

## THE MODELING OF ALUMINUM LAYER FORMATION ON NICKEL ALLOYS BY BI-VELOCITY METHOD.

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**Abstract.** In this paper the model of interdiffusion in multiphase system is discussed and used to simulate a formation of single-phase layers in a binary system and formation of both single- and two-phase layers during diffusion in a ternary system. The model base on the bi-velocity method, in which material velocity and velocities of individual components are considered and allows calculating concentration profiles, spatial distribution of entropy-production rate and diffusion path.

It takes into consideration the mass transport in all phases present in the system (likewise throughout the both phases within two-phase zone). In particular, a formation of two-phase zones by isothermal diffusion is predicted. By using phase-field parameter (here volume fractions of the phases), a smooth transition between neighbouring, single and two – phase, regions is possible and the mass transport equations remain valid when the phase boundaries are crossed. The aluminization of nickel and its superalloy, MAR-M200+Hf, by CVD is studied experimentally and simulated numerically.

### 1 INTRODUCTION

Although much attention has been devoted to aluminization by CVD, the problem of designing the technology and designing the layers formed during aluminization remains open. The main difficulty includes a description of diffusion in multi-component solid which leads to a formation of many layers. The aluminization by CVD is usually carried out in two processing stages. In the first stage, aluminium chlorides are formed in the chemical reactions between solid Al and  $H_2/HCl$  gas mixture. The gaseous products are then transported to the main reactor where they react with solid substrate, Ni or Ni-alloy respectively. The entire process is governed by a combination of gaseous diffusion and solid state diffusion [1, 2].

When pure nickel is aluminized (the interdiffusion in the binary system) sequential layers of intermediate phases and solid solutions can be formed – in agreement with the phase diagram. Depending on the temperature, the following layers can grow in the Ni-Al system:  $\delta$ - $Ni_2Al_3$ ,  $\beta$ -NiAl,  $\gamma'$ - $Ni_3Al$  and solid solution of Al in Ni ( $\gamma$ -phase). The pre-eminent phase is  $\beta$ -NiAl which posses low density 5,9 g/cm<sup>3</sup>, excellent heat resistance (even when compared to other aluminides) and good mechanical properties, like high specific strength. Very good heat

resistance of  $\beta$ -NiAl is because of its propensity to formation of  $\text{Al}_2\text{O}_3$ -rich protective layer [3].

MAR-200 alloy has been designed for application as a base material for the turbine blades in jet engines. It has an improved high-temperature strength, but exhibits poor corrosion resistance when used at elevated temperatures [4]. To eliminate or even reduce the problem, the aluminization is applied in which nickel aluminide phases are formed.  $\text{Al}_2\text{O}_3$ -rich protective layer of good resistance to high temperature oxidation can be also formed [5, 6, 7].

In this work, the bi-velocity method is generalized and combined with the phase field model. The fusion of these two methods, referred to as Bi-velocity Phase Field Method (BPFM), is applied to calculate composition-distribution profiles for the elements present in the diffusion couple. The method shows the possibility of crossing the single-phase, two-phase and three-phase fields. The three-phase zone will not grow in ternary diffusion - in agreement with Gibbs phase rule. Otherwise, the two phase region can grow despite it seems unfavorable because of additional interphase boundaries and related energy dissipation.

## 2 MODEL OF INTERDIFFUSION IN MULTIPHASE SYSTEMS

A purpose of the present model is to provide a method that simulates the interdiffusion in a multiphase binary and ternary system. The model is formulated within Darken method, which is a commonly accepted way of quantifying the Kirkendal effect [8, 9, 10].

### 2.1 Binary system

When pure nickel is aluminized (the interdiffusion in the binary system) sequential layers of intermediate phases and solid solutions can be formed – in agreement with the phase diagram. Depending on the temperature, the following layers can grow in the Ni-Al system:  $\text{Ni}_2\text{Al}_3$ ,  $\beta$ -NiAl,  $\gamma'$ - $\text{Ni}_3\text{Al}$ , and solid solution of Al in Ni [11]. The two phase zones do not grow. The concentration profiles reproduce the compositions of pure phases and solid solutions with the jumps at the interphase boundaries. In the present approach, the mass transport through the phase boundary zone and the equilibrium at both interphases of each phase boundary zone are considered [10].

The fundamental physical laws used in the description of the mass transport are given by mass-balance, Nernst-Planck [12] and volume-continuity equations. The final form of the continuity equation calculated in each phase separately in binary system is:

$$\frac{\partial N_2}{\partial t} = -\frac{\partial J_2}{\partial x} = \frac{\partial}{\partial x} \left[ (N_1 D_2 + N_2 D_1) \frac{\partial N_2}{\partial x} \right], \quad (1)$$

where:  $N_2$  denote the molar fraction of the second component and  $D_i$  is diffusion coefficient.

