Interdiffusion Issues in Pt Modified NiAl Coatings

S. Datta\(^1\), R. Filipiek\(^2\) and M. Danielewski\(^2\)

\(^1\) Advanced Materials Research Institute, University of Northumbria, U.K.
\(^2\) Faculty of Materials Science & Ceramics, University of Mining & Metallurgy, Cracow, Poland.

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**Abstract.**
Platinum aluminide diffusion coatings act as a remedy against the aggressive environments in which modern aero-gas turbines operate. The increase in operating temperatures of industrial energy systems and gas turbines, often coupled with the decrease in fuel quality being employed, has led to the extensive use of coatings capable of providing improved service life. Interdiffusion plays a critical role in understanding the integrity of such coatings.

This paper presents a review of the interdiffusion issues in Pt-modified nickel aluminide coatings. The mathematical model for interdiffusion in multi-component open systems which allows for the description of a wide range of processes (e.g., processes stimulated by reactions at interfaces) is employed for the modeling of interdiffusion in the Pt-modified $\beta$-NiAl on MAR M002 superalloy and in the Pt/ $\beta$-NiAl coatings systems. The Inverse Method which permits calculation of the intrinsic diffusivities, for an arbitrary number of components in a system, is presented.

**Introduction**
The design of gas turbine nickel base superalloys to provide improved high temperature creep resistance through the precipitation of a strengthening $\gamma'$ phase undermines the corrosion resistance of these materials. The high temperature corrosion resistance is then provided by nickel aluminide diffusion coatings [1-3]. However, the ability of nickel aluminide coatings in providing protection against high temperature corrosion is severely undermined by the incorporation within the scale of the outwardly diffusing damaging substrate elements often accentuated by the presence of increasingly severe corrosive environments. Significant progress was achieved in overcoming the limitations of conventional nickel aluminide coatings by incorporation of Pt in the nickel aluminide coating systems. Even the improved Pt-aluminide coatings suffer eventual failure caused by thermal stress generated during thermal cycling, depletion of Al in the coating following spallation of $\text{Al}_2\text{O}_3$, and sulphur segregation at the coating/scale interface. The major cause of failure is still the migration and incorporation of the substrate elements in the coating and the scale.

The design of high performance Pt-nickel-aluminide requires a knowledge of the interdiffusion of the substrate elements in the coating system formed on the superalloy. Until recently this area has not been studied extensively. In this paper the mathematical modeling of interdiffusion in Pt-Ni-Al system providing design strategies to improve its performance, thermal stability and resistance to oxygen/sulphur degradation at elevated service temperatures is demonstrated. Some background information on nickel aluminide and noble-metal-modified diffusion coatings is presented to provide the context for considering the interdiffusion issues during the operation of these coatings in preventing high temperature degradation of the aero-gas turbines.

**Nickel Aluminide Coatings**
Nickel aluminide coatings are the most widely used intermetallic coatings. Nickel aluminide is an ordered intermetallic and exists over a composition range of 45 - 60 at % Al. [7]. Because of its high oxidation resistance combined with low density, nickel aluminide is used as a structural
coating to prevent the high temperature environmental degradation generally encountered in aero
gas turbines. Nickel aluminide coatings are produced by two types of pack processes [1,3]. In one
variant the component is placed in contact with a pack consisting of aluminium, a halide activator
(NH4Cl, NaCl or CrF\textsubscript{2}) and an inert filler and subjected to a diffusion treatment (for 2 to 24h)
within a temperature range of 750 to 1000 °C. The Al halide formed, aided by the decomposition of
the halide activator, undergoes dissociation on the surface allowing Al diffusion into the substrate
and leaving halide ions free to react with more Al and cause the cycle to continue. A modification
of this technique, termed “out-of-pack”, is similar to the chemical vapour deposition process (CVD)
in that the components to be coated are not in contact with the powder of the pack, the aluminium
halide gas generated being transported over the component/substrate surface by a carrier gas [1].

