BI-VELOCITY REACTIVE MASS TRANSPORT PHENOMENOLOGY; MODELING OF CVD PROCESS

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Abstract

This paper presents a numerical method to determine the concentration profile during the aluminization process. The quantitative description of the diffusion controlled Chemical Vapor Deposition (CVD) of the coating formation is shown. The method is based on volume fixed frame of reference. It allows computing the material velocity in the reacting system in which reactions at several moving interfaces occur. All reactions lead to the lattice shift due to the difference of intrinsic diffusivities and different molar volumes. It is shown that the derived set of partial differential equations describing the reactive diffusion is thermodynamically consistent and can be used in advanced modeling.

Key words: CVD, multiphase system, Kirkendall shift, volume continuity equation

1. INTRODUCTION

CVD is a technique to improve the oxidation resistance of metallic materials like nickel and iron based alloys. It is crucial where parts like turbine blades are operated in a high temperature environment (Kohlscheen and Stock, 2007) and provides corrosion resistance at high temperatures and in corrosive environments (Wood at al., 1987; Goward, 1998). In oxidizing environment aluminum based coatings provide a self-healing, slow-growing, protective oxide scale on the surface, which prevent further oxidation and corrosion (John, Srinivasa et al., 2004; John, Kale at al., 2004). These coatings are produced by the diffusion of aluminum into the surface of a component by solid, liquid and vapor processes. Development of a model for the coating formation is useful to provide a theoretical basis for the advance CVD technology. In this work the following peculiarities are considered (1) the deviation from local equilibrium at both interfaces of each

moving inter-phase zone (i.e., at each side of the moving phase-boundary); (2) different mobility of the components in the interphase zone; (3) nonzero steps of molar volumes for each component from phase to phase and (4) different physicochemical properties of the interphase zones.

The bi-velocity (Darken) method is commonly accepted in materials science, where two velocities are always necessary to quantify the Kirkendall shift in solid solutions (Darken, 1948; Danielewski and Wierzba, 2010). The method is based on the postulate that each component's velocity must be divided into two parts: (i) the unique diffusion velocity, which depends on diffusion potential gradient (Balluffi at al., 2005) and is independent of the choice of the reference frame; and (ii) the drift velocity, which is common for all components and depend on the choice of the external reference frame.

In this article the effective use of the bi-velocity method and practical applications in the multiphase

systems as well as the quantitative description of the diffusion controlled processes from nano- to meter scale during the coatings formation is presented.

2.1. The conservation of mass

The core of the bi-velocity method is the mass balance equation:

$$\frac{\partial c_i^j}{\partial t} + \nabla \cdot \left(c_i^j {}^d \upsilon_i^j + c_i^j {}^D \upsilon^j \right) = 0$$

$$\text{for } i = 1, 2, ..., r \text{ and } j = 0, 1, ..., n \qquad (1)$$

where c_i^j denote concentration of the i-th component in the j-th phase, ${}^d J_i^j = c_i^j {}^d \upsilon_i^j$ is diffusion flux and ${}^d \upsilon_i^j$, ${}^D \upsilon^j$ are the unique diffusion and the drift (Darken) velocity.

The component diffusion flux, ${}^d J_i^j = c_i^j {}^d \upsilon_i^j$, should be expressed by the proper constitutive formula. In this work the Nernst-Planck flux equation is used (Nernst, 1889 and Planck, 1890):

$$^d \upsilon_i^j = -B_i^j \nabla \mu_i^j, \qquad (2)$$

where: B_i^j denote the mobility of the i-th component and μ_i^j is the diffusion potential, defined e.g. as a sum of chemical and mechanical potentials (Danielewski and Wierzba, 2010):

$$\mu_i^j = {}^{ch}\mu_i^j + {}^m\mu_i^j = {}^{ch}\mu_i^j + \Omega_i^j p^j \qquad (3)$$

The bi-velocity method implies the Darken drift velocity as a new variable that requires a new general relation, Volume Continuity Equation, shown in next section.

2.2. The Volume Continuity Equation

The Volume Continuity Equation (Danielewski and Wierzba, 2009; 2010) in case of "pure" Darken interdiffusion in j-th phase is reduced to the following form (the effects of stress is neglected):

$$^D \upsilon^j = -\sum_{i=1}^{r} \Omega_i^j {}^d J_i^j \qquad \text{for } j = 0, 1, ..., n \qquad (4)$$

where: Ω_i^j is the partial molar volume of the i-th component in the j-th phase.

