Diffusion of Al and Al-Substituting Elements in Ni₃Al at Elevated Temperatures

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Diffusion of Ti, V, Nb, Mo and Ta in Ni₃Al phase was investigated at different temperatures using Ni–Al–X (X = Ti, V, Nb, Mo, Ta) pseudo-binary diffusion couples. The magnitude of the interdiffusion coefficients was in the descending order of V, Mo, Ti, Nb and Ta at all experimental temperatures ranging from 1423 to 1573 K. Diffusion data obtained in this study was compared with those of Re and Ru available in the literature as Re and Ru are recently being added in modern Ni-based superalloys. Diffusion retardation occurred for Ti, V, Nb, Mo and Ta as compared to Ru, and this can be explained by the anti-site diffusion mechanism. The high activation energy for anti-site formation is required for α-site (Al-site) elements, such as Ti, V, Nb, Mo and Ta. However, as Ru can diffuse either by α- (Ni-site) or β-site preferences without creating local disorder, Ru diffusion is not retarded by the anti-site diffusion mechanism. [doi:10.2320/matertrans.M2012218]

(Received June 20, 2012; Accepted September 5, 2012; Published October 17, 2012)

Keywords: nickel-based superalloys, nickel aluminide, diffusion couple, interdiffusion coefficient, activation enthalpy

1. Introduction

Nickel based superalloys comprise a class of materials developed particularly for superior properties at elevated temperatures, and they are being widely used as materials for bladed in aircraft engines and land-based gas turbines.¹ Nickel aluminide, Ni₃Al (γ”), has attracted much attention as an important phase in these superalloys as it exhibits the inverse temperature dependence of strength.² The ordered γ’ lattice, denoted as L₁₂, is stable up to the melting temperature, T_m (T_m = 1668 K for pure Ni₃Al). However, this phase in a pure binary form shows poor high-temperature creep strength and this strength can be improved by alloying. The elements replacing Al in Ni₃Al, such as Ti, Nb, Ta etc. strengthen the γ’ phase and thus contribute in strengthening the superalloys, whereas the Ni substituting elements (Co, Fe, Cr etc.) improve ductility.³ Furthermore, considerable amounts of Re have been added to Ni-based superalloys in the process of alloy evolution for improving both creep strength and hot corrosion resistance. Re and other refractory elements introduced so far are γ stabilizing elements,⁴ and their addition increases the negative mismatch between γ and γ’ phases in superalloys. Therefore, the addition of γ’-stabilizing elements, such as Ti, V, Nb, Mo and Ta is necessary for maintaining coherency between γ and γ’ phases.

The diffusion parameters of the alloying elements in Ni₃Al-based superalloys are important for understanding the excellent high-temperature properties attributed by the alloying elements in high-temperature processes, including homogenization and precipitation of the γ’ phase in γ matrix.⁵ Despite the obvious importance of the diffusion phenomena of Ni-based superalloys, little attention has been paid to obtaining diffusion parameters. Information concerning the interdiffusion of Re in a binary Ni–Re system has been reported by Karunaratne et al.,⁶ while Hattori et al.⁷ reported the interdiffusion in ternary Ni–Al–Re and Ni–Al–W systems. Moreover, the activation enthalpy of Nb in Ni₃Al, reported by Jiri Cermak et al.,³ shows a substantially lower value than in the literature,⁸ although the authors suggested some possible explanations for this discrepancy. Jiri Cermak et al.⁹ got the activation enthalpy of Nb in Ni₃Al to be 306 kJ/mol where as Divinski et al.¹⁰ mentioned the value to be 476 kJ/mol in their respective experiments. Thus, further research on the diffusion of Al and Al-substituting solute atoms should be necessary. In this study, the intrinsic diffusion of Ti, V, Nb, Mo and Ta in Ni₃Al was studied systematically in Ni–Al–X (X = Ti, V, Nb, Mo, Ta) systems in the temperature range of 1423–1573 K.