Aluminide coatings grow by two mechanisms depending on the use of a low or high activity
pack. The high aluminium activity process involves the inward diffusion of aluminium to form δ-
Ni\textsubscript{2}Al\textsubscript{3} with a minor amount of NiAl. The coating is heat treated to allow Ni diffusion from the
substrate to form β-NiAl, a much more ductile and oxidation resistant phase than the Ni\textsubscript{2}Al\textsubscript{3} phase.
A three-zone structure develops comprising an outer zone containing α-Cr and other substrate
phases in a β-NiAl matrix, a middle zone of a single phase β-NiAl with Cr, Ti, Mo and Co in
solution and a β-matrix inner zone containing carbides and σ phases [1,12].

The low aluminium activity process leads to the formation of a two-zoned structure by the
outward diffusion of Ni from the substrate reacting with Al. The outer zone consists of a single
phase β-NiAl with alloying elements diffusing out from the substrate along with Ni. The inner zone
contains carbides and/or phases formed by the Ni withdrawal from the β-NiAl matrix [1].

The protectivity of aluminide (NiAl) coatings stems from their ability to form α-Al\textsubscript{2}O\textsubscript{3} scale.
α-Al\textsubscript{2}O\textsubscript{3} has an hcp structure of oxygen anions with two thirds of the octahedral sites filled by
trivalent cations.

The high temperature protection afforded by the α-Al\textsubscript{2}O\textsubscript{3} results from the oxide having low
concentrations and mobilities of both ionic and electronic defects [4]. The slow growth rate of the
oxide is related to its low nonstoichiometry and large band gap width, which makes electronic
conduction difficult. In the main, α-Al\textsubscript{2}O\textsubscript{3} acts as an ionic conductor in which both oxygen and aluminium are mobile [5,6].

There appears to be some contention over the growth mechanism of the alumina scale. It has
been reported that the columnar structure of α-alumina is indicative of oxide formation at the
scale/substrate interface [4]. Tracer studies of the oxide formed by overlay coatings [5] and bulk
β-NiAl [7] have indicated alumina growth by inward diffusion of oxygen. However, the growth rate
cannot be accounted for by the rate of oxygen diffusion along alumina grain boundaries [8]. It has
been proposed that the growth of the oxide formed by overlay coatings is by anion transport and the
growth of alumina by outward diffusion of cations or is a combination of anion and cation transport
[4,9,10]. The morphology and microstructure of the scales formed on the β-NiAl indicates its
growth mechanisms. The formation of a characteristic ridge morphology of the scale has been
ascribed to the transformation (at ~1100 °C) of transitional aluminas, formed by the outward
diffusion of aluminium to α-Al\textsubscript{2}O\textsubscript{3} where growth occurs by both inward and outward diffusion. The
alumina cells nucleate and then grow laterally across the surface consuming the transient phases
until the cells impinge. The large grain size of β-NiAl promotes outward diffusion. The views
concerning the growth of the oxides are not consistent.

The effectiveness of aluminide coatings in preventing high temperature corrosion is undermined
by the incorporation within the scale of the outwardly diffusing, damaging substrate elements. The
high activity aluminide coatings being inwardly grown facilitate this incorporation. Such
incorporation of the damaging elements is more difficult in the outwardly grown, low activity
coatings [1]. The effectiveness of aluminides is further compromised by the increased attack by
impurities in combustion gases caused by engines operating on lower grade fuel and in harsher
environments. The limitations in the use of conventional nickel aluminide coatings deposited on Ni-
base superalloys, e.g., MAR M002, to provide oxidation and hot-corrosion resistance, are well known [11].

Pt Modified NiAl Coatings

A major advance was made by the addition of Pt to nickel aluminide coatings; such coatings outperform the unmodified conventional aluminide coatings [4]. Two main types of Pt-Al coatings are used:

1. a single phase structure with a continuous PtAl$_2$ surface layer, and
2. a two phase PtAl$_2$ + (Ni,Pt)Al structure with varying amounts and morphologies of Pt-rich phases and with varying amounts and extent of substrate intervention in the (Ni,Pt)Al layer.

The Pt-aluminide coatings have displayed improved oxidation resistance and a greater resistance to type-I [1] hot corrosion and a marginal improvement in type-II hot corrosion resistance. There is now a consensus that improved adherence of a slow growing $\alpha$-Al$_2$O$_3$ scale, preventing spallation and cracking, is a major factor. This overall improvement may be associated with a number of key factors:

1. promotion of the selective oxidation of Al,
2. an ability for the oxide to reform following spallation, probably associated with enhanced Al diffusion in the coating,
3. the creation of an Al reservoir through the affinity of Al for Pt,
4. the inhibition of the coating/substrate interdiffusion,
5. the exclusion or limitation of concentration of substrate refractory elements in the outer zone of the coatings – such elements undermine the integrity of the coatings, and
6. a reduction in the oxide growth stresses.

