On the interplay between tungsten and tantalum atoms in Ni-based superalloys: An atom-probe tomographic and first-principles study

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The partitioning behavior of W in a multicomponent Ni-based superalloy and in a ternary Ni-Al–W alloy is investigated using atom-probe tomography (APT) and first-principles calculations. APT observations indicate that whereas W partitions preferentially to the γ′(L12)-precipitates in the ternary alloy, its partitioning behavior is reversed in favor of the γ(fcc)-matrix in the multicomponent alloy. First-principles calculations of the substitutional formation energies of W and Ta predict that Ta has a larger driving force for partitioning to the γ′ phase than W. This implies that Ta displaces W from the γ′-precipitates into the γ-matrix in multicomponent alloys.

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A multicomponent Ni-14.6 Al-8.18 Cr-7.74 Co-1.95 Ta-0.95 Mo-2.31 W-1.47 Re-0.63 C-0.05 Hf (at. %) alloy and a ternary Ni-14 Al-3 W (at. %) alloy were directionally solidified employing the Bridgman technique to form (100)-oriented single crystals. APT microtip samples were prepared by electrochemical polishing. Pulsed-laser APT was performed using local-electrode atom-probe (LEAP™) tomography, at a specimen temperature of 40 ± 0.3 K, a 200 kHz pulse repetition rate, an energy of ~0.6 nJ pulse−1, and a pressure ~<5 × 10−9 Pa. These experimental conditions were found to yield optimal compositional accuracy in a model Ni-based alloy. Data analysis was performed using IVAS® (Imago Scientific Instruments), and compositional information was obtained with proximity histograms.

Figure 1 displays typical three-dimensional (3D) APT reconstructions from both alloys, which contain the γ and γ′-phases, separated by 8.2 at. % Cr and 12 at. % Al isoconcentration surfaces for the (a) multicomponent and (b) ternary alloys, respectively. For clarity, only the Ni, Al, and W distributions are displayed, showing the predominance of Ni (green) in the γ-phase and of Al (red) in the γ′-phase. Pronounced partitioning of W (represented as large spheres) to the γ′-phase in the ternary alloy is observed, with K_W^γ'/γ = 1.4 ± 0.1. Conversely, in the multicomponent alloy, W partitions to the γ-phase, resulting in K_W^γ'/γ = 0.92 ± 0.06. The calculated partitioning ratios are based on bulk analyses of ~10^5 atoms in each of the γ and γ′-phases. The other alloying additions to the multicomponent alloy (Cr, Co, Mo, Re, C, and Hf) exhibit pronounced partitioning to the γ-phase.

High-temperature strength and creep resistance are the major prerequisites for materials for turbine blades of aerospace jet engines and land-based power generators. Ni-based superalloys are the ideal materials for these applications, owing to their unique two-phase, single-crystal microstructure, comprised of a high volume fraction of Ni3Al-type γ′(L12)-precipitates that are dispersed in a γ(fcc)-matrix. Both phases contain refractory elements, which promote solid-solution strengthening of the γ-matrix (e.g., Mo, W, and Re) and the formation of γ′-precipitates (e.g., Ta). The partitioning of elements to the γ and γ′-phases in Ni-based superalloys determines the lattice parameter misfit at the coherent γ/γ′ interface, which strongly correlates with the mechanical properties of the material at high temperatures. The lattice parameter misfit is particularly sensitive to variations in the concentration of W on both sides of this heterophase interface due to its large atomic size.

The partitioning behavior of W has been investigated in commercial multicomponent Ni-based superalloys using atom-probe tomography (APT) and analytical electron microscopy. These works indicate that W has a tendency to occupy the γ-matrix, yielding partitioning ratios (K_W^γ/γ) slightly smaller than unity, where K_W^γ/γ is the ratio of the concentration of an element i in the γ′-precipitates to its concentration in the γ-matrix. To our knowledge, a value of K_W^γ/γ > 1 has not been reported for a multicomponent Ni-based superalloy. Studies of the partitioning behavior of W in model Ni-based alloys with less than four components by analytical transmission electron microscopy and APT have, however, reported K_W^γ/γ values ranging between 1.2 and 2.0. This difference between the K_W^γ/γ values measured for different Ni-alloys has not been explained on a scientific basis.

