Modelling of Interdiffusion and Reactions at the Boundary; Initial-value Problem of Interdiffusion in the Open System

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Abstract. The application of the Danielewski-Holly model of interdiffusion for modelling of selective and concurrent oxidation of multi-component alloys is presented. This model enables prediction of the evolution of components distributions taking into account interdiffusion and the reactions at the boundary, e.g., due to the oxidation/sulphidation processes. The model is subsequently reformulated to the form suitable for numerical calculation. For illustrating its capabilities modelling of the selective oxidation of Ni-Pt alloys is presented. The results are compared with those obtained from Wagner model. Both models give exactly the same results for the longer reaction times. In Wagner model the equilibrium concentration of the elements at the boundary is reached instantly while in this model it changes with time. Consequently the model allows modelling of initial stages of oxidation.

Introduction

The phenomenological description of interdiffusion proposed by Darken [1] was extended by Danielewski and Holly [2,3]. The Danielewski-Holly model describes the process in the bounded mixture (i.e., diffusion couple of finite thickness) showing constant concentration (e.g., in solid or liquid solutions) and for variable diffusivities of the elements. It allows description of thermal oxidation of the thermodynamically ideal alloys [4]. This model was subsequently developed for the modelling of interdiffusion in non-ideal closed systems [5].

In this work the formulation of the model is extended to non-ideal reacting alloy (open system). The boundary conditions for selective and concurrent oxidation are presented. This model can be subsequently reformulated to the form, which will be used for the mathematical analysis and obtaining a solution [6]. For illustrating the capabilities of the model the modelling of selective oxidation of Ni-Pt alloys is presented. The results are compared with those obtained from the Wagner model.

Mathematical Model

Formulation of the Model. In this section mathematical model of thermal oxidation is formulated. The initial boundary-value problem is presented in a classical way, i.e., presenting data, physical laws, initial and boundary conditions and finally the unknowns to be calculated.

Data
1. $M_1,\ldots,M_r$ - molar masses of the elements, where $r$ - is the number of components in the system;
2. $\Lambda$ - a position of the right end of the system;
3. $\varrho_i^0 = \varrho_i(x),\ldots,\varrho_r^0 = \varrho_r(x)$ - the initial distributions of the components $\varrho_i^0 : [-\Lambda,\Lambda] \rightarrow \mathbb{R}_+^r, \ i = 1,\ldots,r$, such that $c = \sum_{i=1}^{r} \frac{1}{M_i} \varrho_i^0 = \text{const.}$

where $c > 0$ is the molar concentration of the system;
4. \( D_i^r = D_i^r(\varrho) \), \( D_r^r = D_r^r(\varrho) \) - self (tracer) diffusion coefficients† of the components, which may depend on components’ densities, \( \varrho = (\varrho_1, \ldots, \varrho_r) \);
5. \( a_i = a_i(\varrho), a_r = a_r(\varrho) \) - the thermodynamic activities of the components as functions of components’ densities;
6. \( \hat{t} \) - the time of the process duration;
7. \( j_{ia}, \dot{j}_{ia} [0, \hat{t}] \to \mathbb{R} \) - evolution of mass flow of the \( i \)-th component through the left and right boundary. As a consequence of constant concentration of the system the fluxes must satisfy the following relation [4]:
   \[
   \sum_{i=1}^{r} \frac{1}{M_i} j_{ia}(t) = \sum_{i=1}^{r} \frac{1}{M_i} \dot{j}_{ia}(t) \quad \text{for} \quad t \in [0, \hat{t}].
   \]  
   Therefore only \( 2r - 1 \) fluxes are independent.

**Physical Laws**

1. Law of the mass conservation of an \( i \)-th element. That law tells that a local change of density of an \( i \)-th element is a result of its net in- or outflow only (reactions within diffusion zone are neglected):
   \[
   \frac{\partial \varrho_i}{\partial t} + \frac{\partial }{\partial x} \hat{J}_i = 0 \quad i = 1, \ldots, r.
   \]  
   Following Darken’s drift flow idea [1], it is postulated that the flux of an \( i \)-th element, \( \hat{J}_i \), is a sum of its diffusion flux, \( J_{id}^i \), and the drift flux, \( (\varrho_i \nu) \):
   \[
   \hat{J}_i := J_{id}^i + \varrho_i \nu,
   \]  
   where the diffusion flux is expressed by [8,5]:
   \[
   J_{id}^i = -\sum_{j=1}^{r} D_y \frac{\partial \varrho_j}{\partial x}.
   \]  
   The partial intrinsic diffusivities, \( D_y \) in the equation (4), are defined as follows
   \[
   D_y(\varrho) := D_y^r(\varrho) \rho_i \frac{\partial \ln a_{i\mu}}{\partial \varrho_j}(\varrho).
   \]  
   One can notice that in the ideal system, when activity coefficients equal one, the diffusion flux becomes
   \[
   J_{id}^i = -D_y \frac{\partial \varrho_i}{\partial x}.
   \]
   2. A postulate of the constant molar volume of the system. Consequently the molar concentration of the system being a sum of the concentrations of all elements at any position for every time is constant:
   \[
   \frac{1}{M_1} \varrho_1 + \ldots + \frac{1}{M_r} \varrho_r = c = \text{con}.
   \]

