# Experimental and Simulation Study of Uphill Diffusion of Al in a Pt-Coated γ-Ni-Al Model Alloy

**Bo Sundman, Stewart Ford, Xiao-Gang Lu, Toshio Narita, and Daniel Monceau**

An experimental study of diffusion of Al, Ni, and Pt in a Pt-coated binary Ni-Al alloy has been made and compared with a computer simulation. Assessed thermodynamic and kinetic descriptions have been used. Starting from the measured experimental concentration profiles after 1 h heat treatment at 1173 K the simulation is compared to the experimentally determined profiles after 11 h continuous heat treatment. The experimental finding that Al will diffuse against its concentration gradient is explained by the strong lowering of the chemical potential by Pt. The simulation predicts that Al will reach a concentration maximum at the surface, larger than its bulk composition.

## 1. Introduction

The corrosion resistance of Ni-based superalloys can be enhanced by coating with Pt. Coatings are typically 5-10 μm thick and at elevated temperatures, there will be diffusion of all elements in the coating as well as in the bulk. This leads to a $\gamma/\gamma'$ coating enriched in Pt.[1] This coating can also be enriched in Al.[2] The optimization of the coating fabrication process, and also the durability of the $\gamma/\gamma'$ coating, depends on the diffusion of Pt into the bulk and of the diffusion of Al toward the external surface. There have been reports[3] that Al will diffuse against its composition gradient because Pt significantly lowers its chemical potential. It is interesting to investigate if a simulation based on assessed thermodynamic data can correctly reproduce experimental findings as it is much simpler to simulate long time heat treatments than to perform the experimental work, particularly since coatings as well as the bulk material are usually multicomponent alloys. However, this study is based on the first available assessment of Al-Ni-Pt,[4] and a binary Ni-Al alloy was used as substrate with a coating of pure Pt in order to have as simple a system as possible.

If uphill Al diffusion toward the coating surface can be shown experimentally in a model Pt-Ni-Al system and simulated thanks to adequate thermokinetic data, the consequences are threefold. First, it proves the assumption that this effect is due to the Pt effect on Al activity. Second, it shows that the use of simple Fick's laws with the concentration gradients being the driving force for diffusion is inadequate to model the composition evolution of coated superalloys. Third, it opens the way to an optimization of the fabrication of coated systems and to a better simulation of the lifetime of coated superalloys including thermal barrier coating (TBC) systems.

## 2. Thermodynamic and Kinetic Models

The Calphad method means that each phase in a system is modeled with a single Gibbs energy function with parameters fitted to experimental and theoretical data.[5,6] These models can also be extrapolated in composition and temperature outside the stable range of the phase. They can thus be used to calculate gradients in chemical potentials and thermodynamic factors when there is an on going diffusion process or phase transformation.

The DICTRA software[6] can solve diffusion problems in one dimension expressing the flow $J_k$ of the components $k$ in a lattice fixed frame as

$$\tilde{J}_k = -c_k y_{\text{Va}} \Omega_{k\text{Va}} \frac{\partial \mu_k}{\partial z} \qquad \text{(Eq 1)}$$

where $c_k$ is the amount of component $k$ per unit volume, $y_{\text{Va}}$ the fraction of vacant sites on the sublattice where $k$ is dissolved, $\Omega_{k\text{Va}}$ is a kinetic parameter, $\mu_k$ is the chemical potential of component $k$, and $z$ is the length coordinate. For substitutional diffusion, the phenomenological parameters $L_{kk}$ are defined as

$$L_{kk} = c_k y_{\text{Va}} \Omega_{k\text{Va}} \qquad \text{(Eq 2)}$$

Transforming to the volume fixed frame gives

$$J_k = -\sum_{i=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial z}, \qquad \text{(Eq 3)}$$