2. Experimental Procedure

Button ingots of Ni–23Al (mol%) and five kinds of ternary Ni alloys were prepared by arc melting under high-purity argon (Ar) gas atmosphere for the diffusion experiments. Their terminal compositions are shown in Table 1. These alloys were prepared from high-purity nickel (99.99 mass pct), aluminum (99.99 mass pct), titanium (99.5 mass pct), vanadium (99.9 mass pct), niobium (99.9 mass pct), molybdenum (99.95 mass pct) and tantalum (99.95 mass pct). The compositions placed the alloys in the single γ’ phase region of the ternary phase diagram at all experimental temperatures. The ingots were cut into rectangular samples (10 × 10 × 3 mm) and then polishes using diamond and aluminum oxide abrasive papers. The samples were annealed at 1573 K in an argon gas atmosphere for 100 h, and then quenched in ice-water solution to get a single γ’ phase.
2 mm), and then annealed at 1573 K for 240 h in order to promote homogenization and grain growth. Sufficiently large grain sizes for the diffusion experiments were obtained after this heat treatment in all six alloys, as shown in Fig. 1. In the cases of Ni–23Al–2Ti and Ni–23Al–2Nb, no grain boundary is seen in the figure because of their larger grain sizes than the respective micrograph sizes.

The homogenized samples were ground flat into plates, and then polished with a 0.25-µm diamond slurry for finishing. The plate specimens were then cleaned with acetone in an ultrasonic cleaner. Each diffusion couple listed in Table 1 was assembled with inert markers of alumina fibers 0.3 µm in diameter, placed between the polished surfaces of two plate specimens, and clamped using a molybdenum holder. Before this arrangement, the surfaces of the holder were coated with alumina powders 1 µm in diameter to prevent direct contact with the alloys. Five types

<table>
<thead>
<tr>
<th>No.</th>
<th>Diffusion couple (mol%)</th>
<th>Homogenization</th>
<th>Diffusion annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni–23Al/Ni–23Al–2Ti</td>
<td>1573 K, 240 h</td>
<td>1523 K, 168 h, 1473 K, 265 h, 1423 K, 360 h</td>
</tr>
<tr>
<td>2</td>
<td>Ni–23Al/Ni–23Al–2V</td>
<td>1573 K, 240 h</td>
<td>1523 K, 96 h, 1473 K, 120 h, 1423 K, 144 h</td>
</tr>
<tr>
<td>3</td>
<td>Ni–23Al/Ni–23Al–2Nb</td>
<td>1573 K, 240 h</td>
<td>1523 K, 96 h, 1473 K, 120 h, 1423 K, 144 h</td>
</tr>
<tr>
<td>4</td>
<td>Ni–23Al/Ni–23Al–2Mo</td>
<td>1573 K, 240 h</td>
<td>1523 K, 189 h, 1473 K, 328 h, 1423 K, 600 h</td>
</tr>
<tr>
<td>5</td>
<td>Ni–23Al/Ni–23Al–2Ta</td>
<td>1573 K, 240 h</td>
<td>1573 K, 96 h, 1523 K, 173 h, 1473 K, 334 h</td>
</tr>
</tbody>
</table>
of diffusion couples were prepared, as shown in Table 1. The diffusion couples were encapsulated in quartz ampoules under Ar gas for diffusion annealing, at three different temperatures for different durations, as shown in Table 1. Then, the couples were quenched into water by breaking the ampoules and then sectioned perpendicular to the diffusion interface. The exposed surface was polished using a 0.3-µm alumina powder finish and cleaned with acetone in an ultrasonic cleaner. The redistribution profiles of the elements along the diffusion zone were measured by SEM/EDX with the position of the inert alumina marker fixed as the origin of the diffusion distance.

3. Analytical Method

Sisson et al. correlated the direct and the cross interdiffusion coefficients with intrinsic diffusion coefficients of elements i in j-k alloys (where i: Ti, V, Nb, Mo, Ta; j: Al; k: Ni). According to Sisson et al. and Shuck et al., the intrinsic diffusion coefficient becomes equal to the intrinsic diffusion coefficient, when the atomic concentration of element i, \( C_i \), approaches zero:

\[
\lim_{C_i \to 0} D_i^u = D_i^\ast (j-k), \quad \lim_{C_i \to 0} D_i^c = 0,
\]

where \( D_i^\ast (j-k) \) is the intrinsic diffusion coefficient of element i in (j-k) binary alloys, \( D_i^u \) the direct interdiffusion coefficient and \( D_i^c \) the cross interdiffusion coefficient. The above relationships were also used by Minamino et al. According to eqs. (1) and (2), the direct coefficient of the \( \gamma' \) phase becomes equal to the intrinsic diffusion coefficient of element i in the \( \gamma' \) phase, because the cross coefficient \( D_i^c \) goes to zero at infinite dilution of element i. Therefore, the interdiffusion flux of element i, denoted by \( J_i \), can be written as

\[
J_i = -D_i^\ast (\gamma') \frac{\partial C_i}{\partial x}.
\]

