

EXPERIMENTAL INVESTIGATION AND COMPUTER SIMULATION OF DIFFUSION IN Pt-COATED BULK Ni

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Abstract

The concentration profiles of thin-film Pt/bulk Ni coatings annealed at 1150, 1250 and 1300 °C for different time were measured by means of electron probe microanalysis. The corresponding interdiffusion coefficients were then determined using the thin-film solution. The calculated concentration profiles based on the presently obtained interdiffusion coefficients agree well with the experimental ones, but better at a higher temperature or a longer time. The comparison between the presently measured concentration profiles and the DICTRA simulated ones indicates that it is promising to apply the well-established atomic mobility databases due to bulk diffusion information in coating systems with some simple modifications for diffusivities.

Keywords: Thin films; Diffusion; Nickel alloys; Electron probe microanalysis; DICTRA

1. Introduction

It is well known that Ni-based superalloys

are widely used for aero engines and gas turbines due to their excellent mechanical properties at high temperature. To improve

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their corrosion and oxidation resistance, Pt is usually employed to coat on Ni-based superalloys followed by aluminizing [1, 2]. The Pt coatings are generally thin films with 5-10 μm thick at elevated temperatures [3].

In order to optimize the coating fabrication processes and improve the durability of the coatings, diffusion information in Pt-coated bulk Ni is indispensable, which is absent in the literature. Most recently, the present authors [4] performed a thorough investigation of diffusion in fcc Ni-Pt alloys, where bulk diffusion coefficients in fcc Ni-Pt alloys were measured, and a critical assessment was then performed to establish the accurate atomic mobility database for Ni and Pt in fcc Ni-Pt alloys. Moreover, as demonstrated in the literature [5, 6], the well-established atomic mobilities, coupled with the available thermodynamic databases [7-9] are valuable for simulating and analyzing various diffusion-controlled transformations in the target alloys. Thus, it would also be extremely interesting to investigate whether the previously established atomic mobility database of fcc Ni-Pt alloys [4] based on bulk diffusion information can be applicable in coatings.

Consequently, the main objectives of the present work are: (i) to measure the concentration profiles of thin-film Pt/bulk Ni coatings annealed at different temperatures for different time, and then determine their interdiffusion coefficients; and (ii) to predict the concentration profiles of the present Pt-coated bulk Ni based on the previous atomic mobility database [4], and analyze the differences between the prediction and the experimental measurements.

2. Experimental procedure

Pure Ni block (Purity: 99.98 wt%) with size of 32 mm \times 15 mm \times 3 mm was first annealed at 1200 $^{\circ}\text{C}$ for 120 h to make the grain size grow large enough to decrease the contribution of boundary diffusion during the subsequent annealing. After that, the Ni block was polished and ultrasonic cleaned. Then Pt was electroplated on the Ni block to form thin-film Pt/bulk Ni coating, and the thickness of the plated Pt layer was kept to be 6 μm by controlling the sample weight gain during the electroplating process. Subsequently, the sample was cut into 12 smaller ones with each size of 6 mm \times 3 mm \times 3 mm. All the Ni-Pt coatings were then sealed in different quartz capsules, and annealed at 1150 $^{\circ}\text{C}$, 1250 $^{\circ}\text{C}$ and 1300 $^{\circ}\text{C}$ for 0.5 h, 1 h, 2 h and 4 h, respectively. After annealing, the twelve Ni-Pt coatings were removed from the furnace and quenched into water. All the annealed thin-film Pt/bulk Ni coatings were polished by standard metallographic preparation and analyzed by scanning electron microscopy/energy dispersive spectroscopy (SEM / EDS, JSM-6500, JEOL, Japan) for morphology observation, and electron probe microanalysis (EPMA, JXA - 8100, JEOL, Japan) for accurate measurements of concentration profiles.

3. Theoretical calculation

In order to determine the interdiffusion coefficients in such thin-film Pt/bulk Ni coatings, the thin-film solution [10], also denoted as Gaussian solutions, was utilized to analyze the concentration profiles. The

initial condition, i.e. at $t = 0$ s, is,

$$c(x, 0) = M\delta(x) \quad \dots(1)$$

where M denotes the number of diffusion species per unit area and $\delta(x)$ is the Dirac delta function. The diffusion species is deposited at the plane $x = 0$ and allowed to spread for $t > 0$. For the thin-film geometry, the solution is

$$c(x, t) = \frac{M}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad \dots(2)$$

where D is the diffusion coefficients, and t is time.

