The partitioning and site preference of rhenium or ruthenium in model nickel-based superalloys: An atom-probe tomographic and first-principles study

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The partitioning behavior and sublattice site preference of Re or Ru in the Ni$_3$Al (L1$_2$) γ'-precipitates of model Ni–Al–Cr alloys are investigated by atom-probe tomography (APT) and first-principles calculations. Rhenium and Ru are experimentally observed to partition to the γ(fcc)-phase, which is consistent with the smaller values of the γ-matrix Re and Ru substitutional formation energies determined by first-principles calculations. APT measurements of the γ'-precipitate composition indicate that Re and Ru occupy the Al sublattice sites of the Ni$_3$Al (L1$_2$) phase. The preferential site substitution of Re and Ru at Al sublattice sites is confirmed by first-principles calculations. © 2008 American Institute of Physics. [DOI: 10.1063/1.2998654]

Nickel-based superalloys, which are widely used in land-based and aerospace turbine engines, have been studied extensively due to their incomparable high temperature strength and resistance to creep and oxidation. These alloys owe their extraordinary high temperature mechanical properties to strengthening of the γ(fcc) matrix by coherent, elastically hard γ'(L1$_2$)-precipitates. Refractory element additions such as Re, Ta, or W improve γ'-precipitate stability by decreasing the coarsening kinetics of the γ'-phase, while simultaneously providing solid-solution strengthening. At temperatures above 1273 K, however, localized supersaturations of Re and W can lead to the precipitation of refractory-rich topologically close-packed (TCP) phases. These TCP phases are deleterious to the mechanical properties of commercial superalloys because they consume refractory additions, reducing both solid-solution and precipitation strengthening. Ruthenium is added to modern nickel superalloys to inhibit the formation of TCP phases, thereby extending the creep capability of single-crystal superalloys to higher temperatures. The mechanisms by which Ru suppresses TCP phase formation have been the subject of some debate, although the effect of Ru on the γ/γ' partitioning of other refractory elements, particularly Re, has been identified as playing a major role.

We investigate the partitioning and site substitution behavior of Re or Ru in Ni–Al–Cr model superalloys aged at 1073 K, employing both atom-probe tomography (APT) and first-principles calculations. Three alloys, Ni-10.0 Al-8.5 Cr, Ni-10.0 Al-8.5 Cr-2.0 Re, and Ni-10.0 Al-8.5 Cr-2.0 Ru at. %, were chill cast in a 19 mm diameter copper mold to form polycrystalline master ingots. The ingots were homogenized at 1573 K for 20 h, then solutionized in the γ-phase field at 1503 K for 3 h and water quenched. Ingot sections were aged at 1073 K under flowing argon for 256 h, then water quenched, and microtip specimens were prepared for study by APT. Pulsed-laser APT data collection was performed at an evaporation rate of 0.04 ions pulse$^{-1}$, a specimen temperature of 40.0±0.3 K, a pulse energy of 0.6 nJ pulse$^{-1}$, a pulse repetition rate of 200 kHz, and a gauge pressure of <6.7 × 10$^{-8}$ Pa. APT data were visualized and analyzed with the IVAS™ 3.0 software program (Imago Scientific Instruments). We note that the details of the phase decomposition of the model alloys studied herein are provided elsewhere, and that the alloys do not contain TCP phases.

First-principles calculations were performed using the plane wave pseudopotential total energy method with local-density approximations, as implemented in the Vienna ab initio simulation package. Projector augmented-wave pseudopotentials were employed with an energy cutoff of 300 eV for plane waves in the 8×8×8 Monkhorst–Pack k-point grids, and were found to give convergent results. The calculated lattice parameter of the relaxed Ni$_3$Al (L1$_2$) structure was determined to be 0.348 nm, in good agreement with the room temperature experimental value of 0.357 nm.

A spheroidal γ'-precipitate from the Ni–Al–Cr–Ru alloy aged at 1073 K for 256 h is visualized by APT (Fig. 1); similar reconstructions are available for the Ni–Al–Cr–Re alloy in the work of Yoon et al. In both alloys, Al is observed to partition strongly to the γ' phase, while Cr and the refractory additions, Re or Ru, partition to the γ-matrix. The concentration profiles across the γ/γ' interface of the Ni–Al–Cr–Re and Ni–Al–Cr–Ru alloys, as measured by the proximity histogram method, are displayed in Fig. 2. The partitioning ratio, defined as the concentration of an element in the γ'-phase divided by the concentration of the same element in the γ-phase, is calculated to quantify the partitioning behavior of an element. Rhenium and Ru were found to partition to the γ-phase, in agreement with previous studies, with partitioning ratios of 0.37±0.03 and 0.37±0.07, respectively.