In this diffusion equation, Hall’s method can be used to estimate the intrinsic diffusion coefficient for i element in \( \gamma' \), \( D_i^\ast (\gamma') \), by analysis of the end of diffusion profiles using the following relationships:

\[
Y_i = \frac{1}{2} (1 + \text{erfc}(u)),
\]

where \( Y_i \) is the normalized concentration defined by \( Y_i = (C_i - C_i^\ast)/(C_i^+ - C_i^\ast) \). \( C_i^+ \) and \( C_i^\ast \) are terminal atomic concentrations of element i of the diffusion couples. In eq. (4), according to Hall, u is represented by

\[
u = \frac{x}{\sqrt{t}} + l = h \lambda + l,
\]

where \( t, x, h \) and \( l \), respectively, are the time, distance, slope and intercept of the line of \( u-l \) curve on the probability paper. Using these parameters, the diffusion coefficient is represented by

\[
D_i(Y_i) = \frac{1}{4h^2} + \frac{l_\pi^2}{2h^2} \exp(u^2) \text{erfc}(u).
\]

In eq. (5), if \( h \) and \( l \) are constants, then \( u-l \) plot gives a straight line. However, \( u-l \) plot sometimes does not give a straight line, as will be shown in section 4. Therefore, in this study, \( h \) and \( l \) are defined at each segment in the \( u-l \) plot, according to Sarafianos.

4. Results and Discussion

Representative redistribution profiles of Ti, V, Nb, Mo and Ta with their corresponding Al profiles in the respective couples after diffusion annealing at 1523 K are shown in Fig. 2. The fitting line in each profile in the figure was drawn using a high-order function as follows:

\[
C_i(x) = C_i^+ + \frac{C_i^- - C_i^+}{1 + \exp \left( \frac{x-x_0}{\Delta x} \right)},
\]

where \( C_i^- \) and \( C_i^+ \) are the terminal atomic concentrations of element i at distance \( x \) of \( -\infty \) and \( +\infty \), respectively, and \( x_0 \) is a constant. In Fig. 2, a difference in diffusion distances is observed among solute elements in their respective systems. For example, Ti, V, and Mo diffused about 200 µm, whereas Nb and Ta diffused less than 100 µm at 1523 K.

According to eqs. (4)-(5), \( u-l \) plots were obtained based on the experimental results shown in Fig. 2. The plots are shown in Fig. 3. As mentioned in section 3, each \( u-l \) plot does not give a straight line, but has a curvature. Thus, \( h \) and \( l \) values are obtained by taking the derivative of the curve in each \( u-l \) plot in Fig. 3. On the basis of these \( h \) and \( l \) values, interdiffusion coefficients are calculated according to eq. (6). The obtained interdiffusion coefficients for the solute elements Ti, V, Nb, Mo and Ta are presented in Fig. 4. Irrespective of the temperature dependence, the interdiffusion coefficients are slightly larger for V, followed by Ti, Mo, Nb, and relatively smaller values are obtained for Ta.

The intrinsic diffusion coefficients obtained from the extrapolation to \( C_i \to 0 \) for Ti, V, Nb, Mo and Ta as \( C_i \) in \( \gamma' \) (\( D_i^{\gamma'}_{\text{Ti}}, D_i^{\gamma'}_{\text{V}}, D_i^{\gamma'}_{\text{Nb}}, D_i^{\gamma'}_{\text{Mo}} \) and \( D_i^{\gamma'}_{\text{Ta}} \), respectively) are obtained from the curves in Fig. 4, and they are presented as a function of the reciprocal absolute temperatures in Fig. 5. The intrinsic diffusion coefficient of ruthenium (Ru) and rhenium (Re) in the \( \gamma' \) phase reported by Mabruri et al. is also displayed in the figure for comparison. Mabruri used Darken-Manning equation for the analysis of intrinsic diffusion coefficients. Figure 5 shows that the diffusivity of Ti, V, Nb, Mo, Ta and Re in the \( \gamma' \) phase is much lower than that of Ru within the range of experimental temperatures. Ta shows the lowest diffusivity among the seven elements.