**Bo Sundman** and **Daniel Monceau**, CIRIMAT, UPS/INPT/CNRS/ENSIACET, 31077 Toulouse, France; **Stewart Ford** and **Toshio Narita**, Research Group of Interface Control Engineering, Hokkaido University, Sapporo 060-8628, Japan; **Xiao-Gang Lu**, Thermo-Calc Software AB, Björnnäsv 21, 11347 Stockholm, Sweden. Contact e-mail: bo.sundman@ensiacet.fr.

where

$$L'_{ki} = \sum_{j=1}^{n} (\delta_{jk} - c_k V_j) L_{ji}, \tag{Eq 4}$$

where $\delta_{jk}$ is the Kronecker delta and $V_j$ is the partial molar volume of component $j$. Finally, this can be transformed to gradients in composition by using the chain rule for derivation

$$J_k = -\sum_{i=1}^{n} L'_{ki} \sum_{j=1}^{n} \frac{\partial \mu_i}{\partial c_j} \frac{\partial c_j}{\partial z} = -\sum_{i=1}^{n} D_{kj} \frac{\partial c_j}{\partial z}, \tag{Eq 5}$$

where

$$D_{kj} = \sum_{j=1}^{n} L'_{ki} \frac{\partial \mu_i}{\partial c_j}. \tag{Eq 6}$$

The diffusion matrix $D_{kj}$ thus consists of a kinetic part $L'_{ki}$, and a thermodynamic part $\partial \mu_i / \partial c_j$ usually called the thermodynamic factor. The mobility coefficients $L'_{ki}$ normally depend much less on temperature and composition than the diffusion coefficients and only the $L_{kk}$ parameters need to be stored in the kinetic database for DICTRA. The thermodynamic factor is a matrix which can be calculated as the second derivatives of the molar Gibbs energy $G_m$:

$$\frac{\partial \mu_i}{\partial c_j} = V_m \frac{\partial \mu_i}{\partial x_j} = V_m \frac{\partial^2 G_m}{\partial x_i \partial x_j}. \tag{Eq 7}$$

There is a relation between the fluxes in Eq 5 and for substitutional diffusion one of the components can be eliminated by introducing $D^n_{kj} = D_{kj} - D_{kn}$ to obtain

$$J_k = -\sum_{i=1}^{n-1} D^n_{kj} \frac{\partial c_j}{\partial z} \tag{Eq 8}$$

The coefficients are usually called interdiffusion coefficients or chemical diffusivities. For more details of diffusion with moving phase interfaces see Andersson et al.[6]

## 3. Thermodynamic and Kinetic Data

The assessed thermodynamic description of Al-Ni-Pt comes from an assessment by Lu et al.,[4] mainly based on the experimental data by Gleeson and coworkers.[7] An isothermal section calculated from the assessed system is shown in Fig. 1. The Ni₃Al, AlNiPt₂, and Pt₃Al phases are ordered forms of the FCC phase. AlNi is a B2 ordered form of the BCC phase.

There is some mobility data for Al, Ni, and Pt in the fcc phase in the mob2 database,[8] consisting of mobilities for Al and Ni in fcc ($\gamma$) from Engström and Ågren[9] and Jönsson,[10] impurity diffusion of Al in Pt from Bergner and Schwartz,[11] impurity diffusion of Pt in Ni from Million and Kucera,[12] and self-diffusion of Pt from Rein et al.[13] The diffusion matrix at 1173 K for small fractions of Al and Pt and with Ni as dependent component is given in Table 1. Both thermodynamic and kinetic data used for the simulation are thus independent of the experimental data.

However, as will be shown later the experimentally measured compositions show that the profiles change more rapidly than the diffusion coefficients allow. That can mean that the thermodynamic data are incorrect or that the mobilities are too small. In order to test the latter, a second simulation was made with mobilities 10 times larger than the database values.

In Table 2, the interdiffusion coefficients calculated from the original mobilities in Table 1 and the thermodynamic factor according to Eq 6 are compared with values obtained by a recent study at 1423 K by Hayashi et al.[14] for a composition close to that used in this paper and the agreement is good. The assessed negative cross terms are about two times larger than the calculated which means that the effect of the gradients in the other elements maybe slightly underestimated in this simulation.

