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Coupled Morphological Stability of the Multiple Phase Boundaries: Oxides in an Oxygen Potential Gradient.
II. Two Oxide Layers

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The morphological stability of the interphase boundaries is a challenging problem, both from mathematical and physical point. In materials that are exposed to thermodynamic potential gradients, *i.e.*, gradients of chemical potentials, electrical potential, temperature, or pressure, transport processes of the mobile components occur. In addition, changes in the morphology of the material surfaces and interfaces may appear. In this paper, a comprehensive formal treatment of the coupled morphological stability of multiple phase boundaries will be given for oxides that are exposed to an oxygen potential gradient. In the Part I of this paper the stability of the diffusionally interacting boundaries of a single oxide layer was explored using the original new method. The exact results obtained by this method where compared to the results obtained by the quasi-stationary approximation, which appeared to be quite precise. In the present communication we study the system of two adjacent oxide layers, *i.e.* the morphological stability of the three diffusionally interacting boundaries.

Key words: morphological stability, multi-phase system, diffusional mass transport.

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Морфологічна стійкість міжфазних границь являє собою серйозну проблему, як з математичної, так і з фізичної точки зору. У матеріалах, підданих дії градієнтів термодинамічних потенціалів, тобто градієнтів хімічних потенціалів, електричних потенціалів, температури або тиску, виникають процеси переносу мобільних компонентів. На додаток до цього можуть виникати зміни морфології поверхонь і міжфазних границь. У цій роботі дається повний формально строгий розгляд зв'язаної морфологічної стійкості множинних міжфазних границь для оксидів під дією градієнта потенціалу кисню. У частині I цієї статті з використанням оригінального нового методу була досліджена морфологічна стійкість дифузійно взаємодіючих границь одного оксидного шару. Точні результати, отримані цим методом, порівнювалися з результатами, отриманими у квазістаціонарному наближенні; це наближення виявилося досить точним. У цьому повідомленні ми вивчаємо систему, що складається із двох межуючих оксидних шарів, тобто морфологічну стійкість трьох дифузійно взаємодіючих границь.

Ключові слова: морфологічна стійкість, багатофазні системи, дифузійне масоперенесення.

Морфологическая устойчивость межфазных границ представляет собой серьёзную проблему, как с математической, так и с физической точки зрения. В материалах, находящихся под действием градиентов термодинамических потенциалов, т.е. градиентов химических потенциалов, электрических потенциалов, температуры или давления, возникают процессы переноса мобильных компонентов. В дополнение к этому могут возникать изменения морфологии поверхностей и межфазных границ. В настоящей работе даётся полное формально строгое рассмотрение связанной морфологической устойчивости множественных межфазных границ для оксидов под действием градиента потенциала кислорода. В части I данной статьи с использованием оригинального нового метода была исследована морфологическая устойчивость диффузионно взаимодействующих границ одного оксидного слоя. Точные результаты, полученные этим методом, сравнивались с результатами, полученными в квазистационарном приближении; это приближение оказалось весьма точным. В настоящем сообщении мы изучаем систему, состоящую из двух примыкающих друг к другу оксидных слоёв, т.е. морфологическую устойчивость трёх диффузионно взаимодействующих границ.

Ключевые слова: морфологическая устойчивость, многофазные системы, диффузионный массоперенос.

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1. INTRODUCTION

In many applications originally homogeneous materials are exposed to thermodynamic potential gradients, which can be gradients of temperature, chemical potential of one or more elements, electrical potential or uniaxial pressure. Well known examples are tarnishing layers on metallic materials [1, 2] which act as corrosion protection, thermal barrier coatings [3] acting as heat shield, solid electrolytes in fuel cells [4], or gas separation membranes [5]. The applied gradients act as a generalized thermodynamic force, and induce directed fluxes of the mobile components. These fluxes may lead to several degradation phenomena of the materials. The original morphology of the material surfaces might become unstable and a new surface morphology might be established (morphological instability) [6]. In addition to the practical implications, this moving-boundary problem is mathematically challenging. In the Part I of this paper [7] the morphological stability of diffusionally interacting boundaries of a single oxide layer was studied. To explore the stability of these boundaries, an original, new method was applied. Based on an integral transformation of a special kind, this method reveals the evolution of the multiple boundaries' perturbations without solving the diffusional problem inside the layer. The study of the morphological stability of the stationary moving boundaries was thereby reduced to exploration of the singular points (in the complex plane) of the corresponding integrands. While being exact, the above approach is quite complicated. So it appeared reasonable to check the simpler but approximate way of solution of the same problem, compare the results, and then use the simpler approach to solve the essentially more complicated problem for the multiple-layer system. The approximate approach is based on the physical fact that the deviations from the stoichiometry at the boundaries are quite small. Correspondingly, it follows from the results of the exact method, that the characteristic time for the development of the instability is large as compared to the characteristic time of the diffusional relaxation inside the layer. Then the quasi-stationary approximation for the diffusion of vacancies can be used, *i.e.*, the time derivative in the diffusion equation can be dropped.

As in the Part I, the class of materials considered here will be limited to oxides. Due to their physical properties oxides are used in many technical applications, which have been mentioned above. Examples are Al_2O_3 tarnishing layers on metallic alloys [1], ZrO_2-layers in thermal barrier coatings [3], Y_2O_3-doped ZrO_2 (YSZ) being the solid electrolyte in solid oxide fuel cells (SOFC) and solid oxide electrolyser cells (SOEC), (La, Sr)MnO_{3-d} being the cathode material in (SOFCs) [4], or (La, Sr)CrO_{3-d} in oxygen separation membranes [5]. Recently, very thin oxide films, *e.g.* $SrTiO_3$ or GaO_x have found increased interest due to their ability for resistive switching [8, 9]. In all of these examples, oxygen potential gradients appear across the oxide layer, either directly applied externally or as a result of another applied gradient.

In Part I of this paper [7] we considered the simplest situation of a semiconducting binary oxide $A_{1-\delta}O$ where oxygen is practically immobile while cations A are mobile *via* cation vacancies V (with cation vacancies fraction $\delta << 1$). In a nonstoichiometric binary transition metal oxide $A_{1-\delta}O$ the concentration of cation vacancies increases with increasing oxygen partial pressure (or increasing temperature). If such an oxide is chemically reduced either by lowering the oxygen partial pressure (or by decreasing the temperature), then cation vacancies, V, and electron holes, $h^{\bullet}$, diffuse to the crystal surface, where reduction of the oxide takes place:

$$O^{2-} + V + 2h^{\bullet} \to (1/2)O_2(g). \tag{1}$$

This reduction process corresponds to the arrival of a vacancy and two electron holes at the surface and the release of oxygen from the crystal. Thus a structural unit composed of a cation vacancy and an anion, is removed from the crystal while the number of cations is conserved. The crystal surface acts as vacancy sink until the new equilibrium state is reached. In contrast to this non-stationary situation a stationary non-equilibrium state can be established by exposing two parallel crystal surfaces of a sample to a gradient of the oxygen partial pressure, resulting in reduction at the low oxygen potential side and oxidation (the reversal of the above reaction) at the high oxygen potential side.

If the oxygen partial pressure on the oxidizing side of the $A_{1-\delta}O$ layer is further increased, the formation of the next oxide, *e.g.* $A_{3-\delta}O_4$ becomes possible (as an example one may consider CoO and Co_3O_4, respectively). If it happens, an additional interphase boundary appears between the oxides (see Fig. 1).

After a transient time, a stationary flux of vacancies and a corresponding flux of A-ions in the opposite direction occur, which are fed by the interface reaction (1), and the reverse of it. As a result of this

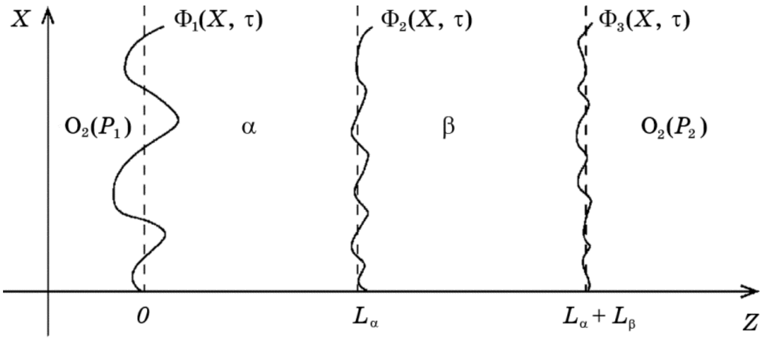

Fig. 1. Schematic presentation of two oxide layers α/β, *e.g.* AO/A_3O exposed to an oxygen potential gradient. P_1 and P_2 ($>P_1$) are the corresponding oxygen partial pressures. Dashed lines represent planar crystal surfaces, solid lines perturbed surfaces.

