1
2
3
4 **The effects of refractory elements on Ni-excesses and Ni-depletions at**
5
6
7 **$\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces in model Ni-based superalloys: Atom-probe**
8
9
10 **tomographic experiments and first-principles calculations**
11
12

13 Yanyan Huang ^{a,b}, Zugang Mao ^b, Ronald D. Noebe ^c, David N. Seidman ^{b,d,*}
14
15

16
17 ^a*School of Aeronautics and Astronautics, Sichuan University, No.24 South Section 1, Yihuan*
18 *Road, Chengdu, 610065, China*
19

20 ^b*Department of Materials Science and Engineering, Northwestern University, 2220 Campus*
21 *Drive, Evanston, IL 60208-3108, USA*
22

23
24 ^c*Materials and Structures Division, NASA Glenn Research Center, 21000 Brookpark Road,*
25 *Cleveland, OH 44135, USA*
26

27 ^d*Northwestern University Center for Atom-Probe Tomography (NUCAPT); 2220 Campus Drive;*
28 *Evanston, IL 60208-3108, USA*
29
30
31

32 **ABSTRACT**
33
34

35 The effects of refractory (R) elements (R = Re, Ru, W, or Ta) on a base Ni-Al-Cr alloy
36 are studied, for an aging temperature of 1073 K (800 °C) and an aging time of 256 h, employing
37 atom-probe tomography (APT) and first-principles calculations. We find that there are strong
38 attractive chemical binding energies between R-elements and solute (S) atoms (S = Al, Cr) in Ni-
39 Al-Cr based alloys utilizing experimental partial radial distribution function (RDF) results, and
40 first-principles calculations performed at 0 K. We demonstrate that correlated R-S binding
41 energies play a key role in the observed Ni retention-excesses at $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ structure)
42 interfaces at aging times as long as 256 h. The total reduction of the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfacial
43
44
45
46
47
48
49
50
51
52
53
54
55
56

57
58 ^{*} Corresponding author: Department of Materials Science and Engineering, Northwestern
59 University, 2220 Campus Drive, Evanston, IL 60208-3108, USA.
60 E-mail address: d-seidman@northwestern.edu (D. N. Seidman)
61

energy, as a result of Ni interfacial-excesses in both γ (f.c.c.)-matrix and γ' (L1₂)-precipitates, lies between $-0.16 \pm 0.06 \text{ mJ m}^{-2}$ and $-0.05 \pm 0.02 \text{ mJ m}^{-2}$. The R-S binding energies cause changes in the compositional diffusion flux-vectors in and out of γ' (L1₂)-precipitates, which result in larger solvent Ni retention-excesses and wider interfacial compositional widths at 256 h, when compared with the base Ni-Al-Cr alloy. Refractory elements are slow diffusers in nickel and the attractive R-Cr binding energies decelerate the solute diffusional fluxes, which results in a decrease of the Ni diffusivity, which in turn hinders the flux of Ni atoms away from the γ (f.c.c.)/ γ' (L1₂) interfaces.

Keywords: Ni-based superalloys, Interfacial excesses, Binding energies, Atom-probe tomography, First-principles calculations

1. Introduction

Ni-based superalloys are the current materials utilized for turbine blades of aerospace jet engines and land-based natural-gas fired power generators, due to their superior mechanical properties and corrosion, oxidation, and creep resistance at elevated temperatures [1-3]. These alloys owe their extraordinary high-temperature properties to their unique two-phase single-crystal microstructure, comprised of a high volume-fraction, ca. 80 %, of coherent Ni₃Al-type γ' (L1₂)-precipitates, which are dispersed in a γ (f.c.c.)-matrix. The crystal structures of the γ (f.c.c.)-matrix and γ' (L1₂)-precipitates are both cubic and the small lattice-parameter mismatch between the two-phases leads to the formation of coherent γ (f.c.c.)/ γ' (L1₂ structure) heterophase interfaces. The nature of the γ (f.c.c.)/ γ' (L1₂ structure) interfaces is of utmost importance for the physical properties of Ni-based superalloys. For instance, interfacial segregation (Gibbsian excess) of different elements at γ (f.c.c.)/ γ' (L1₂-structure) interfaces reduce their interfacial free

energy, which is a key result of the classical Gibbs adsorption isotherm [4-6]. This is important because the morphological evolution of the γ' -precipitates can be understood as a competition between the elastic self-energy of γ' -precipitates and the γ (f.c.c.)/ γ' (L1₂ structure) interfacial free energy [7]. Moreover, the coarsening resistance of γ' -precipitates in Ni-based superalloys is dependent on the interfacial Gibbs free energy of the γ -matrix/ γ' -precipitate interface [8-16], and critically on the diffusivities and interdiffusivities of Ni, Al and the other alloying elements in concentrated multicomponent alloys.

Ternary Ni-Al-Cr systems are important as they represent the basis of commercial superalloys, which can contain as many as 12 or 13 *alloying elements* [1, 2]. Atom-probe tomography (APT) [17-19] has been utilized to investigate phase separation (precipitation) in model Ni-Al-Cr alloys. The research of Schmuck et al. [20, 21] and Pareige et al. [22, 23] combined APT and vacancy-mediated lattice kinetic Monte Carlo (LKMC) simulations to analyze a Ni-Al-Cr ternary alloy. Similarly, we have previously studied a series of ternary Ni-Al-Cr alloys utilizing both APT and LKMC simulations including Ni-7.5Al-8.5Cr, Ni-5.2Al-14.2Cr, and Ni-6.5Al-9.5Cr at.%, all aged at 873 K (600 °C) [24-28], and a Ni-10.0Al-8.5Cr at.% alloy aged at 1073 K (800 °C) [29, 30]. In our previous studies on ternary Ni-Al-Cr alloys [25, 26], localized Ni retention-excesses are observed during the early nucleation and growth stages of γ' (L1₂)-precipitates, which exhibit different diffusional flux couplings across the γ (f.c.c.)/ γ' (L1₂) interface that strongly affect kinetic excesses for the solvent concentration profiles. As a consequence of different diffusional flux couplings two adjacent γ' -precipitates can interact, via the overlap of their diffusion fields, across their interfaces over distances that are greater than the radii of the γ' (L1₂) precipitates, which leads to the formation of interconnecting necks between the γ' -precipitates [26] and this in turn leads to the coagulation-coalescence mechanism of

1
2
3
4 coarsening. The temporally evolving concentration profiles across $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces are
5
6
7 not in local equilibrium and therefore the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfacial free energy is greater than
8
9
10 for fully equilibrated γ' -precipitates at very long aging times.

