Diffusion of Re and Ru in the $\gamma'$ Phase of Ni Based Alloys

Efendi Mabruri$^{1,\ast 1,\ast 2}$, Shingo Sakurai$^{1,\ast 1}$, Yoshinori Murata$^1$, Toshiyuki Koyama$^2$ and Masahiko Morinaga$^1$

$^1$Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
$^2$National Institute for Materials Science, Tsukuba 305-0047, Japan

The diffusion of Re and Ru in the $\gamma'$-Ni$_3$Al phase has been investigated at a range of temperatures 1423–1523 K by using the pseudo-binary diffusion couples. It was found that the concentration gradient of Re appeared to promote the uphill diffusion of Al, whereas that of Ru did not promote the Al uphill diffusion. The cross interdiffusion coefficients of $D_{\text{Al-Re}}$ and $D_{\text{Al-Ru}}$ were independent of the matrix ordering since they were comparable qualitatively between those in the $\gamma'$-Ni$_3$Al and in the $\gamma$-Ni phases. The tracer diffusion coefficients for Re and Ru in Ni$_3$Al were estimated by extrapolation and the obtained activation energies were consistent with the site preferences of the elements reported in the literature. Further, the results of this work suggest that the diffusion of Ru in Ni$_3$Al is mostly governed by the diffusion in Ni sublattice and the diffusion of Re is mainly controlled by the formation of anti-site defects in the Ni sublattice with negligible contribution of the anti-site bridge mechanism. [doi:10.2320/matertrans.MRA2007632]

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1. Introduction

The development of the next generation single crystal Ni based superalloys pays an intensive attention to the roles of Re and Ru as the potent alloying elements. The combination of these two elements has been found to enhance high temperature capability of the superalloys.1–5) Providing mobility data for these elements in nickel based alloys is an important issue since it is indeed required in designing the superalloys with respect to high temperature processes such as the precipitation and growth of the $\gamma'$, creep, rafting, etc. The diffusion of these elements in the $\gamma$ phase of binary and ternary nickel based alloys have been documented in literature.6–12) However, to the author’s knowledge there is no report concerning on the diffusion of these elements in the $\gamma'$ phase. The $\gamma'$ phase has an order structure of L1$_2$ type in which Ni atoms are located at the face center site while Al atoms are at cubic corner site. In the stoichiometric Ni$_3$Al, a Ni atom is surrounded by the nearest neighbors 8 Ni and 4 Al atoms, while an Al atom is surrounded only by 12 nearest neighbor Ni atoms. Due to the order structure, the diffusion of atoms occupying the Al site is expected to be slower than the atoms occupying the Ni site. Thus, the diffusion of solutes in the $\gamma'$ phase depends strongly on their occupation behaviors in the Ni$_3$Al lattice.1,3,14)

The present paper presents the diffusion of Re and Ru in the Ni$_3$Al within a range of temperatures 1423–1523 K. The extrapolated tracer diffusion coefficients in Ni$_3$Al are estimated and the activation energies are correlated with the existing data of the elements from a point of view of the site preferences. In addition, some of the cross interdiffusion coefficients in the systems of Ni$_3$Al-Re and Ni$_3$Al-Ru are also evaluated qualitatively from the redistribution profile of Al which is initially a constant.