## 4. Experimental and Simulation Setup

Computer simulations can assist with prediction of composition profile changes for very long heat treatment times to eliminate the time and expense required to determine them experimentally. Simulations also allow the use of more components and more alloy compositions than can be experimentally determined. But for the present simulation a very simple binary bulk alloy and a pure Pt coating were used in order to verify the simulation method as well as the thermodynamic and kinetic data. The Ni-5at.%Al composition was selected so the whole diffusion process occurred within the fcc ($\gamma$) phase without any moving phase boundaries. This Al content is about half the actual in nickel base superalloys used for blades and vanes in gas turbines.

For the experimental profiles, coupons of Ni-5at.%Al were electroplated to form a 1.5-2 μm layer of Pt. Samples were sealed inside Ar-filled quartz capsules and furnace heated to 1173 K at a rate of 10 K/min, to reduce Pt layer spallation. After heat treatment for 1 or 11 h, samples were removed from the furnace and allowed to air cool. Electron probe micro-analysis (EPMA) was conducted on polished cross sections (see Fig. 2). After 1 h of heat treatment at 1173 K the Pt composition near the surface had decreased significantly to around 15 at.% (see Fig. 3a). This rapid initial diffusion could not be simulated with the available data and may be caused by the very fine grain structure of the electroplated Pt coating. However, the 12-14 μm diffusion depth of Pt is much larger than the initial Pt layer. The composition profile after 1 h was used as the starting profile for the simulation as shown in Fig. 3(a), and the simulation was used to determine the evolution of the profiles at longer times.

## 5. Results

Using the DICTRA software with the thermodynamic and mobility data, the simulated profile after 10 more hours
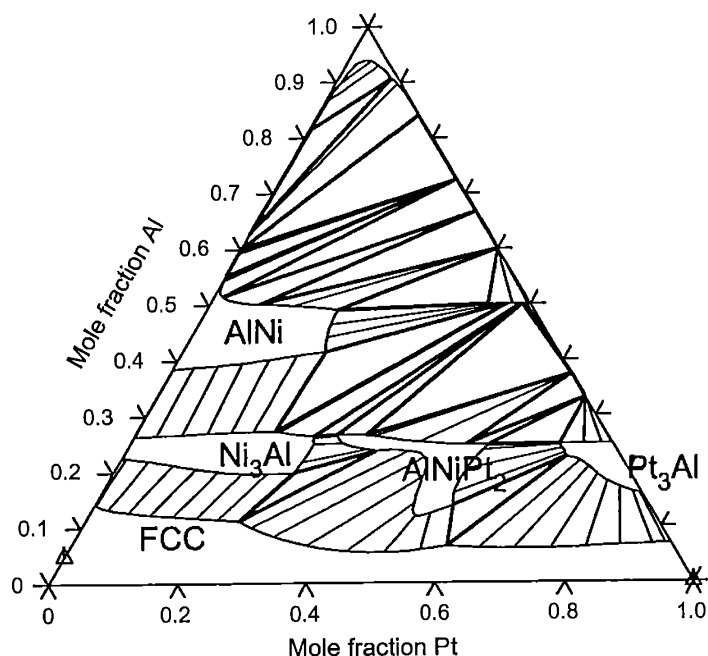
**Fig. 1** The calculated isothermal section for Al-Ni-Pt at 1173 K. The composition of the bulk is Ni-5at.%Al and the coating pure Pt. The diffusion is entirely inside the fcc phase

**Table 1  The diffusion matrix at 1173 K with Ni as dependent component for the composition $\chi_{Al} = 0.05$ and $\chi_{Pt} = 0.1$**

|  | Mobilities from Ref 8 | | Mobilities 10 times faster | |
|---|---|---|---|---|
|  | **Al** | **Pt** | **Al** | **Pt** |
| Al | $3.0 \times 10^{-16}$ | $-9.0 \times 10^{-17}$ | $2.1 \times 10^{-15}$ | $-6.6 \times 10^{-16}$ |
| Pt | $-6.0 \times 10^{-17}$ | $7.7 \times 10^{-17}$ | $-4.5 \times 10^{-16}$ | $5.0 \times 10^{-16}$ |