'vacancy wind' all crystal surfaces move (relative to the immobile oxygen sublattice) towards the side of higher partial pressure.

The corresponding one-dimensional diffusion problem can be solved easily, provided the following assumptions are made: i) the crystal surfaces are assumed to be planar, ii) in each oxide the chemical diffusion coefficient D describing the diffusion processes in the binary oxide is constant, iii) local equilibrium is established at the boundaries, *i.e.* phase boundary reaction kinetics are very fast compared to bulk diffusion. Then, quite analogously to [10, 7] we can obtain a stationary solution by transforming the diffusion equations for the vacancies (or the cations A) and the mass balances at the oxide/oxide and the oxide/gas boundaries to a moving reference frame, $0 \le z \le L_\alpha$ and $L_\alpha \le z \le L_\alpha + L_\beta$ (L_α and L_β are the thicknesses of the layers), in which all interfaces are at rest [10]. Again, the question about the morphological stability of the surfaces of such moving oxide layers naturally arises. Remarkably, despite the huge amount of publications on the subject of morphological stability, to the best of our knowledge the stability of the surfaces coupled by the diffusional mass transfer was not studied. In the present work the problem of linear stability of such surfaces is treated analytically. For three surfaces (two layers of different oxides of the same metal) the problem is solved in a quasistationary approximation, which is shown in the Part I to be quite precise.

2. SETTING OF THE PROBLEM

In Ref. [10] we found that the interfaces of a single layer exhibit different morphological stabilities. While interface where the reduction takes place was morphologically unstable, interface where oxidation takes place was morphologically stable. These experimental results were supported by theoretical investigations that were obtained by means of a linear stability analysis of each interface without any diffusional coupling of the interfaces. In the Part I of the present work [7] the problem of [10] was generalized: in exploring the morphological stability of two crystal surfaces their interaction was taken into account. In the present paper we consider two oxide layers, *i.e.* diffusionally interacting two gas/solid surfaces and one solid/solid interface. The problem is solved analytically; the detailed descriptions of the (necessary) quite lengthy calculations can be found in the Appendixes. In the moving reference frame, moving with a constant velocity V relative to the immobile oxygen sublattice (identical to the laboratory frame, see Fig. 1) the governing equations take the form

$$\frac{\partial C^\alpha}{\partial \tau} - V\frac{\partial C^\alpha}{\partial Z} - D_\alpha\left(\frac{\partial^2 C^\alpha}{\partial X^2} + \frac{\partial^2 C^\alpha}{\partial Z^2}\right) = 0, \qquad (2)$$

$$\frac{\partial C^{\beta}}{\partial \tau} - V\frac{\partial C^{\beta}}{\partial Z} - D_{\beta}\left(\frac{\partial^2 C^{\beta}}{\partial X^2} + \frac{\partial^2 C^{\beta}}{\partial Z^2}\right) = 0, \tag{3}$$

where the index α refers to the AO layer and index β refers to the A_3O_4 layer (see Fig. 1). Here $C^{\alpha} = \delta/\omega_{\alpha}$ and $C^{\beta} = \delta/\omega_{\beta}$ are the vacancy concentrations, D_{α} and D_{β} the chemical diffusion coefficients; ω_{α} and ω_{β} are molar volumes of the α-, and β-phases, which are presumed to be constant *i.e.* independent on δ. X and Z are the spatial coordinates (see Fig. 1), and τ the time.

Looking for small deviations $u^{\alpha}(X,Z,\tau)$ and $u^{\beta}(X,Z,\tau)$ from the stationary solutions $C_s^{\alpha}(Z)$ and $C_s^{\beta}(Z)$, which correspond to constant widths L_{α} and L_{β} of the oxide layers,

$$C^{\alpha} = C_s^{\alpha}(Z) + u(X,Z,\tau), \tag{4}$$

$$C^{\beta} = C_s^{\beta}(Z) + v(X,Z,\tau), \tag{5}$$

and slightly non planar, non-stationary boundaries (see Fig. 1)

$$Z_1(X,\tau) = 0 + \Phi_1(X,\tau), \tag{6}$$

$$Z_2(X,\tau) = L_{\alpha} + \Phi_2(X,\tau), \tag{7}$$

$$Z_3(X,\tau) = L_{\alpha} + L_{\beta} + \Phi_3(X,\tau), \tag{8}$$

the (equilibrium) boundary conditions are

$$C_s^{\alpha}\Big|_{Z=0} + u\Big|_{Z=0} + \frac{\partial C_s^{\alpha}}{\partial Z}\Big|_{Z=0}\Phi_1(X,\tau) = C_1^{\alpha}\left(1 - \tilde{\Gamma}_1\frac{\partial^2\Phi_1}{\partial X^2}\right), \tag{9}$$

$$C_s^{\alpha}\Big|_{Z=L_{\alpha}} + u\Big|_{Z=L_{\alpha}} + \frac{\partial C_s^{\alpha}}{\partial Z}\Big|_{Z=L_{\alpha}}\Phi_2(X,\tau) = C_2^{\alpha}\left(1 + \tilde{\Gamma}_2\frac{\partial^2\Phi_2}{\partial X^2}\right), \tag{10}$$

$$C_s^{\beta}\Big|_{Z=L_{\alpha}} + v\Big|_{Z=L_{\alpha}} + \frac{\partial C_s^{\beta}}{\partial Z}\Big|_{Z=L_{\alpha}}\Phi_2(X,\tau) = C_2^{\beta}\left(1 - \tilde{\Gamma}_2\frac{\partial^2\Phi_2}{\partial X^2}\right), \tag{11}$$

$$C_s^{\beta}\Big|_{Z=L_{\alpha}+L_{\beta}} + v\Big|_{Z=L_{\alpha}+L_{\beta}} + \frac{\partial C_s^{\beta}}{\partial Z}\Big|_{Z=L_{\alpha}+L_{\beta}}\Phi_3(X,t) = C_3^{\beta}\left(1 + \tilde{\Gamma}_3\frac{\partial^2\Phi_3}{\partial X^2}\right). \tag{12}$$

Here $\tilde{\Gamma}_i$, $i = 1, 2, 3$ are the capillary lengths,

$$C_i^{\alpha} = \delta_i^{\alpha}/\omega_{\alpha},\ i = 1, 2, \tag{13}$$

$$C_i^{\beta} = \delta_i^{\beta}/\omega_{\beta},\ i = 2, 3. \tag{14}$$

are the vacancy concentrations at the interfaces δ_i^α and δ_i^β are the deviations from stoichiometry at the corresponding boundaries, and ω_α, ω_β the molar volumes of the α- and β-phases. While C_1^α, C_3^β are determined by the partial pressure of oxygen at the right- and left hand sides of the oxide double layer, the concentrations C_2^α, C_2^β are determined by the local equilibrium between the adjacent oxide phases. The mass balance equations at the interfaces are

$$V + \dot{\Phi}_1(X,\tau) = \frac{\omega_\alpha}{1-\delta_1^\alpha} D_\alpha \left(\left.\frac{\partial C_s^\alpha}{\partial Z}\right|_{Z=0} + \left.\frac{\partial u}{\partial Z}\right|_{Z=0} + \left.\frac{\partial^2 C_s^\alpha}{\partial Z^2}\right|_{Z=0} \Phi_1(X,\tau) \right), \tag{15}$$

$$V + \dot{\Phi}_2(X,\tau) =$$

$$= \left[\frac{3-\delta_2^\beta}{\omega_\beta} - \frac{1-\delta_2^\alpha}{\omega_\alpha} \right]^{-1} \left[D_\beta \left(\left.\frac{\partial C_s^\beta}{\partial Z}\right|_{Z=L_\alpha} + \left.\frac{\partial v}{\partial Z}\right|_{Z=L_\alpha} + \left.\frac{\partial^2 C_s^\beta}{\partial Z^2}\right|_{Z=L_\alpha} \Phi_2(X,\tau) \right) - \right. \tag{16}$$

$$\left. - D_\alpha \left(\left.\frac{\partial C_s^\alpha}{\partial Z}\right|_{Z=L_\alpha} + \left.\frac{\partial u}{\partial Z}\right|_{Z=L_\alpha} + \left.\frac{\partial^2 C_s^\alpha}{\partial Z^2}\right|_{Z=L_\alpha} \Phi_2(X,\tau) \right) \right],$$

$$V + \dot{\Phi}_3(X,\tau) =$$

$$= \frac{\omega_\beta}{3-\delta_1^\beta} D_\beta \left(\left.\frac{\partial C_s^\beta}{\partial Z}\right|_{Z=L_\alpha+L_\beta} + \left.\frac{\partial v}{\partial Z}\right|_{Z=L_\alpha+L_\beta} + \left.\frac{\partial^2 C_s^\beta}{\partial Z^2}\right|_{Z=L_\alpha+L_\beta} \Phi_3(X,\tau) \right). \tag{17}$$