4. Results and discussion

The typical backscatter electron images (BEI) for thin-film Pt/bulk Ni coatings

annealed at 1300 °C for 0.5 h, 1 h, 2 h and 4 h are shown in Fig. 1. As shown in the figure, the Ni/Pt interdiffusion layer increases as time increases, which indicates that interdiffusion goes along the time. Figure 2 presents all the measured concentration profiles (denoted as the open points in the figure) for the thin-film Pt/bulk Ni coatings at 1150 °C, 1250 °C, 1300 °C for 0.5 h, 1 h, 2 h, and 4 h, respectively. The determined interdiffusion coefficients in the present coatings based on Eqs. (1) and (2) are also shown in Table 1. As can be seen, the interdiffusion coefficients in the coatings are time dependent, and decrease as time increases. It may be due to that there exists certain contribution of grain boundary diffusion in the Pt coating side at initial time, and this kind of contribution becomes

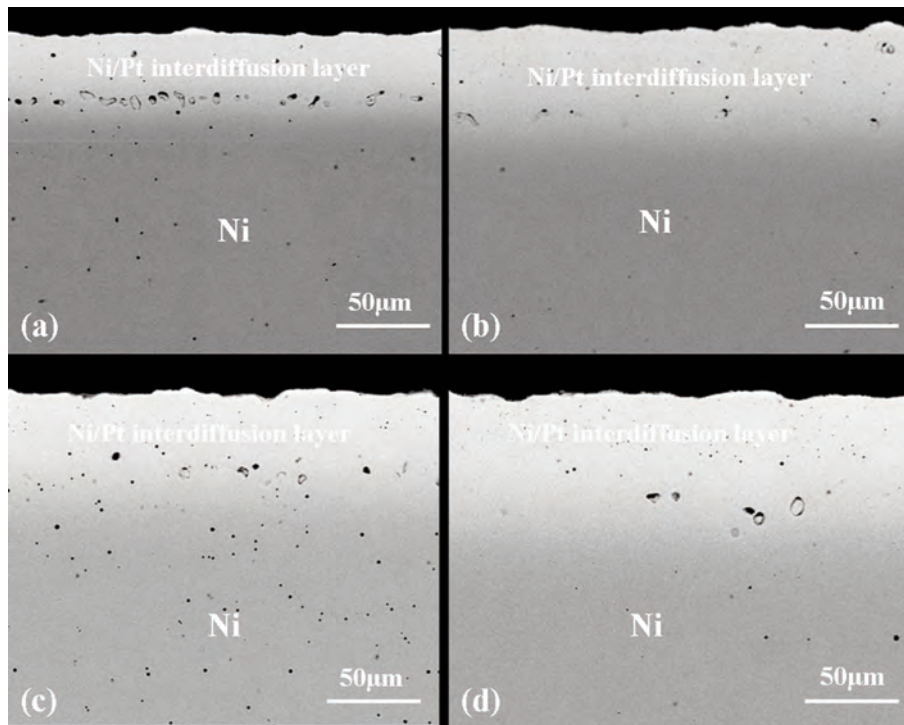


Fig. 1. Backscatter electron images (BEI) for the thin-film Pt/bulk Ni coatings annealed at 1300 °C for (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 4 h.

weaker or even negligible as time increases. The calculated concentration profiles for different Ni-Pt coatings based on the presently obtained interdiffusion coefficients are also appended in Fig. 2 for comparison. It can be seen in Fig. 2 that all the calculated results agree reasonably with the experimental data, and the fit between the calculations and the experiments is better at a higher temperature or a longer time. The main reasons may be due to the small grains and high defect concentration in the coating side of the sample, resulting in the comparable grain boundary diffusion to the volume diffusion. However, the effect of grain boundary diffusion will become weaker or even negligible as time goes on or temperature goes up. That is because grains can grow rapidly at higher temperature, and to be a certain size at a longer time. The presently obtained diffusion coefficients in such thin-film Pt/bulk Ni should be useful

for the further study on diffusion behavior in Pt-coated Ni-based super-alloys.