Two sets of mobility values were used. Units are m²/s

**Table 2  Comparison of the diffusion matrix at 1423 K with Ni as dependent component with mobilities from Ref 8 and thermodynamic data from Ref 4 and that assessed by Hayashi et al.[14] for 8.2at.%Al and 21.5at.%Pt**

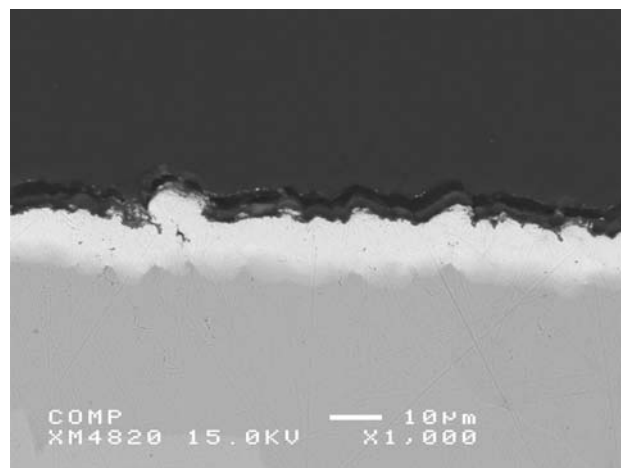|  | Al | | Pt | |
|---|---|---|---|---|
|  | **Calculated** | **Assessed** | **Calculated** | **Assessed** |
| Al | 5.9 | 5.7 | −1.2 | −2.1 |
| Pt | −1.6 | −2.3 | 1.7 | 1.6 |

Units are $10^{-14}$ m²/s



**Fig. 2** A micrograph of the surface layer after 1 h heat treatment

The simulation used experimental data for the initial composition profile and independently determined thermodynamic and kinetic data. It is evident that the mobility data also underestimated the diffusion after 11 h as the calculated composition profile for Pt did not change as much as the experimental. The much more rapid diffusion in the experiments could be due to higher fraction of defects such as vacancies formed by net outward mass transfer.

The experimental data after 10 more hours heat treatment shows the Al profile has a minimum near the maximum diffusion depth of Pt, and this is also predicted in the simulated profile. From this minimum toward the surface,
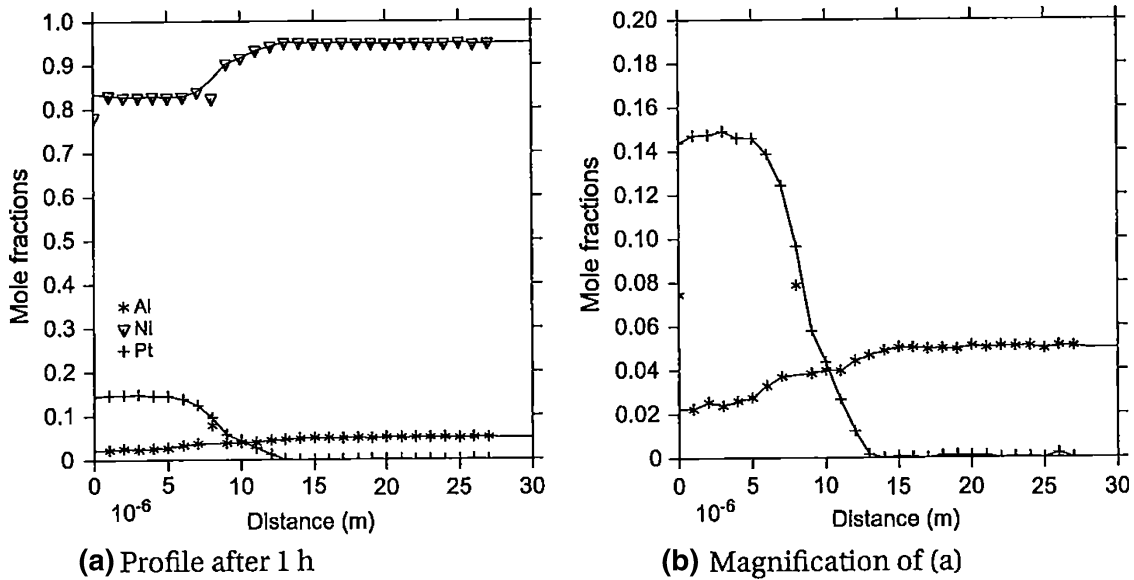
of heat treatment at 1173 K is compared with the experimental data in Fig. 4 together with a magnification of the Al and Pt profiles.