Above mass conservation law in multiphase binary system should be complemented by the initial and boundary conditions between all phases. To define the boundaries we can use the Leibnitz rule of calculus and finally the boundary velocity can be approximated as follow for each phase boundary:

$$\frac{dX_j}{dt} = \frac{J_{2,j} - J_{2,j+1}}{N_{2,j}^{eq} - N_{2,j+1}^{eq}} \quad (2)$$

where:  $N_{2,j}^{eq}$  denote the equilibrium value of the molar fraction of second component in the  $j$ -th phase (this value can be estimated from the phase diagram) and  $J_{2,j}$  denote the second component overall flux.

The initial conditions are as usual: Arbitrary initial distributions of the components  $c_i(t=0, x) = c_i^0(x)$ ; and the initial thickness of the sub-layers (e.g.  $j$ -th phase):  $\Delta X_j(t=0) = X_{j+1}^0(R) - X_{j+1}^0(L)$ .

## 2.2 Ternary system

In multicomponent systems (like an alloy layer), diffusion can lead to the formation of multi-phase regions, next to the layers of solid solutions and intermediate phases. Consequently, the diffusion zone may exhibit a complex morphology. Otherwise, in a two-component system, only solid solutions and intermediate phases can grow. The difference lies in various numbers of degrees of freedom in both cases. For a three-component two-phase system, there is one degree of freedom, which may be the chemical potential of one of the components. Its gradient is a driving force for diffusion. If there are two components, the two-phase region cannot grow in diffusion, because the number of degrees of freedom equals zero and there is no driving force to induce mass transport [13, 14].

In quantitative characteristics of the two-phase region, an average composition of the system and volume fractions of the phases are important. It is convenient to identify the volume fraction of one of the phases with an order parameter, as defined in Phase-Field model [15, 16]. As in previous section the main equation in the mass balance equation:

$$\frac{\partial \bar{N}_i}{\partial t} = -\frac{\partial \bar{J}_i}{\partial x} = \frac{\partial}{\partial x} \left[ \bar{D}_i \frac{\partial \bar{N}_i}{\partial x} - \bar{N}_i \sum_{j=1}^3 \bar{D}_j \frac{\partial \bar{N}_j}{\partial x} \right], \quad i = 1, 2, 3 \quad (3)$$

where:  $\bar{N}_i$  denote the average molar fraction of the  $i$ -th component,  $\bar{J}_i$  is its overall flux and  $\bar{D}_i$  denote the average diffusion coefficient, respectively.

Above equation can be used to calculate diffusion in both single and two-phase zone. Let us assume that the diffusion occur in the two-phase zone, e.g.  $\alpha+\beta$ , than the following equations are valid:

$$\bar{N}_i = f N_{i,\alpha} + (1-f) N_{i,\beta} \quad (4)$$

$$\bar{D}_i = D_{i,\alpha} \frac{\partial c_{i,\alpha}}{\partial \bar{c}_i} + D_{i,\beta} \frac{\partial c_{i,\beta}}{\partial \bar{c}_i} \quad (5)$$

Equation (4) allows to calculate the average concentration of the  $i$ -th component in the two-phase zone. The  $f$  is a volume fraction of a chosen phase (here  $\alpha$ ):  $0 < f < 1$  and  $N_{i,\alpha}$ ,  $N_{i,\beta}$  are the molar fractions of the  $i$ -th component in the  $\alpha$  and  $\beta$  phases (note that in the single phase region  $f=0$  for  $\beta$  phase and  $f=1$  for  $\alpha$  phase). Equation (5) define the average diffusion coefficient in the two phase region.

The diffusion in the ternary A-B-C system represents some other circumstance because it can lead to the grow of the two-phase zone. The solution requires a knowledge of the initial conditions and thermodynamics of the system. One simply needs the isothermal section of the phase diagram (for the processing temperature). Specifically, the margins of the single and two-phase regions (phase boundaries) and the conodes in the two phase-region (tie-lines connecting the compositions of the two phases at the equilibrium) must be known. In the present calculations, we are basing on the Ni-Cr-Al phase diagram by Huang and Chang [17].