2.3. Initial conditions

Initial conditions are arbitrary, e.g., can be given by any known functions:

1) arbitrary initial distributions of the components (in the solid solutions, alloys, only):

$$c_i(0, x) = c_i^0(x) \text{ for } i = 1, 2, ..., r \qquad (5)$$

2) the initial thickness of sub-layers (e.g. j-th phase):

$$\Delta X^j(t = 0) = X_0^j(R) - X_0^j(L) \quad \text{for } j = 0, ..., n$$

3) constant thicknesses of the phase boundary zones, δ^j

2.4. Boundary conditions at interfaces of the phase boundary

On each interface of the phase boundary zone one can postulate the para- or ortho-equilibrium conditions, figure 1. The boundary conditions are used to calculate the concentrations of the components on each side of the phase boundary zone and to calculate the reaction rates of each phase.
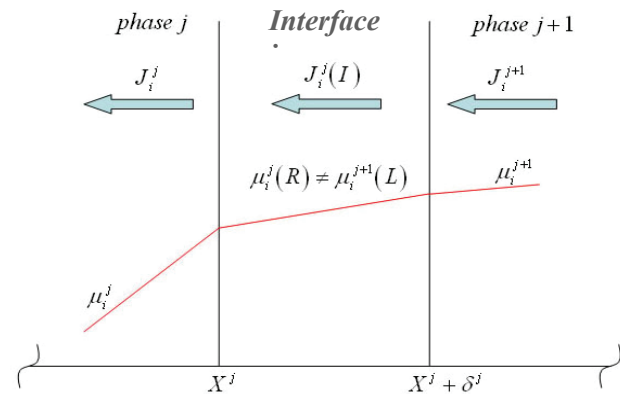
Fig. 1. Schema of the heterogeneous solid state reaction in the multiphase system. Mass transport within the phase boundary. The nanometer phase boundary zone between neighboring phases where on both interfaces the ortho-equilibrium conditions hold.

The volume produced due to the reaction (unbalanced fluxes) at the moving boundaries of j-phase follows from Leibnitz theorem and is given by:

$$\sum_i c_i^j \Omega_i^j \dot{X}^j(R) = \sum_i \left(c_i^j \Omega_i^j {}^d \upsilon_i^j + c_i^j \Omega_i^j {}^D \upsilon^j \right)(R) -$$

$$\sum_i \left(\langle c_i^j \Omega_i^j \rangle {}^d \upsilon_i^j + \langle c_i^j \Omega_i^j \rangle {}^D \upsilon^j \right)(I), \qquad (6)$$

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where $\sum_i \left(c_i^j \Omega_i^j \, {}^d\upsilon_i^j + c_i^j \Omega_i^j \, {}^D\upsilon^j \right)(R)$ and $\sum_i \left(\left\langle c_i^j \Omega_i^j \right\rangle {}^d\upsilon_i^j + \left\langle c_i^j \Omega_i^j \right\rangle {}^D\upsilon^j \right)(I)$ denote the volume fluxes at the right (R) boundary of j-phase and within the interphase (I), boundary zone, respectively, $\dot{X}^j = \mathrm{d}X^j / \mathrm{d}t$ denote the velocity of the j-phase right interface.

The mass balance at moving interfaces can be written as:

$$\left(c_i^j(R) - \left\langle c_i^j(I) \right\rangle \right) \dot{X}^j =$$

$$J_i^j(R) - {}^d J_i^j(I) - \left\langle c_i^j(I) \right\rangle {}^D\upsilon^j(I), \qquad (7)$$

$$\left(c_i^{j+1}(L) - \left\langle c_i^j(I) \right\rangle \right) \dot{X}^j =$$

$$J_i^{j+1}(L) - {}^d J_i^j(I) - \left\langle c_i^j(I) \right\rangle {}^D\upsilon^j(I), \qquad (8)$$

For $i = 1,...,r$ $j = 0,...,n$, where $c_i^j(R) = c_i^j\left(X^j(t) \right)$ denotes the concentration of the i-th component at the right side of the j-th phase and ${}^d J_i^j(I)$ is the time dependent diffusion flux in j-th boundary zone (interface), namely for $x \in \left(X^j(t), X^j(t) + \delta^j \right)$.