**(a)** Profile after 1 h

**(b)** Magnification of (a)

**Fig. 3** The symbols are measured compositions from the surface (*left side*) into the bulk. In (a) all fractions, and in (b) a magnification of the Al and Pt compositions. Note that two points of the Al composition, at the surface and at 7 μm have been smoothed. The line is the initial profile for the simulation
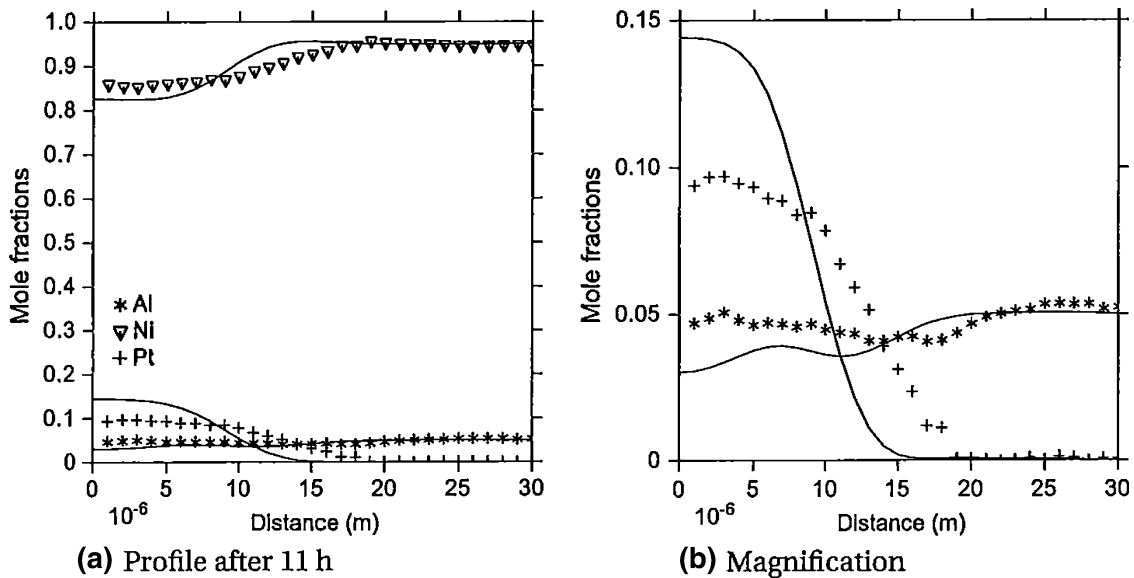


**(a)** Profile after 11 h

**(b)** Magnification

**Fig. 4** In (a) the measured and simulated compositions after a total time of 11 h heat treatment is shown with a magnification in (b)

the experimental data shows a continuous increase in Al concentration whereas the simulated profile shows a slight increase, a maximum and then a decrease. This difference could again be attributed to the contribution of grain boundary diffusion at the surface; however, both profiles show some increase in Al composition after the minimum. This increase occurs because Al diffusion is governed by the gradient in chemical potential of Al and the chemical potential of Al is constantly decreasing from the bulk to the surface as shown in Fig. 5(a) due to the increasing amount of Pt.

The simulation also showed that the surface composition of Al will exceed that of the bulk after a period of time due to the effect of Pt on the Al activity. Figure 5(b) shows how the Al composition at the surface increases rapidly during the first 20 h and then levels off.