2. Experimental Procedure

The experiments used the pseudo-binary diffusion couples with a constant Al concentration. Due to the limited solubility of Re and Ru in the Ni$_3$Al (about 2 mol% for Re at 1313 K15) and about 4 mol% for Ru at 1373 K16) dilute concentration of these elements was used in the alloys for the diffusion couples. The composition of the diffusion couples in mol% after homogenization and the heat treatment condition used in this study are presented in Table 1. The aluminum concentration of the alloys shown in the table deviates slightly from stoichiometric composition of Ni$_3$Al and this may be due to the melting condition. Thus, these alloys can be considered to be the Al-rich Ni$_3$Al. The button ingots of the alloys were prepared by arc melting in high purity argon gas atmosphere. The ingots were annealed at 1523 to promote homogenization and grain growth. Sufficient large grain sizes were obtained for the three alloys as shown in Fig. 1. Then, the ingots were cut into plate-shape and ground flat and parallel. The plates were polished with a 0.25 mm finish of diamond slurry and cleaned by acetone in an ultrasonic cleaner. The diffusion couples were assembled with alumina fibers of several micrometers in diameter placed between the polished surfaces of the plates as the inert marker of initial interface. The diffusion couples were then clamped with molybdenum holders. Before the arrangement, the surfaces

Table 1 Composition (mol%) of the diffusion couples and condition of diffusion annealing.

<table>
<thead>
<tr>
<th>No.</th>
<th>Diffusion Couple</th>
<th>Diffusion Annealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-25.5Al/Ni-25.5Al-1Re</td>
<td>1423 K, 516.06 ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1473 K, 486.24 ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1523 K, 240.55 ks</td>
</tr>
<tr>
<td>2</td>
<td>Ni-25.5Al/Ni-25.5Al-1Ru</td>
<td>1423 K, 516.06 ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1473 K, 399.60 ks</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1523 K, 259.20 ks</td>
</tr>
</tbody>
</table>
of the holders were coated by 0.3 μm in diameter alumina powders to prevent direct contact with the alloys. The diffusion couples were sealed in quartz ampoules under an argon atmosphere and then annealed at the given temperatures for the given times presented in Table 1. After diffusion annealing the ampoules were quenched in water by breaking them. The diffusion couples were then sectioned perpendicular to the diffusion interface and polished to a 0.3 μm alumina-powders finish and cleaned by 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 marker fixed as origin of the distance.

3. Results and Discussion

Figure 2(a) and (b) presents the typical redistribution profiles for Re and Ru in their respective diffusion couples after annealing at 1523 K for 240.55 ks and for 259.2 ks, respectively. The full line is the fitting profile representing the measured profiles by the error-function type equation as follows:  

\[ C_x(x) = C_{x^-} + \frac{C_{x^+} - C_{x^-}}{2} [1 + \text{erf}(fx)], \]

where \( C_{x^-} \) and \( C_{x^+} \) are the terminal concentrations of element \( i \) at the distance \( x \) of \( -\infty \) and \( +\infty \), respectively and \( fx \) is the polynomial function upon \( x \). The examples for redistribution profiles of Al which has an initially constant concentration in the couples are shown in Fig. 3(a) and (b) in the Re-containing and Ru-containing diffusion couples, respectively, after annealing at 1523 K. It is observed from this figure that the Al redistribution profile shows uphill diffusion in the presence of the Re concentration gradient (Fig. 3(a)) and it stays roughly constant along the diffusion zone in the presence of the Ru concentration gradient (Fig. 3(b)). It indicates that Re in Ni₃Al changes the chemical potential of Al to drive the Al diffusion but Ru does not. The Re addition into Ni₃Al is expected to increase the activity of Al considering that the diffusion of Al originated from the area of higher content of Re. Further, as the uphill diffusion is attributable to the cross interdiffusion coeffi-
coefficients, the cross terms of $\tilde{D}_{\text{AlRe}}^\text{Ni}$ and $\tilde{D}_{\text{AlRu}}^\text{Ni}$ which represent the influence of Re and Ru concentration gradients, respectively, on the Al fluxes can be deduced qualitatively from the redistribution profile of Al. The results are displayed in Table 2 in the form of the ratio of cross to major interdiffusion coefficients in $\gamma$ and $\gamma'$ phases of both Ni-Al-Re and Ni-Al-Ru systems. It is shown that both $\tilde{D}_{\text{AlRe}}^\text{Ni}$ and $\tilde{D}_{\text{AlRu}}^\text{Ni}$ are qualitatively consistent between those in the $\gamma/C13$ and $\gamma/C13^0$ phases indicating that these coefficients are independent of the matrix ordering.