### 3 RESULTS

#### 3.1 Amunization of pure Ni

Following the phase diagram between Al and Ni solid solution at 1273 K the two phases are formed, mainly  $\beta$ -NiAl and  $\gamma$ -Ni<sub>3</sub>Al. The concentration profiles show jumps in the concentrations at the interfaces. The Al and Ni concentration profiles for the  $\beta$ -NiAl phase formed by the dominating inward Al diffusion show a presence of a sharp concentration gradient. It appears at the distance where the  $\beta$ -NiAl composition reaches the stoichiometry 50:50. Such behaviour is connected with the strong dependence of the interdiffusion coefficient in  $\beta$ -NiAl on the composition. For stoichiometric NiAl this coefficient reaches a minimum. The results of the calculations compared with the SEM microphotograph is presented in Fig. 1. The following data were used in calculations of aluminization of pure nickel: 1) the diffusion coefficients in pure Ni, Al,  $\beta$ -NiAl and AlNi<sub>3</sub>, have been given by the integral diffusion coefficients. The Al and Ni diffusivities are:  $D_{Ni} = 1,91 \cdot 10^{-15} m^2 s^{-1}$ ,  $D_{Al} = 5,29 \cdot 10^{-10} m^2 s^{-1}$ , the diffusion coefficient in  $\beta$ -NiAl base on the Campbell approximation [18]  $D_{\beta-NiAl} = 1,0 \cdot 10^{-14} m^2 s^{-1}$  and  $D_{AlNi_3} = 5,01 \cdot 10^{-15} m^2 s^{-1}$  [19, 20, 21]; 2) duration of the process:  $t = 6h$ ; 3) the simulations were made for constant temperature:  $T = 1273 K$ .

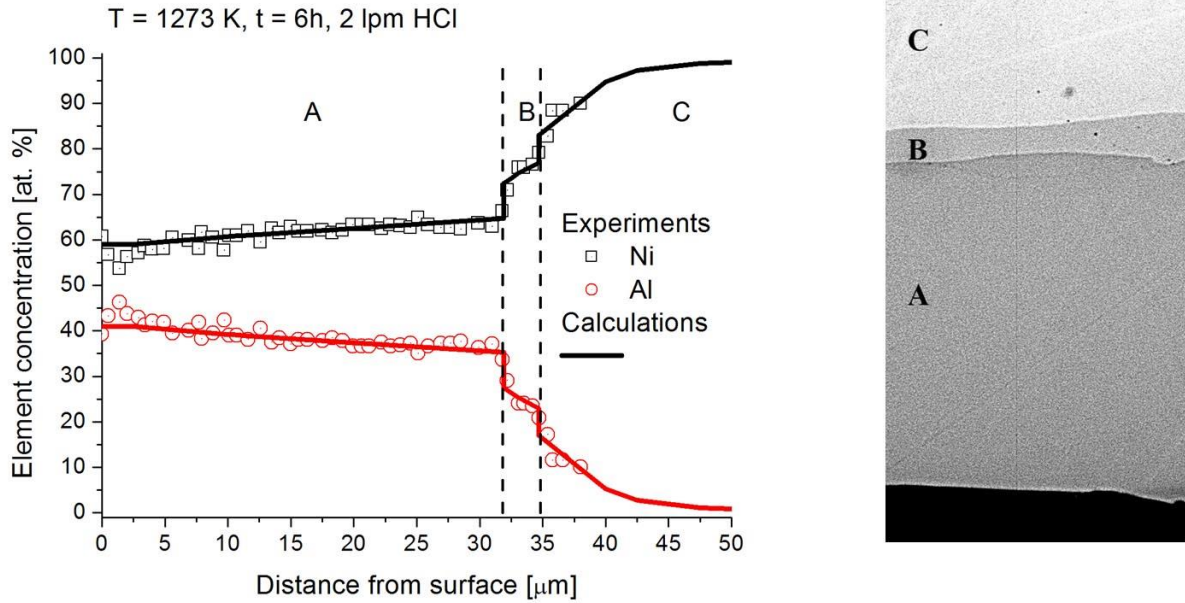


Figure 1. Aluminized zone of the nickel subjected to aluminization by CVD: concentration profile (left) and SEM image of the cross sections (right). Computational results are drawn with solid lines, experimental data are represented by the markers. The phases present in the aluminized zone: A:  $\beta$ -NiAl, B:  $\gamma'$ -Ni<sub>3</sub>Al, C:  $\gamma$ -Ni (solid solution). Interphase boundaries are drawn by dotted lines

### 3.2 Amunization of Ni-based super alloys

The remaining initial data, necessary in the calculations, include: time of the diffusion, terminal compositions of the diffusion couple and diffusion coefficients in all phases. The data for the systems considered in this work MAR-M200+Hf alloy subjected to aluminization, are given in Table 1. The terminal compositions of the diffusion couple represent the terminal points of the diffusion path and are taken from the experiment.

**Table 1.** The diffusion coefficients and terminal composition used in the simulations of reactive diffusion in the Al-Cr-Ni system, at 1273 K.