To test the effect of higher mobilities, a second set of diffusion coefficients listed in Table 1 were used for a simulation with the same initial composition profile and the results are shown in Fig. 6. The fit is now much better in the outer high Pt region but slightly worse in the bulk. This strongly indicates that diffusion in the inner and outer regions
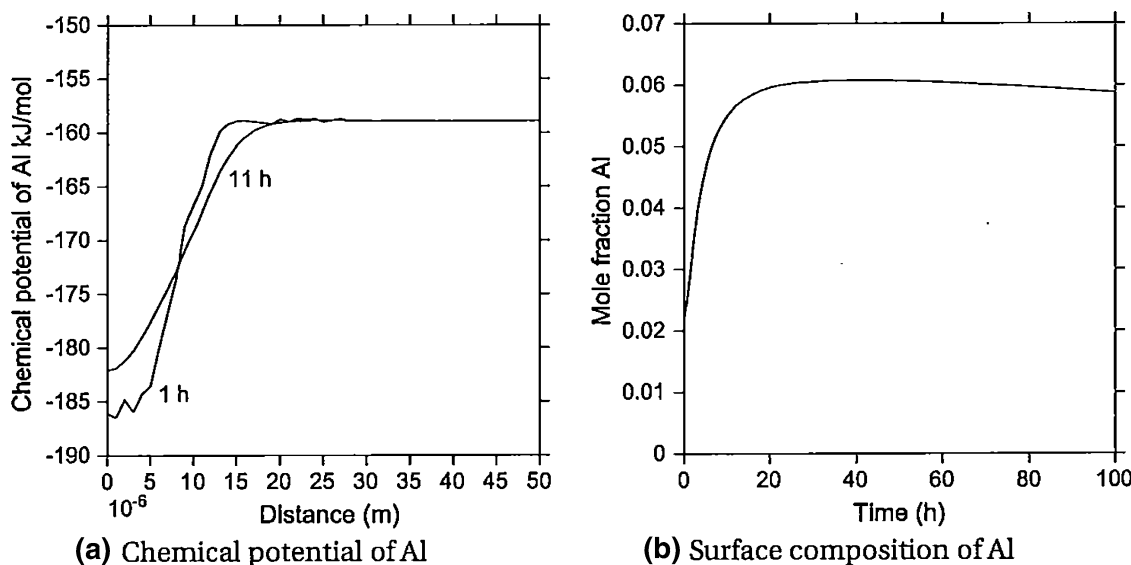
**(a)** Chemical potential of Al

**(b)** Surface composition of Al

**Fig. 5** The calculated profile for the chemical potential of Al after 1 and 11 h heat treatment is shown in (a) and in (b) the variation of the surface concentration of Al with time
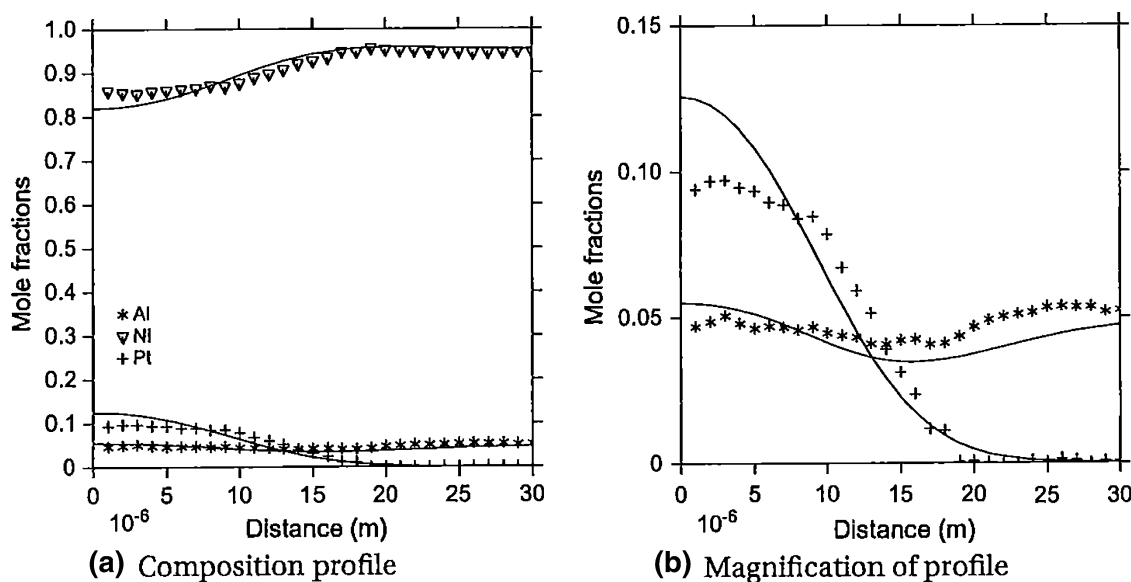