11
12
13 Additionally, we have implemented different techniques to study systematically the roles
14
15 of small additions (2 at.%) of refractory elements on the γ/γ' decompositions when a model
16
17 ternary Ni-10.0Al-8.5Cr at.% superalloy is aged at 1073 K (800 °C) for seven aging times
18
19 varying from 0 to 256 h [5, 29-35]. More specifically, we reported previously on four quaternary
20
21 alloys Ni-10.0Al-8.5Cr-2.0Re [5, 31], Ni-10.0Al-8.5Cr-2.0W [29, 30], Ni-10.0Al-8.5Cr-2.0Ta
22
23 [32, 33] and Ni-10.0Al-8.5Cr-2.0Ru at.% [34], one quinary alloy Ni-10.0Al-8.5Cr-1.0Re-1.0Ru
24
25 at.% [35] and one alloy with six elements Ni-10.0Al-8.5Cr-1.0W-0.5Re-0.5Ru at.% [35], which
26
27 focus mainly on the temporal evolution of the nanostructures and chemistry during phase
28
29 separation. The temporal evolution of precipitates' characteristics, e.g., morphology, volume
30
31 fraction, mean radii and number density are investigated utilizing TEM and/or SEM micrographs
32
33 and APT, along with predictions of coarsening models and PrecipiCalc simulations. For instance,
34
35 a 2.0 att.% addition of W [29, 30] yields a larger microhardness, earlier onset of spheroidal-to-
36
37 cuboidal precipitate morphological transition, larger volume fraction, reduction in coarsening
38
39 kinetics by one-third and a larger number density of smaller mean radii precipitates. Additionally,
40
41 the chemistry evolution of the precipitates and the matrix, including the partitioning behavior of
42
43 all alloying elements between the two phases and the segregation behavior at γ/γ' interfaces has
44
45 also been studied in great detail mainly based on APT results. Overall, Al, Ta and W partition to
46
47 the precipitates, while Ni, Cr, Re and Ru prefer the matrix. As precipitates grow, the former three
48
49 elements diffuse to the γ' -precipitates, while the latter four diffuse away from the γ' -precipitates.
50
51 The addition of W, Ta or Re leads to stronger partitioning of Al to the γ' -precipitates, and of Cr
52
53
54
55
56
57
58
59
60
61

to the γ -matrix, than was measured for the base Ni-Al-Cr alloy, while the effectiveness of Ru for such enhancements is insignificant.

Unlike Ni retention-excesses in ternary Ni-Al-Cr alloys [25, 26], which emerge during the early stages of phase separation and disappear at later stages, an accumulation of Ni is observed to develop on the γ -matrix side of the γ (f.c.c.)/ γ' (L1₂) interface during aging times 0-256 h in Ni-10.0Al-8.5Cr-2.0Ta at.% [32, 33]. But in just one Ni-Al-Cr-Ta alloy has a Ni interfacial excess been reported, which is lacking an in-depth explanation. In this research, we discover that localized Ni retention-excesses can exist at aging times as long as 256 h in Ni-Al-Cr based alloys with refractory elemental additions, as a result of thermodynamic and kinetic effects associated with strong attractive binding energies among the refractory elements and solute elements, which causes changes in the diffusional fluxes across γ (f.c.c.)/ γ' (L1₂) interfaces. Therefore, it is significant to implement a deep and systematic study to explore the details and mechanisms of Ni retention-excesses after 256 h aging, when alloys are in a quasi-stationary (or stationary) condition.

Given the above we study in detail, in this article, the effects of four R (R = Re, Ru, W or Ta) elements on Ni retention-excesses in six model Ni-Al-Cr based superalloys aged at 1073 K (800 °C) for 256 h, which is based on the diffusion theory presented in our prior research on ternary Ni-Al-Cr alloys [25, 26]. We calculate Ni-excesses and Ni-depletions, Γ_{Ni} , the total reduction of interfacial free energy, $\Delta\sigma_{Ni}$, caused by the Ni retention-excesses, changes of Ni, Al and Cr diffusion flux vectors $\Delta\tilde{C}$ due to R-additions, and interfacial compositional widths, δ_{Ni} , across γ (f.c.c.)/ γ' (L1₂ structure) interfaces, from our experimental APT data. We also present the spatial correlations and the binding conditions among R and S (S = Al, Cr) elements,

combining the experimental APT partial radial distribution function (RDF) results and first-principles calculations of the binding energy between R and S atoms.

2. Methodologies

2.1. Atom-probe tomography (APT)

Atom-probe tomography (APT) specimens were cut from the aged samples into $0.2 \times 0.2 \times 10 \text{ mm}^3$ rods using electrical discharge machining (EDM) and then subjected to standard electro-polishing techniques [36] at room temperature; coarse-polishing in a 10% perchloric acid in glacial acetic acid solution at 15-20 Vdc, followed by fine-polishing in a 2% perchloric acid in 2-butoxyethanol solution at 5-10 Vdc to form needle-like nanotips with a radius of curvature of $<40 \text{ nm}$. The specimens were analyzed using a pulsed ultraviolet (UV) picosecond laser-assisted local-electrode atom-probe (LEAP) tomograph [17, 18], a LEAP 4000X Si (Cameca, formerly Imago Scientific Instruments, Madison, WI), at a specimen base temperature of $40.0 \pm 0.3 \text{ K}$ and an ambient gauge pressure of $<6.7 \times 10^{-8} \text{ Pa}$. APT analyses were performed using the following parameters [37]: (i) an UV wavelength of 355 nm ; (ii) a laser pulse energy of 20 pJ pulse^{-1} ; (iii) a pulse repetition rate of 200 kHz ; and (iv) a detection rate (ions per pulse) of 5%. The times-of-flight of all detected ions were converted to mass-to-charge-state (m/n) spectra, enabling the elemental identifications of all collected ions. Subsequently, the x-, y- and z- position data were employed to construct 3D tomographic reconstructions of the analyzed volumes [19] using IVAS 3.6.4 (Cameca, Madison, WI) software.