Numbers of recent work demonstrate that reliable computer simulations can assist with prediction of various diffusion phenomena, especially for those with very long heat treatment time to decrease or even eliminate the time and expense required to experimental measurements [3]. Thus, it should be extremely interesting to check whether the previously established atomic mobility database of fcc Ni-Pt alloys [4] based on bulk diffusion information can be also used in the present coating system, as just mentioned in the first part. As described in the work of Gong et al. [4], two sets of the atomic mobility databases were provided based on different thermodynamic databases [11, 12]. To simplify the problem, only the set of atomic mobility database corresponding to the thermodynamic database from Lu et al. [11] was chosen in

Table 1. Comparison between the determined interdiffusion coefficients from the present Ni-Pt coating, and the calculated ones based on atomic mobilities from Gong et al. [4]

Annealing Temperature	Thin-film Pt/bulk Ni case (This work)		Bulk Ni/Pt (Gong et al. [4])	
	Annealing time (h)	\tilde{D} (m ² /s)	Annealing time (h)	\tilde{D} (m ² /s)
1150 °C	0.5	6.2×10^{-14}	120	5.33×10^{-15}
	1	5.6×10^{-14}		
	2	1.5×10^{-14}		
	4	1.4×10^{-14}		
1250 °C	0.5	7.1×10^{-14}	74	2.37×10^{-14}
	1	4.6×10^{-14}		
	2	2.5×10^{-14}		
	4	2.0×10^{-14}		
1300 °C	0.5	1.1×10^{-13}	40	4.81×10^{-14}
	1	6.0×10^{-14}		
	2	5.8×10^{-14}		
	4	4.5×10^{-14}		

