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Combined atom probe tomography and first-principles calculations for studying atomistic interactions between tungsten and tantalum in nickel-based alloys

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Abstract

We investigate the partitioning behavior of tungsten to the γ(face-centered cubic) and γ′($L1_2$) phases in Ni-based alloys employing atom probe tomography (APT), first-principles calculations and computational thermodynamics. Several APT studies of Ni-based alloys indicate that the partitioning of tungsten atoms to the γ′($L1_2$) phase is reversed in favor of the γ phase due to tantalum atom additions. First-principles calculations of substitutional formation energies at 0 K indicate that tungsten and tantalum atoms share the aluminum sublattice sites of the γ′($L1_2$) phase, and that tantalum has a larger tendency to partition to the γ′($L1_2$) phase than does W. We also calculate the binding energies of W–W and Ta–W dimers in the γ(fcc) and γ′($L1_2$) phases, respectively, and use these values in a quantitative model to demonstrate that interatomic interactions between tungsten and tantalum atoms play a significant role in the partitioning reversal of tungsten.

Keywords: Ni-based superalloys; Partitioning ratio; Atom probe tomography; First-principles calculations; Binding energy

1. Introduction

Extraordinary strength and creep and oxidation resistance at high temperatures permit nickel-based superalloys to be widely used for turbine blades of aerospace jet engines and land-based power generators [1,2]. Understanding the basic rules for designing Ni-based superalloys is driven by ongoing efforts to increase the thermodynamic efficiency of turbine engines; that is, obtaining a high ratio of energy yield to fuel consumption [1,3]. The latter requires elevating the operating temperature of a turbine engine (>1200 °C) [3], which implies improving the high-temperature properties of these superalloys [1,4]. Nickel-based superalloys for turbine blades are single crystals with a two-phase microstructure, containing a high volume fraction of Ni_3Al-based γ′($L1_2$) precipitates, which are dispersed in a Ni-based γ(face-centered cubic, fcc) matrix. Both phases contain different refractory elements to promote solid-solution strengthening of the γ matrix, for example, Mo, W, Re and Ru, and to stimulate the formation of γ′($L1_2$) precipitates, such as Ta, Nb and Ti [5]. The partitioning of elements to the γ(fcc) and γ′($L1_2$) phases in Ni-based superalloys determines the lattice parameter misfit at the coherent γ(fcc)/γ′($L1_2$) interface [6–12], which strongly correlates with the mechanical properties of these alloys at elevated temperatures [10,13–19]. The lattice

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parameter misfit is particularly sensitive to variations in the concentrations of tungsten on both sides of the γ(fcc)/γ′($L1_2$) interface due to its large atomic diameter [1,20]. A quantitative metric for the phase preference of elements is the partitioning ratio defined by:

$$K_i^{\gamma'/\gamma} = \frac{C_i^{\gamma'}}{C_i^{\gamma}} \quad (1)$$

where $C_i^{\gamma'}$ and C_i^{γ} are the atomic fractions of an element i in the γ′($L1_2$) and γ(fcc) phases, respectively.

We have reported on a reversal of the partitioning behavior of W, from a preference for the γ′($L1_2$) phase in model Ni alloys, $K_W^{\gamma'/\gamma} > 1$, to the γ(fcc) matrix preference in multicomponent Ni-based alloys, $K_W^{\gamma'/\gamma} < 1$ [21,22]. This trend is evident from a comparison of atom probe tomography (APT) [23–26] and analytical electron microscopy studies of phase compositions in aged commercial multicomponent Ni-based superalloys [27–35], with other studies of model Ni-based alloys having a small number of elements (three to six) including W [20,36–38]. We suggested that Ta atoms are responsible for the rejection of W atoms from the γ′($L1_2$) to the γ(fcc) phase, and supplemented our hypothesis with first-principles calculations of the substitutional formation energies of W and Ta at 0 K [21]. We have also demonstrated that thermodynamic computations predict the partitioning reversal of W due to Ta additions, and demonstrated the role of electronic structure in determining the phase preference of W and Ta atoms by calculating the electron charge distributions in their vicinities [22]. A lingering question is, however, what is the governing mechanism for the reversal of W partitioning driven by Ta atoms? Its answer can shed additional light on the interplay between these atoms, and provide us with quantitative estimates of the optimal concentrations of these elements in Ni-based alloys, which is technologically important.