2.2. Computational methods

Our first-principles calculations employ the plane-wave pseudo-potential total-energy methodology, with the generalized-gradient approximation (GGA) for exchange-correlation, as

implemented in the Vienna ab initio simulation package (VASP) [38-42]. We utilized the projector augmented wave (PAW) potentials [43], and we relaxed fully all the structures according to its unit-cell volume and individual atomic coordinates, and tested the convergence of energy cutoff and k-points. The optimized energy cutoff is 300 eV, which represents the Kohn-Sham wave functions. A 12×12×12 Monkhorst–Pack k-point mesh was used for summing over the Brillouin zone for the bulk structures for all calculations. A 3×3×3 f.c.c. Ni superlattice was utilized for all binding energy calculations at 0 K.

2.3. *Preparation of alloys and their processing*

Six model Ni-based superalloys were investigated with a base-line composition of Ni-10Al-8.5Cr at.%, with the addition of 2 at.% total refractory elements (R) from the group W, Re, Ru, and Ta. The nominal compositions of the alloys are as follows (all concentrations are in at.% unless otherwise noted): (E) Ni-10.0Al-8.5Cr-2.0Ru; (F) Ni-10.0Al-8.5Cr-2.0Ta; (G) Ni-10.0Al-8.5Cr-2.0Re; (H) Ni-10.0Al-8.5Cr-2.0W; (I) Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (J) Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%. In this article, we use the lettering scheme of Ref. [34] for identifying the alloys, starting with the letter E, to make it easy to interconnect with our other articles on Ni-Al-Cr based alloys.

To produce master alloy ingots, high-purity constituent elements were vacuum induction melted under a partial Ar atmosphere to minimize oxidation and then chill cast in a 19 mm diameter copper mold. The cast ingots were processed using the following three steps: (i) homogenization; (ii) vacancy annealing; and (iii) aging annealing. All heat treatments were performed in vacuum or a flowing Ar atmosphere to reduce external oxidation. For homogenization, the cast ingots were placed in a vacuum furnace at 1573 K (1300 °C) for 20 h followed by a *power-off* furnace cool to room temperature. The ingots were then sectioned into

10 mm lengths and the pieces wrapped in Ta foil and placed in a tube furnace under flowing argon and vacancy annealed at a temperature above the solvus curve of the γ' -phase (in the single phase γ -matrix) and held for a fixed time, followed by water quenching to room temperature. Specifically, the temperatures and holding times for alloys E to J for the vacancy annealing step are as follows: 1380 K (1107 °C) and 0.5 h for alloy F (with Ta); 1363 K (1090 °C) and 0.5 h for alloy H (with W); and 1503 K (1230 °C) and 3 h for alloys G (with Re), E (with Ru), I (with Re and Ru) and J (with W and Re). The vacancy annealing treatment is performed to re-solution the alloy while decreasing the vacancy concentration to minimize the nucleation and growth of γ' -precipitates during the subsequent water quench. Finally, ingot sections 10 mm in length were aged at 1073 K (800 °C) for 256 h in a preheated furnace, followed by a water quench to room temperature, to freeze in the nanostructure.

3. Results and analysis

3.1. 3-D reconstructions from atom-probe tomography

Data analyses were performed on the 3D tomographic reconstructions, employing Cameca's IVAS 3.6.4 code. Fig. 1 displays 3D reconstructions for Ni-based superalloys E to J, with each comprising ~70 million (alloy E) to ~85 million (alloy G) atoms. Only a fraction of the Al (red), Cr (blue), Ta (magenta), W (purple), Re (dark yellow) and Ru (dark cyan) atoms are displayed, and the Ni atoms are omitted for the sake of clarity. The γ -matrix and γ' -precipitates are identified unambiguously, as a result of the strong partitioning of Cr atoms (blue) to the γ -matrix and Al atoms (red) to the γ' -precipitates. Nickel, Re and Ru atoms partition preferentially to the γ -matrix, while the W and Ta atoms partition to the γ' -precipitates. The partitioning preference of each element is in agreement with prior experimental results on multi-component

Ni-based superalloys, except for W [44-56]. A discussion concerning the W reversal effect from a preference for the γ' (L1₂)-precipitates, $K_W^{\gamma'/\gamma} > 1$, in model Ni-based alloys containing three to six elements, such as alloy H, to a preference for the γ (f.c.c.)-matrix, $K_W^{\gamma'/\gamma} < 1$, in multi-component Ni-based alloys is presented in Refs. [57, 58]. $K_W^{\gamma'/\gamma}$ is the partitioning ratio of W, and by convention, the partitioning ratio of an element i ($K_i^{\gamma'/\gamma}$) is defined as the concentration of this element i in the γ' -precipitates divided by its concentration in the γ -matrix. For reference, the partitioning ratios ($K_i^{\gamma'/\gamma}$) of the refractory elements Ta, W, Re and Ru in alloys F, H, G and E, after aging for 256 h are 10.25 ± 0.07 , 2.09 ± 0.04 , 0.40 ± 0.03 and 0.38 ± 0.03 , respectively [5, 29, 31, 32, 34].

[Fig. 1]

Alloys E to J yield γ' -precipitates with different characteristics, due to the addition of different refractory elements at a concentration of 2 at.%. Here, we review γ' -morphology, γ' -mean radii ($\langle R \rangle$), γ' -number density (N_v), edge-to-edge γ' -inter-precipitate distance (λ_{e-e}), and γ' -volume fraction (ϕ) in the four quaternary model alloys E to H, containing only one refractory elemental addition, R, at a time, based on our prior research [5, 30-34]. The morphological evolution of the γ' -precipitates in the base Ni-Al-Cr alloy [30], and alloys F (with Ta) [30] and H (with W) [32, 33] follows the trend observed for most Ni-based superalloys [59, 60]; that is, a sphere-to-cuboid transition in the later stage of coarsening. The transition for alloys F [30] and H [32, 33] occurs at a smaller $\langle R \rangle$ value than the base Ni-Al-Cr alloy because of their *increased lattice parameter misfit*, due to the Ta or W additions. In contrast, the morphology of the γ' -precipitates in alloys G (with Re) [5, 31] and E (with Ru) [34] is spheroidal through 256 h of

aging as a result of the Re or Ru additions, which *decrease the lattice parameter misfit* between two phases.

