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Grain boundary interdiffusion and stresses in thin polycrystalline films

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Abstract We consider the kinetics of tensile stress relaxation in thin metal film attached to inert substrate, controlled by chemical interdiffusion along the grain boundaries. We assume that the source of diffusing atoms is located at the surface of the film. We show that the kinetics of stress relaxation in the film can be either accelerated or slowed down if compared with the same kinetics in a single-component film, depending on the difference of intrinsic GB diffusion coefficients of the two components. In the case of faster matrix atoms, the tensile stress in the film significantly increases beyond its initial value at the beginning of interdiffusion process, while in the case of faster diffuser atoms, the compressive stresses develop in the film at the intermediate stages of stress evolution.

Introduction

It is well known that thin metal films deposited on inert substrates are in most cases highly stressed [1]. The stresses, which can be both compressive and tensile, are building up either during deposition process or as a result of subsequent heat treatments (in this case, the stresses may be generated due to the grain growth in the film or due to the mismatch of thermal expansion coefficients of the film and the substrate [2]). Grain boundary (GB) self-diffusion of the film atoms is an important mechanism of stress relaxation in unpassivated films. Gao et al. [3] developed a theory describing the relaxation of tensile stresses in the polycrystalline thin films rigidly attached to the inert substrate with elastic constants identical to those of the film. In their model, the only driving force for GB self-diffusion was the reduction of elastic strain energy of the film.

In many technological applications, thin metal films are deposited on or covered by a thin film of another metallic material (i.e., diffusion barriers in microelectronics or thin film multilayers exhibiting desired functional properties [1]). In this case, the relevant kinetic process occurring in the GBs of the film at elevated temperatures is the chemical interdiffusion, rather than self-diffusion. A main component of the driving force for GB interdiffusion is the reduction of the chemical Gibbs free energy of the intermixing components due to formation of solid solution in the GB. In a first approximation this contribution does not depend on the second component of the driving force associated with elastic strain energy of the film. A characteristic feature of chemical interdiffusion mediated by point defects (vacancies and interstitials) is the inequality of intrinsic diffusion fluxes of the components. In our recent study, we demonstrated that this inequality leads to a build-up of the normal stresses at the GB during GB interdiffusion process, which can be both compressive and tensile [4]. Thus, one can conclude that the GB interdiffusion can both accelerate and slow down the kinetics of stress relaxation in the host thin film, depending on the sign of the difference of intrinsic GB diffusion coefficients. The main aim of this study is to analyze the process of stress relaxation mediated by the GB interdiffusion in a thin film rigidly attached to an inert substrate. In our treatment, we will follow the scheme proposed by Gao et al. [3].

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The model

Let us consider a columnar polycrystalline thin film of the component A on a solid inert substrate (Fig. 1). For simplicity, we will consider a quasi one-dimensional film, with the stripe-like grains of width L. The component B penetrates from the surface of the film A along the GBs. Component A, generally, moves in opposite direction. We will assume that the atoms A leave the GBs in the film at the free surface or at the A/B interface without any hindrance. We will also assume that the component B does not have any effect on the elastic deformation field in the film A, for which the same boundary conditions for stress as used by Gao et al. [3] could be employed. Therefore, our model is suitable for description of the GB interdiffusion process when the source of B-atoms is the gas or the liquid phase, or the film of solid B deposited on the top of film A is ultra-thin and discontinuous (island-, or beaded film), so that the effect of this ultrathin B-layer on the deformation in film A is negligible. It is important that the layer of B, unlike the surface passivation layer on thin metal films which hinders the GB diffusion process, allows for free escape of A-atoms either along the A/B interface or to the free surface. For example, in the case of beaded film B this means that the fraction of surface area of film A occupied by islands of B is small, and that the A-atoms escaping the GBs in the film A are homogeneously distributed at the surface by a fast process of surface diffusion. This assumption is not unreasonable since in the typical face centered cubic (fcc) metal at the temperatures below $0.5T_\mathrm{m}$ (where T_m is the melting temperature of component A) the surface self-diffusion coefficient exceeds the GB self-diffusion coefficient by more than an order of magnitude [5]. Furthermore, we neglect the diffusion in the bulk, which approximately corresponds to the temperatures below $0.4T_\mathrm{m}$.