The activation energy and the frequency factor for the intrinsic diffusivities obtained from the Arrhenius plot in Fig. 5 are shown in Table 2. The Arrhenius parameters of each element in the \( \gamma' \) phase reported so far are also listed in Table 2 for comparison. Table 2 shows that the activation energies of Ti, V, Nb, Mo, Ta and Re in the \( \gamma' \) phase are significantly larger than those in the \( \gamma' \) phase indicating that these elements diffuse in Ni3Al in a similar mechanism. This mechanism is discussed in the following paragraph. On the other hand, Ru exhibits comparable values both in the \( \gamma' \) and \( \gamma' \) phases which means that Ru diffuses in the \( \gamma' \) phase by a similar mechanism with that in the \( \gamma' \) phase. The site
occupancy of Ru in γ' phase in reported by Mabruri et al.\textsuperscript{15}) Although the Ru site occupancy reported here is supported by some other authors,\textsuperscript{2,11,19} \textsuperscript{21} it is a speculation from the low and comparable activation energy values of Ru in both γ and γ' phases and further study is necessary for its verification. Figure 6 shows the variation of activation energies with the bond order of elements. Bond order implies the strength of interaction in Ni–X (X = Al-substituting elements) system.\textsuperscript{22} In the same d-orbital energy level group, the large bond order element needs the large activation energy for diffusion. For example, Ti and V belong to 3d energy level. V has the larger bond order than Ti. The activation energy of V is found larger than Ti in this study. This means that the strength of Ni–X affects the activation energy. Other experimental elements within the same d-orbital energy level also satisfy the same scheme.

It is well accepted that the diffusion of elements in Ni$_3$Al (L1$_2$-type structure) depends strongly on the site preference of the element.\textsuperscript{2,11,23} An α-site (Ni site) in L1$_2$ structure has eight nearest neighbor α-sites and four nearest neighbor β-sites, whereas β-sites (Al site) are exclusively surrounded by twelve α-sites. From this configuration, it is naturally expected that α-site atoms (e.g., Ni atom) can migrate over their own sublattice without disturbing the long range order, by the ordinary vacancy mechanism (the sublattice vacancy mechanism\textsuperscript{28}). The migration of β-site atoms (e.g., Al or Al-substituting solutes), however, appears to be less easy because their jump to a neighboring site must disrupt the ordered atomic arrangement. This can be explained by the anti-structure bridge (ASB) mechanism.\textsuperscript{2} There are always some Al atoms present on α sublattice sites. These atoms (anti-structure Al atoms) can also migrate through the α
sublattice by exchanging their positions with Ni vacancy at α sublattice. To perform an elementary migration an Al anti-site atom and a Ni vacancy must occupy nearest neighbor positions of the Ni sublattice. The anti-structure bridge (ASB) mechanism consists in the following sequences of atomic jump as shown in Fig. 7: (a) a nearest neighbor jump of a Ni vacancy into an adjacent Al site. Here an additional anti-structure Al atom is created at the initial position of the Ni vacancy, (b) a nearest neighbor jump of an initial anti-structure Al atom into the new vacant position on the Al sublattice. Vanaccy on the Ni sublattice is restored now. Final structure of this two-step ASB jump is shown in Fig. 7(c). As a result of accomplishing two vacancy jumps, the anti structure Al atom and the Ni vacancy exchange their positions:

\[ A_{\text{Al}}^{\text{Ni}} + V_{\text{Ni}} \rightarrow A_{\text{Al}}^{\text{Ni}} + A_{\text{Al}}^{\text{Ni}} + V_{\text{Al}} \rightarrow A_{\text{Al}}^{\text{Ni}} + V_{\text{Ni}} \]  

(8)