In all four alloys, with increasing aging time from 0 to 256 h, the value of $\langle R \rangle$ increases and the value of N_v decreases, while λ_{e-e} increases [5, 30-32, 34]. After aging for 256 h, the γ' -precipitates of the base Ni-Al-Cr alloy have the following characteristics: $\langle R \rangle = 141.1 \pm 15.0$ nm; $N_v = 0.70 \pm 0.13 \times 10^{20} \text{ m}^{-3}$; and $\lambda_{e-e} = 62 \pm 10$ nm [30]. Adding Ta, W, Re or Ru leads to a reduction in the value of $\langle R \rangle$ and an increase in the value of N_v [5, 30-32, 34]. Compared to λ_{e-e} in the base Ni-Al-Cr alloy, alloys F and H have smaller values of λ_{e-e} , while alloys G and E have larger values of λ_{e-e} [5, 30-32, 34]. The γ' -volume fraction (ϕ) value is increased by different percentages for the dissimilar refractory elemental additions in alloys E to H compared to the base Ni-Al-Cr alloy. The value of ϕ is $19.3 \pm 1.9\%$ in the base Ni-Al-Cr alloy [30], while the ϕ values for alloys F, H, G and E [5, 30-32, 34] are, respectively, 37.2 ± 8.9 , 35.1 ± 0.7 , 25.0 ± 1.5 and $20.7 \pm 0.9\%$, after 256 h aging, implying that the effectiveness of individual refractory elements for increasing ϕ follows the order Ta>W>Re>Ru. Strengthening generally scales with precipitate volume fraction and as expected in this case, microhardness values in the 256 h aged alloys E to H follows the sequence F>H>G>E [5, 29, 31, 32, 34], which is consistent with their increasing ϕ values.

3.2. *Nickel concentration profiles and interfacial retention-excesses across the γ/γ' interface*

The concentration profiles of Ni across the γ (f.c.c.)/ γ' (L1₂-structure) interface for alloys E to J were created using a 0.1 nm bin size with respect to the Ni iso-concentration surfaces,

utilizing the proximity histogram methodology [61], and are displayed in Fig. 2. The standard error of the Ni concentration is associated with the statistical variance of values from different 3D volumes [19]. The $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces are depicted as a threshold Ni iso-concentration-surface, where the Ni threshold values of the iso-concentration surface represent the average of the far-field plateau concentrations of the two phases, by employing the inflection-point methodology [29]. The solid vertical lines are placed at the inflection points of the measured Ni concentration profiles, indicating, by definition, the location of the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface at zero on the abscissa axis. Negative values are into the γ -matrix and positive values are into the γ' -precipitate. It is evident that Ni is slightly preferentially distributed in the γ -matrix, yielding $K_{\text{Ni}}^{\gamma'/\gamma}$ values between 0.90 and unity. The shaded areas indicate the interfacial retention-excesses of Ni in the vicinity of the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface. It is emphasized strongly that the shaded areas contain three-dimensional (3D) information even though this is a two-dimensional (2D) plot. Nickel retention-excesses in the vicinity of the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface are observed in all alloys, with the actual values dependent on the different refractory elemental additions. Note that Ni concentration profiles as demonstrated in Fig. 2 (a), (b), (c) and (d) are consistent with the profiles for the same quaternary alloys in Refs. [29, 31, 32, 34] in most cases, but the new data is more accurate and all profiles exhibit Ni interfacial excesses. This is because we have been studying some of these alloys for over a decade, employing different APT instruments. In this research, we utilize the newer LEAP 4000X Si, featuring a pulsed ultraviolet (355 nm wavelength) laser at pulse repetitions rates up to 1 MHz, with a local-electrode design, wide-angle field-of-view up to 250 nm, and a nanotip array capability, and employ the same experimental parameters [37], section 2.1.

[Fig. 2]

The calculated maximum positive accumulation (at.%) on the γ -matrix side and minimum negative depletion values (at.%) on the γ' -precipitate side, for the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface of alloys E to J aged at 1073 K (800 °C) for 256 h are listed in Table 1. The maximum positive accumulation (or minimum negative depletion) of an element i is defined to be the difference between the maximum (or minimum) concentration of this element at the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface on the matrix (or precipitate) side and its far-field plateau concentration of the γ -matrix (or γ' -precipitates). The maximum Ni accumulation values range from 0.41 ± 0.09 at.% in alloy J to 0.85 ± 0.12 at.% in alloy H at the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface on the γ -matrix side, while the minimum Ni depletion values range from -0.81 ± 0.14 at.% in alloy H to 0 at.% in alloys E and I (both containing Ru) on the γ' -precipitate side.

[Table 1]

A new more accurate integral methodology [62] is utilized to calculate the interfacial excess and the corresponding local reduction in interfacial free energy. In this new methodology, a profile of excess concentration is first calculated using a method based on J. W. Cahn's approach to the Gibbsian interfacial excess, and then the corresponding local reduction in the Gibbs interfacial free energy is calculated using the Gibbs adsorption isotherm. The Gibbsian interfacial excess of an element i , Γ_i , is defined by the excess number of i atoms per unit area, and it can be obtained for an arbitrary interface of any convexity, by integrating the following function [62]:

$$d\Gamma_i = (C_i^m(x) - C_i^0(x)) dx; \quad (1)$$

where $C_i^m(x)$ is the local measured concentration of i , and $C_i^0(x)$ is the local measured reference concentration of i . The continuous reference concentration profile of Ni was calculated by fitting a Ni concentration profile precisely to a hyperbolic tangent curve, with the plateaus of the profiles matching the far-field concentrations in the γ -matrix and γ' -precipitates, Fig. 2.

According to this definition, a positive value of Γ_i implies an accumulation of Ni atoms; conversely, a negative Γ_i implies a depletion of Ni atoms. The interfacial excesses are a result of a decrease in the interfacial free energies of an interface [4, 6, 63-67]. Using the Gibbs adsorption isotherm, a local change in interfacial free energy due to specie i , $d\Delta\sigma_i$, can be calculated using the following equation [62]:

$$d\Delta\sigma_i = -d\Gamma_i k_B T \cdot \ln\left(\frac{C_i^m(x)}{C_i^0(x)}\right); \quad (2)$$

The total reduction of interfacial free energy, $\Delta\sigma_i$, is then calculated by integrating the above function to obtain an integral value. When discretized it can be applied to a measured concentration profile, which yields [62]:

$$\Delta\sigma_i = \sum_{n=1}^N -\left(C_i^m(n) - C_i^0(n)\right) \Delta x k_B T \cdot \ln\left(\frac{C_i^m(x)}{C_i^0(x)}\right); \quad (3)$$

where n is the index of the bins of the concentration profile, N is the total number of bins, and Δx is the bin width of the concentration profile.