The energetic driving force for the partitioning of Re or Ru to the γ-matrix was determined by first-principles calculations in a system of 12×2×2 unit cells (192 atoms) con-
FIG. 1. LEAP tomographic reconstruction of a spheroidal γ'-precipitate in a model Ni-10.0 Al-8.5 Cr-2.0 Ru at. % alloy aged at 1073 K for 256 h. The elements that partition to the γ(fcc)-matrix, Cr and Ru atoms, are shown in white, while Al atoms, which partition to the γ'-(L12) precipitates, are shown in black; Ni atoms are omitted for clarity.

structured along the (100) direction. The supercell was divided by a (100) interface, and the two halves of the supercell were occupied by the γ-Ni and γ'-Ni3Al phases, respectively. Every Ni atom on the γ-Ni side of the interface was treated as a potential substitutional site for the Re or Ru atoms, while on the Ni3Al side, the Ni and Al sublattice sites were treated as separate substitutional sites. To ensure coherency of the {100} γ'/γ' interface, the structures on either side of the interface were relaxed within the constraints of the Ni3Al crystal structure. The substitutional formation energies of Re or Ru as a function of distance from the {100} interface were calculated employing

\[ E_{Z-M} = \left( E_{\text{Z precipitate}}^{\text{tot}} + n_M \mu_M - (E_{\text{Z matrix}}^{\text{tot}} + n_Z \mu_Z) \right) / n_Z, \]

(1)

\[ E_{Z-Ni} = \left( E_{\text{Ni precipitate}}^{\text{tot}} + n_{Ni} \mu_{Ni} - (E_{\text{Ni matrix}}^{\text{tot}} + n_Z \mu_Z) \right) / n_Z, \]

(2)

where \( M \) is Ni or Al, \( Z \) is Ru or Re, \( E_{\text{tot}} \) is the total energy prior to substitution, \( E_{\text{Z precipitate}}^{\text{tot}} \) and \( E_{\text{Z matrix}}^{\text{tot}} \) are the total energies when elements \( Z \) partition to the precipitate or matrix phase, respectively, and \( n_Z \) is the number of \( Z \) atoms. The chemical potentials per atom of the pure bulk elements \( \mu_i \) are calculated by assuming the same cell symmetry and are determined to be -6.538, -4.195, -10.512, and -13.682 eV atom\(^{-1}\) for Ni, Al, Re, and Ru, respectively. The calculated substitutional formation energies of Re and Ru are smaller in the γ'-matrix than in the γ'-precipitate (Fig. 3), providing the energetic driving force for the partitioning of Re and Ru in the γ'-phase. It is noted that the addition of Re and Ru leads to an increase in the total energy of the L12 crystal structure.

Table I summarizes the γ'-phase compositions of the three alloys studied herein for samples aged at 1073 K for 256 h. The sum of the γ'-precipitate concentrations of Al, Cr, and Re or Ru is \( \sim 25 \) at. % for the investigated alloys, indicating that the four solute elements substitute preferentially to the Al sublattice sites of the Ni3Al structure.

The site preference of Re or Ru is studied by first-principles calculations by substituting one Re or Ru atom at one of the Ni or Al sublattice sites in the Ni3Al superlattice, resulting in four substitutional structures: (Ni1-Re1-x)1Al, (Ni1-Re1-x)1Al, (Ni1-Re1-x)1Al, and (Ni1-Re1-x)1Al. A three-dimensional periodic supercell with \( 2 \times 2 \times 2 \) unit cells was constructed for the substitutional energy calculations, and the total energies of the cells converged to \( 2 \times 10^{-5} \) eV atom\(^{-1}\), while residual forces converged to 0.005 eV nm\(^{-1}\). Table I lists the calculated total energies of the relaxed structures, \( E_{\text{tot}} \), and the site substitutional energies, \( E_{Z-Ni} \) and \( E_{Z-Al} \), which are defined as

\[ E_{Z-Ni} = \left( E_{\text{Ni precipitate}}^{\text{tot}} + n_{Ni} \mu_{Ni} - (E_{\text{Ni matrix}}^{\text{tot}} + n_Z \mu_Z) \right) / n_Z, \]