Even the improved Pt-aluminide coatings eventually suffer failure. The failure mechanisms identified include:

1. thermal stress generated within the coating during thermal cycling,
2. depletion of Al in the coating and the failure to regenerate Al$_2$O$_3$,
3. associated growth of Ni- and Cr-spinels at the oxide coating/substrate interface and their eventual inclusion in the scale, lowering scale adhesion,
4. outward diffusion of substrate elements such as Ti from the diffusion zone to the coating/oxide interface increasing the scale growth rate leading to localized scale thickening and eventual spallation,
5. for Hf-containing superalloys (e.g. MAR M002) large Hf peg formation (10-20µm deep) at the oxide/coating interface, and
6. sulphur segregation at the oxide/scale interface.

However, there has been/and is, a continued demand to improve further the effectiveness of Pt-modified NiAl coatings. Several avenues have been explored: improved understanding of the processes of scale formation in oxidizing and hot corrosion environments; a) better insight of the mechanisms responsible for the loss of integrity of the protective Al$_2$O$_3$ scale due to the incorporation of the substrate elements, e.g., Ti; b) through the modification of the coatings by incorporating other noble metals – Rh, Ir – in combination or singly and semi-reactive elements such as Hf or Zr; and c) by improving the manufacturing methods for producing these coatings so as to minimize the sulphur content. There has been some renewed interest in the last two methods [4,12,13].

One approach has been to incorporate iridium, with or without platinum, in the coating. Analysis of the Ir-aluminide coating system in the as-processed condition shows a layer morphology – a Ni-rich outer layer and Ir-rich inner layer. Al concentration decreases with depth through the coating and concentrations of W and Ta appear within the Ir-rich layer. Ir-Pt-aluminide also produces, in the as-processed condition, a dual layered structure ($\beta$-NiAl outer layer), similar to that of the Ir-Pt
system with Ir concentrated in the inner layer, and the outer layer rich in Ni and Pt; Ti is excluded from the outer layer. The oxidation (200h at 1000 °C) of an Ir-Pt-aluminide on MAR M002 reveals: i) the formation of Al₂O₃, which suffers less spallation than that shown by the Ir-aluminide system; ii) the presence of voids at the coating/substrate interface; iii) the absence of Hf peg formation; iv) internal oxidation and outward diffusion of W, Ta and Ti [4,12,13]. The conclusion is that the reason for the beneficial effects of incorporating Ir over that derived from Pt alone is unclear.

Similar efforts considered the use of rhodium. Some improvement in the hot corrosion behavior of Pt aluminide and Pt-Rh aluminide coatings on MAR M002 was noted. The beneficial effect of this system was further demonstrated by the absence of the substrate elements (W and Ta) in the outer layer [11].

Computer Modeling of the Mass Transport in the Multi-component Systems

It is clear from the background information given above that platinum aluminide diffusion coatings are commonly used as a remedy against aggressive environments in which modern nickel based gas turbine blades operate [19,20]. Both experimental and theoretical studies of interdiffusion in the Pt-aluminide coatings on nickel-based superalloys carried out so far show a complexity of the transport processes occurring during the processes of oxidation, sulphidation and hot corrosion [14-18]. It is assumed that the addition of platinum contributes towards achieving enhancement in diffusion of aluminium necessary for the formation of a protective Al₂O₃ scale.

In the further part of this paper the interdiffusion in the Pt/Ni-Al on MAR M002 systems are analyzed. A special attention is put on the Pt-Ni-Al system which is a base of the platinum-modified nickel aluminide coatings. The objective of this study is to calculate the intrinsic diffusivities of Pt, Ni, and Al in Pt/β-NiAl system and examine the influence of the addition of platinum on transport properties in nickel aluminide coatings.

The Generalized Darken Method (GDM) of interdiffusion and the Inverse Method (IM) have been used for the calculations of the intrinsic diffusivities of Pt, Ni, Al and other elements. These diffusivities have subsequently been employed to compute the concentration profiles in the Pt/β-NiAl system for various temperatures and times of the annealing and been compared with the experimental results.