The resulting interfacial excesses Γ_{Ni} (atom nm⁻²) and the corresponding local reductions in the Gibbs interfacial free energy $\Delta\sigma_{Ni}$ (mJ m⁻²), for alloys E to J aged at 1073 K (800 °C) for 256 h, were calculated employing the new integral method, and are displayed in Table 2 (a). The Ni concentration profiles of alloys F and G yield almost the same largest Ni accumulation excess

values, 0.99 ± 0.13 atom nm⁻² and 0.99 ± 0.15 atom nm⁻², respectively, while alloy J exhibits the smallest Ni accumulation effect 0.33 ± 0.05 atom nm⁻² in the vicinity of the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface in the γ -matrix phase. Alloy F has the largest minimum Ni depletion excess value, -0.89 ± 0.12 atom nm⁻², and alloy H has the second largest minimum Ni depletion effect, -0.67 ± 0.12 atom nm⁻² at the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface in the γ' -precipitates. Nickel depletions aren't found in alloy E, with a 2.0 at.% Ru addition and alloy I with 1.0 at.% Re and 1.0 at.% Ru additions on the γ' -precipitates side. The total integral interfacial free energy reduction $\Delta\sigma_{Ni}$, as a result of Ni interfacial excesses in both phases, varies from -0.16 ± 0.06 mJ m⁻² for alloy F (with Ta) to -0.05 ± 0.02 mJ m⁻² for alloy E (with Ru), which are small compared to the experimentally determined Gibbs interfacial free energies, 22 to 25 mJ m⁻², for two ternary base alloys, Ni-7.5Al-8.5Cr and Ni-5.2Al-14.2Cr at.% at 873 K (600 °C) [27, 28].

[Table 2]

The interfacial excesses Γ_{Ni} (atom nm⁻²) and the corresponding local reductions in the Gibbs interfacial free energy $\Delta\sigma_{Ni}$ (mJ m⁻²) for alloys E to J aged at 1073 K (800 °C) for 256 h, were also calculated using our prior approach [65, 67-69], Table 2 (b). The Γ_{Ni} values on the γ -matrix side range from 0.24 ± 0.03 atom nm⁻² in alloy J to 0.83 ± 0.08 atom nm⁻² in alloy G, while the Γ_{Ni} values on the γ' -precipitate side are between -0.67 ± 0.06 atom nm⁻² in alloy F to zero in alloys E (with Ru) and I (with Re and Ru). The total interfacial free energy reduction, $\Delta\sigma_{Ni}$, due to interfacial excesses in both phases ranges from -0.14 ± 0.04 mJ m⁻² for alloy F (with Ta) to -0.03 ± 0.01 mJ m⁻² for alloy E (with Ru). Overall, the traditional method yields Γ_{Ni} values ~13 to ~57% in magnitude smaller than those calculated by the new method as well as different decreases in the interfacial free energy $\Delta\sigma_{Ni}$. This is because it uses constant far-field Ni

concentrations in the γ -matrix and γ' -precipitates as Ni reference concentrations and only takes into account the peak (or bottom-most) concentrations of Ni at the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface on the matrix (or γ' -precipitate) side, whereas the new method employs a continuous Ni reference concentration profile, which takes into account the actual transient shape of the Ni concentration profile at each data point.

3.3. *The effects of refractory elements on the compositional diffusion fluxes*

The interfacial excesses of the solvent Ni are related to different diffusional flux couplings across the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface. The kinetic compositional paths of Ni, Al and Cr can be described by a unit vector ΔC proposed in Ref. [26], whose components $[x(\text{Ni}) + y(\text{Al}) + z(\text{Cr})]$ are proportional to the differences of the equilibrium γ' -precipitate and initial supersaturation concentrations. ΔC is a compositional deviation from the thermally stable final composition in the matrix. This deviation is caused by the current diffusional flux, which is different from the final thermally stable diffusional flux. Such deviation can be represented using the composition differences for each element. In this study, the processes of precipitate growth and coarsening imply that Ni- and Cr-fluxes diffuse out of the γ' -precipitates toward the γ -matrix, while the Al flux is toward the γ' -precipitates. Thus, a positive term means the flux is toward the γ' -precipitates, while a negative term implies the flux is toward the γ -matrix.

We calculated the components of the flux vector (unit vector ΔC), for the base Ni-Al-Cr alloy from the APT data in Ref. [29] and the Ni-Al-Cr based alloys E to J from APT results in this research. The detailed results are presented in Table 3. The components of the unit vector for the base Ni-Al-Cr alloy are: -0.537(Ni), 0.801(Al), and -0.264(Cr). We find that for all the alloys studied, there are similar diffusional flux vector trends in ΔC : negative Ni components (-0.403

in alloy E to -0.318 in alloy H); positive Al components (0.717 in alloy F to 0.853 in alloy E); and negative Cr components (-0.578 in alloy F to -0.330 in alloy E), implying that Ni and Cr diffuse away from the γ' -precipitates and Al diffuses toward the γ' -precipitates.

[Table 3]

The addition of refractory elements changes the directions of the components of the flux vector due to strong attractive binding energies among the refractory elements and Cr or Al. The driving force for changes in the signs of the Ni, Al and Cr compositional flux components is given by a vector $\Delta\tilde{C}$ (Table 3), where $\Delta\tilde{C} = \Delta C - \Delta C(base)$; that is, the difference of the unit vector between a given alloy and the base Ni-Al-Cr alloy. The magnitude of $\Delta\tilde{C}$ is the result of binding energy effects caused by the addition of an element R to the base Ni-Al-Cr alloy. We have determined that Ta and W have the largest effects and Ru has the smallest effect on the directional change of the flux vector, $\Delta\tilde{C}$, which causes large interfacial retentions of Ta and W and a relatively small retention of Ru: Section 3.2. The positive Ni components of $\Delta\tilde{C}$ (0.134 to 0.219) in alloys E to J suggest that fewer Ni atoms diffuse away from the γ' -precipitates, which is in agreement with their larger Ni partitioning ratio values, 0.93 to 0.95 [5, 29, 30, 33, 34], compared with the Ni partitioning value of 0.927 ± 0.002 in the base Ni-Al-Cr alloy [29]. The negative values of the Al components of $\Delta\tilde{C}$ of alloy F (with Ta) and alloy H (with W) indicate that Ta and W atoms partition to the γ' -precipitates and substitute on the Al-sublattice of the $L1_2$ structure [57, 58]. The Al positive components of $\Delta\tilde{C}$ of alloy G (with Re), alloy E (with Ru), alloy I (with Re and Ru) indicate repulsive binding energies between Re (or Ru) and Al, which drives Re and Ru away from γ' -precipitates toward the γ -matrix. The absolute value of the Cr component of $\Delta\tilde{C}$ is greater than that of the Al component in all alloys, implying that the effect of the refractory elements on the directions of the Al flux is not as significant as it is on Cr. All

