2\delta\right), \\ c_m^e = \dfrac{c_{s1}^e}{K_1\left(T\right)} = \dfrac{c_{s2}^e}{K_2\left(T\right)}. \end{cases} \tag{11}$$

Exactly,

$$c_m^e = \frac{c_0\left(d + 2\delta\right)}{K_1\delta + K_2\delta + d} \approx \frac{c_0}{\left(K_1 + K_2\right)/\beta + 1}, \tag{12}$$

$$c_{s1}^e \approx \frac{c_0 K_1}{\left(K_1 + K_2\right)/\beta + 1},\ c_{s2}^e \approx \frac{c_0 K_2}{\left(K_1 + K_2\right)/\beta + 1}, \tag{13}$$

where $\beta = d/\delta$ is the dimensionless film thickness.

The maximum of the concentration profile in the impurity-containing layer $x = b(t)$, which can be interpreted as the border between two depleted regions is derived from

$$\left.\frac{\partial c\left(x,t\right)}{\partial x}\right|_{x=b(t)} = 0. \tag{14}$$

The amount of impurity in the bulk can be sufficient to fill totally segregation layers before the intersection of exhausted areas. If the impurity is insufficient, the exhausted areas merge and the dividing line shifts toward the boundary with lower coefficient of enrichment.

The ratio of the enrichment coefficients and the thickness of the film determine the variant to be realized in practice.

If $K_1 \sim K_2 << d/\delta$, i.e. the enrichment coefficients are comparatively small, the segregation occurs almost independently at the both boundaries, and the equilibrium values are $c^e_{s1} \approx c_0 K_1$, $c^e_{s2} \approx c_0 K_2$. If one of the coefficients significantly exceeds the other one, $K_1 >> K_2 \sim d/\delta >> 1$, then $c^e_{s1} \sim c_0\, d/\delta$, $c^e_{s2} \sim c_0$, and the second boundary is not almost enriched. At similar, but large enough values of the enrichment coefficients, $K_1 \sim K_2 >> d/\delta$, the equilibrium values of concentrations are about

$$c_{s1}^e \approx c_0 \frac{d}{\delta}\frac{K_1}{K_1 + K_2},\quad c_{s2}^e \approx c_0 \frac{d}{\delta}\frac{K_2}{K_1 + K_2}. \tag{15}$$

The moment when segregation becomes close to the equilibrium is determined by a natural estimation

$$t_1 = \frac{\delta^2}{D}\left(c_{s1}^e\right)^2, \quad t_2 = \frac{\delta^2}{D}\left(c_{s2}^e\right)^2. \tag{16}$$

At the same initial impurity content in the bulk, the result of the segregation, i.e. the equilibrium value of impurity concentration within the segregation layer, can differ in orders. At the temperatures above some critical one, the equilibrium value of concentration within the segregation layer becomes close to unity. Therefore, not only the area adjacent to the boundary is depleted significantly, but also the whole grain or film. At low temperatures, such depletion may be not required. Thus, depending on the temperature, impurity segregation at the boundaries of thin film can result in significant reduction of the amount of impurity in the bulk or not. When we have access to the data about energy parameters, i.e. the enrichment coefficients, we can approximately determine what part of the impurity is attracted by each of the boundaries.

To describe the impurity motion through the bulk of material toward two segregation layers, it is necessary to solve the diffusion equation. We use again the simplest Henry isotherm and reformulate the problem, measuring time and distance in units of δ^2/D and δ, respectively. The solution takes the form

$$c(x,t) = c_0\left(1 + 2\frac{d}{\delta}\right)\left(1 - \frac{K_1 + K_2}{K_1 + K_2 + \dfrac{d}{\delta}}\right) + \sum_{n=0}^{\infty} A_n \exp\left(-\lambda_n^2 t\right), \tag{17}$$

where $\lambda_n \approx \pi(n\text{-}1)/$□, n=2,3,… and

$$A_n = \frac{2\left(\dfrac{\sin\left(\lambda_n d/\delta\right)}{\lambda_n} - K_1 + K_1\cos\left(\lambda_n d/\delta\right)\right)\left(\cos\lambda_n x - K_1\lambda_n \sin\lambda_n x\right)}{\dfrac{1-K_1^2\lambda_n^2/2}{2\lambda_n}\sin\left(2\lambda_n d/\delta\right) + K_1\cos\left(2\lambda_n d/\delta\right) + K_1^2\lambda_n^2\, d/\delta - K_1 + d/\delta}. \tag{18}$$

The maximum of the concentration profile (17) is shifted within the film according to the law

$$b(t) \approx \frac{1}{2} + 4\frac{A_2}{A_1}\exp\left(-3\pi^2 t\right). \tag{19}$$

3. Results and Discussion

Now we shall consider the kinetics of segregation process. The values of enrichment factors and energies associated with cooper, gold and silver were used for calculation [9]. In [9], the segregation energies at the interfaces in fcc metals were calculated using methods of molecular dynamics. The authors of [9] have confirmed that the energy values u1, u2¬ are the key parameters controlling the segregation process.