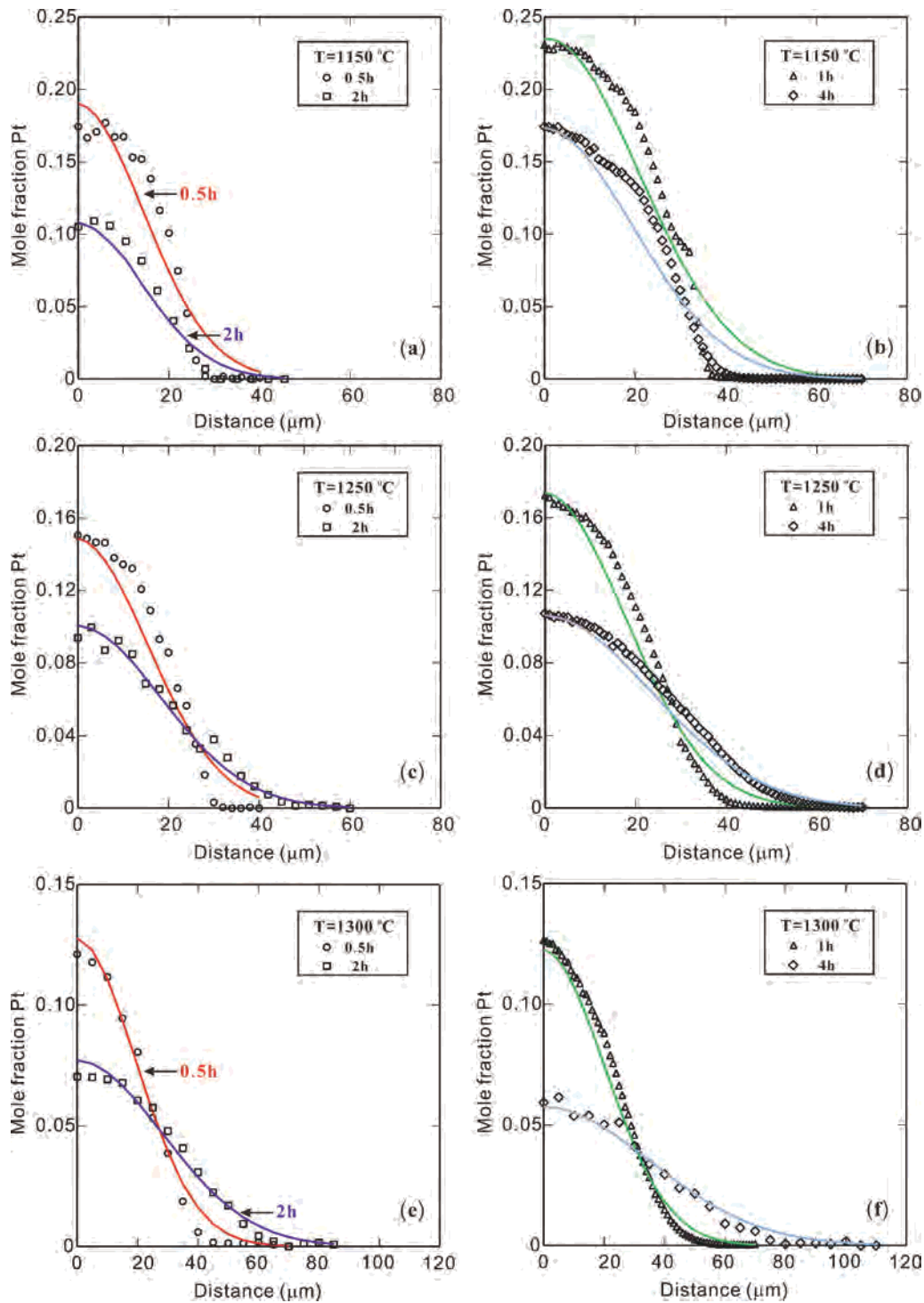


Fig. 2. Experimentally measured (open points) and calculated concentration profiles (solid lines) of the thin-film Pt/bulk Ni coating annealed at (a) 1150 °C for 0.5 and 2 h, (b) 1150 °C for 1 and 4 h, (c) 1250 °C for 0.5 and 2 h, (d) 1250 °C for 1 and 4 h, (e) 1300 °C for 0.5 and 2 h, and (f) 1300 °C for 1 and 4 h.

the present work. All the calculations and simulations associated with the atomic mobility were performed in DICTRA (Diffusion Controlled TRAnsfOrmations) software [13] under the frame work of CALPHAD (CALculation of PHase Diagram) method [14].

The direct comparison between the presently obtained interdiffusion coefficients in Ni-Pt coatings and the average values calculated based on the previous atomic mobility database [4] are shown in Table 1. As can be seen, the experimental data are higher than the calculated values by almost one order at 1150 °C, and gradually approach to the calculated value at higher temperatures and longer annealing time. It can be clearly found that the calculated interdiffusion coefficient at 1300 °C agree excellently with the experimental one at 4 h and 1300 °C. The reason should also be that certain contribution of grain boundary diffusion in the Pt coating side exists at initial time, but it becomes weaker or even negligible as time increases and temperature goes up when the grains grow large enough.

Considering that the experimental interdiffusion coefficients at 1300 °C agree best with the corresponding calculated ones, the comparison between the simulated concentration profiles based on our previously obtained atomic mobilities [4] and the presently measured ones were performed in the present work, as presented in Fig. 3. As shown in the figure, the calculated concentration profiles agree well with the experimental ones at bulk Ni side, while differ largely at Pt coating side. Obviously, the effect of the relatively rapid diffusion in the electroplated Pt coating at

initial stage on concentration profile is large, and cannot be easily eliminated by simply increasing annealing time because it is an accumulated process. Thus, we also compared the experimental concentration profiles with the calculated ones based on 10 times of the interdiffusion coefficients due to the original atomic mobilities [4]. It can be seen that the calculated concentration profiles with $10\tilde{D}$ agree more or less with the experimental data at Pt coating side, while show certain difference with the experimental data at bulk Ni side. That is because diffusion in the Pt coating region and the bulk Ni region is governed by different diffusion coefficients, as the same reason in the Al-Ni-Pt system by Sundman et al. [3]. It is anticipated that the simulation with different mobilities for different regions should be promising to reproduce the experimental data in coating systems. However, it is a very complex process to accurately obtain the different diffusivities in different region. As a first try, a simple set of mixed interdiffusion coefficients, i.e. $10\tilde{D}$ in Pt coating side and \tilde{D} in the Ni bulk side was employed for simulation.

The result is shown in Fig. 3(d), where the simulated concentration profile (The pink solid line) due to the mixed interdiffusion coefficients agrees best with the experimental data.

Though the fit is still not excellent, the trend is promising.

The try to achieve the better fit can make the obtained atomic mobility databases based on bulk diffusion information applicable in coating systems with some simple modifications for diffusivities, as will be the subject of the future work.