Cr components for $\Delta\tilde{C}$ are negative, implying that the diffusional driving force for the Cr flux increases with the addition of these refractory elements. This trend of a large Cr flux diffusing away from the γ' -precipitates is in agreement with the decrease in the Cr partitioning ratios reported earlier [5, 29, 30, 33, 34]. The Cr component for $\Delta\tilde{C}$ in alloy F (with Ta) has the largest negative value due to a strong repulsive binding energy between Ta and Cr. The correlations and binding conditions between the refractory and solute elements are discussed in detail below, as are the experimental partial radial distribution function (RDF) [70] results, and the calculated first-principles binding energies.

3.4. *The effects of refractory elements on the interfacial compositional width at the γ/γ' interface*

The interfacial compositional width, $\delta_i(t)$, defined as the horizontal distance between the 10 and 90% values of the concentration difference between the plateau concentrations of the γ -matrix and γ' -precipitates, was calculated from the measured concentration profiles of each element based on a spline-function fitting procedure [34]. The measured interfacial compositional widths for the elements Ni, Al, Cr, and the refractory elements (W, Re, Ru, and Ta) of alloys E to J aged at 1073 K (800 °C) for 256 h are listed in Table 4. Note that by 256 h, the interfacial compositional width values in the model alloys are small, implying that the interface becomes sharp for long annealing times. These results are consistent to our previous studies on model Ni-based superalloys [5, 29, 31, 32, 34, 35, 71] thereby demonstrating that the interfacial compositional widths decrease as the γ' -precipitate mean radii increase with increasing aging time, which is in complete disagreement with Ardell's so-called trans-interface diffusion-controlled (TDIC) model of coarsening (Ostwald ripening) [72-75].

The elemental interfacial compositional widths of Ni, Al, Cr of the base Ni-Al-Cr alloy, for the same aging condition, are 1.07, 1.74 and 2.02 nm, respectively, based on the APT data [29]. In general, alloys E to J have wider Ni interfacial compositional widths, varying from 1.14 nm (alloy G) to 1.52 nm (alloy F). The increased value of $\delta_{Ni}(t = 256 \text{ h})$ agrees with a decrease of the calculated Ni diffusivity in the γ -matrix of alloys E to J, ranging from 33.3% for alloy F [32, 33] to 97.2% for alloy E [34] of the base Ni-Al-Cr alloy [30]. Additionally, the $\delta_{Ni}(t = 256 \text{ h})$ values in alloys F (with Ta), H (with W) are larger than those in alloys G (with Re) and E (with Ru). These findings are consistent with the magnitude of the compositional change, $\Delta\tilde{C}$, due to the addition of refractory elements, Table 3. For the solute elements Al and Cr, the $\delta_{Al}(t = 256 \text{ h})$ values are between 1.28 nm in alloy I and 1.99 nm in alloy H, and the $\delta_{Cr}(t = 256 \text{ h})$ values vary from 1.65 nm in alloy I to 2.30 nm in alloy H. For the base Ni-Al-Cr alloy or any of the alloys E to J, aluminum has a larger diffusivity value and it exhibits a sharper interfacial compositional width than does Cr. Alloys F (with Ta), H (with W) exhibit a large value of the compositional change, $\Delta\tilde{C}$ (Table 3), and they exhibit a wider Al (or Cr) interfacial compositional width than alloys G (with Re), E (with Ru), which is consistent with their smaller Al (or Cr) diffusivity values [5, 30, 32-34]. The interfacial compositional widths for the refractory elements W, Re, Ru and Ta are 2.11, 2.34, 1.98 and 1.61 nm, respectively, in the corresponding quaternary alloys. The interfacial compositional widths of W and Re in alloy J are 2.43 and 2.19 nm, respectively, and for Re and Ru in alloy I they are 1.57 and 2.22 nm, respectively. In summary, we find that the interfacial compositional width is strongly affected by the addition of refractory elements to the base Ni-Al-Cr alloy. The larger the changes of the compositional flux vector, the broader are the interfacial compositional widths. These effects are related to correlations, as measured by

partial radial distribution functions (RDFs), among the refractory elemental additions and solute atoms, which we discuss next.

[Table 4]

3.5. *Spatial correlations and the binding energy conditions among the refractory elements and solutes*

Now we discuss the binding energy states among the refractory and solute elements, Al and Cr, using experimental APT partial RDF results, followed by first-principles calculations in section 3.6. A partial RDF at a given radial distance, r , from any atom is defined as the average concentration distribution of component i around a given solute species, X, $\langle C_i^X(r) \rangle$, normalized to the overall concentration of i atoms, $C_i^{overall}$, in the sampled volume [70]:

$$Partial\ RDF_i^X(r) = \frac{\langle C_i^X(r) \rangle}{C_i^{overall}} = \frac{1}{C_i^{overall}} \sum_{k=1}^{N_X} \frac{N_i^k(r)}{N_{total}^k(r)} \frac{1}{N_X}; \quad (4)$$

where $N_i^k(r)$ is the number of i atoms in a radial shell around the k^{th} X atom that is centered at r , $N_{total}^k(r)$ is the total number of atoms in this shell, and N_X is the number of X atoms in this volume. Partial RDF values of unity describe perfectly random distributions of atoms, while values that differ from unity describe either clustering (anti-ordering) or ordering. The absolute magnitude of these processes can be compared with an RDF's amplitude, $A_i^X(r)$, $A_i^X(r) = [RDF_i^X(r) - 1]$, where $A_i^X(r) > 0$ indicates a greater concentration than the overall concentration (positive correlation) and $A_i^X(r) < 0$ implies a smaller one (negative correlation).