Based on the fitted redistribution profiles expressed by eq. (1) the interdiffusion coefficients for Re and Ru at the range of temperatures 1423–1523 K are calculated by Sauer and Freise method\textsuperscript{18) using the following equation:

$$
\tilde{D} = \frac{1}{2t} \left( 1 - Y_1 \right) \int_x^{+\infty} Y_i dx + Y_i \int_x^{-\infty} (1 - Y_i) dx,
$$

where $Y_i$ is the normalized concentration defined by $Y_i = (C_i - C_i^-)/(C_i^+ - C_i^-)$, $t$ and $x$ are the time and the distance, respectively. The estimated interdiffusion coefficients of Re and Ru are presented in Fig. 4. Both coefficients appear to vary slightly with the respective element concentration. However, they all can be represented by linear lines. Further, as the systems concerned here are assumed as the pseudo-binary solution, the tracer diffusion coefficient for both Re and Ru in Ni$_3$Al can be deduced from these lines by considering the Darken-Manning equation\textsuperscript{19,20) as follows:

$$
\tilde{D} = \tilde{D}_A^N + \tilde{D}_B^N \Phi S,
$$

where $\tilde{D}$, $\tilde{D}_A^N$, and $\tilde{D}_B^N$ are the interdiffusion coefficient, the A-tracer diffusion coefficient and the B-tracer diffusion coefficient, respectively. $N_A$ and $N_B$ are the atomic fraction for element A and B, respectively, $\Phi$ is the thermodynamic factor and $S$ is the vacancy wind factor. By taking the $N_B$ is zero for the very dilute solution, both $\Phi$ and $S$ will be equal to unity. At this point ($N_B = 0$) the interdiffusion coefficient $\tilde{D}$ is expected to be identical with the tracer diffusion coefficient $\tilde{D}_B^N$. Then, the extrapolated value of $\tilde{D}$ to the zero concentration of B can be considered as $\tilde{D}_B^0$.

Table 2 The ratio of cross to major interdiffusion coefficients in $\gamma$ and $\gamma'$ phases of both Ni-Al-Re and Ni-Al-Ru systems.

<table>
<thead>
<tr>
<th>Phase</th>
<th>$\tilde{D}<em>{\text{AlRe}}^\text{Ni}/D</em>{\text{AlAl}}^\gamma$</th>
<th>$\tilde{D}<em>{\text{AlRu}}^\text{Ni}/D</em>{\text{AlAl}}^\gamma$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma'$</td>
<td>Positive</td>
<td>$\approx 0$</td>
<td>This work</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.2$^*$</td>
<td>0.05$^{**}$</td>
<td>$^*$Mabruri et al.\textsuperscript{9) }$^**$Hattori et al.\textsuperscript{10) }</td>
</tr>
</tbody>
</table>

Fig. 3 Typical redistribution profiles of Al in (a) Re- and (b) Ru-containing diffusion couples after diffusion annealing at 1523 K for 240.55 ks and for 259.2 ks, respectively.

Fig. 4 The interdiffusion coefficients of (a) Re and (b) Ru in Ni$_3$Al as a function of their respective concentrations at various temperatures.
By considering that the term A is for Ni and B is for Re or Ru, the extrapolated tracer diffusion coefficients for Re and Ru in $\gamma'$-Ni$_3$Al ($D^\text{ex}_{\text{Re}}$ and $D^\text{ex}_{\text{Ru}}$, respectively) are obtained from Fig. 4 and they are presented in Fig. 5 as a function of the reciprocal absolute temperatures. It is seen from Fig. 5 that the diffusion coefficient of Re in the $\gamma'$ phase is lower than that of Ru along the range of experimental temperatures and this is consistent with their difference in the $\gamma$ phase.

