THE INFLUENCE OF H₂/HCl RATIO ON ALUMINIZING BY CVD METHOD

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S u m m a r y

In this manuscript the theoretical studies of aluminisation by CVD method is shown. The bi-velocity model of multicomponent and multiphase diffusion is used to calculate the growth of β-NiAl phase under different ranges of miscibility (HCl to H_2 ratio). The composition dependent diffusivities of β-NiAl and Ni_3Al at 1350 K are presented and used in calculations.

Keywords: CVD, multiphase system, alloys, volume continuity equation

**Wpływ składu chemicznego mieszaniny gazów reakcyjnych H₂/HCl
na kinetykę procesu aluminiowania metodą CVD**

S t r e s z c z e n i e

W artykule zaprezentowano matematyczny model procesu aluminiowania metodą osadzania z fazy gazowej – CVD. Model matematyczny opracowano na podstawie uogólnionej metody Darkena – dwu-prędkości. Był podstawą oszacowania kinetyki powstawania kryształów fazy β-NiAl w zależności od natężenia przepływu dostarczonego gazu reakcyjnego – proporcja HCl:H_2. W symulacji numerycznej uwzględniono wzrost kryształów dwóch faz pośrednich – β-NiAl oraz Ni_3Al w temperaturze 1350 K – określono zmienne cząstkowe współczynniki dyfuzji składników.

Słowa kluczowe: CVD, układy wielofazowe, stopy, zasada zachowania gęstości objętości

1. Introduction

Metallic components operated at high temperatures and in corrosive environments are protected against oxidation and other forms of degradation by a variety of coatings. Intermetallic compounds such as nickel aluminides are very attractive for practical applications. The main futures of such materials are good corrosion resistance and high electrical and thermal conductivities [1, 2]. The aluminide coatings applied on the surface of iron, nickel and cobalt based superalloys exhibit fairly good resistance to high temperature oxidation by forming an Al_2O_3-rich protective layer [1, 3].

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The CVD (Chemical Vapor Deposition method) is one of the methods to apply the aluminide coatings on metals. In this technique the hydrogen/HCl gas mixtures is used as activator gas. The coating is formed by solid state diffusion of Al, and/or substrate species, so the kinetics of the process is governed by a combination of gaseous diffusion and solid state diffusion in the coating [4]. The Kohlscheen and Stock [5] reported, that a high amount of hydrogen added to the HCl gas flow has been found to increase the coating growth rate (ratio of approx. 10:1).

The goal of this work is to investigate the aluminium layer formation on Ni substrate in the CVD process under varying process parameters, i.e. initial carrier/reactive gas ratio (respectively H_2/HCl). The comparison of the experimental and simulated results are shown. Presented modelling approach link the local thermochemical equilibrium at the solid-gas interface with the solid-state diffusion simulated with the generalized Darken method.

2. Experiments and results

The substrate samples were cut from the nickel bars (99.95% Ni) into cylinders of 14 mm diameter and 4 mm height. The samples were ground with the SiC abrasive paper to a 500-grade finish, ultrasonically cleaned in ethanol, dried and placed at the half height of the reactor. The aluminising process was carried out in the CVD Bernex BPXpro 325S commercial apparatus provided by IonBond Company, schematically presented in Fig. 1.
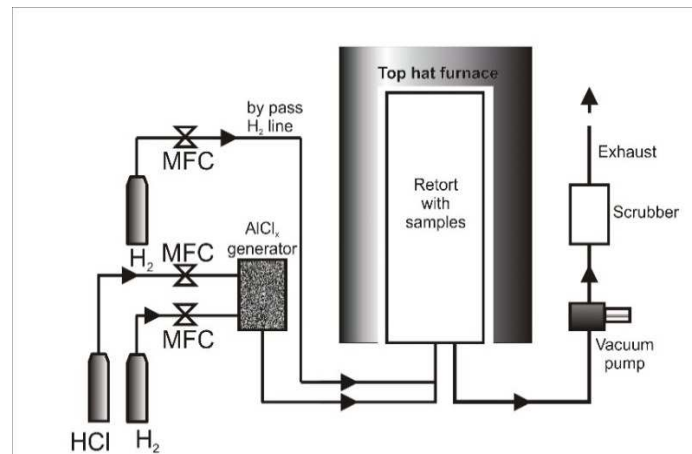

Fig. 1. Schematic representation of the CVD apparatus used
for the aluminizing process

The source of aluminium consisting of 99.99% Al round pellets of approx. 10 mm in diameter was placed in the external retort. The aluminium precursors

were formed at 260°C by reaction of the Al source with a reactive stream consisting of various amount of HCl (see Table 1) dissolved in H_2 (constant flow of 3.5 dcm³/min). The gaseous species ($AlCl_x$) were transported through a heated pipe to the main reactor containing the sample to be coated. All deposition experiments were performed at 1000°C. An additional stream of H_2 (7 dcm³/min) was supplied to the main reactor in order to prevent the backflow of the gases and to ensure the high mass flow. The constant pressure in the main reactor was maintained by pumping out the redundant vapours.