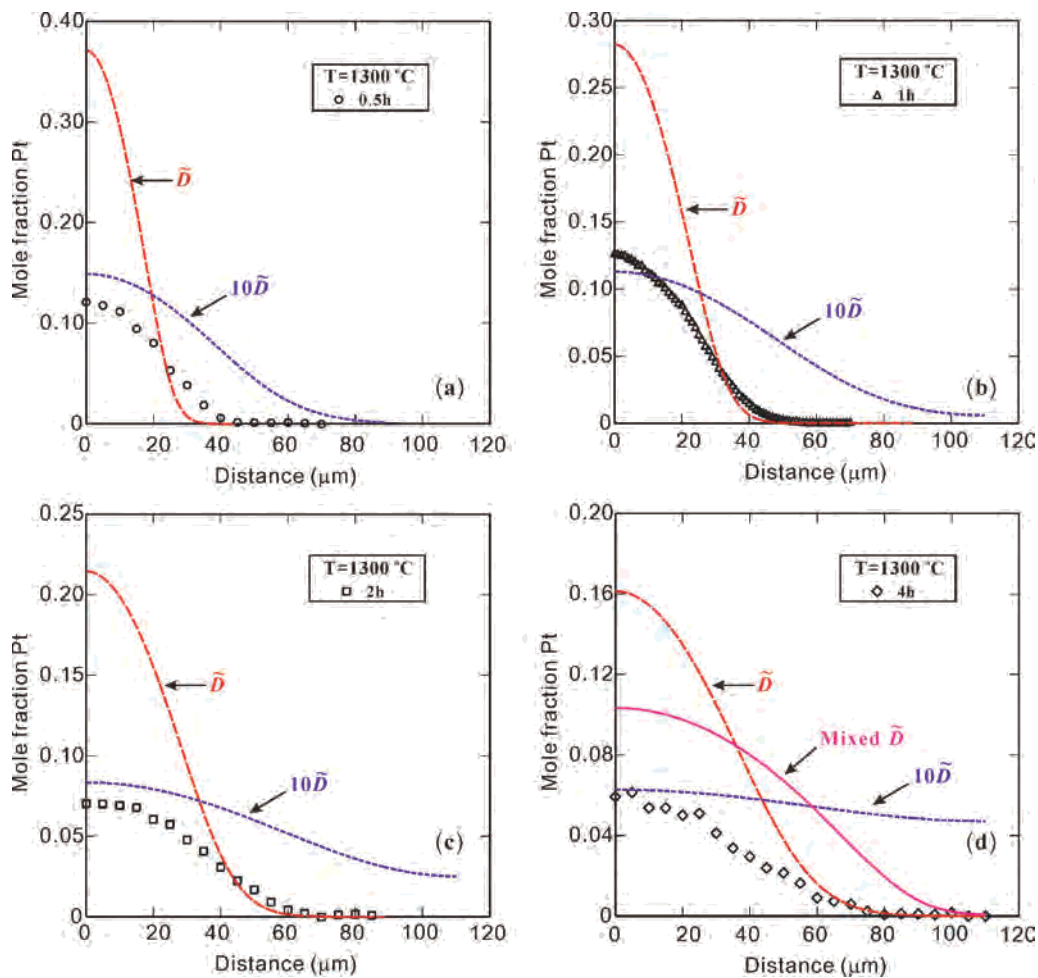


Fig. 3. (a) DICTRA simulated and experimentally measured concentration profiles in the thin-film Pt/bulk Ni coating annealed at 1300 °C for (a) 0.5 h, (b) 1 h, (c) 2 h and (d) 4 h.

The red dash lines are the DICTRA simulated ones due to the original atomic mobilities [4], while the blue dot lines are the DICTRA simulated ones based on 10 times of the interdiffusion coefficients due to the original atomic mobilities [4]. The pink solid lines are calculated with mixed interdiffusion coefficients, i.e. $10\tilde{D}$ in Pt coating side and \tilde{D} in the Ni bulk side.

5. Conclusions

In summary, the concentration profiles of thin-film Pt/bulk Ni coatings annealed at different temperatures for different time were measured by means of EPMA, and the corresponding interdiffusion coefficients were determined using the thin-film solution. It was found that grain boundary diffusion exists in Pt coating side at initial time due to

the very fine grain structure, and the effect of grain boundary diffusion becomes weaker or even negligible as time goes on or temperature goes up. In order to check whether the previously established atomic mobility database of bulk fcc Ni-Pt alloys [4] can be applicable in the present coatings, the presently measured concentration profiles were compared with the DICTRA simulated ones based on the original \tilde{D} , $10\tilde{D}$ and the

mixed diffusion coefficients (i.e. $10\tilde{D}$ for Pt coating side, and \tilde{D} for bulk Ni side). The results indicate that the original atomic mobilities based on bulk information cannot describe the coating case, but the simulation with different mobilities for different regions seems promising to accurately reproduce the experimental data.

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