If we look for the stationary ('zero order') solution, which is only Z-dependent, both the equation (2) and the boundary conditions (9)–(17) simplify essentially. The corresponding system of equations and the boundary conditions are given in Appendix 1; the stationary values of the layer widths L_α, L_β and the velocity V are now

$$L_\alpha = L_0 D_\alpha \frac{1-\delta_0^\alpha}{\omega_\alpha} \left[\frac{D_\alpha}{\omega_\alpha}\left(\delta_2^\alpha - \delta_1^\alpha\right) + \frac{D_\beta}{\omega_\beta}\left(\delta_3^\beta - \delta_2^\beta\right) \right]^{-1} \ln \frac{1-\delta_1^\alpha}{1-\delta_2^\alpha}, \tag{18}$$

$$L_\beta = L_0 D_\beta \frac{1-\delta_0^\alpha}{\omega_\alpha} \left[\frac{D_\alpha}{\omega_\alpha}\left(\delta_2^\alpha - \delta_1^\alpha\right) + \frac{D_\beta}{\omega_\beta}\left(\delta_3^\beta - \delta_2^\beta\right) \right]^{-1} \ln \frac{3-\delta_2^\beta}{3-\delta_3^\beta}, \tag{19}$$

$$V = \frac{\omega_\alpha}{L_0\left(1-\delta_0^\alpha\right)} \left[\frac{D_\alpha}{\omega_\alpha}\left(\delta_2^\alpha - \delta_1^\alpha\right) + \frac{D_\beta}{\omega_\beta}\left(\delta_3^\beta - \delta_2^\beta\right) \right]. \tag{20}$$

Naturally, setting $\delta_3^\beta = \delta_2^\beta$ in (18) we regain the expression for the stationary width of a single α-layer [10, 7], and setting $\delta_2^\alpha = \delta_1^\alpha$ in (19) we obtain the similar expression for the single β-layer.

3. STABILITY ANALYSIS FOR TWO OXIDE LAYERS

In the Part I this paper [7], we have studied the coupled morphological stability of two phase boundaries for oxides that are exposed to an oxygen potential gradient. For a single oxide layer this problem was first considered in [10], both experimentally and theoretically. It was shown that the oxidizing boundary is morphologically stable, while the reducing boundary becomes unstable. In the Part I [7] of the present work the problem of [10] was generalized in an important way: in exploring the morphological stability of two solid/gas interfaces their diffusional interaction was taken into account. In the present communication we study the system of two adjacent oxide layers, *i.e.* the morphological stability of the three diffusionally interacting boundaries.

For two oxide layers, that is three interphase boundaries (see Fig. 1), the governing equations for the first order perturbations are, see (2)–(5):

$$\frac{1}{D_\alpha}\frac{\partial u}{\partial \tau} = \frac{V}{D_\alpha}\frac{\partial u}{\partial Z} + \frac{\partial^2 u}{\partial X^2} + \frac{\partial^2 u}{\partial Z^2}, \tag{21}$$

$$\frac{1}{D_\beta}\frac{\partial v}{\partial \tau} = \frac{V}{D_\beta}\frac{\partial v}{\partial Z} + \frac{\partial^2 v}{\partial X^2} + \frac{\partial^2 v}{\partial Z^2}, \tag{22}$$

From (9)–(12) and (15)–(17), the boundary conditions and the mass balance equations for the first order perturbations are

$$u\big|_{Z=0} + \frac{V}{D_\alpha}\frac{1-\delta_1^\alpha}{\omega_\alpha}\Phi_1(X,\tau) + \frac{\delta_1^\alpha}{\omega_\alpha}\tilde{\Gamma}_1\frac{\partial^2\Phi_1}{\partial X^2} = 0, \tag{23}$$

$$u\big|_{Z=L_\alpha} + \frac{V}{D_\alpha}\frac{1-\delta_2^\alpha}{\omega_\alpha}\Phi_2(X,\tau) - \frac{\delta_2^\alpha}{\omega_\alpha}\tilde{\Gamma}_2\frac{\partial^2\Phi_2}{\partial X^2} = 0, \tag{24}$$

$$v\big|_{Z=L_\alpha} + \frac{V}{D_\beta}\frac{3-\delta_2^\beta}{\omega_\beta}\Phi_2(X,\tau) + \frac{\delta_2^\beta}{\omega_\beta}\tilde{\Gamma}_2\frac{\partial^2\Phi_2}{\partial X^2} = 0, \tag{25}$$

$$v\big|_{Z=L_\alpha+L_\beta} + \frac{V}{D_\beta}\frac{3-\delta_3^\beta}{\omega_\beta}\Phi_3(X,\tau) - \frac{\delta_3^\beta}{\omega_\beta}\tilde{\Gamma}_3\frac{\partial^2\Phi_3}{\partial X^2} = 0, \tag{26}$$

$$\frac{1}{D_\alpha}\frac{\partial \Phi_1}{\partial \tau} = \frac{\omega_\alpha}{1-\delta_1^\alpha}\frac{\partial u}{\partial Z}\bigg|_{Z=0} - \left(\frac{V}{D_\alpha}\right)^2\Phi_1(X,\tau), \tag{27}$$

$$\frac{\partial \Phi_2}{\partial \tau} = \left[\frac{3-\delta_2^\beta}{\omega_\beta} - \frac{1-\delta_2^\alpha}{\omega_\alpha}\right]^{-1}\left[D_\beta\left(\frac{\partial v}{\partial Z}\bigg|_{Z=L_\alpha} - \frac{3-\delta_2^\beta}{\omega_\beta}\left(\frac{V}{D_\beta}\right)^2\Phi_2\left(X,\tau\right)\right) - \right. \tag{28}$$

$$-D_\alpha\left(\left.\frac{\partial u}{\partial Z}\right|_{Z=L_\alpha} - \frac{1-\delta_2^\alpha}{\omega_\alpha}\left(\frac{V}{D_\alpha}\right)^2 \Phi_2(X,\tau)\right)\Bigg],$$

$$\frac{1}{D_\beta}\frac{\partial \Phi_3}{\partial \tau} = \frac{\omega_\beta}{3-\delta_3^\beta}\left.\frac{\partial v}{\partial Z}\right|_{Z=L_\alpha+L_\beta} - \left(\frac{V}{D_\beta}\right)^2 \Phi_3(X,\tau). \tag{29}$$

Here we have used the formulae (91)–(94) from the Appendix 1. Taking the stationary width L_α of the α-phase layer as the length scale and, correspondingly rescaling all other lengths $Z/L_\alpha = z$, $X/L_\alpha = x$, $\Phi_i/L_\alpha = \varphi_i$, $\tilde{\Gamma}_i/L_\alpha = \Gamma_i$, and time $\tau/(L_\alpha^2/D_\alpha) = t$, measuring u, v in molar fractions $\omega_\alpha u = \tilde{u}$, $\omega_\beta v = \tilde{v}$, and defining $l = L_\beta/L_\alpha$, we are led to the dimensionless system of equations for the perturbations of concentration fields

$$\frac{\partial \tilde{u}}{\partial t} = 2\xi\frac{\partial \tilde{u}}{\partial z} + \frac{\partial^2 \tilde{u}}{\partial x^2} + \frac{\partial^2 \tilde{u}}{\partial z^2},\ 0 < z < 1, \tag{30}$$

$$\theta\frac{\partial \tilde{v}}{\partial t} = 2\xi\theta\frac{\partial \tilde{v}}{\partial z} + \frac{\partial^2 \tilde{v}}{\partial x^2} + \frac{\partial^2 \tilde{v}}{\partial z^2},\ 1 < z < l, \tag{31}$$

where

$$\xi = \frac{VL_\alpha}{2D_\alpha} = \frac{1}{2}\ln\frac{1-\delta_1^\alpha}{1-\delta_2^\alpha},\ \theta = \frac{D_\alpha}{D_\beta}. \tag{32}$$