**(a)** Composition profile

**(b)** Magnification of profile

**Fig. 6** The lines are the calculated composition profile using the higher diffusion coefficients in Table 1. The symbols show the experimental values (same as in Fig. 4)

is governed by different effective diffusion coefficients, due to the differences in microstructure and in the concentration of diffusion assisting defects. It would be of interest to model the system with different mobilities for the different regions although this may make the simulations very complex.

## 6. Discussion

Computer simulations for predicting changes in phase composition after long time heat treatments or for materials used at high temperatures can be very useful to predict how their properties may change. Experimental validation of the simulation is very important to test the available databases. Validated databases for thermodynamic and kinetic data are needed to allow reasonable predictions for multicomponent alloys.

The simulations presented in this paper show a reasonable agreement with experiments, in particular the uphill diffusion of Al toward the surface of a Pt-coated Ni-Al alloy. This "pull" of Al to the surface due to the lowering of the chemical potential of Al by Pt is a major factor to improve the corrosion resistance. The complexities of the

very small grain size and high defect concentration in the experimental samples are the main reason that the experimental results deviate from the simulations which are based on bulk equilibrium thermodynamics and steady-state determinations of kinetic data. Using a recent assessment of mobilities in the Ni-Pt system,[15] not available when this work was done, could possibly also improve the results.

## 7. Conclusions

Three main conclusions can be made from this study. The first concerns the Pt effect on the high temperature oxidation resistance of alumina-forming alloys. This work confirms Gleeson's et al.[3] idea that Pt reduces Al activity and causes its outward migration toward the surface when a Pt coating is applied on a Ni-base superalloy. The fact that Al flux toward the surface is increased improves the ability of the alloy to form a protective pure alumina layer. Indeed, the Wagner theory of oxidation[16] shows that Al activity should be not only higher than a critical value to make alumina the most stable oxide for a given atmosphere, but also that the outward flux of Al should be higher than a critical value which depends on diffusion and solubility of oxygen in the alloy. The first condition will be always fulfilled in Ni-base superalloys for gas turbine blades but the second condition not always. This can lead to detrimental internal oxidation of aluminum, but a surface layer of Pt will favor external alumina scale formation. It would also be interesting to analyze the thermodynamic effect of Pt on Al diffusion in Pt-coated β-NiAl in order to explain the various aspects of the Pt improvements on β-(Ni, Pt)Al high temperature oxidation.

The second consequence of the Pt effect on Al activity and diffusion in γ-Ni(Al) concerns the Ni-Pt-Al coating fabrication. The kinetics of formation of a γ/γ′ Pt-rich coating at the surface of the superalloy from a pure Pt coating (as in Ref 1) could be optimized from a diffusion analysis as done in this paper. It was shown that Pt deposition on a nickel base superalloy increases the rate of aluminization from the vapor phase by Benoist et al.[17] The rate of aluminization of a superalloy from the vapor phase will depend on the difference of Al activity between the gas and the alloy surface, and the modeling of the kinetics of aluminization presented here can take into account the thermodynamic effects.