The Generalized Darken Method will be used for the modeling of the diffusion mass transport in the multi-component systems. In this method the Darken’s postulate [19] that the total mass flow is a sum of the diffusion and drift flows, is applied for the description of the diffusion transport in multi-component solid solutions. The equations of mass conservation (continuity equations), the appropriate expressions describing the fluxes and the postulate of constant molar volume of the system allow a quantitative description of the diffusion transport process both for the open and closed systems and when component diffusivities vary with composition. The detailed information about this model and its solution can be found elsewhere [20,23]. The brief formulation of the model necessary for understanding the Inverse Method, used for calculating the intrinsic diffusivities of the components, is presented schematically in the Figure 1.
1) Intrinsic diffusivities of the components, $D_1, \ldots, D_r$, where $r$ – the number of the components in the system.

2) Initial profiles of the components, $ho_1(x), \ldots, \rho_r(x)$.

3) Thickness of the system, $2\Lambda$.

4) Time of the process duration, $\hat{t}$.

5) The functions describing the fluxes of the components through the left and right boundary: $J_{L}(t), J_{R}(t)$ for $i = 1, \ldots, r$ and $0 \leq t \leq \hat{t}$.

**Physical laws, initial and boundary conditions**

1) Law of the mass conservation:
   \[ \partial \rho_i / \partial t = - \partial J_i / \partial x. \]

2) Darken’s flux definition:
   \[ J_i = -D_i (\partial \rho_i / \partial x) + \rho_i \nu. \]

3) Postulate of the constant concentration of the system:
   \[ \rho_1 + \cdots + \rho_r = \text{const.} = c. \]

4) Initial density distributions of the elements in the system:
   \[ \rho_i(0,x)=\rho_i(x) \quad \text{for} \quad i = 1, \ldots, r. \]

5) Fluxes at the boundaries equal the fluxes which flow through the boundaries:
   \[ J_i(t,-\Lambda) = J_{L}(t), \quad J_i(t,\Lambda) = J_{R}(t) \]
   \[ \text{for} \quad i = 1, \ldots, r. \]

**Known**

- Density distributions of the elements $\rho_1(t,x), \ldots, \rho_r(t,x)$

**Unknowns**

- 1) Drift velocity $\nu(t,x)$ in the system for any time $t$.

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**Figure 1 Schematic formulation of the Generalized Darken Method.**

The Inverse Method of Calculation the Intrinsic Diffusivities. A single experiment at any $t \geq 0$ (given the components’ concentration profiles) allows calculation of the average intrinsic diffusivities of the unrestricted number of elements in the system. The uniqueness of solution of the Generalized Darken Method [21] permits the formulation of the inverse problem of interdiffusion in the closed system:

**Given:** 1) Molecular masses of the elements; 2) Thickness of the system, $2\Lambda$; 3) Initial distribution of elements: $\hat{\rho}_1(x), \ldots, \hat{\rho}_r(x)$ for $-\Lambda \leq x \leq \Lambda$; 4) Measured experimental distributions of the elements after arbitrary time $t$, $\hat{\rho}_1(x), \ldots, \hat{\rho}_r(x)$ for $-\Lambda \leq x \leq \Lambda$.

For any positive numbers $\Theta_1, \ldots, \Theta_r$, we denote $\rho_i^j \Theta$ - the calculated density of the $i$-th element for time $\hat{t}$ and for these numbers inserted in the place of the intrinsic diffusivities. Let us define a function $err$, given by formula:

$$
err(\Theta_1, \ldots, \Theta_r) := \int_{-\Lambda}^{\Lambda} \sum_{i=1}^{r} \left( \hat{\rho}_i(x) - \rho_i^j \Theta(x) \right)^2
$$

We are looking for such parameters $\Theta_1, \ldots, \Theta_r$, that minimize objective function $err$. Calculated for such determined numbers, concentration profiles of the all components in the diffusion couple are the best fitted to the experimental (measured) ones. These numbers correspond to the intrinsic diffusivities for the GDM of interdiffusion. The calculation of the intrinsic diffusivities in “r”-component system was carried out by optimizing the objective function err, in “r”-dimensional space.