Both components move under the actions of the concentration and stress gradients, but with the different diffusion mobilities. The difference of diffusion coefficients of two species along the GBs is associated with the fact that at low homological temperatures the GB diffusion is dominated by random walks of vacancies and self-interstitials [6]. The divergence of the total diffusion flux along the GB causes plating out of an additional material at the GB in the form of extra material wedge. It modifies the internal stresses, which, in turn, affect the GB diffusion. Let us analyze this effect quantitatively.

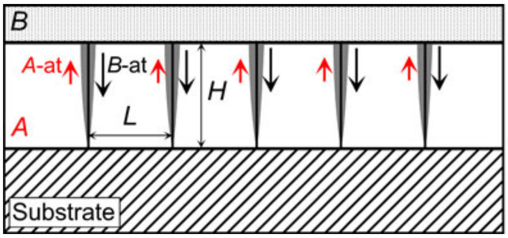

Fig. 1 Schematic illustration of a thin film of A with columnar microstructure and a source of a diffuser B at the surface. The unequal GB diffusion fluxes of A- and B-atoms are shown by the *short* and *long arrows*, respectively. The imbalance of the GB diffusion fluxes causes the formation of extra material wedges at the GBs

In the framework of ideal solid solution model, the chemical potentials of the atoms at the GB subjected to a normal stress σ are (here we assume that σ is positive for compressive stress):

$$\mu_i = \mu_i^0 + kT\ln C_i + \Omega\sigma; \quad (i = A, B) \tag{1}$$

where Ω is the atomic volume supposed to be equal for both components, C_A and C_B are the molar fractions of the respective components, and μ_A^0 and μ_B^0 are the standard chemical potentials of respective components. The factor kT has its standard thermodynamic meaning. In fact, σ is the normal traction at the GB which, for the sake of simplicity, will be identified with the stress in the film throughout this study. At this point, we would like to emphasize that the phenomena considered in this study are different from the phenomenon of diffusion-generated coherency stresses in thin films considered by Wang et al. [7]. Indeed, an essential element of the latter phenomenon is the dependence of the lattice parameter of the host lattice on the concentration of substitutional impurities. In our approach, we assume equal atomic volumes of both components and neglect any possible dependence of the lattice parameter on the concentration of B-atoms. It should be also noted that Eq. 1 is applicable only to the GBs which are perfect sources/sinks for vacancies, such as random high-angle GBs [8]. Atomic fluxes of the components are governed by the gradients of the chemical potentials along GB:

$$j_i = -\frac{D_i n_i}{kT}\frac{\partial \mu_i}{\partial y} = -\frac{\delta D_i}{\Omega}\left(\frac{\partial C_i}{\partial y} + \frac{\Omega C_i}{kT}\frac{\partial \sigma}{\partial y}\right); \tag{2}$$

where n_A and n_B are the numbers of atoms of respective components per unit area of the GB, and D_A and D_B are the respective intrinsic GB diffusion coefficients. δ is the diffusion thickness of the GB (typically, 0.5 nm [8]). It should be noted that in the framework of ideal GB solid solution model employed in this study, D_A and D_B coincide with respective self-diffusion coefficients of A- and B-atoms along the GBs. We will further suppose that a total number of atoms of both components per unit area of the GB are constant:

$$n_i = C_i\delta/\Omega; \quad C_A + C_B = 1; \tag{3}$$

Mass balance equations for each component can be written down in the following form:

$$\delta\frac{\partial C_i}{\partial t} = -\Omega\frac{\partial j_i}{\partial y} - \frac{\partial w}{\partial t}\begin{cases} C_i, & \partial w/\partial t > 0 \\ C_i^w & \partial w/\partial t < 0 \end{cases}; \tag{4}$$