Table 1. Characteristics of experiments carried out in this study

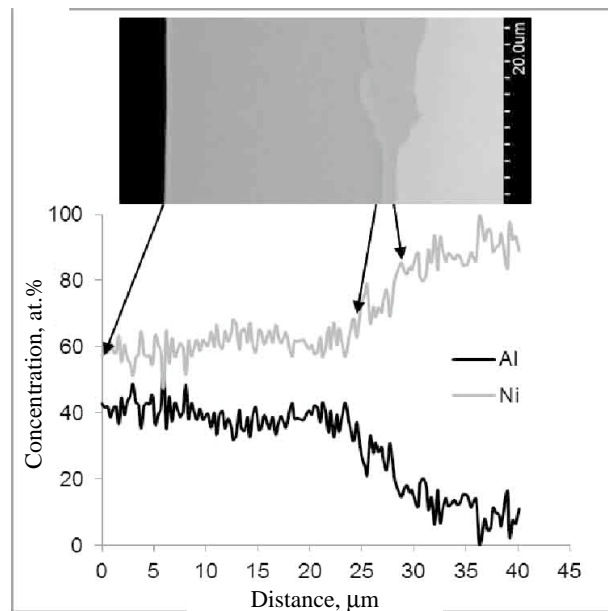| Process no.	HCl, dcm³/min	Processing time, h	Layer thickness, μm	
			β-NiAl	γ'-Ni₃Al
1	1.4	1	10.0±0.8	3.6±1.3
2	1.4	2	13.8±0.8	2.9±1.1
3	2.0	4	19.3±1.9	4.2±1.9
4	1.4	8	24.8±1.0	3.7±1.5

Fig. 2. SEM microstructure of aluminised Ni profile after 8 h

After the required processing time, the supply of Al precursors was shut off and the samples were cooled during approx. 3 hours in a pure H_2 atmosphere. Then the samples were cleaned with cold water and dried. Prior to the analyses, the specimens were cut and cross sections were prepared.

The chemical compositions and thicknesses of the aluminide coatings were determined using scanning electron microscopy (SEM, S-3400 Hitachi Scanning Electron Microscope). While the SEM images showed the microstructure of the sample cross sections, energy dispersive spectrometry (EDS) was employed to determine the elemental concentration depth profiles in the cross sections as well as the aluminium concentration at the surface of selected specimens.

The cross-sectional SEM images of the sample microstructure and the corresponding concentration depth profiles obtained after 8-hour treatment is shown in Fig. 2. Chemical composition measurements confirmed the presence of the β-NiAl and γ'-Ni₃Al phases. The results of the analyses are summarized in Table 1.

3. Modelling of the solid-state diffusion

The aluminising process can be described as semi-infinite, multiphase, volume diffusion. The concentration profiles and the position of interfaces change with the time as the phase layer grow [6]. Simulations of the solid-state diffusion during the CVD process were based on the bi-velocity (Darken) method which enables the calculation of the multiphase and multicomponent diffusion. Bi-velocity method utilizes the postulate that velocity of each component must be divided into two parts [7]. The first one represents the diffusion velocity. It depends only on the diffusion potential gradient [8] and is independent of the choice of the reference frame. The second part represents the drift velocity, which is common for all components and depends on the choice of the external reference frame.

The equations governing calculations carried out in the framework of this study included the mass balance (Eq. 1), the Nernst-Planck flux (Eq. 2), and the volume continuity (Eq. 3):

$$\frac{\partial c_i^j}{\partial t} + \nabla \cdot \left(c_i^{j}\, {}^{d}v_i^{j} + c_i^{j\ drift}v^{j} \right) = 0$$

$$\text{for} \quad i = \text{Ni, Al} \quad \text{and} \quad j = \gamma(\text{Ni}),\ \gamma'\text{-NiAl}_3,\ \beta\text{-NiAl} \tag{1}$$

where c_i^j denotes concentration of the i-th component in the j-th phase. The ${}^{d}v_i^{j}$, ${}^{drift}v^{j}$ are the diffusion and the drift (Darken) velocities,

$$ {}^{d}v_i^{j} = -B_i^{j} \nabla \mu_i^{j} \tag{2}$$

where B_i^{j} denotes the mobility of the i-th component and μ_i^{j} is the diffusion potential.

