Phases equilibria, diffusion growth and diffusivities in Ni-Al-Pt system using Pt/\(\beta\)-NiAl diffusion couples

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Abstract: The phase equilibria, diffusion growth and diffusivities in the Ni-Al-Pt system at 1 150, 1 200 and 1 250 °C were studied using Pt/\(\beta\)-NiAl diffusion couples. Based on the measured concentration profiles coupled with the local equilibrium hypothesis, the tie-lines between neighboring phases were determined. Two intermediate phases, Pt\(_3\)Al and \(\alpha\)-NiPt(Al), are found to develop between the Pt and \(\beta\)-NiAl couples. The thicknesses of Pt\(_3\)Al and \(\alpha\)-NiPt(Al) layers varies linearly with the square of annealing time, indicating that the growth of Pt\(_3\)Al and \(\alpha\)-NiPt(Al) are diffusion-controlled. The calculated Arrhenius equations of the parabolic growth constants, \(k\), for the Pt\(_3\)Al and \(\alpha\)-NiPt(Al) phases are obtained, respectively. The average ternary inter-diffusivities of the Pt\(_3\)Al and \(\beta\)-NiAl phases at different temperatures are determined from an integration of inter-diffusion fluxes calculated directly from the experimental concentration profiles.

Key words: platinum group; nickel aluminides; phase equilibria; thermodynamic; diffusion

1 Introduction

Thermal barrier coatings (TBCs) are widely used in engine blades to provide insulation for hot sections and increase the component durability. TBCs typically consist of the bond coat and the yttria-stabilised zirconia (YSZ) ceramic coat \cite{1−2}. Currently, the Pt-modified \(\beta\)-NiAl alloys are most widely used materials as the bond coat \cite{3} due to their excellent cyclic oxidation resistance. In order to improve the performance of the current bond coats, or even design new bond coats, full interpretation of the oxidation behavior of the Pt-modified aluminide coatings is necessary. However, the major obstacles lie in the lack of sufficient phase equilibria and diffusivities in the Ni-Al-Pt system despite numbers of experimental investigations on the Pt-modified aluminide coatings during the past decades. As early as in 1977, JACKSON and RAIRDEN \cite{4} presented a schematic isothermal section at 1 060 °C, but no ternary phase was reported. Until 1994, KAMM and MILLIGAN \cite{5}, and later MEININGER and ELLNER \cite{6} investigated the same Ni\(_2\)Al-Pt\(_3\)Al join, and observed a ternary phase with \(L1_0\), AuCu-type tetragonal structure. The very recent work from GLEESON’s group \cite{7−8} proposed a relatively complete isothermal section at 1 150 °C of the Ni-Al-Pt system in Al-poor region by employing diffusion couple technique. Besides, the ternary \(L1_0\) phase was also confirmed in their work \cite{7}, and denoted as \(\alpha\)-NiPt(Al). As for the diffusivities in Ni-Al-Pt alloys, only two major contributions exist in the literature. By means of the diffusion couple method, MINAMINO et al \cite{9} determined the impurity diffusion coefficients of Pt in \(\beta\)-NiAl phase with compositions of 43.7%−51.9% (mole fraction) Al at temperature ranging in 1 100−1 400 °C. BOUCHET and MEVREL \cite{10} reported a series of composition-dependent inter-diffusion coefficients of \(\beta\)-(Ni, Pt)Al phase at 1 100 °C by employing single-phase diffusion couples coupled with a numerical inverse analysis \cite{11}.

Thus, there is an urgent need to remedy this situation. Moreover, the phase equilibria and diffusivity information are the basis of the subsequent CALPHAD (CALculation of PHAse Diagram) thermodynamic and atomic mobility databases \cite{12−15}, which are indispensable for quantitative simulation of the
microstructure evolution in Ni-Al-Pt alloys or coatings using the phase-field method [16–18]. Furthermore, the diffusion couple experiments are well known to be very effective in investigating the thermodynamics and kinetics of alloy, in one experiment a large area of the phase space can be screened, and the diffusion coefficients can be extracted. Consequently, the Pt/β-NiAl diffusion couples are employed in the present work to measure the corresponding phase equilibria and diffusion properties in the Ni-Al-Pt system.