The boundary conditions (23)–(29) become

$$\left.\tilde{u}\right|_{z=0} + 2\xi(1-\delta_1^\alpha)\varphi_1(x,t) + \delta_1^\alpha\Gamma_1\frac{\partial^2\varphi_1}{\partial x^2} = 0, \tag{33}$$

$$\left.\tilde{u}\right|_{z=1} + 2\xi(1-\delta_2^\alpha)\varphi_2(x,t) - \delta_2^\alpha\Gamma_2\frac{\partial^2\varphi_2}{\partial x^2} = 0, \tag{34}$$

$$\left.\tilde{v}\right|_{z=1} + 2\xi\theta(3-\delta_2^\beta)\varphi_2(x,t) + \delta_2^\beta\Gamma_2\frac{\partial^2\varphi_2}{\partial x^2} = 0, \tag{35}$$

$$\left.\tilde{v}\right|_{z=1+l} + 2\xi\theta(3-\delta_3^\beta)\varphi_3(x,t) - \delta_3^\beta\Gamma_3\frac{\partial^2\varphi_3}{\partial x^2} = 0, \tag{36}$$

$$\frac{\partial\varphi_1}{\partial t} = \frac{1}{1-\delta_1^\alpha}\left.\frac{\partial\tilde{u}}{\partial z}\right|_{z=0} - 4\xi^2\varphi_1(x,t), \tag{37}$$

$$(\rho-1)\frac{\partial\varphi_2}{\partial t} = \frac{\rho}{\theta\left(3-\delta_2^\beta\right)}\left.\frac{\partial\tilde{v}}{\partial z}\right|_{z=1} - \frac{1}{1-\delta_2^\alpha}\left.\frac{\partial\tilde{u}}{\partial z}\right|_{z=1} + (1-\rho\theta)4\xi^2\varphi_2(x,t), \tag{38}$$

where

$$\rho = \frac{\left(3 - \delta_2^\beta\right)\omega_\alpha}{\omega_\beta\left(1 - \delta_2^\alpha\right)} \tag{39}$$

is the ratio of the metal atoms equilibrium concentrations (per unit volume) for two oxides at their common boundary, and

$$\theta\frac{\partial\varphi_3}{\partial t} = \frac{1}{3 - \delta_3^\beta}\left.\frac{\partial\tilde{v}}{\partial z}\right|_{z=1+l} - 4\theta^2\xi^2\varphi_3(x, t). \tag{40}$$

Introducing the Fourier transforms

$$\varphi_j(x, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\,\exp(ikx)\overline{\varphi}_j(k, t),\ j = 1, 2, 3, \tag{41}$$

$$\tilde{u}(x, z, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\,\exp(ikx)\overline{u}(k, z, t), \tag{42}$$

$$\tilde{v}(x, z, t) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} dk\,\exp(ikx)\overline{v}(k, z, t). \tag{43}$$

We obtain from (30), (31), (33)–(38), and (40):

$$\frac{\partial\overline{u}}{\partial t} = 2\xi\frac{\partial\overline{u}}{\partial z} + \frac{\partial^2\overline{u}}{\partial z^2} - k^2\overline{u}, \tag{44}$$

$$\theta\frac{\partial\overline{v}}{\partial t} = 2\xi\theta\frac{\partial\overline{v}}{\partial z} + \frac{\partial^2\overline{v}}{\partial x^2} - k^2\overline{v}, \tag{45}$$

$$\left.\overline{u}\right|_{z=0} + 2\xi(1 - \delta_1^\alpha)\overline{\varphi}_1 - \delta_1^\alpha\Gamma_1 k^2\overline{\varphi}_1 = 0, \tag{46}$$

$$\left.\overline{u}\right|_{z=1} + 2\xi(1 - \delta_2^\alpha)\overline{\varphi}_2 + \delta_2^\alpha\Gamma_2 k^2\overline{\varphi}_2 = 0, \tag{47}$$

$$\left.\overline{v}\right|_{z=1} + 2\xi\theta(3 - \delta_2^\beta)\overline{\varphi}_2 - \delta_2^\beta\Gamma_2 k^2\overline{\varphi}_2 = 0, \tag{48}$$

$$\left.\overline{v}\right|_{z=1+l} + 2\xi\theta(3 - \delta_3^\beta)\overline{\varphi}_3 + \delta_3^\beta\Gamma_3 k^2\overline{\varphi}_3 = 0, \tag{49}$$

$$\frac{\partial\overline{\varphi}_1}{\partial t} = \frac{1}{1 - \delta_1^\alpha}\left.\frac{\partial\overline{u}}{\partial z}\right|_{z=0} - 4\xi^2\overline{\varphi}_1(k, t), \tag{50}$$

$$(\rho - 1)\frac{\partial\overline{\varphi}_2}{\partial t} = \frac{\rho}{\theta\left(3 - \delta_2^\beta\right)}\left.\frac{\partial\overline{v}}{\partial z}\right|_{z=1} - \frac{1}{1 - \delta_2^\alpha}\left.\frac{\partial\overline{u}}{\partial z}\right|_{z=1} + (1 - \rho\theta)4\xi^2\overline{\varphi}_2(k, t), \tag{51}$$

$$\theta\frac{\partial\overline{\varphi}_3}{\partial t} = \frac{1}{3 - \delta_3^\beta}\left.\frac{\partial\overline{v}}{\partial z}\right|_{z=1+l} - 4\theta^2\xi^2\overline{\varphi}_3(k, t), \tag{52}$$

Following the approach in Part I [7], we again introduce a new variable that is we add a fictitious ‘dissipation’, which may be adjusted to compensate the possible instability:

$$w^{\alpha} = \bar{u}\exp(-\eta t), \tag{53}$$

$$w^{\beta} = \bar{v}\exp(-\eta t), \tag{54}$$

$$\gamma_i = \bar{\varphi}_i \exp(-\eta t),\ i = 1, 2, 3, \tag{55}$$

where the constant $\eta > 0$ is undetermined; the upper index α refers to the AO layer (α-phase), and the index β refers to the A_3O_4 layer (β-phase). In terms of these new variables (44), (45) become:

$$\frac{\partial w^{\alpha}}{\partial t} = 2\xi\frac{\partial w^{\alpha}}{\partial z} + \frac{\partial^2 w^{\alpha}}{\partial z^2} - (k^2 + \eta)w^{\alpha}, \tag{56}$$

$$\theta\frac{\partial w^{\beta}}{\partial t} = 2\xi\theta\frac{\partial w^{\beta}}{\partial z} + \frac{\partial^2 w^{\beta}}{\partial z^2} - (k^2 + \eta)w^{\beta}. \tag{57}$$

The boundary conditions (46)–(49) do not change their form:

$$w^{\alpha}\Big|_{z=0} + \left[2\xi(1-\delta_1^{\alpha}) - \delta_1^{\alpha}\Gamma_1 k^2\right]\gamma_1 = 0, \tag{58}$$

$$w^{\alpha}\Big|_{z=1} + \left[2\xi(1-\delta_2^{\alpha}) + \delta_2^{\alpha}\Gamma_2 k^2\right]\gamma_2 = 0, \tag{59}$$

$$w^{\beta}\Big|_{z=1} + \left[2\xi\theta(3-\delta_2^{\beta}) - \delta_2^{\beta}\Gamma_2 k^2\right]\gamma_2 = 0, \tag{60}$$

$$w^{\beta}\Big|_{z=1+l} + \left[2\xi\theta(3-\delta_3^{\beta}) + \delta_3^{\beta}\Gamma_3 k^2\right]\gamma_3 = 0, \tag{61}$$

and the boundary conditions (50)–(52) become

$$\frac{\partial\gamma_1}{\partial t} = \frac{1}{1-\delta_1^{\alpha}}\frac{\partial w^{\alpha}}{\partial z}\Bigg|_{z=0} - \left[4\xi^2 + \eta\right]\gamma_1(k,t), \tag{62}$$

$$\begin{aligned}(\rho-1)\frac{\partial\gamma_2}{\partial t} = {} & \frac{\rho}{\theta\left(3-\delta_2^{\beta}\right)}\frac{\partial w^{\beta}}{\partial z}\Bigg|_{z=1} - \frac{1}{1-\delta_2^{\alpha}}\frac{\partial w^{\alpha}}{\partial z}\Bigg|_{z=1} + \\ & + \left[(1-\rho)\eta + (1-\rho\theta)4\xi^2\right]\gamma_2(k,t),\end{aligned} \tag{63}$$

$$\theta\frac{\partial\gamma_3}{\partial t} = \frac{1}{3-\delta_3^{\beta}}\frac{\partial w^{\beta}}{\partial z}\Bigg|_{z=1+l} - \left[4\theta^2\xi^2 + \theta\eta\right]\gamma_3(k,t). \tag{64}$$

As in the Part1, in the present work we are mainly targeting the effect of the diffusional interaction of the moving boundaries on their morphological stability. All renormalized capillary lengths are quite small ($\Gamma_i = \tilde{\Gamma}_i/L \sim 10^{-6}$ or less). That is, the influence of surface tension may be essential only for the perturbations with the very short wave lengths. So, to make our further considerations most transparent we take again $\Gamma_1 = \Gamma_2 = \Gamma_3 = 0$, and, additionally $\theta = 1$, *i.e.* we presume equal diffusion coefficients for both oxide phases as this simplifies all formulae essentially, in analogy to the 'Stationary symmetric model' of Langer [14]. The influence of the different diffusion coefficients and non-zero surface tension will be studied elsewhere.