The above method was used for calculations of the intrinsic diffusivities in Pt-modified $\beta$-NiAl coating on MAR M002 and in Pt/\$\beta$-NiAl systems.
Interdiffusion in Pt-Modified Nickel Aluminide Coatings on MAR M002 Superalloy.

**Experimental Procedure.** The nominal composition of the superalloy MAR M002 is presented in Table 1. The details on the materials, experimental procedure and used techniques of analysis has been already published [16].

| Table 1 Nominal chemical composition of MAR M002 substrate material (wt.%). |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Cr | Al | Ti | Co | W | Ta | Mo | Hf | Fe | Zr | B | C | Ni |
| 9 | 5.5 | 1.5 | 10 | 10 | 2.5 | 0.5 | 1.25 | <0.5 | 0.1 | 0 | 0 | Bal |

Calculating of the intrinsic diffusivities. The diffusion annealing experiments at selected temperatures in the 1073 – 1373 K range have been performed in an argon atmosphere. Because the studied alloys contain precipitations of the gamma prime phase, the average concentration profiles of the components have been determined using the EDS (Energy Dispersive Spectrometer) technique. For simplicity we reduced the number of components to five Pt, Al, Cr, Ni, Co - the other components were omitted. Using the measured average concentration profiles of the components before and after diffusion annealing and employing the presented method (Inverse Method) the corresponding average intrinsic diffusivities of Pt, Al, Cr, Ni and Co in Pt-modified β-NiAl/MAR M002 (the multi-phase) system were calculated - see Table 2.

| Table 2 Computed average intrinsic diffusivities in the coating-alloy system (Pt-modified β-NiAl coating on MAR M002) [16]. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Temperature [K] | $D_{Al}$ [cm$^2$s$^{-1}$] | $D_{Cr}$ [cm$^2$s$^{-1}$] | $D_{Co}$ [cm$^2$s$^{-1}$] | $D_{Ni}$ [cm$^2$s$^{-1}$] | $D_{Pt}$ [cm$^2$s$^{-1}$] | Annealing time, [h] |
| 1073 | 2.73·10^{-12} | 8.59·10^{-13} | 9.42·10^{-13} | 2.50·10^{-13} | 8.3·10^{-13} | 200 |
| 1173 | 9.28·10^{-12} | 2.78·10^{-12} | 4.17·10^{-12} | 1.39·10^{-11} | 6.28·10^{-13} | 100 |
| 1273 | 2.49·10^{-11} | 1.43·10^{-11} | 1.05·10^{-11} | 1.68·10^{-11} | 2.17·10^{-11} | 150 |
| 1373 | 5.08·10^{-11} | 2.77·10^{-11} | 2.27·10^{-11} | 1.06·10^{-10} | 4.22·10^{-11} | 97 |

In Figure 2, the average intrinsic diffusivity of Pt, Al, Cr, Ni and Co in Pt-modified β-NiAl/MAR M002 system as a function of temperature and calculated activation energies of the components are shown. The scatter of the calculated intrinsic diffusivities of the nickel and the platinum in Figure 2 is too big and at present the values calculated from the plots of lnD/(1/T) do not represent the true activation energies. It is probably due to the simplifying assumption that in such complex multi-component and multi-phase system like Pt-modified β-NiAl/MAR M002 the diffusivities do not depend on the alloy composition.

In Figure 3 the calculated and experimental profiles of the components after 150 h of diffusion annealing in argon atmosphere at 1273 K are shown.

Interdiffusion in the Oxidized Pt-Modified β-NiAl Coating on MAR M002. In this section we will present the predicted and measured distributions of elements in the coating/alloy system (diffusion couple) produced by the oxidation of Pt-modified β-NiAl coating on MAR M002 leading to the formation of an α-Al$_2$O$_3$ scale. Using the calculated average intrinsic diffusivities - see Table 2, we have done the simulations of interdiffusion in the selectively oxidized coating (i.e., Al is the reacting metal that forms Al$_2$O$_3$ scale). The estimated values of oxygen uptake ($k_p = 10^{-12}$ g$^2$cm$^{-4}$s$^{-1}$) were used to calculate the flux of oxygen as a function of time and the equivalent flux of Al through the coatingSCALE interfaces. The computed densities of Al, Ni and Pt in the Pt-modified β-NiAl coating on MAR M002 after oxidation at 1173 K for 100 h are shown in Figure 4. Satisfactory
agreement can be seen in the case of Al and Ni distributions, however, the measured Pt densities markedly exceed the calculated values.