where $w(y,t)$ is a thickness of the extra material wedge, and C_i^w is a bulk concentration in the immediate vicinity of the GB. Though in this treatment the contribution of bulk diffusion is neglected, the bulk concentration close to the GB does change due to the plating out of an additional material there. To calculate C_i^w, let us introduce an effective thickness of the bulk zone, w^+, where the concentrations significantly deviate from the initial ones C_i^{bulk} ($C_A^{\text{bulk}} = 1,\ C_B^{\text{bulk}} = 0$):

$$\frac{\partial w^+}{\partial t} = \frac{\partial w}{\partial t}, \quad \text{if } w^+ > 0 \tag{5}$$

In contrast with w, w^+ is always positive or zero (note that w can be negative: this means that the GB acts as material sink and the centers of neighboring grains drift toward the GB separating them). Denoting a total volume occupied by B-atoms in this zone per unit area of the GB as q_i^+, and neglecting the concentration inhomogeneity across this zone yields:

$$C_i^w = \begin{cases} q_i^+/w^+ & w^+ > 0 \\ C_i^{\text{bulk}} & w^+ = 0 \end{cases} \tag{6}$$

With the definitions (5), (6) the mass balance condition in the wedge can be written in the following form:

$$\frac{\partial q_i^+}{\partial t} = \frac{\partial w}{\partial t}\begin{cases} C_i, & \partial w/\partial t > 0 \\ q_i^+/w^+, & \partial w/\partial t < 0,\ w^+ > 0 \end{cases} \tag{7}$$

The extra material wedge can be represented as an ensemble of edge dislocations with the Burgers vector density $\partial w/\partial y$ [3]. The corresponding normal stress at the GB can be written as

$$\sigma(y,t) = \sigma_0 + E^* \int_0^H K(y,z)\frac{\partial w(z,t)}{\partial z}\mathrm{d}z \tag{8}$$

where $E^* = \dfrac{E}{4\pi(1-v^2)}$ is the effective elastic modulus, σ_0 is an initial stress in the film, H is a thickness of the film, and kernel $K(y,z)$ is a stress of an array of unit edge dislocations located at the GBs on distance z from the film surface [9]:

$$\begin{aligned} K(y,z) = {} & \frac{2\pi}{L}\Big[\coth(\pi\frac{y-z}{L}) - \coth(\pi\frac{y+z}{L})\Big] \\ & - \pi^2\frac{y-z}{L^2}\operatorname{csch}^2\left(\pi\frac{y-z}{L}\right) \\ & + \pi^2\frac{y+3z}{L^2}\operatorname{csch}^2\left(\pi\frac{y+z}{L}\right) \\ & - 4\pi^3\frac{yz}{L^3}\coth\left(\pi\frac{y+z}{L}\right)\operatorname{csch}^2\left(\pi\frac{y+z}{L}\right) \end{aligned} \tag{9}$$

The kernel given by Eq. 9 represents the Green's function of the full elastic problem for the extra material wedge [9], see Eq. 8. The set of Eqs. 2–9 has to be complemented by the following boundary conditions:

$$C_B|_{y=0} = 1, \quad \sigma|_{y=0} = 0, \quad w|_{y=H} = 0, \quad \left.\frac{\partial\sigma}{\partial y}\right|_{y=H} = 0 \tag{10}$$

The last condition follows from the requirement of zero diffusion fluxes of both components at $y = H$.