To explore the stability of diffusionally interacting boundaries in Part I the method developed in [11, 12] was applied. Based on integral transformation of a special kind which was introduced by Chekmaryova [13], this method exactly reveals the evolution of the boundaries' perturbations without solving the diffusional problem inside the layer. It followed from the exact approach that the characteristic time for the development of the instability is $\sim 1/(2\xi k)$, where k is the wave vector and the non-dimensional parameter ξ was introduced in (32). The deviations from the stoichiometry at the boundaries are quite small; then ξ is a small parameter too. This means that the characteristic time for the development of the instability is large as compared to the characteristic time of the diffusional relaxation inside the layer (which we have taken as a time scale, see Section 2). Then we can use the quasi-stationary approximation, that is, drop the time derivative in the diffusion equation. It was shown in Part I [7] that the approximate analysis of morphological stability based on the quasi-stationary solution yields essentially the same results as the exact approach. Now it is evident that for a multi-layer system the ratio of characteristic times will not change qualitatively (if the diffusion coefficients in the layers are not too different), so application of the much simpler approximate method is again justified.

In the quasi-stationary approximation instead of (56), (57) we consider

$$\frac{\partial^2 w^\alpha}{\partial z^2} + 2\xi \frac{\partial w^\alpha}{\partial z} - (k^2 + \eta) w^\alpha = 0, \tag{65}$$

$$\frac{\partial^2 w^\beta}{\partial z^2} + 2\xi \frac{\partial w^\beta}{\partial z} - (k^2 + \eta) w^\beta = 0 \tag{66}$$

with the boundary conditions, see (58)–(61),

$$w^\alpha \Big|_{z=0} = -2\xi(1 - \delta_1^\alpha)\gamma_1, \tag{67}$$

$$w^\alpha \Big|_{z=1} = -2\xi(1 - \delta_2^\alpha)\gamma_2, \tag{68}$$

$$w^\beta \Big|_{z=1} = -2\xi(3 - \delta_2^\beta)\gamma_2, \tag{69}$$

$$w^\beta \Big|_{z=1+l} = -2\xi(3 - \delta_3^\beta)\gamma_3. \tag{70}$$

Here we only outline the most essential steps of the quite tedious solution procedure, moving all the details to the Appendix 2. First, the solutions (95), (96) of equations (65), (66) satisfying the boundary conditions (67)–(70) are obtained. Then the values of the derivatives $\frac{\partial w^{\alpha}}{\partial z}$ and $\frac{\partial w^{\beta}}{\partial z}$ at the corresponding boundaries are calculated, see Eqs. (97)–(100), and substituted into the boundary conditions (62)–(64); in this way we obtain the system of three ordinary linear equations (Eqs. (101)–(103) in Appendix 2) governing the time evolution of the renormalized boundary perturbations $\gamma_1(k,t)$, $\gamma_2(k,t)$, and $\gamma_3(k,t)$. Solution of this system is obtained in the same way as for the case of two boundaries, see [7]: substitution of $\gamma_1 = A\exp(\sigma t)$, $\gamma_2 = B\exp(\sigma t)$, and $\gamma_3 = C\exp(\sigma t)$ yields a linear homogeneous algebraic system for A, B, and C. For solutions of this system to exist the determinant (115) of this system should equal zero. After some algebra this yields the following equation for σ

$$\begin{aligned}\det(G_{ij}) &= \left[(2\xi^2+\eta+\sigma)^2-(2\xi\zeta)^2\right]\times\\ &\times\left[2\xi\zeta\operatorname{cth}\zeta l+2\rho\xi\zeta\operatorname{cth}\zeta+(1-\rho)(2\xi^2+\eta+\sigma)\right]=0.\end{aligned} \tag{71}$$

The very fact that the determinant (115) (with the elements given by (108)–(114)) is exactly reduced to the short expression (71), which is additionally decomposed in two parts, is remarkable! This is a direct consequence of the special feature both of the stationary solutions for the plain boundaries, and solutions (95), (96): *i.e.* the width of the layer and velocity are expressed *via* boundary conditions, and *vice versa*.

This equation has three roots: two roots are given by

$$(2\xi^2+\eta+\sigma)^2-(2\xi\zeta)^2=0 \tag{72}$$

and the third by

$$2\xi\zeta\operatorname{cth}\zeta l+2\rho\xi\zeta\operatorname{cth}\zeta+(1-\rho)(2\xi^2+\eta+\sigma)=0. \tag{73}$$

Now, ρ is the ratio of the metal atoms equilibrium concentration (per unit volume) for the higher oxide to that for the lower oxide at their common boundary, see (39); that is in most cases, *e.g.* AO and A_3O_4 (A = = Co, Ni, Fe....) $\rho < 1$. This means that the root of (73) is always negative, so only roots of (72) are of interest from the point of the possible instability:

$$\sigma_{1,2}=-(2\xi^2+\eta)\pm 2\xi\zeta. \tag{74}$$

The margin of stability corresponds to zero value of the largest root $\sigma_1 = 0$. In its turn this means $\eta = 2\xi k$. Again, as in the Part I [7], in terms of the Fourier modes of the boundaries' perturbations $\bar{\varphi}_i, i = 1, 2$ this means the increment $\eta = 2\xi k$ for the k-th mode. Correspondingly, to compare the amplitudes at the onset of instability we need only A_1, B_1, and C_1. Exact (quite complicated) expressions for these amplitudes are given in Appendix 2. For the sake of simplicity, we discuss here only the case when $l = L_\beta/L_\alpha$ is not a small parameter, which means that the stationary widths of the layers are comparable. Then for k larger than one, *i.e.* for the perturbations with the wave length smaller than the widths of the layers, these expressions simplify drastically, see (137)–(139), and in terms the Fourier modes of the boundaries' perturbations $\bar{\varphi}_1(k,t)$, $\bar{\varphi}_2(k,t)$, and $\bar{\varphi}_3(k,t)$ we obtain:

$$\begin{aligned} &\bar{\varphi}_1(k,t) = A_1 \exp(2\xi k t), \\ &A_1 \approx \bar{\varphi}_1(k,0) - (1-\rho)\exp(-2\xi - k)\bar{\varphi}_2(k,0) - \rho\exp(-(2+l)\xi - k)\bar{\varphi}_1(k,0), \end{aligned} \tag{75}$$

$$\begin{aligned} &\bar{\varphi}_2(k,t) = B_1 \exp(2\xi k t), \\ &B_1 \approx \exp(-k)\bar{\varphi}_1(k,0) - (1-\rho)\exp\big(-2(\xi+k)\big)\bar{\varphi}_2(k,0) - \\ &- \rho\exp\big(-(2+l)\xi - 2k\big)\bar{\varphi}_3(k,0), \end{aligned} \tag{76}$$

$$\begin{aligned} &\bar{\varphi}_3(k,t) = C_1 \exp(2\xi k t), \\ &C_1 \approx \exp\big(-k(1+l)\big)\bar{\varphi}_1(k,0) - (1-\rho)\exp\big(-2\xi - k(2+l)\big)\bar{\varphi}_2(k,0) - \\ &- \rho\exp\big(-(2+l)\xi - k(2+l)\big)\bar{\varphi}_3(k,0). \end{aligned} \tag{77}$$

It's worth mentioning that for $\rho = 0$, *i.e.* only for a single oxide layer A_1 in (75) and B_1 in (76) are reduced to

$$A_1 \approx \gamma_1(0,k) - \exp(-2\xi - k)\gamma_2(0,k), \tag{78}$$

$$B_1 \approx \exp(-k)\gamma_1(0,k) - \exp\big(-2(\xi+k)\big)\gamma_2(0,k), \tag{79}$$

i.e. to corresponding expressions for the single layer [7].

It is evident from (75)–(77) that for the double oxide layer, *e.g.* AO/A_3O_4, the surface on the reducing side is again unstable. The stability of the intermediate boundary is practically the same (up to coefficient of order unity) as of the oxidizing surface for the single-oxide case. On the other hand the surface of the higher oxide on oxidizing side is even much more morphologically stable.

4. SUMMARY AND CONCLUSIONS

In this paper, we have studied the coupled morphological stability of multiple phase boundaries for oxides that are exposed to an oxygen potential gradient. For a single oxide layer this problem was considered in [10], both experimentally and theoretically. It was shown that while the oxidizing boundary is morphologically stable, the reducing boundary becomes unstable. In the present work the problem of [10] is generalized in two ways: first, in exploring the morphological stability of the interfaces their diffusional interaction is taken into account; second we consider two oxide layers with two solid/gas interfaces and one solid/solid interface. Considering a single layer in [7] we first applied original exact method.