The calculated segregation curves for residual impurity of silver in the copper and gold films are presented in Fig.2. Here it is supposed that the enrichment factor of the right boundary is 12 times more than the one of the left boundary. This ratio corresponds to the structure of “substrate–film–free surface”, because the enrichment factor of a free surface mostly exceeds that of an internal interface by one or two orders of magnitude [10].

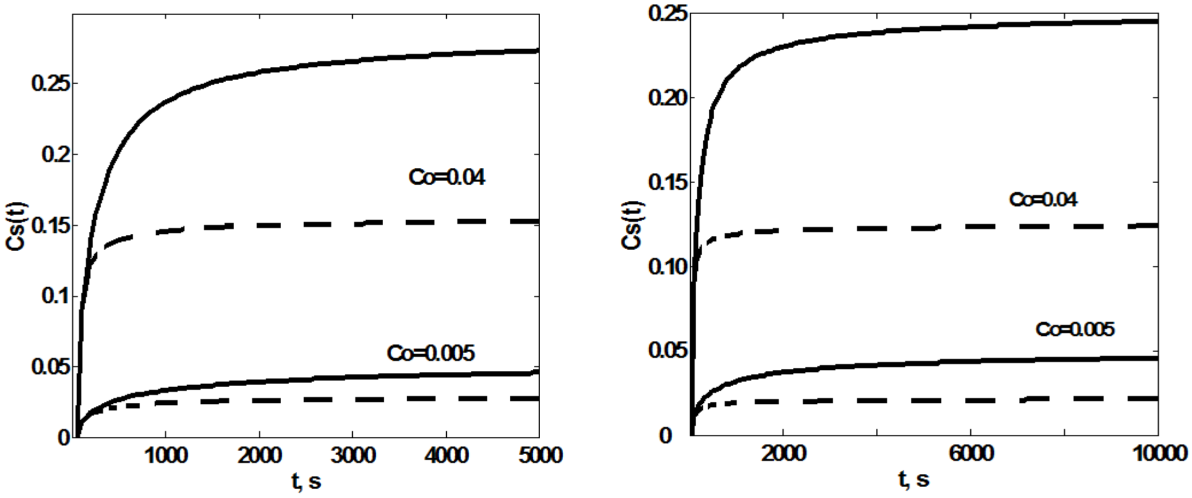

Figure 2: Segregation of Ag impurity in copper (*a*) and gold (*b*) films at the substrate-film boundary (dashed line) and at the free surface (solid line) at varied initial concentration.

The total duration of the segregation process ranges from a few hours to a day in both cases. It is determined not only by the diffusion coefficient value, but also by the amount of impurity required by segregation layer enrichment, i.e. by the enrichment factor.

Now we shall consider the impurity movement within an impurity-containing film (see Fig.3).

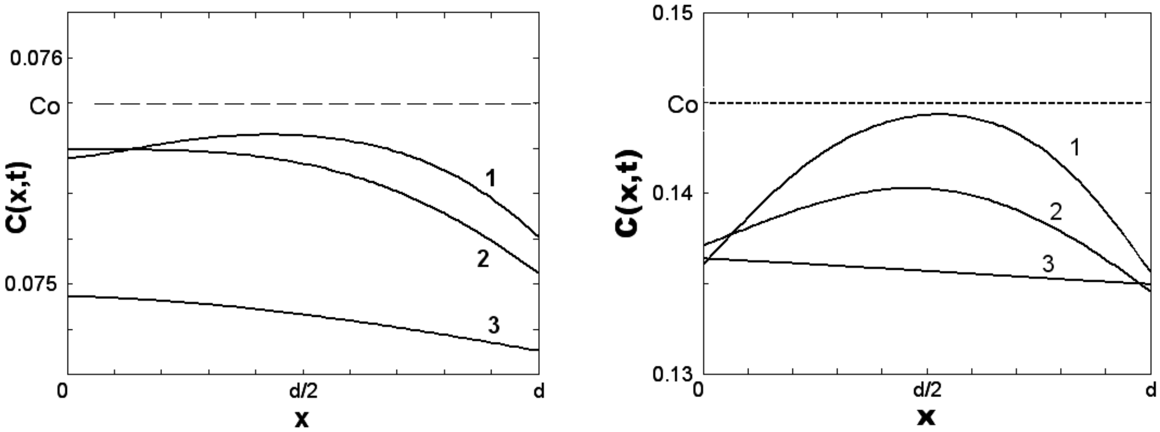

Figure 3: Concentration profiles of impurity distribution (Ag) in the copper (a) and gold (b) film: (a) – the curves are calculated for the time of 4000, 10000, 100000 sec; (b) 3000, 10000, 100000 sec, correspondingly.

It is clearly seen that the maximum of concentration profile is shifted step-by-step toward the boundary with a smaller redistribution coefficient. The rate of the maximum shift and the general film depletion are determined by the value of the enrichment factor of the boundary.