All the reactions studied show that the distribution of all alloy components is affected by the oxidation process. The computed distributions of alloy components and scale composition do not show a satisfactory quantitative agreement with the experimental measurements. Actual coating composition shows markedly higher Pt concentration. These differences may be due to the underrated values of intrinsic diffusivities used (neglecting thermodynamic factor). Clearly more precise measurements of intrinsic diffusivities of the Pt, Ni and Al in the Pt/β-NiAl system are necessary to explain why the addition of the platinum to basic aluminide coatings significantly improves the oxidation resistance of these coatings. These studies are presented bellow.
Concentration profiles:  
- initial  
- experimental  
- calculated

Figure 3 The measured and calculated density profiles in Pt-modified β-NiAl coating on MAR M002 after 150h of the diffusion annealing at 1273 K in argon.

Interdiffusion studies in the Pt/β–NiAl system.

Experimental Procedure. The 2 mm thick slices have been cut from an extruded β–NiAl rod and polished up to 0.25 µm diamond paste. A 8.0±0.5 µm thick layer of platinum was electroplated on the specimens. Such prepared diffusion couples were heat treated at constant temperature at 1073–1273 K temperature range in argon atmosphere (a_o2 < 10^{-15} atm) for varying times - see Table 3. The couples were sectioned for the purpose of analyzing the concentration profiles which were measured using the EDS technique.

Table 3 The conditions of diffusion annealing of the Pt/Ni-Al diffusion couples.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>Time [h]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>64.5</td>
</tr>
<tr>
<td>1123</td>
<td>18</td>
</tr>
<tr>
<td>1173</td>
<td>5</td>
</tr>
<tr>
<td>1223</td>
<td>5</td>
</tr>
<tr>
<td>1273</td>
<td>1</td>
</tr>
</tbody>
</table>

Calculating of the intrinsic diffusivities. The average intrinsic diffusivities of platinum, nickel and aluminium at various temperatures were obtained by analyzing the annealed Pt/β–NiAl diffusion couples. Using the measured concentration profiles and the Inverse Method (described above) the diffusivities of Pt, Ni and Al for various temperatures were calculated [25] and are
presented in Table 4. The calculated average intrinsic diffusivities of Pt, Ni and Al are plotted in the logarithmic scale as a function of the reciprocal temperature – see Figure 8. The apparent activation energies and pre-exponential factors for the intrinsic diffusion in Pt-Ni-Al system were calculated and presented in Table 5.

![Graph showing density of Al, Ni, and Pt as a function of distance.](image)

Figure 4 The measured and calculated (using the GDM) densities of Al, Ni and Pt in the oxidized Pt-modified β-NiAl coating on MAR M002 superalloy. The distance measured from the MAR M002/coating interface. EDS data after oxidation at 1173 K for 100h.

<table>
<thead>
<tr>
<th>Temperature [K]</th>
<th>$D_{Al}$ [$\text{cm}^2\text{s}^{-1}$]</th>
<th>$D_{Ni}$ [$\text{cm}^2\text{s}^{-1}$]</th>
<th>$D_{Pt}$ [$\text{cm}^2\text{s}^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1073</td>
<td>$6.23\times10^{-12}$</td>
<td>$2.12\times10^{-13}$</td>
<td>$1.41\times10^{-13}$</td>
</tr>
<tr>
<td>1123</td>
<td>$2.48\times10^{-11}$</td>
<td>$3.29\times10^{-13}$</td>
<td>$1.07\times10^{-12}$</td>
</tr>
<tr>
<td>1173</td>
<td>$4.64\times10^{-11}$</td>
<td>$4.94\times10^{-12}$</td>
<td>$6.44\times10^{-12}$</td>
</tr>
<tr>
<td>1223</td>
<td>$1.04\times10^{-10}$</td>
<td>$1.07\times10^{-11}$</td>
<td>$1.78\times10^{-11}$</td>
</tr>
<tr>
<td>1273</td>
<td>$4.19\times10^{-10}$</td>
<td>$2.60\times10^{-11}$</td>
<td>$7.81\times10^{-11}$</td>
</tr>
</tbody>
</table>

Table 4 Calculated intrinsic diffusivities in the Pt/β-NiAl system for various temperatures [25].