Based on an integral transformation of a special kind, this method reveals the evolution of the multiple boundaries' perturbations without solving the diffusional problem inside the layer. The study of the morphological stability of the stationary moving boundaries was thereby reduced to exploration of the singular points (in the complex plane) of the corresponding integrands. While being exact, the above approach is quite complicated. So it appeared reasonable to check the simpler but approximate way of solution of the same problem, compare the results, and then use the simpler approximate approach to solve the essentially more complicated problem for the two-layer system. The approximate approach is based on the important result of the exact method: the characteristic time for the development of the instability is large as compared to the characteristic time of the diffusional relaxation inside the layer. Then the quasi-stationary approximation for the diffusion of vacancies can be used.

As it was mentioned in [7], from the formal point the result of [10] may look paradoxical: if the interaction of the boundaries is taken into account the perturbations of the boundaries are governed by a coupled linear system; a linear system could be either stable, or unstable as a whole; so formally both boundaries with necessity should be either stable or unstable. However, comparing (75)–(77) it is easily seen that the ratio of the perturbation amplitudes at the oxidizing side and solid/solid boundary to that at the reducing side decreases exponentially with the wave number k. This means that the boundary at the oxidizing side and solid/solid boundary are practically morphologically stable indeed. So to obtain a morphologically stable oxide layer it may be expedient to grow it on the base of lower oxide.

To unify notations with the Part 1 let us rewrite (75)–(77) as

$$\overline{\varphi}_i(k,t) = \sum_j \tilde{F}_{ij}\overline{\varphi}_j(k,0), \quad i,j = 1,2,3. \tag{80}$$

Here

$$\begin{aligned}\tilde{F}_{11} &= \exp(2\xi kt),\\ \tilde{F}_{12} &= -(1-\rho)\exp(-2\xi - k)\exp(2\xi kt),\\ \tilde{F}_{13} &= -\rho\exp\left(-(2+l)\xi - k\right)\exp(2\xi kt),\end{aligned} \tag{81}$$

$$\begin{aligned}
\tilde{F}_{21} &= \exp(-k)\exp(2\xi kt),\\
\tilde{F}_{22} &= -(1-\rho)\exp\left(-2(\xi+k)\right)\exp(2\xi kt),\\
\tilde{F}_{23} &= -\rho\exp\left(-(2+l)\xi-2k\right)\exp(2\xi kt),
\end{aligned} \tag{82}$$

$$\begin{aligned}
\tilde{F}_{31} &= \exp\left(-k(1+l)\right)\exp(2\xi kt),\\
\tilde{F}_{32} &= -(1-\rho)\exp\left(-2\xi-k(2+l)\right)\exp(2\xi kt),\\
\tilde{F}_{33} &= -\rho\exp\left(-(2+l)\xi-k(2+l)\right)\exp(2\xi kt).
\end{aligned} \tag{83}$$

Here the $\tilde{F}_{ij}$, $i, j = 1, 2, 3$ are introduced for three boundaries in the same way, as they were introduced in Part 1 for two. To visualize the mutual influence of the boundaries' perturbations it is practical to plot the $\ln\left|\tilde{F}_{ij} / \tilde{F}_{11}\right|$ against the wave number k. However, there is now a dependence on the ratio of the layer widths $l = L_\beta / L_\alpha$: for $l < 1$, see Fig. 2, and for $l > 1$, see Fig. 3.

Thus, for $l < 1$ both the self-influence of the solid/solid boundary and the influence of the oxidizing boundary on it decrease faster with

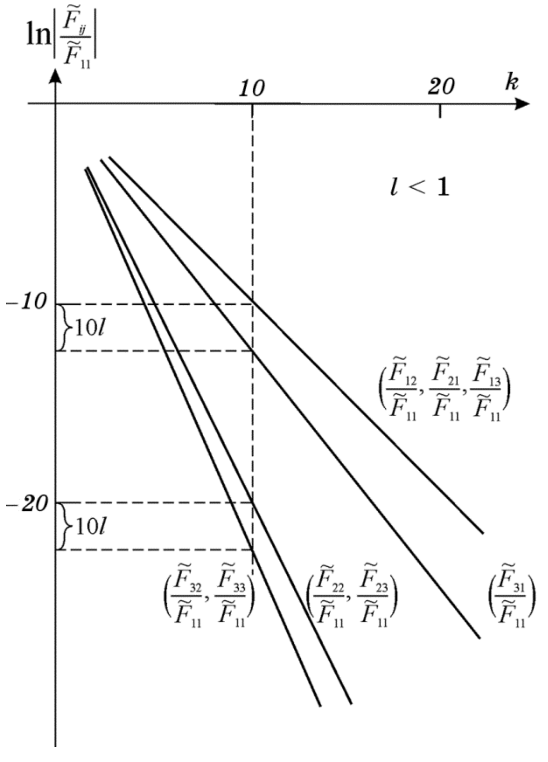

Fig. 2. The k-dependence of $\ln\left|\tilde{F}_{ii} / \tilde{F}_{11}\right|$ for the case $l < 1$.

the wave number than the influence of the reducing surface on the oxidizing surface. The situation is inversed when $l > 1$, *i.e.* when the width L_β is larger than the width L_α.

APPENDIX 1

If we look for the stationary ('zero order') solution which is only Z-dependent, the equations (2), (3), the equilibrium boundary conditions (9)–(12), and the mass balance equations (15)–(17) are reduced to

$$V\frac{dC_s^\alpha}{dZ} + D_\alpha \frac{d^2C_s^\alpha}{dZ^2} = 0, \; 0 < Z < L_\alpha, \tag{84}$$

$$V\frac{dC_s^\beta}{dZ} + D_\beta \frac{d^2C_s^\beta}{dZ^2} = 0, \; L_\alpha < Z < L_\alpha + L_\beta, \tag{85}$$

$$C_s^\alpha\Big|_{Z=0} = C_{\alpha 1}, \; C_s^\alpha\Big|_{Z=L_\alpha} = C_{\alpha 2}, \tag{86}$$

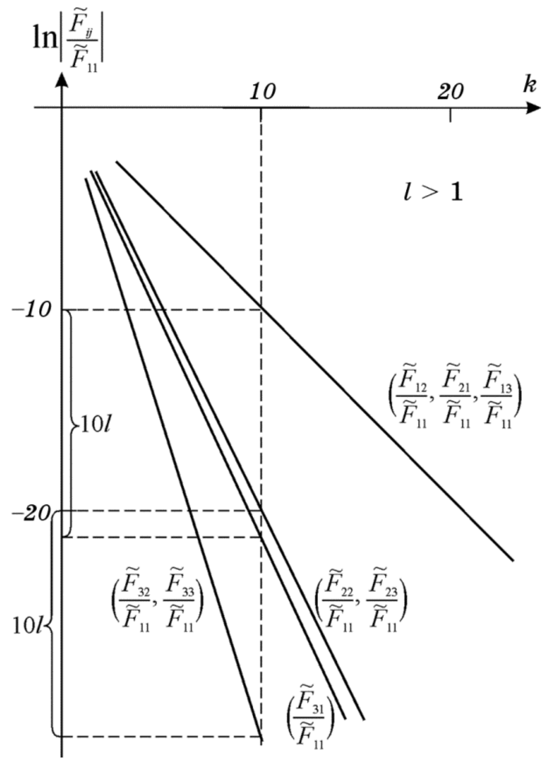

Fig. 3. The k-dependence of $\ln|\tilde F_{ii} / \tilde F_{11}|$ for the case $l > 1$.

$$C_s^\beta\Big|_{Z=L_\alpha} = C_{\beta 2}, \quad C_s^\beta\Big|_{Z=L_\alpha+L_\beta} = C_{\beta 3}, \tag{87}$$

$$V = \frac{\omega_\alpha}{1-\delta_1^\alpha} D_\alpha \frac{\partial C_s^\alpha}{\partial Z}\Bigg|_{Z=0}, \tag{88}$$

$$V = \left[\frac{3-\delta_2^\beta}{\omega_\beta} - \frac{1-\delta_2^\alpha}{\omega_\alpha}\right]^{-1}\left(D_\beta \frac{\partial C_s^\beta}{\partial Z}\Bigg|_{Z=L_\alpha} - D_\alpha \frac{\partial C_s^\alpha}{\partial Z}\Bigg|_{Z=L_\alpha}\right), \tag{89}$$

$$V = \frac{\omega_\beta}{3-\delta_3^\beta} D_\beta \frac{\partial C_s^\beta}{\partial Z}\Bigg|_{Z=L_\alpha+L_\beta}. \tag{90}$$