Herein, we present the results of APT analyses of the γ and γ′-phases of both a ternary Ni–Al–W alloy and a multicomponent Ni-based superalloy to illustrate the reversal of the partitioning preference of W in multicomponent alloys. We hypothesize that the addition of Ta to Ni-superalloys is responsible for the reversal of the partitioning behavior of W. We prove this by employing first-principles calculations of the substitutional formation energy of W and Ta in the γ(fcc) and γ′(L12) phases, in conjunction with APT studies.
except Ta, which is the only element that partitions strongly to the $\gamma'$-phase with $K_{Ta}^{\gamma'} = 18.4 \pm 0.4$. A very high value of $K_{Ta}^{\gamma'} = 10.25 \pm 0.07$ has also been observed in a model quaternary Ni-10.0 Al-8.5 Cr-2.0 Ta (at.%) alloy aged at 1073 K.\(^{17,18}\)

What is the reason for the reversal of the partitioning behavior of W in multicomponent alloys? Since Ta is the only element that partitions preferentially to the $\gamma'$-precipitates, and given that both W and Ta occupy the same Al substitutional sublattice sites in the $\gamma'(L1_2)$-phase,\(^{4,17,19}\) we can reasonably assume that Ta is responsible for this effect, by displacing W from the Al-sublattice of the $\gamma'$-precipitates into the $\gamma$-matrix. To illustrate this effect, the W and Ta compositional profiles across the $\gamma'$-$\gamma$ interfaces of the ternary and multicomponent alloys, determined by 3D-APT, are shown in Fig. 2. The concentration of W on the $\gamma'$-precipitate side of the interface in the Ni–Al–W alloy (empty circles) is considerably larger than on the $\gamma$-side. In the multicomponent alloy, however, this trend is reversed (full circles). The strong partitioning of Ta to the $\gamma'$-phase in the multicomponent alloy (empty squares) suggests that Ta has a stronger affinity for the Al-sublattice sites of the $\gamma'$-precipitates than W does, leading to the displacement of W to the $\gamma'$-matrix.

To test this hypothesis quantitatively, we performed first-principles calculations of the substitutional formation energy of W and Ta in the $\gamma$(Ni, fcc) phase as well as at the Ni- and Al-sublattice sites of the $\gamma'(Ni_3Al,L1_2)$ phase at 0 K. The first-principles calculations were performed using the plane wave pseudopotential total energy method with the general gradient approximation, as implemented in the Vienna \textit{ab initio} simulation package (VASP).\(^{20-22}\) The lattice parameter of the relaxed Ni3Al structure was calculated to be 0.3566 nm, in agreement with the experimental room temperature value of 0.3570 nm.\(^{1}\)

A model W- and Ta-microalloyed Ni–Al system was built to simulate the experimental conditions. Three supercells were simulated. Each was divided by one of the \{100\}, \{110\}, and \{111\} heterophase interfaces, and the two-halves of the supercells were occupied by the $\gamma$-Ni and $\gamma'$-Ni3Al phases, respectively. Projector-augmented-wave pseudopotentials\(^{23}\) were employed with an energy cutoff of 300 eV for plane waves in optimized 8 × 8 × 1 Monkhorst-Pack \textit{k}-point grids. The ground-state atomic geometries of the structures were obtained by minimizing the total energy using Hellmann–Feynman forces with a cutoff value of 5 meV nm\(^{-1}\). The total energies of the relaxed structures were converged with respect to an energy cutoff of 0.02 meV atom\(^{-1}\). The substitutional formation energies of W and Ta were calculated when W or Ta was placed at different sites close to each of the three simulated interfaces. The construction of these interfaces and the locations of these sites are described elsewhere.\(^{19}\)