Introducing the dimensionless variables according to

$$W = w/\delta, \quad S = \sigma\Omega/kT, \quad Y = y/H, \quad \tau = tD_A/H^2, \quad C \equiv C_B,$$

yields the following set of equations providing a self-consistent description of simultaneous stress and concentration evolution in the film:

$$\frac{\partial W}{\partial \tau} = (\varphi - 1)\left[\frac{\partial^2 C}{\partial Y^2} + C\frac{\partial^2 S}{\partial Y^2} + \frac{\partial C}{\partial Y}\frac{\partial S}{\partial Y}\right] + \frac{\partial^2 S}{\partial Y^2} \tag{11}$$

$$\begin{aligned} \frac{\partial C}{\partial \tau} = {} & \varphi\frac{\partial^2 C}{\partial Y^2} + \varphi C\frac{\partial^2 S}{\partial Y^2} + \varphi\frac{\partial C}{\partial Y}\frac{\partial S}{\partial Y} \\ & - \frac{\partial W}{\partial \tau}\begin{cases} C & \partial W/\partial\tau > 0 \\ C^w & \partial W/\partial\tau < 0 \end{cases} \end{aligned} \tag{12}$$

$$C^w = \begin{cases} Q^+/W^+ & W^+ > 0 \\ 0 & W^+ = 0 \end{cases} \tag{13}$$

$$\frac{\partial W^+}{\partial \tau} = \frac{\partial W}{\partial \tau}\begin{cases} 1 & W^+ > 0 \\ 0 & W^+ = 0 \end{cases} \tag{14}$$

$$\frac{\partial Q^+}{\partial \tau} = \frac{\partial W}{\partial \tau}\begin{cases} C, & \partial W/\partial\tau > 0 \\ Q^+/W^+ & \partial W/\partial\tau < 0,\ W^+ > 0 \end{cases} \tag{15}$$

$$S(Y,\tau) = S_0 + \alpha\int_0^1 K(Y,Z)\frac{\partial W(Z,\tau)}{\partial Z}\mathrm{d}Z \tag{16}$$

In these equations $\varphi = D_B/D_A$, $\alpha = \delta\Omega E^*/kTH$, $S_0 = \sigma_0\Omega/kT$. Additional dimensionless parameter H/L is incorporated in the function $K(Y, Z)$. The Eqs. 11–16 were solved numerically (for the details of the numerical scheme, see Ref. [4]).

Results and discussion

In our calculations, we assumed $L = H$ (grain size in thin polycrystalline films is in most cases comparable to their thickness [1]), and employed the following values of parameters: $S_0 = 1$, and $\alpha = 0.1$. These values were derived employing the parameters for a typical fcc metal: $E = 100$ GPa, $v = 0.33$, $\Omega = 10^{-29}$ m^3/at. We also assumed the film thickness $H \approx 129\delta \approx 65$ nm and $\sigma_0 \approx 700$ MPa.

The calculated distributions of the dimensionless stress, S, across the film thickness for different annealing times and relative diffusion coefficients φ are shown in Figs. 2 and 3. The case $\varphi = 1$ corresponds to tensile stress relaxation by the GB self-diffusion considered by Gao et al. [3]. Figure 2 shows that for $D_B < D_A$ the relaxation of