The j-th phase volume follows from Eq. (6):

$$\dot{X}^j = \sum_i c_i^j \Omega_i^j \frac{\left(c_i^{j+1}\Omega_i^{j+1}\,{}^d\upsilon_i^{j+1} + c_i^{j+1}\Omega_i^{j+1}\,{}^D\upsilon^{j+1} \right)(L) - \left(c_i^j\Omega_i^j\,{}^d\upsilon_i^j + c_i^j\Omega_i^j\,{}^D\upsilon^j \right)(R)}{c_i^{j+1}\Omega_i^{j+1}(L) - c_i^j\Omega_i^j(R)}$$
$$\text{for } j = 0,...,n-1 \qquad (9)$$

The phase thickness may be calculated from Eq. (9):

$$\Delta X^j = X^{j+1} - X^j = \int \left(\dot{X}^{j+1} - \dot{X}^j \right) \mathrm{d}t$$

$$\text{for } j = 0,...,n\text{ - }1 \qquad (10)$$

In the phase boundary zone the diffusion fluxes are expressed by the Nernst-Planck formula, figure 1:

$$^d J_i^j(I) = -B_i^j(I) c_i^j(I) \nabla \mu_i^j(I) =$$

$$B_i^j(I) c_i^j(I) \frac{\mu_i^j(R) - \mu_i^{j+1}(L)}{\delta^j}, \qquad (11)$$

where $B_i^j(I)$ is the invariant i-th component mobility in the boundary zone; $c_i^j(I)$ for $x \in \left(X^j(t), X^j(t) + \delta^j \right)$ denotes the constant i-th component concentration; $\mu_i^{j+1}(L) = \mu_i^{j+1}\left(X^j(t) + \delta^j \right)$ and $\mu_i^j(R) = \mu_i^j\left(X^j(t) \right)$ are time dependent chemical potentials at the interfaces of the $j \,|\, j+1$ phase boundary zone[1].

The driving force in Eq. (11): $F_i^j(I) = \left(\mu_i^j(t,R) - \mu_i^{j+1}(t,L) \right) / \delta^j$ is due to the transport through the phase boundary and depend on thermodynamics of neighboring phases. Thus, instead of a postulate of local equilibrium between all components at the phase boundary the ortho-equilibrium at both interfaces of the phase boundary zone is postulated, figure 1.

The diffusion flux in the phase boundary zone is now determined by the deviations from the equilibrium at interfaces and by the transport properties of the phase boundary zone:

$$J_1^j(I) \cong -\frac{B_1^j(I) c_1^j(I)}{\delta^j} \left(\left({}^{eq}N_1^{j+1} - N_1^{j+1}(L) \right) N_2^{j+1}(L) g''^{j+1} - \left({}^{eq}N_1^j - N_1^j(R) \right) N_2^j(R) g''^j \right)$$

$$J_2^j(I) \cong -\frac{B_2^j(I) c_2^j(I)}{\delta^j} \left(\left({}^{eq}N_2^{j+1} - N_2^{j+1}(L) \right) N_1^{j+1}(L) g''^{j+1} - \left({}^{eq}N_2^j - N_2^j(R) \right) N_1^j(R) g''^j \right)$$

$$(12)$$

3. RESULTS

The Ni-Al binary system has several intermetallic phases (Ansara at al, 1997). Two of them (β-NiAl and γ'-Ni₃Al) are considered here. The data used in simulations are shown in table 1. According to Campbell (2008) the interdiffusion coefficient in β-NiAl depend on concentration. In this work the integral interdiffusion coefficient $\tilde{D}_{NiAl}^{Int}$ basing on Campbell approximation is used. The thermodynamic function g was calculated based on the estimations by Ansara et al. (Ansara et al, 1997 and FactStage).

For proposed model evaluation, the concentration profile during the reactive diffusion in Al-Ni system was investigated experimentally. Samples of pure nickel, 99.99% purity, were used for the experiments. Specimens with dimensions 20×10 mm were cut from nickel foil 2 mm thick. The CVD (Chemical Vapour Deposition) process was carried out in the commercial apparatus: CVD BPXpro 325S in Research and Development Laboratory for Aerospace Materials in Rzeszow.

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[1]In this work it is assumed that the phase boundary zone has constant thickness denoted by δ.