To address this question, we present herein APT results demonstrating the reversal in the partitioning of W. Then, we present first-principles calculations of the substitutional formation energies of W and Ta, and of the interatomic binding energies of W–W and W–Ta dimers in model γ(Ni) and γ′(Ni_3Al) phases for different nearest-neighbor (NN) positions. Consequently, we construct a model elucidating the role of Ta in diminishing or reversing $K_W^{\gamma'/\gamma}$.

2. Experimental procedures

2.1. Materials and processes

We study two multicomponent Ni-based alloys, ME-9 and ME-15 [39], containing Ni, Al, Cr, Co, Mo, W, Ta, Re, Hf and C (Table 1). The three samples were directionally solidified by Precision Casting Corporation – Airfoils (Beachwood, OH) employing the Bridgman technique (2.5 mm min^{-1} withdrawal rate, without a cooling liquid) to form ⟨1 0 0⟩-oriented single crystals [39]. Additionally, we analyze two model alloys, a Ni–Al–Cr–W quaternary and a Ni–Al–Cr–Ta–W quinary alloy (Table 1), to examine directly the effect of Ta on W partitioning. Both alloys were homogenized at 1573 K for 20 h and aged at 1073 K for 264 h [22].

2.2. Atom probe tomography (APT)

APT microtip samples are prepared by cutting $0.2 \times 0.2 \times 10\ mm^3$ rods and electrochemical polishing [40] in an electrolyte of 10% perchloric in a glacial acetic acid at 10–15 V dc, followed by fine-polishing in a 2% perchloric acid in butoxyethanol solution at 5 V dc to form needle-like tips with a radius of curvature <40 nm. We analyze the microtips using a laser-pulsed local-electrode atom-probe (LEAP) tomograph [24–26] (Cameca, formerly Imago Scientific Instruments, Madision, WI) at 40 ± 0.3 K and a gauge pressure $<5 \times 10^{-9}$ Pa. Pulses of 532 nm wavelength (green) laser with an energy of 0.6 nJ per pulse are applied at a pulse repetition rate of 200 kHz, in addition to a V dc bias between the specimen and a local electrode. The ions evaporated during each laser pulse are accelerated toward a position-sensitive detector, and their original x-, y- and z-locations in a specimen are determined from their impact positions on a high-gain two-dimensional detector. The chemical identities of the different ions are determined from their times-of-flight [23], which are translated into a mass-to-charge-state spectrum. Fig. 1 shows an example of such a spectrum collected from ME-15, in which the peaks indicating the W and Ta isotopes are well-resolved from each other and from the Re- and Hf-peaks. Thus, three-dimensional tomographic reconstructions of a specimen are obtained in direct space with subnanoscale spatial resolution.

Data analyses are performed using IVAS 3.4 software, and compositional information is obtained employing the proximity histogram methodology [41]. Further details on data analysis and measurement accuracy are found elsewhere [22].

2.3. First-principles calculations

To supplement and complement our experimental findings, we perform first-principles calculations of the total

Table 1
The nominal compositions of the Ni-based alloys investigated in at.%.

Alloy	Al	Cr	Co	Ta	Mo	W	Re	C	Hf	Ni
ME-9	14.6	8.18	7.74	1.95	0.95	2.31	1.74	0.63	0.05	Bal.
ME-15	15.1	7.73	7.31	1.97	0.90	0.75	0.46	0.67	0.05	Bal.
Quaternary	10.0	8.5	–	–	–	2.0	–	–	–	Bal.
Quinary	10.0	8.5	–	1.0	–	1.0	–	–	–	Bal.