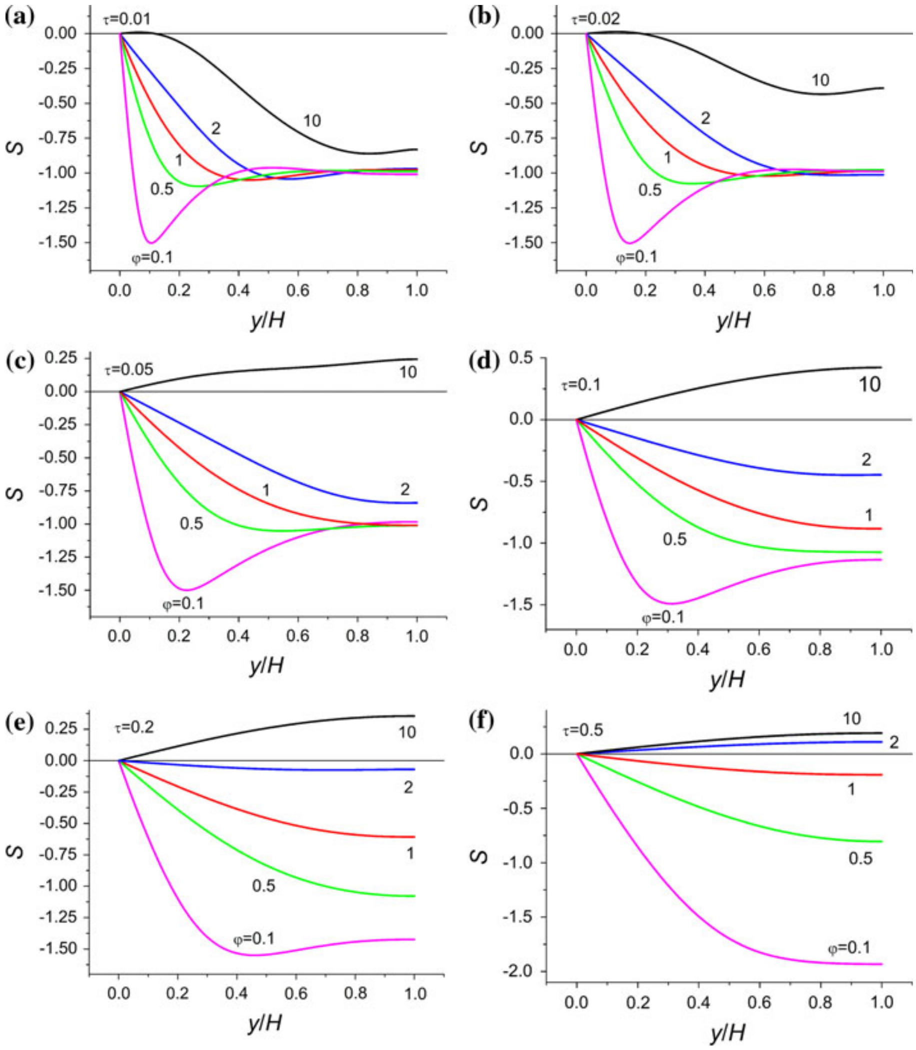

Fig. 2 The dependencies of the dimensionless stress in the film on the distance from the *A*/*B* interface for $\tau = 0.01$ (**a**), $\tau = 0.02$ (**b**), $\tau = 0.05$ (**c**), $\tau = 0.1$ (**d**), $\tau = 0.2$ (**e**), $\tau = 0.5$ (**f**), and various relative intrinsic diffusivities φ. In most cases, the stresses in the systems with $\varphi < 1$ and $\varphi > 1$ are more tensile and more compressive, respectively, than in the single-component film ($\varphi = 1$)

initial tensile stress in the film is significantly slower than in the case of stress relaxation by self-diffusion (which corresponds to $D_B = D_A$). Moreover, for the short annealing times the tensile stress at certain locations in the film significantly exceeds the initial stress level $S = 1$. For example, for $\tau = 0.5$ the tensile stress at the film/substrate interface is by a factor of 2 higher than initial stress in the film (see Fig. 2f). This is because for $D_B < D_A$ the number of *A*-atoms leaving the film is larger than the number of *B*-atoms penetrating into the film, especially for the short annealing times for which the concentration gradients driving chemical interdiffusion are high. This leads to the temporary increase of the average tensile stress in the film. For the longer annealing times the concentration gradients in the GBs level off, and the stress gradient takes a lead as main driving force for diffusion. This leads to a slow process of stress relaxation (see Fig. 3a).

For $D_B > D_A$ the relaxation of initial tensile stress in the film for the short annealing times is significantly faster than in the case of GB self-diffusion (see Fig. 2a, b). This is because the chemical driving force for GB interdiffusion in this case joins forces with the stress-related driving force, leading to a faster mass gain in the film. For longer annealing times an interesting phenomenon of "over-shooting" can be observed: after achieving a stress-free state, the film continues to gain mass (because the chemical driving force for interdiffusion is still there), which leads to the increase of compressive stresses in the film (Fig. 2c–f). After reaching a maximum, these compressive stresses eventually relax toward the stress-free state (Fig. 3d, e).