In the whole range of temperatures 1073–1273 K the intrinsic diffusivity of the aluminium is approximately one order of magnitude higher than the diffusivities of the nickel and platinum. The results obtained show that the fast diffusion of aluminium in Pt-Ni-Al system can be a factor that is responsible for the very good protective properties of the platinum-aluminide coatings on
superalloys. Additional studies of interdiffusion in binary Ni-Al system are necessary to confirm the crucial influence of the addition of platinum on the transport properties of nickel and aluminium.

![Density profiles](image)

**Figure 5** The measured and calculated profiles of the components in the Pt/β-NiAl system at 1073 K and 64.5 h of the diffusion annealing in argon.

![Density profiles](image)

**Figure 6** The measured and calculated profiles of the components in the Pt/β-NiAl system at 1173 K and 5 h of the diffusion annealing in argon.

Such preliminary studies have been already done. An example concentration profile of Ni at 1273 K for 20 h of diffusion annealing in argon is presented in Figure 9. Unsymmetrical concentration profiles indicate a strong concentration dependence of the intrinsic diffusivities of Ni and Al in β-NiAl. The thermodynamic activity data also show a big change of the thermodynamic factor in the range of stability of the β-NiAl phase [26]. Consequently the variable intrinsic diffusivities have to be calculated including a non-ideality of the β-NiAl system. These studies are now in progress.
Figure 7 The measured and calculated profiles of the components in the Pt/β–NiAl system at 1273 K and 1 h of the diffusion annealing in argon.

Figure 8 The calculated intrinsic diffusivities of Al, Ni and Pt in the Pt/β-NiAl system in the Arrhenius plot. Temperature range 1073 – 1273 K.

**Modeling of interdiffusion in Pt/β–NiAl system.** Using the calculated intrinsic diffusivities from Table 4 the concentration profiles of the elements in Pt/β–NiAl system at various temperatures have been calculated [25]. In the Figures 5–7 the calculated profiles of the Pt, Ni and Al are shown.
The computed concentration profiles are in good agreement with the experimental in the whole temperature range 1073–1273 K.

Table 5 Activation energy, $Q$, and pre-exponential factor $D_0$, for intrinsic diffusion in Pt/β–NiAl system at 1073–1273 K [25].

<table>
<thead>
<tr>
<th>Element</th>
<th>$Q$ [kJmol$^{-1}$]</th>
<th>$D_0$ [cm$^2$s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>223±19</td>
<td>0.48</td>
</tr>
<tr>
<td>Ni</td>
<td>297±42</td>
<td>50.97</td>
</tr>
<tr>
<td>Pt</td>
<td>351±16</td>
<td>9.95·10$^5$</td>
</tr>
</tbody>
</table>

Figure 9 The measured concentration profile of nickel in β-NiAl system at 1273 K and for 20 h of the diffusion annealing.

Summary

A review on the current position of the Pt-modified nickel aluminide diffusion coating has been presented. The possibility of adopting a theoretical approach for describing the complex processes occurring in coating/alloy multi-component system (the Pt-aluminide coating on MAR M002 alloy) has been shown. The Inverse Method has been used for calculating the intrinsic diffusivities of the components. For such obtained intrinsic diffusivities the modeling of thermal stability of a coating/alloy system has been performed. It can be seen that even for a much more simple ternary system – Pt/β-NiAl – the simplifying assumption that intrinsic diffusivities of the components do not depend on composition of the system is not valid – see in particular the nickel concentration profile in the Figure 5. The calculated intrinsic diffusivities of Al and Ni in Pt-modified β-NiAl coating on MAR M002 and in Pt/β-NiAl system are significantly different. The differences can stem from the fact that diffusion of these elements in the case of Pt-modified β-NiAl coating on MAR M002 occurred in the presence of the gamma prime phase precipitation and such microstructure can strongly affect transport properties.

This analysis shows potential of using the GDM in description of the interdiffusion process in multi-component systems. However further improvement in modeling such real complex systems will be possible using the concentration dependent intrinsic diffusivities. Some initial work in this direction have already been done and the results obtained for the Cu-Fe-Ni system are quite promising [27].
Acknowledgments

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