The difference of the concentration profiles in Figs. 3a and 3b is that the depletion of the copper film near substrate-film interface is slower in comparison with the gold film due to half value of u_{s1} [9] and 8 times lower value of the enrichment coefficient, respectively. The impurity concentration within the film reaches the equilibrium value in 10^5 sec, i.e. in about 28 hours. Here we can say about significant difference in segregation rates in these alloys and iron-based compounds [8] due to higher diffusion coefficients [10]. Besides, thin-film structures demonstrate the diffusion coefficient higher than this parameter of macroscopic samples.

A separate discussion should touch upon the degree of depletion of impurity-containing layer that was many times considered before [7]. Depending on the difference between the equilibrium value of impurity concentration in the bulk and the initial value, the layer can be considered as a “thin” one (where the amount of impurity atoms is insufficient for segregation layer saturation without significant drop of impurity concentration in the bulk) or as a “thick” one, where the change of concentration due to segregation is insignificant. As a rule, the layer of thickness more than 1000 interatomic distances can be considered as a “thick” one and we may use the formula derived for semi-infinite medium. But from thin film viewpoint, it becomes apparent that this criterion is too rough. It is necessary to know not only the initial value of impurity concentration in the bulk, but also the impurity redistribution coefficient determined by energy parameters of interatomic interaction and boundary properties, in order to refer the specimen of a layered or a small-grained material to the “thin” or “thick” type. The principal role in this choice belongs to such thermodynamic parameter as the temperature; it may be illustrated as follows.

Figure 4 demonstrates calculated phase diagrams in $\beta - T$ coordinates, which illustrates film classification with respect to their segregation characteristics. As seen from (15), thin films are associated with the area below the curve $K_1(T)+K_2(T)$. Thick film area is located above the curve. At low temperatures, the horizontal line $\beta=c_0-1$ becomes the natural border of thin film area where all impurity atoms leave the film, being accumulated in segregation layers.

At the same temperature, any film can be called thin or a thick one depending on the initial impurity content. The more impurity in the film, the higher probability is that segregation kinetics will coincide with that in half-infinite medium. At a lower initial content of impurity, the range of the temperature, where the film thickness affects the kinetics and the result of segregation, will broaden.

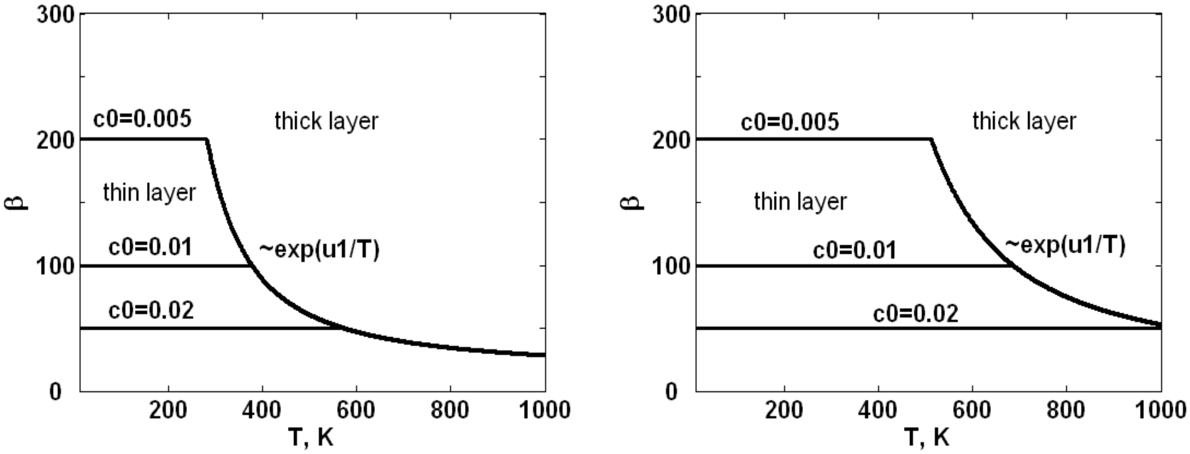

Figure 4: Phase diagrams in β – T coordinates illustrating film classification for silver segregation in the copper (*a*) and gold (*b*) film.

It is seen in Figure 4 that the copper film of approximately 100 nm in size can be classified as a thin film at the maximum value of the initial concentration of Ag equal to 0.01.

4. Conclusion

In the present work, the peculiarities of impurity segregation at the boundaries of a thin layer of substance separating two different materials are analyzed. The results can be also applied to the case of internal and external boundaries of a film.

As the materials outside the layer are different, the rate of impurity motion toward the boundaries depends on the energy characteristics of the impurity at the boundaries. Together with the temperature and the initial impurity concentration, segregation energies control both kinetics and equilibrium result of segregation. The segregation energies should be surely taken into account when discussing possible distinctions of segregation in a concrete thin film and in a bulk sample.

Acknowledgments

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