Table 1. *Thermodynamic and kinetic data used to simulate reactions in Ni-Al system at 1273 K.*

Phase, j	Molar ratio N_{Ni} (L)	Molar ratio N_{Ni} (R)	Thermodynamic function $\partial^2 g / \partial N_{Al}^2$ [kg cm^2 s^{-2}]	Integral interdiffusion coefficient, $\tilde{D}_{Ni,Al}^{j}$ [cm^{2}s^{-1}]	Interdiffusion coefficient within the boundary zone [cm^{2}s^{-1}]
Ni	1	0.85		4.24 10^{-12}	1.7e-11
AlNi$_3$	0.77	0.725	2.40418 10^{-14}	2.92 10^{-11}	9.2e-11
AlNi	0.625	0.45	1.18485 10^{-14}	1.55 10^{-10}	8.8e-11
Al	0	0		2.15 10^{-11}	

The substrates were cleaned and dried prior to the experiment, then were suspended in the center of the reactor. Aluminum chlorides from an external bath were used as Al precursor. The substrate temperature was 1273 K. The processing time was 2.5h. After this time the AlCl$_3$ supply was stopped. The sample was cooled for 24 hours in a hydrogen atmosphere to avoid the oxidation. Than, the samples were removed, cleaned thoroughly in cold water and dried. The transverse sections of the selected specimens were observed in an optical microscope and the thickness of the various layers were measured using a Nikon microscope EPIPHOT 300. The layers compositions were evaluated using scanning electron microscope (EDX), the phase compositions were determined by X-ray diffraction (XRD).
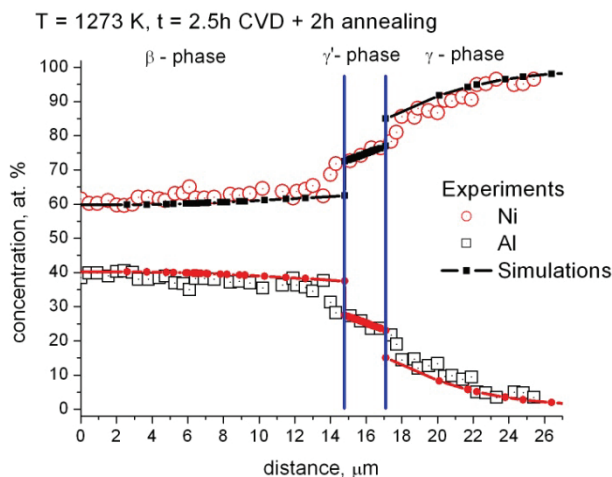

Fig. 2. *The concentration profile after the CVD process. Dots show the experimental results and line are simulations.*

Figure 2 show the results obtained during the commercial CVD process followed by the cooling procedure. The dots refer to the experimental concentration profile, the lines show the simulation. The aluminization process was performed for 2.5h than the 2h of the diffusional annealing was calculated (to simplify the calculations 2 hours of diffusional annealing at 1273 K instead of cooling procedure at variable temperature was assumed). A good agreement of the values calculated for 2-hour annealing with experimental data is seen.

3. CONCLUSIONS

In this paper the original bi-velocity method and the effective use of the volume continuity equation was presented. It was shown, that the volume continuity equation allows defining the material drift velocity and can be used in practical computations. The commercial aluminization process, CVD was successfully modeled. The transport at nanoscale by considering the processes within the phase boundary zone was analyzed.

Presented method allows quantitative description of the diffusion controlled processes, the diffusional coatings formation, the life time of the material, i.e., the critical consumption of the reacting element. The resulting system of physical laws, initial and boundary conditions (i.e., the initial boundary value problem) allows using the bi-velocity method in a case of non-ideal systems.

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Streszczenie

W artykule zaprezentowana została metoda wyznaczania profili stężeń podczas procesu aluminizowania. Pokazano ilościowy oraz jakościowy opis tworzenia powłok metodą osadzania chemicznego z fazy gazowej (CVD). W niniejszej pracy zaprezentowano rozwiązanie w układzie odniesienia jakim jest sieć krystaliczna materiału. Takie podejście pozwala na wyznaczenie prędkości materiału uwzględniając wiele poruszających się granic międzyfazowych. Przesuwanie się granic faz jest wynikiem różnicy we współczynnikach dyfuzji oraz objętości molowych tworzących się faz. Pokazane zostało, że przedstawiony model opisujący dyfuzję reakcyjną jest zgodny z termodynamiką procesów nieodwracalnych i pozwala na modelowanie złożonych układów wielofazowych.