(3)

TABLE I. The experimental compositions of the γ'-(L12) precipitates of the Ni-10.0 Al-8.5 Cr, Ni-10.0 Al-8.5 Cr-2.0 Ru, and Ni-10.0 Al-8.5 Cr-2.0 Re at. % alloys aged at 1073 K for 256 h.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni (at. %)</th>
<th>Al (at. %)</th>
<th>Cr (at. %)</th>
<th>Ru or Re (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Al-Cr</td>
<td>75.69 ± 0.28</td>
<td>18.06 ± 0.30</td>
<td>6.24 ± 0.20</td>
<td>...</td>
</tr>
<tr>
<td>Ni-Al-Cr-Ru</td>
<td>75.71 ± 0.29</td>
<td>18.06 ± 0.26</td>
<td>5.36 ± 0.15</td>
<td>0.87 ± 0.06</td>
</tr>
<tr>
<td>Ni-Al-Cr-Re</td>
<td>75.61 ± 0.16</td>
<td>17.57 ± 0.30</td>
<td>5.93 ± 0.32</td>
<td>0.86 ± 0.17</td>
</tr>
</tbody>
</table>

FIG. 2. Nickel, Al, Cr, and Re (Ru) concentration profiles across the γ'/γ' heterophase interface for alloys Ni-10.0 Al-8.5 Cr-2.0 Re and Ni-10.0 Al-8.5 Cr-2.0 Ru at. %, both aged at 1073 K for 256 h.

FIG. 3. The substitutional formation energies of Re and Ru atoms as a function of distance from the γ(fcc)/γ'-(L12) heterophase interface from first-principles calculations for a γ(Ni)/γ'(Ni3Al) system.
TABLE II. Total and site substitutional energies determined by first-principles calculations. (For this calculation, $x = 0.042$ and $y = 0.125$, and $Z = \text{Re or Ru}$.)

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{tot}}$ (eV)</th>
<th>$E_{Z=\text{NiAl}}$ (eV atom$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_3$Al</td>
<td>−206.587</td>
<td>⋯</td>
</tr>
<tr>
<td>(Ni$<em>3$Re)$</em>{1−x}$Al</td>
<td>−212.494</td>
<td>1.237</td>
</tr>
<tr>
<td>Ni$<em>3$(Al,Re)$</em>{1−x}$</td>
<td>−215.282</td>
<td>0.792</td>
</tr>
<tr>
<td>(Ni$<em>3$Ru)$</em>{1−x}$Al</td>
<td>−209.621</td>
<td>0.940</td>
</tr>
<tr>
<td>Ni$<em>3$(Al,Ru)$</em>{1−x}$</td>
<td>−212.200</td>
<td>0.705</td>
</tr>
</tbody>
</table>

$$E_{Z=\text{Al}} = [(E_{\text{tot}}(\text{Al}_{1−x}Z_x) + n_\text{Al}Z_x) - (E_{\text{tot}}(\text{Ni}_3\text{Al}) + n_\text{Z}Z_x)]/n_\text{Z}.$$ (4)

The site substitutional energies of Re or Ru are significantly smaller at the Al sublattice sites than at the Ni sites (Table II), confirming that these refractory additions prefer to occupy the Al sublattice sites of the Ni$_3$Al structure. A study of the Ru $γ'$ precipitate site substitution in a ternary Ni–Al–Ru alloy, employing the atomic site location by channeling enhanced microanalysis technique, showed that Ru is five times more likely to occupy the Al sublattice sites, in qualitative agreement with the first-principles results determined above. We note that a previous study employing methods similar to those used herein showed that Ta also occupies the Al sublattice sites of the $γ'$-phase.

The average atomic displacements and forces at the first nearest-neighbor distance associated with the local strains and stresses resulting from the site substitution of Re or Ru at the Ni or Al sublattice sites are displayed in Table III. The average atomic displacements and forces are found to be smaller for substitution of Re or Ru at the Al sublattice sites, providing supporting evidence that the refractory additions prefer to occupy the Al sublattice sites.

To conclude, Re and Ru partition strongly to the $γ$-matrix phase in model Ni–Al–Cr alloys because the values of the site substitutional energies of the refractory additions are smaller in the $γ$ phase than in the $γ'$ phase. Additionally, the APT experimental results and first-principles calculations demonstrate that Re and Ru substitute preferentially at the Al sublattice sites in the Ni$_3$Al ($L_1_2$) structure.

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