Here \( A_{\text{Al}}^{\text{Ni}} \) denotes an Al atom at the Ni sublattice (the anti structure Al atom); \( V_{\text{Al}} \) and \( V_{\text{Ni}} \) are the vacancies on Al and Ni sublattices, respectively. In true sense, initial and final Al atoms are different Al atoms as denoted by the primed symbol in eq. (8). Two Al atoms participate in an elementary ASB jump, namely nearest neighbor site and anti site atoms, and finally they exchange the host lattices: the Al atom jumps from the Al to the Ni sublattice and the anti structure Al atom goes to the Al sublattice. Thus diffusion of Al atoms in the β-sites must overcome the energy associated with local disordering caused by the exchanging positions between \( A_{\text{Al}}^{\text{Ni}} \) and \( V_{\text{Ni}} \). This means that diffusion of Al atoms needs a larger activation enthalpy including the atomic ordering energy. For simplicity, this activation enthalpy, \( Q_{\text{ord}} \), is assumed to be the sum of the activation enthalpy for diffusion in the disordered γ' phase, \( Q_{\text{dis}} \), and the ordering energy, \( E_{\text{ord}} \), then

\[ Q_{\text{ord}} = Q_{\text{dis}} + E_{\text{ord}}. \]  

(9)

In the case of the α-sites atoms migrate from α-sites to one of the nearest eight α-sites, they can diffuse without creating local disordering. Thus, the solutes substituting for Al show higher activation enthalpy than the elements substituting for Ni. This corresponds to the additional contribution needed for

![Image](image-url)

Fig. 3  ν–λ profiles in the diffusion couples of (a) Ni–23Al/Ni–23Al–2Ti, (b) Ni–23Al/Ni–23Al–2V, (c) Ni–23Al/Ni–23Al–2Nb, (d) Ni–23Al/Ni–23Al–2Mo and (e) Ni–23Al/Ni–23Al–2Ta, annealed at 1523 K.
Fig. 4 Interdiffusion coefficients determined as a function of concentration at different temperatures for the solute elements of (a) Ti, (b) V, (c) Nb, (d) Mo and (e) Ta in Ni₃Al.

Fig. 5 Extrapolated intrinsic diffusion coefficients for Ti, V, Nb, Mo, Ta, Re\(^{15}\) and Ru\(^{15}\) in Ni₃Al.
antisite formation\textsuperscript{2,29} i.e., the low mobilities of Ti, V, Nb, Mo, Ta and Re atoms in Ni$_3$Al compared to those in Ni is due to this anti structure bridge diffusion mechanism. The elements occupying both sites (\(\alpha\)- or \(\beta\)-sites) can diffuse by a similar mechanism to that for Ni substituting elements. Ru can diffuse either by \(\alpha\)- or \(\beta\)-site preference, and hence its diffusion is not retarded by the anti structure bridge diffusion mechanism. Thus, Fig. 5 shows more rapid diffusion of Ru than of Ti, V, Nb, Mo, Ta and Re.

5. Conclusion

The diffusion of Ti, V, Nb, Mo and Ta in Ni$_3$Al phase was investigated at four different temperatures of 1423, 1473, 1523 and 1573 K using pseudo-binary diffusion couples. Irrespective of the temperature dependence, the magnitudes of interdiffusion coefficients were in the descending order of Ru, V, Mo, Ti, Nb, Re and Ta. On the basis of modified Hall method, the activation enthalpy (\(Q\)) for solute element diffusion in Ni$_3$Al was estimated from experimental data. The activation enthalpies of Ti, V, Nb and Mo in Ni$_3$Al were calculated in this study. The results of this study are summarized as follows:

\[
D_{\text{Ti}}^{(\gamma)} = 1.8 \times 10^7 \exp(426 \text{kJmol}^{-1}/RT) \\
D_{\text{V}}^{(\gamma)} = 1.7 \times 10^7 \exp(446 \text{kJmol}^{-1}/RT) \\
D_{\text{Nb}}^{(\gamma)} = 3.5 \times 10^7 \exp(470 \text{kJmol}^{-1}/RT) \\
D_{\text{Mo}}^{(\gamma)} = 5.2 \times 10^8 \exp(550 \text{kJmol}^{-1}/RT) \\
D_{\text{Ta}}^{(\gamma)} = 7.16 \times 10^9 \exp(462 \text{kJmol}^{-1}/RT)
\]

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research of Japan Society for the Promotion of Science (JSPS), Japan.

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