Refractory-element-centered partial RDF results as a function of radial distance are utilized to analyze the γ -matrix phase of the four quaternary model Ni-based superalloys: alloy E, Ni-10.0Al-8.5Cr-2.0Ru; alloy F, Ni-10.0Al-8.5Cr-2.0Ta; alloy G, Ni-10.0Al-8.5Cr-2.0Re; and alloy H, Ni-10.0Al-8.5Cr-2.0W at.%, which were aged at 1073 K (800 °C) for 256 h. The following partial RDF results are displayed in Fig. 3: (a) R-Cr partial RDF and (b) R-Al partial RDF, where R = Ta, W, Re, or Ru. The vertical lines indicate the nearest-neighbor (NN) distances through the 10th NN distance for an ordered Ni₃Al (L1₂ structure) precipitate, exhibiting almost perfect long-range order (LRO) [76]. The dashed horizontal lines correspond to partial RDF values of unity, which describe a perfectly random solid-solution distribution. In the R-Cr partial RDF profile (Fig. 3a), Ta has a negative correlation with Cr, suggesting that a repulsive binding energy exists between Ta and Cr atoms. Alternatively, Re and Ru reveal positive correlations with Cr, suggesting that a chemical affinity exists between Re and Cr atoms, and between Ru and Cr atoms due to significant Re-Cr and Ru-Cr negative binding energies, which are listed in Table 5 and discussed in section 3.6; we utilize the sign convention that a negative binding energy is attractive and a positive binding energy is repulsive. Additionally, we find that the W-Cr partial RDF is weakly correlated and hence W does not have a strong preference for Cr. The R-Al partial RDF profile, Fig. 3b, demonstrates that Ta and W have strong positive correlations with Al, whereas Re and Ru have negative correlations with Al. These findings indicate that Ta and W have strong effects on both the Al diffusional flux toward γ' -precipitates and their partitioning to γ' -precipitates.

[Fig. 3]

3.6. *The binding energies between refractory elements and solute atoms*

The binding energy between a refractory element and a solute atom was studied by first-principles calculations. A 3×3×3 f.c.c. Ni superlattice was utilized for all binding energy calculations at 0 K. In this study, one refractory element (R = Re, Ru, W, or Ta) replaces one Ni atom and one solute atom (S = Al or Cr) replaces one of the i^{th} NN Ni atoms. The R-S binding energy, $E_{R-S, \text{binding}}^i$, for each NNst shell is calculated from:

$$E_{R-S, \text{binding}}^i = E_{\text{total}}^i - E_{\text{total}}^{\infty} ; \quad (5)$$

where $E_{\text{total}}^{\infty}$ is the total energy of the system when the refractory element (R) atom is far from the solute (S) atom, and E_{total}^i is the total energy of the system when the refractory element (R) is at an i^{th} NN distance from a solute (S) atom.

The calculated R-S binding energy values are listed in Table 5. Utilizing the above definition, a negative value of the binding energy, $E_{R-S, \text{binding}}^i$, implies an attractive interaction between a refractory element and a solute atom, while a positive binding energy is repulsive. These binding energies are in agreement with the partial RDF results discussed above. We find that Re and Ru have attractive binding energies with Cr at 1st and 2nd NN distances. Hence, the Cr and Re (or Ru), both prefer the γ -matrix, bind together, and diffuse away from the γ' -precipitates. Tungsten and Ta have strong repulsive interaction energies with Cr in 1st NN sites, which indicates that W and Ta have the opposite partitioning behavior compared to Cr, again in agreement with the experimental concentration profiles. In contrast, W-Cr and Ta-Cr have attractive binding energies with Cr at a 2nd NN site, which decreases the Cr flux away from the γ' -precipitates. The R-Cr attractive binding energies, either at the 1st or 2nd NN distance, tend to decelerate the outward flux of Cr from the γ' -precipitates. For R-Al binding energies, all four

refractory elements exhibit alternating positive and negative binding energies from 1st to 4th NN sites, respectively, which indicates that all four refractory elements are substituting on the Al-sub-lattice and form an L1₂ ordered-structure with Ni [57, 58, 77, 78].

[Table 5]

See Fig. 4: (a) R-Cr binding energy; and (b) R-Al binding energy, where R = Ta, W, Re, or Ru, displays the binding energies for R-S as a function of their interatomic distance, corresponding to different NN positions through 6th NN distances. The binding energies decay to essentially zero when they reach the 6th NN, as anticipated. We find that the interactions are only significant through the 4th NN, which is not surprising as in a metallic alloy the charges on the ion cores are screened strongly by the conduction free electrons. It is noteworthy that there are oscillations in the R-Cr and R-Al binding energies as a function of NN distance, Fig. 4. Such oscillations with NN distance are observed for binding energies for W-Ta in the γ' -phase and W-W in the γ -phase in other Ni-based alloys [79], and for Mg-Mg, Mg-Sc and Sc-Sc binding energies in a ternary Al-Sc-Mg alloy [80].

[Fig. 4]

3.7. *The effects of refractory elements on solute diffusional behavior*

In prior studies [25, 26], Ni excesses emerge only during the early stages of the temporal evolution of γ' -precipitates and disappear at later stages in ternary Ni-Al-Cr alloys. The kinetic pathways involved in the formation of γ' -precipitates during aging of concentrated Ni-Al-Cr alloys at 873 K (600 °C), for three distinct alloy compositions Ni-5.35Al-9.4Cr, Ni-3.4Al-15.23Cr and Ni-5.42Al-10.3Cr at.%, were studied experimentally by APT and computationally with vacancy-mediated lattice kinetic Monte (LKMC) simulations [25]. It was found that during

the early stages the fastest diffusion eigenmode contributes to the formation of γ' -precipitates; the fast diffusion eigenmode is dominated by Al, whose flux is accompanied by Ni and Cr fluxes, and the flux of Al atoms to the γ' -precipitates opposes the outward flux of Cr and Ni atoms. As a consequence, the concentration profiles exhibit Ni and Cr excesses (accumulations) and an Al depletion in the vicinity of the γ' -precipitates [25]. In this research it is noteworthy that a chemical binding affinity exists between refractory elements R (Re, Ru, W, or Ta) and Cr when their solute fluxes cross the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces; the latter is based on both experimental partial RDF results and first-principles calculations. The R-Cr binding correlations affect the delayed Ni retention-excesses at aging times as long as 256 h.