† The vacancy-wind factor in multi-component alloys doesn’t differ much from unity [7] and correlation effects are often neglected. Moreover one has to accept the fact that the experimental error(s) are the same order of magnitude or exceed expected effect. Thus, one can assume that self- and tracer diffusion coefficients are equivalent in multi-component alloys.
Initial and boundary conditions

1. The initial density distributions of the components in the system:

\[
\bar{\rho}_i(x) = \rho_i(0,x) \quad \text{for } x \in [-\Lambda, \Lambda], \quad i = 1, \ldots, r.
\]  

(7)

2. The following boundary conditions are postulated:

\[
J_i(t,-\Lambda) = j_{in}(t), \quad J_i(t,\Lambda) = j_{in}(t),
\]

for \( t \in [0, \hat{t} ] \), \( i = 1, \ldots, r \).

(8)

In practice, e.g., for modelling the oxidation process, it is assumed that oxidation takes place on the one side of the system (e.g., right side, i.e., for \( x = \Lambda \)), while on the other side a semi-finite geometry of the system (boundary conditions) is assumed:

\[
\frac{\partial \rho_i}{\partial x}(t,-\Lambda) = 0 \quad \text{and} \quad \rho_i(t,-\Lambda) = \rho^*_i(-\Lambda) \quad \text{for } t \in [0, \hat{t} ], \quad i = 1, \ldots, r.
\]  

(9)

The functions, \( j_{in}(t) \), have to be known (measured and/or calculated). They can be calculated e.g., from the known rate of reactions at the boundary or from the experimental data. The analysis of the boundary conditions for the selective and concurrent oxidation is discussed in the next section.

It was shown [3] that in the closed system the gradients of all the components at both boundaries vanish, i.e., the flux of an \( i \)-th component at the boundary equals zero,

\[
J_i(t,\pm \Lambda) = 0 \quad \text{for } t \in [0, \hat{t} ], \quad i = 1, \ldots, r.
\]

The unknowns

1. Densities of the components as functions of time and position, \( \rho_i(t, x) \), \( i = 1, \ldots, r \).

2. A drift velocity in the system (alloy) as a function of time and position, \( \nu(t, x) \).

Boundary Conditions for Thermal Oxidation

It initially uniform, the alloy changes its composition near the alloy/scale boundary due to the oxidation process only. In multi-component alloy the chemical reaction (oxide formation) at the boundary effects concentration of all the elements in the alloy. Modelling of such process involves formulation of the proper boundary conditions.

The flux of component at the boundary, (i.e. for \( x = \Lambda \)), which is oxidised (forms a scale) can be expressed as follows

\[
J_i(t, \Lambda) = J_i^{\text{diff}}(t, \Lambda) + c_i(t, \Lambda) \frac{d\Delta X}{dt}(t),
\]

(10)

where \( d\Delta X / dt \) is the rate of the alloy consumption due to oxidation process.

If some element in the alloy does not form a scale, then its flux through the boundary equals zero

\[
J_i(t, \Lambda) = 0
\]

(11)

and consequently

\[
J_i^{\text{diff}}(t, \Lambda) = -c_i(t, \Lambda) \frac{d\Delta X}{dt}(t).
\]

(12)

Expressions (10) - (12) introduced into equation (8) allow to postulate functions describing fluxes of the components, Eq. (8).
If the scale (oxide) is compact and adheres to the alloy, the rate of the alloy consumption is inversely proportional to instantaneous thickness of the oxide layer, which in turn is proportional to the displacement of the alloy surface $\Delta X$. Thus the rate of the alloy consumption is \[ (13) \]
$$ \frac{d\Delta X}{dt} = \frac{k_c}{\Delta X} $$
where $k_c$ is a parabolic rate constant of an alloy consumption. Solving the equation (13), the displacement of the alloy surface due to oxidation can be obtained: $\Delta X = \sqrt{2k_c t}$. Consequently \[ (14) \]
$$ \frac{d\Delta X}{dt} = \frac{k_c}{\sqrt{2t}} $$
Expressions (10), (11) and (14) introduced into equation (8) describe fluxes of the components, Eq. (8), assuming that oxidation is governed by parabolic growth kinetics [11].