The solutions of the linear Eqs. (84), (85), satisfying boundary conditions (86), (87) are easily obtained. We will omit presenting here these lengthy expressions; substituting of these solutions into the mass balance equations (88)–(90) for the C_s^α and C_s^β, and accounting for the conservation of metal atoms, yields the expressions for the widths of the layers (18), (19) and the stationary velocity (20). Actually, for the exploration of stability we will need only these formulae for the widths of the layers (18), (19), for the stationary velocity (20), and for the values of the derivatives $\frac{\partial C_s^\alpha}{\partial Z}$, $\frac{\partial C_s^\beta}{\partial Z}$ and $\frac{\partial^2 C_s^\alpha}{\partial Z^2}$, $\frac{\partial^2 C_s^\beta}{\partial Z^2}$ at corresponding boundaries:

$$\frac{\partial C_s^\alpha}{\partial Z}\Bigg|_{Z=0} = \frac{V}{D_\alpha}\frac{1-\delta_1^\alpha}{\omega_\alpha}, \quad \frac{\partial^2 C_s^\alpha}{\partial Z^2}\Bigg|_{Z=0} = -\left(\frac{V}{D_\alpha}\right)^2 \frac{1-\delta_1^\alpha}{\omega_\alpha}, \tag{91}$$

$$\frac{\partial C_s^\alpha}{\partial Z}\Bigg|_{Z=L_\alpha} = \frac{V}{D_\alpha}\frac{1-\delta_2^\alpha}{\omega_\alpha}, \quad \frac{\partial^2 C_s^\alpha}{\partial Z^2}\Bigg|_{Z=L_\alpha} = -\left(\frac{V}{D_\alpha}\right)^2 \frac{1-\delta_2^\alpha}{\omega_\alpha}, \tag{92}$$

$$\frac{\partial C_s^\beta}{\partial Z}\Bigg|_{Z=L_\alpha} = \frac{V}{D_\beta}\frac{3-\delta_2^\beta}{\omega_\beta}, \quad \frac{\partial^2 C_s^\beta}{\partial Z^2}\Bigg|_{Z=L_\alpha} = -\left(\frac{V}{D_\beta}\right)^2 \frac{3-\delta_2^\beta}{\omega_\beta}, \tag{93}$$

$$\frac{\partial C_s^\beta}{\partial Z}\Bigg|_{Z=L_\alpha+L_\beta} = \frac{V}{D_\beta}\frac{3-\delta_3^\beta}{\omega_\beta}, \quad \frac{\partial^2 C_s^\beta}{\partial Z^2}\Bigg|_{Z=L_\alpha+L_\beta} = -\left(\frac{V}{D_\beta}\right)^2 \frac{3-\delta_3^\beta}{\omega_\beta}. \tag{94}$$

APPENDIX 2

The solutions of (65), (66) satisfying boundary conditions (67)–(70) are easily obtained

$$w^{\alpha} = \frac{2\xi}{\exp(\lambda_1) - \exp(\lambda_2)} \Big\{ \Big[(1 - \delta_1^{\alpha}) \exp(\lambda_2)\gamma_1 - (1 - \delta_2^{\alpha})\gamma_2 \Big] \exp(\lambda_1 z) + \\ + \Big[(1 - \delta_2^{\alpha})\gamma_2 - (1 - \delta_1^{\alpha}) \exp(\lambda_1)\gamma_1 \Big] \exp(\lambda_2 z) \Big\}, \tag{95}$$

$$w^{\beta} = \frac{2\xi}{\exp(\lambda_1 l) - \exp(\lambda_2 l)} \Big\{ \Big[(3 - \delta_2^{\beta}) \exp(\lambda_2 l)\gamma_2 - (3 - \delta_3^{\beta})\gamma_3 \Big] \times \\ \times \exp(\lambda_1 (z - 1)) + \Big[(3 - \delta_3^{\beta})\gamma_3 - (3 - \delta_2^{\beta}) \exp(\lambda_1 l)\gamma_2 \Big] \exp(\lambda_2 (z - 1)) \Big\}, \tag{96}$$

where $\lambda_1 = -\xi + \zeta$, $\lambda_2 = -\xi - \zeta$, and $\zeta = \left|\sqrt{\xi^2 + k^2 + \eta}\right|$. Below we need $\left.\frac{\partial w^{\alpha}}{\partial z}\right|_{z=0}$, $\left.\frac{\partial w^{\alpha}}{\partial z}\right|_{z=1}$, $\left.\frac{\partial w^{\beta}}{\partial z}\right|_{z=1}$, and $\left.\frac{\partial w^{\beta}}{\partial z}\right|_{z=1+l}$ only, that is the values of derivatives at the boundaries.

$$\frac{1}{1 - \delta_1^{\alpha}} \left.\frac{\partial w^{\alpha}}{\partial z}\right|_{z=0} = 2\xi \left[(\xi + \zeta \operatorname{cth}\zeta)\gamma_1 - \frac{\zeta \exp(-\xi)}{\operatorname{sh}\zeta} \gamma_2 \right], \tag{97}$$

$$\frac{1}{1 - \delta_2^{\alpha}} \left.\frac{\partial w^{\alpha}}{\partial z}\right|_{z=1} = 2\xi \left[(\xi - \zeta \operatorname{cth}\zeta)\gamma_2 + \frac{\zeta \exp(\xi)}{\operatorname{sh}\zeta} \gamma_1 \right], \tag{98}$$

$$\frac{1}{3 - \delta_2^{\beta}} \left.\frac{\partial w^{\beta}}{\partial z}\right|_{z=1} = 2\xi \left[(\xi + \zeta \operatorname{cth}\zeta l)\gamma_2 - \frac{\zeta \exp(-\xi l)}{\operatorname{sh}\zeta l} \gamma_3 \right], \tag{99}$$

$$\frac{1}{3 - \delta_3^{\beta}} \left.\frac{\partial w^{\beta}}{\partial z}\right|_{z=1+l} = 2\xi \left[(\xi - \zeta \operatorname{cth}\zeta l)\gamma_3 + \frac{\zeta \exp(\xi l)}{\operatorname{sh}\zeta l} \gamma_2 \right]. \tag{100}$$

Substituting these values into (62)–(64) we obtain the system of three ordinary differential equations for γ_1, γ_2, and γ_3:

$$\frac{\partial \gamma_1}{\partial t} = \left[2\xi\zeta \operatorname{cth}\zeta - 2\xi^2 - \eta \right] \gamma_1 - \frac{2\xi\zeta}{\operatorname{sh}\zeta} \exp(-\xi)\gamma_2, \tag{101}$$

$$(\rho - 1) \frac{\partial \gamma_2}{\partial t} = -\frac{2\xi\zeta}{\operatorname{sh}\zeta} \exp(\xi)\gamma_1 + P\gamma_2 - \frac{2\rho\xi\zeta}{\operatorname{sh}\zeta l} \exp(-\xi l)\gamma_3, \tag{102}$$

$$\frac{\partial \gamma_3}{\partial t} = \frac{2\xi\zeta}{\operatorname{sh}\zeta l} \exp(\xi l)\gamma_2 - \left[2\xi\zeta \operatorname{cth}\zeta l + 2\xi^2 + \eta \right] \gamma_3, \tag{103}$$

where we have denoted for brevity

$$P = \rho \left[2\xi\zeta \operatorname{cth}\zeta - 2\xi^2 - \eta \right] + \left[2\xi\zeta \operatorname{cth}\zeta l + 2\xi^2 + \eta \right]. \tag{104}$$

Solution of this system is obtained in the standard way: substitution of $\gamma_1 = A\exp(\sigma t)$, $\gamma_2 = B\exp(\sigma t)$, and $\gamma_3 = C\exp(\sigma t)$ yields a linear homogeneous algebraic system for A, B and C

$$G_{11}A + G_{12}B = 0, \tag{105}$$

$$G_{21}A + G_{22}B + G_{23}C = 0, \tag{106}$$

$$G_{32}B + G_{33}C = 0. \tag{107}$$

Here

$$G_{11} = 2\xi\zeta\,\mathrm{cth}\zeta - 2\xi^2 - \eta - \sigma, \tag{108}$$

$$G_{12} = -\frac{2\xi\zeta}{\mathrm{sh}\zeta}\exp(-\xi), \tag{109}$$

$$G_{21} = -\frac{2\xi\zeta}{\mathrm{sh}\zeta}\exp(\xi), \tag{110}$$

$$\begin{aligned} G_{22} &= P - (\rho - 1)\sigma = \\ &= \rho\left[2\xi\zeta\,\mathrm{cth}\zeta - 2\xi^2 - \eta - \sigma\right] + \left[2\xi\zeta\,\mathrm{cth}\zeta l + 2\xi^2 + \eta + \sigma\right], \end{aligned} \tag{111}$$

$$G_{23} = -\frac{2\rho\xi\zeta}{\mathrm{sh}\zeta l}\exp(-\xi l), \tag{112}$$

$$G_{32} = \frac{2\xi\zeta}{\mathrm{sh}\zeta l}\exp(\xi l), \tag{113}$$

$$G_{33} = -\left[2\xi\zeta\,\mathrm{cth}\zeta l + 2\xi^2 + \eta + \sigma\right]. \tag{114}$$