$$v^{drift} = -\sum_{i=1}^{r} \Omega_i^j c_i^{j\ d} v_i^j \qquad (3)$$

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

The Initial conditions are the 1) arbitrary initial distributions of the components (in the solid solutions, alloys, only): $c_i(0,x) = c_i^0(x)$, 2) the initial thickness of sub-layers (e.g. j-th phase): $\Delta X^j(t=0) = X_0^j(R) - X_0^j(L)$ and 3) constant thicknesses of the phase boundary zones, δ^j

In the bi-velocity method 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:

• the mass balance at moving interfaces (left (L) and right (R) side of the phase):

$$\left(c_i^j(R) - \left\langle c_i^j(I) \right\rangle\right)\overset{\bullet}{X}^j = \left(c_i^j \Omega_i^{j\ d} v_i^j + c_i^j \Omega_i^{j\ D} v^j\right)(R) -$$
$$-\left(\left\langle c_i^j \Omega_i^j \right\rangle^d v_i^j + \left\langle c_i^j \Omega_i^j \right\rangle^D v^j\right)(I) \qquad , \qquad (4)$$

$$\left(c_i^{j+1}(L) - \left\langle c_i^j(I) \right\rangle\right)\overset{\bullet}{X}^j = \left(c_i^{j+1} \Omega_i^{j+1\ d} v_i^{j+1} + c_i^{j+1} \Omega_i^{j+1\ D} v^{j+1}\right)(L) -$$
$$-\left(\left\langle c_i^j \Omega_i^j \right\rangle^d v_i^j + \left\langle c_i^j \Omega_i^j \right\rangle^D v^j\right)(I) \qquad , \qquad (5)$$

• the volume produced due to the reaction of j-phase:

$$\overset{\bullet}{X}^j = \sum_i c_i^j \Omega_i^j \frac{\left(c_i^{j+1} \Omega_i^{j+1\ d} v_i^{j+1} + c_i^{j+1} \Omega_i^{j+1\ D} v^{j+1}\right)(L) - \left(c_i^j \Omega_i^{j\ d} v_i^j + c_i^j \Omega_i^{j\ D} v^j\right)(R)}{c_i^{j+1} \Omega_i^{j+1}(L) - c_i^j \Omega_i^j(R)}$$
$$(6)$$

• the phase thickness:

$$\Delta X^j = X^{j+1} - X^j = \int_t \left(\overset{\bullet}{X}^{j+1} - \overset{\bullet}{X}^j\right) d\tau \qquad (7)$$

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

$$
\left.
\begin{array}{c}
J_1^j(I) \cong -\dfrac{B_1^j(I)c_1^j(I)}{\delta^j} \times \\[2mm]
\times\left(\left({}^{eq}N_1^{j+1} - N_1^{j+1}(L)\right)N_2^{j+1}(L)\,g''^{\,j+1} - \left({}^{eq}N_1^j - N_1^j(R)\right)N_2^j(R)\,g''^{\,j}\right) \\[3mm]
J_2^j(I) \cong -\dfrac{B_2^j(I)c_2^j(I)}{\delta^j} \times \\[2mm]
\times\left(\left({}^{eq}N_2^{j+1} - N_2^{j+1}(L)\right)N_1^{j+1}(L)\,g''^{\,j+1} - \left({}^{eq}N_2^j - N_2^j(R)\right)N_1^j(R)\,g''^{\,j}\right)
\end{array}
\right\}
\qquad (8)
$$

where: $g''^{\,j} = \partial\mu_i^j / \partial N_i^j = \partial^2 g^j / \partial\left(N_i^j\right)^2$ denote the second derivative of the Gibbs free energy and ${}^{eq}N_i^j$ are the molar ratios at the equilibrium state.

The details of the bi-velocity model and method of calculations applied in this work can be found elsewhere [7, 9-11].

Calculations of solid-state diffusion simulated the growth of β-NiAl and γ'-Ni₃Al at 1077°C. The initial conditions included pure Ni as the substrate and various concentrations of deposited Al (in the range of β-NiAl phase) being dependent on the [H₂]/[HCl] ratio. The relation between the values of interdiffusion coefficient and the chemical composition in the β-NiAl and γ'-Ni₃Al was estimated according to the Campbell approximation [12] (Fig. 3 and 4) respectively.