The calculations are described by the relationships:

$$E_{M\rightarrow Ni \text{ or } Al} = \left[ \left( E_{tot}^{M\text{ in } \gamma'} + n_{Ni} \mu_{Ni} \text{ or } \mu_{Al} \right) - \left( E_{tot}^{M\text{ in } \gamma} + n_{M} \mu_{M} \right) \right]/n_{M}$$

for the $\gamma'$-precipitate, and

$$E_{M\rightarrow Ni} = \left[ \left( E_{tot}^{M\text{ in } \gamma} + n_{Ni} \mu_{Ni} \right) - \left( E_{tot}^{M\text{ in } \gamma'} + n_{M} \mu_{M} \right) \right]/n_{M}$$

for the $\gamma$-matrix. In this notation, $M$ represents the substitutional atom W or Ta, and $n_{i}$ is the number of $i$ atoms. $E_{tot}$ is the total energy of the supercell, including the interface, prior to substitution. $E_{tot}^{M\text{ in } \gamma'}$ and $E_{tot}^{M\text{ in } \gamma}$ are the total energies of the $M$-microalloyed supercell calculated for substitution in the $\gamma'$ or $\gamma$, respectively. $\gamma$ denotes a fcc-based substitutional solid solution of Ni; $\gamma'$ has several alternative structural forms: (Ni$_{1-x}$)$_j$(Al$_x$)$_{3-x}$ for substitution on the Ni-sublattice and Ni$_3$(Al$_{1-x}$)$_x$ for substitution on the Al-sublattice. $\mu_{i}$ represents the chemical potential of the bulk pure element $i$, and is calculated assuming same cell symmetry. The values of $\mu_{i}$ are $-5.432, -3.697, -12.644, \text{ and } -11.478$ eV atom\(^{-1}\) for Ni, Al, W, and Ta, respectively. Additionally, the average atomic forces and displacements due to substitution at the first nearest-neighbor sites were calculated. No atomic force was measured for relaxed bulk, either $\gamma'(Ni_3Al)$ or $\gamma$(Ni), prior to site substitution. While the substitutional formation energy, $E_{M\rightarrow Ni \text{ or } Al}$, indicates the preference of $M$ at specific sublattice sites originating from interatomic electronic interactions, the force and displacement terms yield the elastic energy due
However, is observed in the and into the the calculations support firmly the hypothesis that the addition of atomic forces and displacements associated with substitution of W and Ta at the Al-sublattice sites results in smaller values of the atomic forces and displacements than the substitution of W and Ta at the Ni-sublattice sites. The atomic forces and displacements associated with substitution in the γ-matrix have intermediate values. All the results of the calculations support firmly the hypothesis that the addition of Ta to multicomponent alloys leads to the displacement of W from the Al-sublattice sites of the γ'-precipitates, and into the γ-matrix. This displacement effect results in an inversion of the partitioning ratio of W from $K_W^{\gamma'/\gamma} > 1$ to $K_W^{\gamma'/\gamma} < 1$, as demonstrated by the results presented in Fig. 2. Figure 3 is a graphic representation of the substitutional formation energies of (a) W and (b) Ta as a function of their distance from the {100}, {110}, or {111} interface.

The results clearly indicate the existence of an energetic driving force for the partitioning of both elements to the γ'-precipitates. The driving force for the partitioning of Ta to the γ'-precipitates of 0.225 eV atom$^{-1}$ is about twice as large as the value of W of 0.101 eV atom$^{-1}$. The difference in the driving force for partitioning is responsible for the reversal of the partitioning ratio of W in alloys that also contain Ta. We note that the partitioning behavior is the same for all crystallographic planes separating the γ'- and γ-phases, keeping in mind that the set of {100}, {110}, and {111} planes is representative of the space of crystallographic orientations.

In summary, we find that W prefers to partition strongly to the γ'-phase in a model ternary Ni–Al–W alloy, while this behavior is reversed in multicomponent Ni-based alloys. This effect is explained by first-principles calculations of the substitutional formation energies of W and Ta in both phases, which reveal that the driving force for the partitioning of Ta to the γ'-phase is nearly twice as large as the value calculated for W. These findings imply that Ta atoms replace W atoms in the γ'-precipitates, leading to a reversal of the partitioning behavior of W between the two phases.

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