2 Experimental

One single-phase β-NiAl alloy was prepared by arc-melting Al (purity of 99.98%, mass fraction) and Ni (purity of 99.9%) rods in an vacuum arc furnace. The button was re-melted five times to improve its homogeneity. This alloy was then annealed at 1 200 °C for 0.5 h in a vacuum furnace at 1 Pa, followed by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) with energy-dispersive X-ray analysis (EDX) to check the phase structure and microstructure homogenous. Then, this β-NiAl alloy was cut into blocks with approximate dimension of 3 mm×3 mm×3 mm. After annealing at 1 200 °C for 120 h, pure Pt pieces (purity of 99.95%) were cut into blocks with dimension of 3 mm×3 mm×1.5 mm. After grounding and polishing, the β-NiAl and the Pt blocks were bound together in a vacuum furnace at 1 200 °C for 0.5 h to make 12 semi-infinite Pt/β-NiAl diffusion couples. All the Pt/β-NiAl diffusion couples were sealed in different quartz capsules, and annealed at (1 150±1) °C, (1 200±1) °C and (1 250 ±1) °C for 30, 60, 90 and 110 h, respectively, in tube furnaces (GSL-1600X MTI, produced by Hefei Kejing Materials Technology Co., Ltd., China) under flowing argon. The diffusion couples were removed from the furnace and quenched into water. The annealed Pt/β-NiAl diffusion couples were analyzed by SEM/EDX for morphology observation, and electron probe microanalysis (EPMA, JXA–8100, JEOL, Japan) for accurate measurements of concentration profiles.

3 Theory-determination of ternary inter-diffusivities

The inter-diffusion flux ( ) at any section x for each component can be directly calculated from the concentration profile from the relation as [19–20]

( )

(3)

where is the time, and are the terminal compositions, and is the location of the Matano plane, which is usually determined by averaging the calculated Matano plane positions of 3 components for a ternary system. This fact can result in additional errors for inter-diffusivity calculation. In order to avoid such errors, DAYANANDA and SOHN [21] proposed a new method to compute without calculating the Matano plane positions,

(2)

where is the relative concentration variable, denoted by

(3)

The inter-diffusion flux determined from Eq. (2) can be integrated over a selected region, to , to yield an expression as [21]

(4)

where and refer to the average main inter-diffusion coefficients, and and are average cross inter-diffusion coefficients in a fictitious ternary 1-2-3 system.

Taking and as constants, the Fick’s law in ternary system can be rewritten as

(5)

If both sides of the Eq. (5) are multiplied by and integrated over the diffusion zone between and , the following expression can be obtained [21]:

(6)

Eqs. (4) and (6) provide four equations to solve for , , and . This method has been successfully applied in various alloy systems [22–24] to determine average ternary inter-diffusion coefficients.

4 Results and discussion

Figure 1(a) presents a typical SEM micrograph of the inter-diffusion zone of the Pt/β-NiAl diffusion couple annealed at 1 150 °C for 30 h, and the corresponding concentration profiles of the elements Ni, Al and Pt are shown in Fig. 1(b). It is obvious that two new intermediate phases, Pt3Al and α-NiPt(Al), formed between the Pt and β-NiAl couples, with the resulting three interfaces identified in Fig. 1 as 1, 2 and 3. The integers 1, 2 and 3
denote the interfaces of Pt/Pt$_3$Al, Pt$_3$Al/α-NiPt(Al) and α-NiPt(Al)/β-NiAl, respectively. The observation of the α-NiPt(Al) phase confirms the previous work [5–8]. Moreover, a large solubility of Pt exists in the β-NiAl phase, which is consistent with the previous experimental work [7]. According to the local equilibrium hypothesis [25], the tie-lines between adjacent phases can be obtained from the concentration profiles. The detailed procedure can be referred to HAYASHI et al [7]. The tie-lines at different temperatures obtained in the present work are as follows: for Pt/Pt$_3$Al, 5.56–92.81/19.04–74.28 at 1150 °C, 5.69–91.89/18.88–75.06 at 1200 °C, and 5.78–90.47/17.81–74.16 at 1250 °C; for Pt$_3$Al/α-NiPt(Al), 23.44–63.20/28.10–57.06 at 1150 °C, 24.51–61.29/27.72–55.54 at 1200 °C, and 21.98–63.56/26.46–56.36 at 1250 °C; for α-NiPt(Al)/β-NiAl, 34.08–44.72/34.30–40.28 at 1150 °C, 33.30–45.20/35.86–39.77 at 1200 °C, and 33.59–44.09/35.89–40.84 at 1250 °C (Al–Pt, in mole fraction, the remaining amount is for Ni). The tie-lines should be important supplement to the isothermal sections at the three temperatures.

The thicknesses of the Pt$_3$Al and α-NiPt(Al) phases formed between the Pt and β-NiAl couples were determined from the SEM micrographs and the EPMA concentration profiles. The results are plotted in Figs. 2(a)

![Cross-sectional microstructure and concentration profiles](image)

**Fig. 1** Cross-sectional microstructure (a) and concentration profiles (b) across inter-diffusion zone of Pt/β-NiAl diffusion couple annealed at 1150 °C for 30 h
and (b) in terms of the layer thickness versus the square root of time. As can be seen that, the layer thicknesses for both the Pt$_3$Al and $\alpha$-NiPt(Al) vary linearly with $t^{1/2}$, indicating that the growth of the Pt$_3$Al and $\alpha$-NiPt(Al) phases are diffusion-controlled. Figure 2(c) shows the Arrhenius plot of the parabolic growth constants $k$ for the Pt$_3$Al and $\alpha$-NiPt(Al) phases with $k^{1/2}$ being slopes obtained from Figs. 2(a) and (b). The calculated Arrhenius equations of the parabolic growth constants, $k$, for the Pt$_3$Al and $\alpha$-NiPt(Al) phases are $k = 3.701 \times 10^2 \exp[-4.506 \times 10^{-5} / (RT)]$ and $k = 1.395 \times 10^{-7} \exp[-2.084 \times 10^{-2} / (RT)]$, respectively.