A well-established paradigm of the Physical Metallurgy claims that at elevated temperatures allowing some diffusion mobility of atoms, the internal stresses in the system gradually relax [10]. Yet the above examples show that predicting the temporal behavior of internal stresses in the thin film bi- and multi-layers based on this paradigm may lead to wrong conclusions. Indeed, the phenomena of initially increasing tensile stress in the film ($D_B < D_A$, Fig. 3a, b) or a transition from tensile to compressive stresses ($D_B > D_A$, Fig. 3d, e) seem to be illogical because

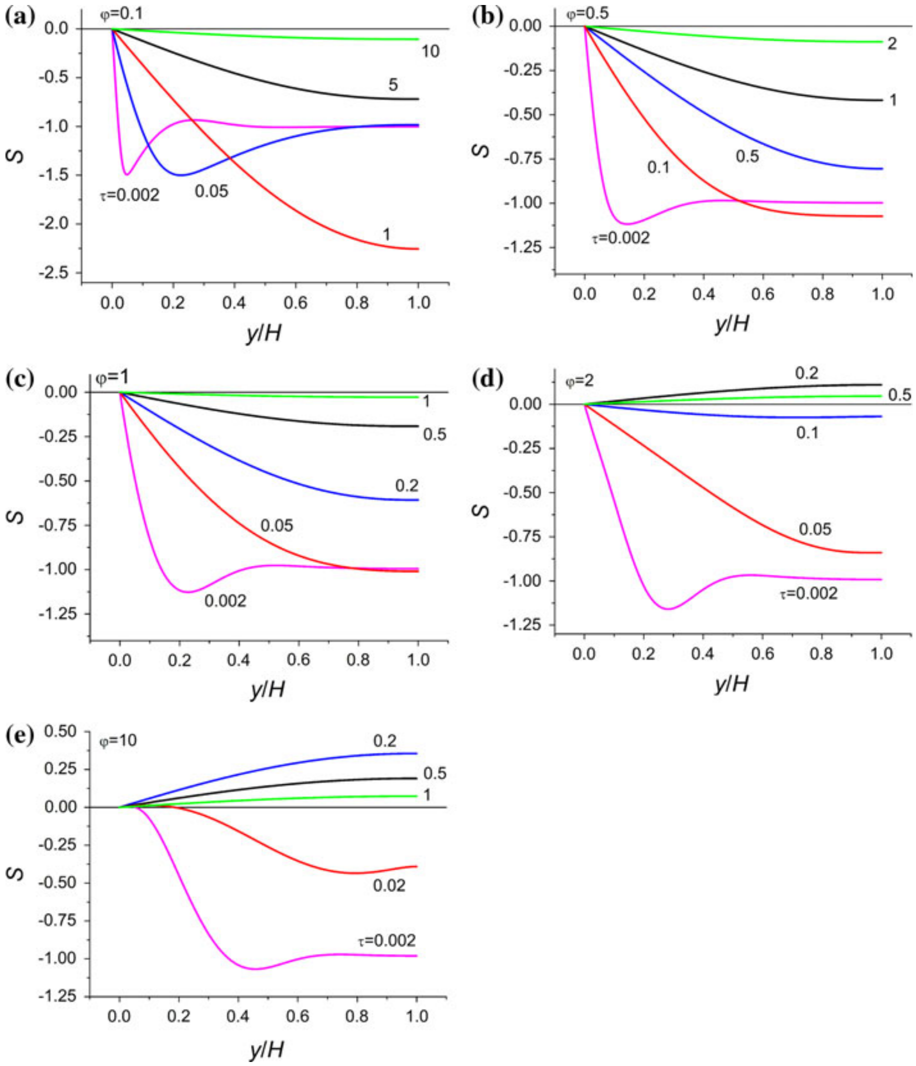

Fig. 3 The dependencies of the dimensionless stress in the film on the distance from the A/B interface for $\varphi = 0.1$ (**a**), $\varphi = 0.5$ (**b**), $\varphi = 1$ (**c**), $\varphi = 2$ (**d**), $\varphi = 10$ (**e**), and various annealing times τ. Note the similarity of Fig. 3c and Fig. 9a from the study of Gao et al. [3] (tensile stresses correspond to $S < 0$ in our study)