The activation energy and the frequency factor for the tracer diffusion of Re and Ru obtained from Arrhenius plot in Fig. 5 is shown in Table 3. The Arrhenius parameters for diffusion of Re and Ru in the $\gamma$ phase and of other elements in the $\gamma'$ phase reported in the literature are also displayed in Table 3 for comparison. It can be seen from the table that the activation energy for diffusion of Re in the $\gamma'$ phase is significantly larger than that in the $\gamma$ phase. Also, this energy is comparable with those for Nb and Ti in the $\gamma'$ phase as shown in Table 3, and hence it is likely that Re diffuses in Ni$_3$Al in a similar mechanism with that of the two latter elements. As for Ru, the activation energy shows a comparable value in both phases, indicating that Ru diffuses in the $\gamma'$ phase by a similar mechanism with that in the $\gamma$ phase, i.e. through the Ni vacancies in the Ni sublattice. The migration of Ru atoms from Al site to Ni site or vice versa seems to be negligible and do not contribute to the total diffusion activation energy. This behavior is similar to the cases of Ni and Co as the diffusion activation energies for the three elements (Ni, Co, Ru) in the $\gamma'$ phase are comparable as listed in Table 3.

It is well accepted that the diffusion of elements in Ni$_3$Al depends strongly on the elements site preferences. The elements occupying Ni site diffuse via Ni vacancies, whereas the elements occupying Al site diffuse as anti-site defects in Ni sublattice. The elements occupying both sites may diffuse by the mechanism similar to that for Ni substituting elements. The ordinary diffusion activation energy for Ru resulted in this study reflects that Ru occupies Ni site more preferentially or for both sites. On the other hand, the large diffusion activation energy for Re in the $\gamma'$ phase reflects that Re occupies Al site preferentially. The site preference of the elements of 3d, 4d and 5d in Ni$_3$Al has been reported to depend on the composition and on the temperature. In Al-rich Ni$_3$Al alloys, as this kind of alloy is used in this work, Ru shows a preference for Ni site at low temperature, but with increasing temperature the fraction of Ru in the Ni sublattice decreases to such extent that their site preference is reversed. At a range of temperatures applied in this work, about 55–65% fraction of Ru is located at Al site. Due to the vacancy concentration in the Ni site is five times larger than that in Al site, the diffusion of Ru in Ni$_3$Al is mostly governed by the diffusion in Ni sublattice. This gives the activation energy for diffusion of Ru in Ni$_3$Al to be comparable with that for Ni and the Ni substituting element Co.

On the other hand, Re shows consistently a predominant preference for the Al site at all temperatures. At a range of temperatures concerned in this work, about 80% or 98% fraction of Re atoms are located at the Al site. Considering that the disordering activation energy of Ni$_3$Al alloyed with the elements Nb, V, Ti and W which substitute strongly for the Al site, is much larger than the ordering activation energy, it is hard to be expected that the atoms occupying Al site diffuse accompanied by this kind of disordering. If this is true for Re, then the diffusion of Re atoms in the Ni$_3$Al will be controlled by the formation of the anti-site atoms in the Ni sublattice. The anti-site atoms in Ni sublattice are the atoms of Al or Al-substituting elements available in Ni sublattice as an impurity.

Furthermore, it is shown also in Table 3 that activation energies for Re, Ti and Nb are much larger with respect to that for Ge and Ga even though all these elements occupy the Al site predominantly. This indicates that the contribution of the so called anti-site bridge (ASB) mechanism to the diffusion of anti-site atoms of Re, Ti, Nb seems to be negligible. It has been proposed that the ASB mechanism enhances the diffusion of Al, Ge and Ga in Ni$_3$Al by enhancing the number of probable sites which can be reached by the anti-site atoms. The ASB mechanism enables the anti site atoms in Ni sites and the nearest neighbor atoms in Al sites exchange their host lattices while maintaining the order state. Since the effective activation enthalpy for the
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REFERENCES