For solutions of this system to exist the determinant of this system should equal zero

$$\det\begin{pmatrix} G_{11} & G_{12} & 0 \\ G_{21} & G_{22} & G_{23} \\ 0 & G_{32} & G_{33} \end{pmatrix} = 0. \tag{115}$$

After some algebra (115) is exactly reduced to the following equation for σ

$$\begin{aligned} \det(G_{ij}) &= \left[(2\xi^2 + \eta + \sigma)^2 - (2\xi\zeta)^2\right] \times \\ &\times \left[2\xi\zeta\,\mathrm{cth}\zeta l + 2\rho\xi\zeta\,\mathrm{cth}\zeta + (1 - \rho)(2\xi^2 + \eta + \sigma)\right] = 0. \end{aligned} \tag{116}$$

As it is explained in Section 3, the root given by

$$2\xi\zeta\,\mathrm{cth}\zeta l + 2\rho\xi\zeta\,\mathrm{cth}\zeta + (1 - \rho)(2\xi^2 + \eta + \sigma) = 0 \tag{117}$$

is negative, so from the point of possible instability only the roots of

$$(2\xi^2 + \eta + \sigma)^2 - (2\xi\zeta)^2 = 0 \tag{118}$$

are of interest. Two roots of (118) are

$$\sigma_{1,2} = -(2\xi^2 + \eta) \pm 2\xi\zeta. \tag{119}$$

The solution of the system (105)–(107) is

$$\gamma_1 = A_1 \exp(\sigma_1 t) + A_2 \exp(\sigma_2 t) + A_3 \exp(\sigma_3 t), \tag{120}$$

$$\gamma_2 = B_1 \exp(\sigma_1 t) + B_2 \exp(\sigma_2 t) + B_3 \exp(\sigma_3 t), \tag{121}$$

$$\gamma_3 = C_1 \exp(\sigma_1 t) + C_2 \exp(\sigma_2 t) + C_3 \exp(\sigma_3 t). \tag{122}$$

The margin of stability corresponds to zero value of the largest root $\sigma_1 = 0$. In its turn this means $\eta = 2\xi k$. The coefficients A_n, B_n, and C_n are calculated in a standard way using initial values of $\gamma_i(0, k)$. Setting $t = 0$ in (120)–(122) yields

$$A_1 + A_2 + A_3 = \gamma_1(0, k), \tag{123}$$

$$B_1 + B_2 + B_3 = \gamma_2(0, k), \tag{124}$$

$$C_1 + C_2 + C_3 = \gamma_3(0, k). \tag{125}$$

Additionally, for each root σ_n Eqs. (105) and (107) give a link between A_n, B_n, and C_n:

$$G_{11}(\eta, \sigma_n)A_n + G_{12}(\eta)B_n = 0, \tag{126}$$

$$G_{32}(\eta)B_n + G_{33}(\eta, \sigma_n)C_n = 0. \tag{127}$$

We are looking for the amplitudes at the onset of instability, so we need only ‘marginal’ values of G_{ij}, that is

$$M_{ij}^n = G_{ij}(\eta, \sigma_n)\Big|_{\eta = 2\xi k}. \tag{128}$$

For off-diagonal elements which don’t depend on σ_n we drop the upper index. To calculate the diagonal elements we need the ‘marginal’ values of σ_n:

$$\sigma_1 = 0, \quad \sigma_2 = -4\xi(\xi + k), \tag{129}$$

$$\sigma_3 = -2\xi(\xi + k)\left[1 + \frac{\rho\,\mathrm{cth}(\xi + k) + \mathrm{cth}(l(\xi + k))}{1 - \rho}\right]. \tag{130}$$

Calculation of M_{ij}^n yields

$$M_{11}^n = 2\xi(\xi + k)[\mathrm{cth}(\xi + k) - 1] - \sigma_n, \tag{131}$$

$$M_{33}^n = -2\xi(\xi + k)[\mathrm{cth}(l(\xi + k)) + 1] - \sigma_n, \tag{132}$$

$$M_{12} = -2\xi(\xi + k)\frac{\exp(-\xi)}{\mathrm{sh}(\xi + k)}, \tag{133}$$

$$M_{32} = 2\xi(\xi + k)\frac{\exp(l\xi)}{\mathrm{sh}(l(\xi + k))}. \tag{134}$$

From (126), (127) we obtain

$$B_n = -\frac{M_{11}^n}{M_{12}}A_n, \quad C_n = \frac{M_{11}^n M_{32}}{M_{12}M_{33}^n}A_n. \tag{135}$$

To compare the amplitudes at the onset of instability we need only A_1, B_1, and C_1. Using (123)–(125) and (135) we finally get

$$\begin{gathered} A_1 = \left[(M_{11}^3 - M_{11}^1)\left(1 - \frac{M_{11}^1 M_{33}^2}{M_{11}^2 M_{33}^1}\right)\right]^{-1} \times \\ \times\left[\gamma_{10}M_{11}^3 + \gamma_{20}M_{12}\left(1 - \frac{M_{33}^2}{M_{11}^2}\right) - \gamma_{30}\frac{M_{12}M_{33}^3 M_{33}^2}{M_{32}M_{11}^2}\right], \end{gathered} \tag{136}$$

as well as corresponding expressions for B_1 and C_1. For large k the approximate expressions for these amplitudes become:

$$\begin{gathered} A_1 \approx \gamma_1(0, k) - (1 - \rho)\exp(-2\xi - k)\gamma_2(0, k) - \\ - \rho\exp(-(2 + l)\xi - k)\gamma_3(0, k), \end{gathered} \tag{137}$$

$$\begin{gathered} B_1 \approx \exp(-k)\gamma_1(0, k) - (1 - \rho)\exp(-2(\xi + k))\gamma_2(0, k) - \\ - \rho\exp(-(2 + l)\xi - 2k)\gamma_3(0, k), \end{gathered} \tag{138}$$

$$\begin{gathered} C_1 \approx \exp(-k(1 + l))\gamma_1(0, k) - (1 - \rho)\exp(-2\xi - k(2 + l))\gamma_2(0, k) - \\ - \rho\exp(-(2 + l)\xi - k(2 + l))\gamma_3(0, k). \end{gathered} \tag{139}$$

REFERENCES

1. P. O. Mchedlov-Petrosyan and M. Martin, *Metallofiz. Noveishie Tekhnol.*, **41**, No. 11: 1433 (2019).
2. G. H. Meier, *Oxidation of Intermetallics* (Eds. H. J. Grabke and M. Schütze) (Weinheim: Wiley-VCH: 1997), p. 15.
3. U. Koops, D. Hesse, and M. Martin, *J. Mater. Res.*, **17**: 2489 (2002).
4. E. Ryshkewitch and D. W. Richerson, *Oxide Ceramics* (Orlando: Academic:

1985).
5. A. Hammou and J. Guindet, *The CRC Handbook of Solid State Electrochemistry* (Eds. P. J. Gellings and H. J. M. Bouwmeester) (Boca Raton: CRC Press: 1996), p. 407.
6. H. J. M. Bouwmeester and A. J. Burggraaf, *The CRC Handbook of Solid State Electrochemistry* (Eds. P. J. Gellings and H. J. M. Bouwmeester) (Boca Raton: CRC Press: 1996), p. 481.
7. J. S. Langer, *Rev. Modern Phys.*, **52**: 1 (1980).
8. Y. Aoki, C. Wiemann, V. Feyer, H.-S.Kim, C. M. Schneider, H.-S. Yoo, and M. Martin, *Nat. Commun.*, **5**: 3473 (2014).
9. D.-H. Kwon, S. Lee, C. S. Kang, Y. S. Choi, S. J. Kang, H. L. Cho, W. Sohn, J. Jo, S.-Y. Lee, K. H. Oh, T. W. Noh, R. A. De Souza, M. Martin, and M. Kim, *Adv. Mater.*, **31**: 1901322 (2019).
10. M. Martin and H. Schmalzried, *Ber. Bunsenges. Phys. Chem.*, **89**: 124 (1985).
11. P. O. Mchedlov-Petrossyan, *Dopov. Nac. Akad. Nauk Ukr.*, No. 1: 78 (2002).
12. P. O. Mchedlov-Petrossyan, *Metallofiz. Noveishie Tekhnol.*, **24**: 25 (2002).
13. O. M. Chekmareva, *J. Techn. Phys.*, **XLI**: 1115 (1971) (in Russian).
14. J. S. Langer and L. A. Turski, *Acta Metalurgica*, **25**: 1113 (1977).