**Mathematical Reformulation of the Problem**

For mathematical convenience and obtaining the solution, the presented model has to be reformulated. Let us multiply by $1/M_i$ and add equations of local mass conservation (Eqs. (2))

\[ (15) \]
$$ \sum_{i=1}^{r} \frac{1}{M_i} \frac{\partial \rho_i}{\partial t} + \frac{1}{M_i} \frac{\partial J_i}{\partial x} = 0. $$
Taking into account Eq. (6) we get
$$ \frac{\partial}{\partial t} c + \frac{\partial}{\partial x} \sum_{i=1}^{r} \frac{1}{M_i} J_i = 0. $$
Because $c = \text{const}$ (see Eq.(6)) one can notice that $\sum_{i=1}^{r} \frac{1}{M_i} J_i$ does not depend on a position in the system, consequently exists $K(t) \in \mathbb{R}$ such that $\sum_{i=1}^{r} \frac{1}{cM_i} J_i(t,x) = K(t)$ for $t \geq 0$, $x \in [-\Lambda, +\Lambda]$.

After inserting the expression for the flux $J_i(t,x)$ we have
$$ \sum_{i=1}^{r} \frac{1}{M_i} \left( - \sum_{k=1}^{r} D_{ik}(\varphi) \frac{\partial \varphi_k}{\partial x} + \varphi \nu \right) = cK(t), $$
and finally after rearrangements
$$ \nu = K(t) + \sum_{k=1}^{r} \sum_{i=1}^{r} \frac{1}{cM_i} D_{ik}(\varphi) \frac{\partial \varphi_k}{\partial x}. \quad (15) $$
For further transformations let us introduce the following notations
$$ \mathcal{M}_i(t) = \frac{1}{2\Lambda cM_i} \int_{-\Lambda}^{\Lambda} \varphi_i(t,x)dx \quad \text{and} \quad w_i(t,x) = \frac{1}{cM_i} \varphi_i(t,x) - \mathcal{M}_i(t), \quad (16) $$
where
$$ \mathcal{M}_i(t) = \frac{1}{2\Lambda cM_i} \int_{-\Lambda}^{0} \varphi_i(x)dx + \frac{1}{2\Lambda cM_i} \int_{0}^{t} \left( j_{i,L} - j_{i,R} \right)(\tau)d\tau, \quad (17) $$
which means that $\mathcal{M}_i(t)$ is known function of time.
One can notice that the following relations are fulfilled
\[
\sum_{i=1}^{r} w_i(t,x) = 0, \quad \int_{-\Lambda}^{\Lambda} w_i(t,x) dx = 0 \quad i = 1, \ldots, r.
\]  

Using defined variables (16) and (2)-(6) we obtain:

\[
\frac{\partial w_i}{\partial t}(t,x) = \frac{\partial J_i^M}{\partial x}(t,x) - \mathcal{M}_i(t), \quad i = 1, \ldots, r,
\]

where \( J_i^M(t,x) = \frac{1}{cM_i} J_i(t,x) \) and \( \mathcal{M}_i = \frac{d\mathcal{M}_i(t)}{dt} \).

Consequently we can write initial and boundary conditions using variable, \( w_i \):

\[
\begin{aligned}
w_i(0,x) &= w_i^0(x) & \text{for} & \quad x \in [-\Lambda, \Lambda], \\
J_i^M(t,-\Lambda) &= j_{il}^M(t) & \text{and} & \quad J_i^M(t,\Lambda) = j_{ir}^M(t) & \text{for} & \quad i = 1, \ldots, r & \text{and} & \quad t \geq 0,
\end{aligned}
\]

where \( j_{il,R}^M = \frac{j_{il,R}}{cM_i} \).

**The Solution to the Model**

In the last section the model of thermal oxidation given by Eqs. (2) - (9), was transformed to the initial-boundary problem (Eqs. (19)-(20)), which will be solved numerically in several steps:

1. formulation of the generalized solution to the model,
2. numerical solution using Galerkin-like method,
3. solving the resulting system of ordinary differential equations.

The details on numerical solution to the model can be found elsewhere [6,10].