Third, the modeling of long-term lifetimes of coated superalloys requires modeling of Al and Pt diffusion in the system (e.g., Bacos et al.[18]). There are complications due to different phase transformations, but nevertheless the very small grain size and high defect concentration in the strong effect of Pt on Al activity suggests that thermodynamic effect on diffusion should be carefully considered in the modeling of the lifetime of coated superalloys.

## References

1. D.S. Rickerby, Patent US005667663A, 1997
2. B. Gleeson, D. Sordelet, and W. Wang, Patent US2004022907A1, 2004
3. B. Gleeson, W. Wang, S. Hayashi, and D. Sordelet, Effects of Platinum on the Interdiffusion and Oxidation Behavior of Ni-Al-Based Alloys, *Mater. Sci. Forum*, 2004, **461-464**, 213-222
4. X.-G. Lu, B. Sundman, and J. Ågren, Thermodynamic Assessment of the Ni-Pt and Al-Ni-Pt Systems, *CALPHAD*, 2009, **33**(3), p 450-456
5. H.L. Lukas, S.G. Fries, and B. Sundman, *Computational Thermodynamics*, Cambridge Univ Press, Cambridge, 2007
6. J.-O. Andersson, T. Helander, L. Höglund, P. Shi, and B. Sundman, *Calphad*, 2002, **26**(2), p 273-312
7. S. Hayashi, S.I. Ford, D.J. Young, D.J. Sordelet, M.F. Besser, and B. Gleeson, α-NiPt(Al) and Phase Equilibria in the Ni-Al-Pt System at 1150 °C, *Acta Mater.*, 2005, **53**(11), p 3319
8. DICTRA Mobility Database 2002, http://www.thermocalc.se
9. A. Engström and J. Ågren, Assessment of Diffusionalmobilities in fcc Ni-Cr-Al Alloys, *Z. Metallkd.*, 1996, **87**, p 92-97
10. B. Jönsson, Assessment of Mobilities of Cr, Fe and Ni in Binary fcc Cr-Fe and Cr-Ni Alloys, *Scand. J. Metall.*, 1995, **24**(1), p 21-27
11. D. Bergner and K. Schwartz, Diffusion of Other Metals in Platinum, *Neue Hutte*, 1978, **23**(6), p 210-212
12. B. Million and J. Kucera, Diffusion of $^{193}$Pt in Pt, γ-Fe, Co and Ni, *Kovove Mater.*, 1973, **11**(4), p 300-306
13. G. Rein, H. Mehrer, and K. Meier, Diffusion of $^{197}$Pt and $^{199}$Au in Platinum at Low Temperatures, *Phys. Status Solidi (a)*, 1978, **45**(1), p 253-261
14. S. Hayashi, D.J. Sordelet, L.R. Walker, and B. Gleeson, Interdiffusion in Pt-Containing γ-Ni and γ′-Ni$_3$Al alloys at 1150 °C, *Mater. Trans. Jpn*, 2008, **49**, p 1550-1557
15. W.Y. Gong, L.J. Zhang, D.Z. Yao, and C.E. Zhou, Diffusivities and Atomic Mobilities in fcc Ni-Pt Alloys, *Scripta Mater.*, 2009, **61**(1), p 100-103
16. C. Wagner, Oxidation of Alloys involving Noble Metals, *J. Electrochem. Soc.*, 1956, **99**(10), p 571-580
17. J. Benoist, K.F. Badawi, A. Malié, and C. Ramade, Microstructure of Pt Modified Aluminide Coatings on Ni-Based Superalloys Without Prior Pt Diffusion, *Surf. Coat. Technol.*, 2005, **194**, p 48-57
18. M.-P. Bacos, P. Josso, N. Vialas, D. Poquillon, B. Pieraggi, D. Monceau, J.R. Nicholls, N. Simms, A. Encinas-Oropesa, T. Ericsson, and S. Stekovic, ALLBATROS Advanced Long Life Blade Turbine Coating Systems, *Appl. Therm. Eng.*, 2004, **24**(11-12), p 1745-1753