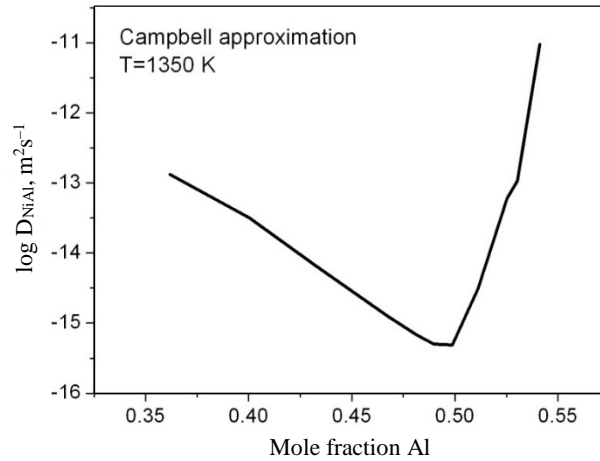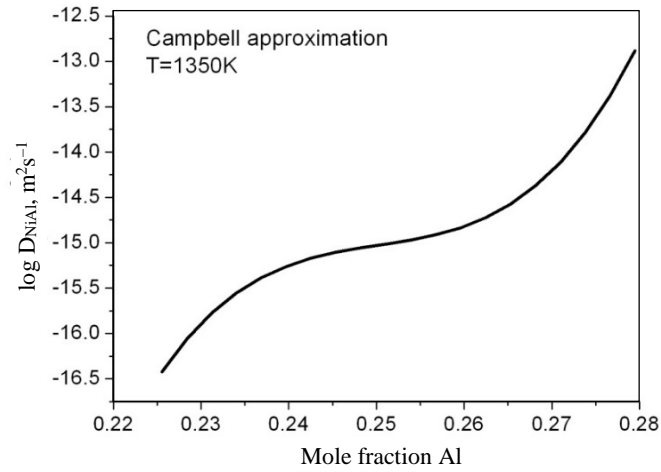Fig. 3. The interdiffusion coefficient in β-NiAl phase at 1350 K

Fig. 4. The interdiffusion coefficient in Ni₃Al phase at 1350 K

Table 2 summarizes the thermodynamic and kinetic data used in the simulations of the Ni-Al system. Symbols N_{Ni} (L) and N_{Ni} (R) denote the equilibrium Ni molar ratio at the moving interfaces at the left and right side of the phase zone, respectively. Calculations of the Gibbs' free energy were based on the estimations made by Ansara et al. [13]. The thickness of β-NiAl zone was calculated for each chosen phase composition. The results gained for the simulations of 2-h process at 1077°C are in a good agreement with experimental data obtained by Kolsheen and Stock [14]. Figure 5 presents the thickness of β-NiAl phase as the function of [H₂]/[HCl] flow ratio obtained in the simulations and in the experiment. In both cases, for the flow ratio between 0.5 and 2 characteristic reduce in the layer thickness can be observed.

Table 2. Thermodynamic and kinetic data used to simulate reactions
in the Ni-Al system at 1350 K

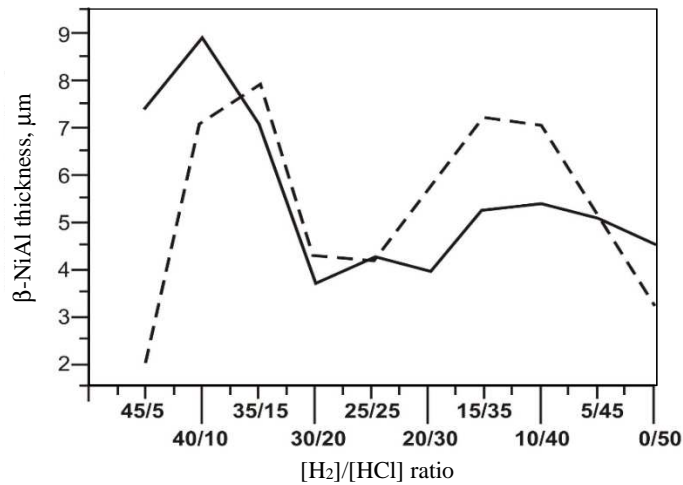| Phase, j	Molar ratio N_{Ni} (L)	Molar ratio N_{Ni} (R)	Gibbs' free energy $\partial^2 g / \partial N_{Al}^2$, kg cm² s⁻²
Ni	1	0.85	–
γ'-Ni₃Al	0.77	0.725	2.40418 10⁻¹⁴
β-NiAl	0.625	0.45	1.18485 10⁻¹⁴
Al	0	0	–

Fig. 5. Thickness of the β-NiAl phase calculated for 2 hour of nickel aluminizing at 1077 °C and various $[H_2]/[HCl]$ ratios. The results of simulations (solid line) compared with the experimental measurements (dashed line) reported by Kohlscheen and Stock for 50 dm^3/h of the total flow [14]

Conclusions

Basing on the bi-velocity method of interdiffusion the multicomponent and multiphase systems can be analyzed. The qualitative analysis of the transport in non-ideal and multicomponent system requires a combined thermodynamic and kinetic approach. The method allows to adopt the composition dependent interdiffusivities for each phase. It is in particular shown that the method can properly predict the growth rate of β-NiAl phase at given temperature (here 1350 K) for different ranges of miscibility. The results show the prospect of the extension of the bi-velocity method in future applications.

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