Phase, j	Al		Cr		Ni	
	Diffusion coefficient	Terminal composition, at. %	Diffusion coefficient	Terminal composition, at. %	Diffusion coefficient	Terminal composition, at. %
MAR - M200	$7.86 \cdot 10^{-12}$	9,11	$2.85 \cdot 10^{-12}$	8,27	$1.44 \cdot 10^{-12}$	82,62
$\gamma' - Ni_3Al$	$3.98 \cdot 10^{-13}$	-	$6.31 \cdot 10^{-13}$	-	$1.58 \cdot 10^{-12}$	-
$\beta - NiAl$	$1.0 \cdot 10^{-10}$	49	$5.31 \cdot 10^{-13}$	0	$1.0 \cdot 10^{-10}$	51
Process duration: $t = 6$ h						
Temperature: 1273 K;						

The aluminization of the nickel-base superalloy, MAR-M200+Hf, was performed for 6 h, at the flow 0,2 lpm, i. e. at the conditions ensuring high-active regime. Figure 2 show the

experimental data next to the concentration profile simulated for Al-Cr-Ni system with application of the present model.

T = 1273 K, t = 6h, 0.2 lpm HCl

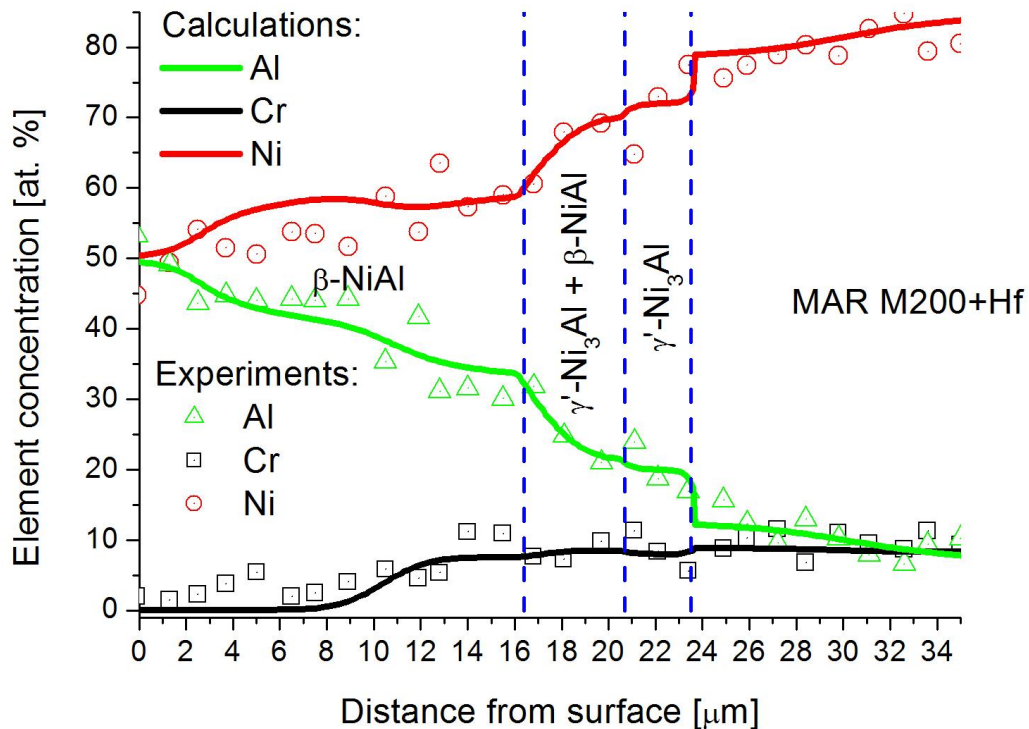


Figure 2. Aluminization of MAR-M200 nickel-base superalloy by CVD; concentration profile after: 6 h of aluminizing. The results for 1273 K and 0,2 lpm of HCl flow.

From the calculations, Fig. 2, the layers can be identified with the phases. Starting from the external layer, the sequence is following:  $\beta$ ,  $\gamma' + \beta$ ,  $\gamma$ ,  $\gamma' + \gamma$  and  $\gamma$ . All layers are indicated in the concentration profiles.

#### 4 CONCLUSIONS

- The solid state diffusion in binary and ternary systems is overall treated and modeled using bi-velocity method. The model follows Darken diffusion theory of and includes drift of the material and diffusion velocities of all components.
- It is shown that the principal difference when the binary and ternary systems are analyzed concerns initial conditions.
- It was presented, that the interdiffusion in the ternary systems can be followed by the formation of the two-phase zone(s).
- The model is applied to simulate interdiffusion during aluminization of nickel and its super-alloy, MAR-M200+Hf. The predictions show good agreement with the performed experiments of aluminization by CVD.

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