**Wagner Model of Diffusion in Selectively Oxidised Ni-Pt Alloys**

It will be shown that Wagner’s Model [11] is a special case of the model presented in this paper. For a sake of simplicity Wagner assumed that the interdiffusion coefficient is independent of composition, i.e.

\[
\tilde{D} = D_{Ni} = D_{Pt} = \text{const}
\]

As a consequence the diffusion of the elements in the alloy can be described by second Fick’s law

\[
\frac{\partial c_{Ni}}{\partial t} = D \frac{\partial^2 c_{Ni}}{\partial x^2} \quad \text{or alternatively} \quad \frac{\partial c_{Pt}}{\partial t} = D \frac{\partial^2 c_{Pt}}{\partial x^2}.
\]

Assuming uniform initial distribution of the components in the alloy

\[
c_{Ni}(0,x) = c_{Ni}^0, \quad c_{Pt}(0,x) = c_{Pt}^0
\]

boundary condition (12) and assuming parabolic rate of the alloy consumption – equation (13) he found the solution – concentration of nickel as a function of time \( t \) and distance \( x \) from the initial surface

\[
c_{Ni}(t,x) = c_{Ni}^A + (c_{Ni}^0 - c_{Ni}^A) \left( \text{erf} \left[ \frac{x}{2\sqrt{Dt}} \right] - \text{erf} \left[ \frac{k_c}{\sqrt{2Dt}} \right] \right) - \left( \text{erf} \left[ \frac{k_c}{\sqrt{2Dt}} \right] \right)
\]

where \( c_{Ni}^A \) is the nickel concentration at the alloy/scale boundary. The characteristic property of the equation (24) is that for any time \( t > 0 \), the nickel concentration of the boundary is constant – stationary.
Modelling of Selective Oxidation of Ni-Pt Alloys

For a selectively oxidised binary Ni-Pt alloy, assuming that Ni is selectively oxidised, the fluxes of nickel and platinum can be written as follows

\[
D_{Pt} \frac{\partial c_{Pt}(t, \Lambda)}{\partial x} = c_{Pt}(t, \Lambda) \frac{d \Delta X_{\text{Alloy}}(t)}{dt} \quad \text{and} \quad j_{Pt(t)} = J_{Pt}(t, \Lambda) = 0.
\]  

(25)

Using boundary conditions (25) and presented above model components’ the evolution of concentration profiles in the oxidised Ni-Pt alloy can be calculated. These results will be subsequently compared with these obtained from the Wagner model [11].

For simulations the following data were used: 1) temperature \( T = 850 \, ^\circ \text{C} \), 2) nickel and platinum diffusion coefficient \( D = 3.1 \times 10^{-12} \, \text{cm}^2 \, \text{s}^{-1} \) and 3) parabolic rate constant of the alloy consumption \( k_c = 2.3 \times 10^{-14} \, \text{cm}^2 \, \text{s}^{-1} \). In calculations the kinetic constrain for the fluxes [12] at the boundary was introduced. This allows to avoid non-physical values of the interdiffusion fluxes.

In the Figure 1a the calculated nickel concentration profile after 1.91 ks is presented and compared with the results obtained for the Wagner’s model. It can be seen (Fig. 1a) that both models give the same solution. However, models behave different for shorter time – Figure 1b. It can be seen (Eq. (24)) that for the Wagner model nickel concentration at the alloy/scale boundary reaches instantly its stationary value, contrary to the Danielewski-Holly model. In the present model the nickel concentration approaches to stationary value with time. The advantage of the present model is a possibility of modelling of the initial stages of oxidation.

Figure 1. Oxidation of Ni-90Pt alloy after a) 1.9 ks and b) 0.01 s of oxidation at 850 \, ^\circ \text{C}.

Comparison of calculated nickel concentration profile using Wagner’s and Danielewski-Holly model.

Summary

The presented model can be used for the modelling of thermal oxidation of multi-component alloys. For the known thermodynamic data (components’ activities), kinetic data (self diffusivities) and reaction rate at the boundary (fluxes of the components) the evolution of the concentration profiles and drift velocity can be found in the oxidized multi-component alloy.

Calculations performed for Ni-Pt alloys shows that presented model and the Wagner model give the same results for longer reaction times. Contrary to the Wagner (stationary equilibrium concentration of the components at the alloy/scale interface) this model can be used for modelling of the initial stages of oxidation.

The presented model has been successfully used for modelling of thermal oxidation of multi-component alloys Fe-Cr and Fe-Cr-Ni [13,14].
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