they are associated with increase of the elastic stress energy of the film. Our model clearly demonstrates that in binary and multicomponent thin film systems the chemical contribution to the Gibbs free energy plays an important role in determining the mechanical stresses in the system. Since (in the framework of our model) the system has only two interdependent ways to decrease its Gibbs energy (either by intermixing or by stress relaxation), it sometimes chooses the path which leads to a steep decrease of the chemical component of the Gibbs energy at the expense of the elastic energy contribution.

Comparing the predictions of our model with experimental data is challenging because a number of additional factors may influence the stress evolution in thin films. For example, formation of intermetallic phases at the A/B interface and at the GBs may overshadow any other contributions to internal stresses in the film [11]. The examples in which the mechanism described in this study may be at work include the study of stress development in Au/Cr/Si multilayer thin films [12], and the recent study of interdiffusion and stress development in Ni–Cu bilayers [13]. For example, Miller et al. [12] observed a fast relaxation of tensile stresses in Au thin film deposited on thin Cr underlayer during annealing at 225 °C in air. An ample presence of chromium oxide on the surface of Au film after annealing indicated that the GB diffusion of Cr through the GBs occurred during this heat treatment. The same system annealed in protective atmosphere of nitrogen did not exhibit any stress relaxation, and no traces of chromium oxide were detected on the surface. Therefore, this example provides a good illustration how the chemical interdiffusion along the GBs accelerates stress relaxation in the film. However, a direct comparison with our model is impossible because of the different diffusion geometries, and a large scatter of experimentally determined self- and hetero-diffusion coefficients of Au and Cr, respectively, along the GBs in Au (the scatter is so large that even determining the sign of the difference $D_B - D_A$ is problematic) [14]. In the study of Sheng et al. [13] a simultaneous diffusion intermixing and tensile stress generation in both Cu and Ni parts of the bi-layer were observed. Though the Authors of Ref. [13] named the GB interdiffusion as one of the possible reasons for tensile stress generation, the fact that tensile stresses were increasing both on the Cu and on the Ni side means that some other factors are contributing to stress evolution (i.e., grain growth or excess vacancy annihilation in the layers).

In conclusion, we would like to emphasize that though no direct comparison of the predictions of our model with the experimental data is possible at this stage; our results clearly demonstrate that the chemical interdiffusion along the GBs in thin metal films is an important factor which should be taken into account while considering the stress evolution in the film. The contribution of the GB interdiffusion to stress development in the film increases with increasing difference of intrinsic GB diffusion coefficients of the components (GB Kirkendall effect). We hope that this study will stimulate further experimental studies of this important effect.

Conclusions

From the results of this study, the following conclusions can be drawn:

1. A model of chemical interdiffusion along the GBs in metal thin films is proposed. The inequality of the GB diffusion fluxes of two components leads to formation of an extra material wedge at the GBs and modifies the stress distribution in the film (GB Kirkendall effect).
2. In the case the diffuser atoms are faster than the matrix ones, the initial relaxation of tensile stress in the film proceeds faster than in the case of a single-component film considered by Gao et al. [3]. However, for long annealing times the sign of the stress changes, and a certain build-up of compressive stress is observed before the film finally relaxes to a stress-free state.
3. In the case the diffuser atoms are slower than the matrix ones, an increase of tensile stress in the film is observed for short annealing times, followed by a slow (slower than in the case of single-component film [3]) relaxation of the film toward a stress-free state.

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