Figure 3 shows the measured concentration profiles of the Pt/$\beta$-NiAl diffusion couples annealed at 1 150, 1 200 and 1 250 °C for 90 h, and the corresponding inter-diffusion fluxes of individual components by means of Eq. (2). As can be seen that, the variation of Pt concentration in the $\beta$-NiAl phase resembles a horizontal mirror reflection of that of the Ni concentration, while the concentration profile of the Al is almost flat. Indicating that the Pt atoms prefer to occupy the Ni sties in $\beta$-NiAl lattice.

Based on the concentration profiles and the inter-diffusion fluxes in Fig. 3, the four average ternary inter-diffusion coefficients of the Pt$_3$Al and $\beta$-NiAl phases were determined using Eqs.(4) and (6), as listed in Table 1.
Fig. 3 Concentration profiles and corresponding inter-diffusion fluxes of Pt, Ni and Al in Pt/β-NiAl diffusion couples annealed at different temperatures for 90 h: (a), (d) 1 150 ºC; (b), (e) 1 200 ºC; (c), (f) 1 250 ºC

Table 1 Comparison between presently calculated average inter-diffusivities of Pt3Al and β-NiAl phases at different temperatures and literature data (m²/s)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Literature²) (1 100 ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 150 ºC</td>
<td>1 200 ºC</td>
<td>1 250 ºC</td>
</tr>
<tr>
<td>(D_{\text{PtNi}})</td>
<td>2.75×10⁻¹⁴</td>
<td>6.64×10⁻¹⁴</td>
<td>2.71×10⁻¹³</td>
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<td>(D_{\text{PtAl}})</td>
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<td>3.49×10⁻¹⁴</td>
<td>1.46×10⁻¹³</td>
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<tr>
<td>(D_{\text{AlNi}})</td>
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<td>-2.13×10⁻¹⁵</td>
<td>-1.63×10⁻¹⁵</td>
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<tr>
<td>(D_{\text{AlAl}})</td>
<td>6.73×10⁻¹⁴</td>
<td>2.84×10⁻¹⁴</td>
<td>9.77×10⁻¹⁴</td>
</tr>
<tr>
<td>(D_{\text{Pt}})</td>
<td>4.48×10⁻¹³</td>
<td>7.17×10⁻¹³</td>
<td>1.76×10⁻¹²</td>
</tr>
</tbody>
</table>
The values of $\beta$ in Table 1 are average values.

It should be pointed that the width of the $\alpha$-NiPt(Al) phase is extremely narrow, and thus the concentration points from EPMA are not enough to compute the reasonable inter-diffusivities. In order to compare with the literature data, the data of ternary inter-diffusivities reported by GLEESON et al [8] and BOUCHET and MEVREL [10] are cited in Table 1. The assumption that the negligible of the cross terms was also made in the present work, and named as Case 2 in order to be different from Case 1, in which all the main and cross terms were considered.

As can be seen from Table 1 that, the presently calculated $\overline{D}_{\beta i j}$ in both Case 1 and Case 2 agree well with the experimental values at 1 100 °C from Refs. [8, 10], while the $\overline{D}_{\beta i j}$ is a little bigger than that by BOUCHET and MEVREL [10]. The present value of the $\overline{D}_{\beta i j}$ agree reasonably with that by GLEESON et al [8], and both are negative, signifying that Al-Pt interaction parameter is negative, which in turn signifies that the Pt decreases the chemical activity of Al [9]. Considering the fact that the inter-diffusivities from the present work and Refs. [8, 10] are based on different methods, but their deviations are with one order (a typical error in diffusivity measurement), the conclusion is that all the data in Table 1 are reasonable.

5 Conclusions

1) Based on the local equilibrium hypothesis, the tie-lines between the respective phases are determined from the measured concentration profiles.

2) The PtAl and $\alpha$-NiPt(Al) layers developed between the Pt and $\beta$-NiAl couples, and their growth was found to be diffusion-controlled. The calculated Arrhenius equations of the parabolic growth constants, $k$, for the PtAl and $\alpha$-NiPt(Al) phases are $k = 3.701 \times 10^5 \exp[-4.506 \times 10^{-5} / (RT)]$ and $k = 1.395 \times 10^{-7} \exp[-2.084 \times 10^{-5} / (RT)]$, respectively.

3) The average inter-diffusivities of the PtAl and $\beta$-NiAl phases at different temperatures were calculated. The values of $\overline{D}_{\beta i j}$ are close to those reported in literature. The value of $\overline{D}_{\beta i j}$ are negative, signifying that the Al-Pt interaction parameter is negative.

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References