The calculated diffusivities of Al and Cr in the γ -matrix of the base Ni-Al-Cr alloy are 13.9×10^{-18} and $5.13 \times 10^{-18} \text{ m}^2\text{s}^{-1}$, respectively [30]. Aluminum is the fastest diffusing solute in alloys E through J and its calculated diffusivity values in the γ -matrix range from 12.6×10^{-18} in alloy F [32, 33] to $14.7 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ in alloy E [34]. The calculated Cr diffusivity in the γ -matrix is smaller than that of Al in all alloys; varying from 4.80×10^{-18} in alloy F [32, 33] to $5.42 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ in alloy E [34]. Thus, compared to the base Ni-Al-Cr alloy, the diffusivities of Al and Cr in alloys E to J do not increase or decrease by more than 11%, implying a small influence of the refractory elemental additions on the diffusivities of Al and Cr. The refractory elements W, Re, Ru, Ta are slow diffusers in the γ -matrix. The diffusivity values of W, Re, Ru and Ta are 4.93×10^{-19} , 1.05×10^{-19} , 5.58×10^{-21} , $5.14 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ in their respective quaternary alloys [5, 30, 32-34]. The R-Cr attractive binding energies, either at the 1st or 2nd NN distance, tend to decelerate the Cr diffusion flux, resulting in a decrease of the Ni diffusivity. As Ni partitions to the γ -matrix during phase separation, the decreased diffusivity of Ni is not sufficiently large to transport all of the Ni atoms away from the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface and an accumulation of Ni

atoms arises in the γ -matrix phase (or a depletion of Ni atoms in the γ' -precipitate phase) is observed. The diffusivity of Ni in the γ -matrix decreases from $6.06 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ in the base Ni-Al-Cr alloy [30] to different values resulting from the addition of different refractory elements. The diffusivity of Ni in alloy F (with Ta) is $2.02 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ [32, 33], which is the smallest among all the analyzed alloys, and the smallest among all atomic species in alloy F. Hence, the inhibition effect on the transport of Ni atoms is significant in alloy F, because Ni is the least mobile element in the γ -matrix. Alternatively, the calculated Ni diffusivity in alloy E (with Ru) is $5.89 \times 10^{-18} \text{ m}^2\text{s}^{-1}$ [34], which is the least affected by the addition of a refractory element, leading to the smallest Ni excess (accumulation) in the γ -matrix and even a zero Ni-depletion in the γ' -precipitates.

4. Summary and conclusions

The effects of adding 2 at.% of the refractory elements, R, (R = Re, Ru, W, or Ta), to a model Ni-based superalloy Ni-10.0Al-8.5Cr at.% aged at 1073 K (800 °C) for 256 h, on the interfacial retention-excesses of the solvent Ni, were studied experimentally using 3D atom-probe tomography (APT) plus first-principles calculations. Our findings and conclusions are summarized as follows:

- There is a strong chemical binding affinity between refractory elements and solute elements, S, (S = Al, Cr), as demonstrated by experimental partial radial distribution functions (RDFs), and first-principles calculations.
- We find that correlated R-S binding energies play a key role in the measured Ni excesses at $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interfaces at an aging time of 256 h. Based on R-Cr partial RDF profiles (Fig. 3a), Ta has a negative correlation with Cr, while Re and Ru reveal positive correlations with

Cr, suggesting a repulsive interaction exists between Ta and Cr atoms and a chemical affinity exists between Re and Cr atoms, and between Ru and Cr atoms, consistent with strong Re-Cr and Ru-Cr attractive binding energies. Additionally, we find that the W-Cr partial RDF is weakly correlated and that W does not have a strong preference for Cr. In the R-Al partial RDF profile (Fig. 3b), Ta and W have strong positive correlations whereas Re and Ru have negative correlations with Al. These findings indicate that Ta and W have strong effects on the Al diffusional-flux into γ' -precipitates and concomitantly partitioning of Al atoms to them.

- The R-S binding energies at 0 K (Table 5 and Fig. 4) were also calculated utilizing first-principles calculations. Rhenium and Ru have attractive binding energies with Cr at 1st and 2nd NN distances. Tungsten and Ta exhibit repulsive binding energies with Cr in the 1st NN shell, but they have attractive binding energies with Cr at the 2nd NN distance. These results are in excellent agreement with our experimental APT partitioning and partial RDF results. The R-Al binding energies for Ta, W, Re and Ru, all have alternating positive and negative values from 1st NN to 4th NN distance, indicating that the four refractory elements substitute on the Al sublattice and form an L1₂ ordered structure with Ni.
- Unlike Ni excesses that emerge during the early stages of phase separation and disappear at later stages in ternary Ni-Al-Cr alloys [25, 26], we observe Ni interfacial excesses at the $\gamma(\text{f.c.c.})/\gamma'(\text{L1}_2)$ interface at an aging time of 256 h for alloys E to J with refractory elemental additions, Fig. 2. The calculated Γ_i values on the matrix side range from 0.33 ± 0.05 atom nm⁻² in alloy J to 0.99 ± 0.13 atom nm⁻² in alloy F and 0.99 ± 0.15 atom nm⁻² in alloy G, while the Γ_i values on the precipitate side range from -0.89 ± 0.12 atom nm⁻² in alloy F to zero atom nm⁻² in alloy E and I. These interfacial excesses are related to the R-S binding energies

between refractory elements and solute atoms, which reflect changes in the compositional vectors as indicated below. The total reduction of the interfacial free energy, as a result of the Ni interfacial excesses in both phases, lies between $-0.16 \pm 0.06 \text{ mJ m}^{-2}$ for alloy F (with Ta) to $-0.05 \pm 0.02 \text{ mJ m}^{-2}$ for alloy E (with Ru).

- The addition of refractory elements affects the compositional values and the directions of the components of the compositional diffusion flux vectors in and out of $\gamma'(L1_2)$ -precipitates, due to strong R-S binding energies (Table 3). Tantalum and W have the largest effects and Ru has the smallest effect on the directional change of the flux vector, causing large interfacial excesses for Ta and W and a relatively small excess for Ru.
- The interfacial compositional width, δ_i ($t = 256 \text{ h}$), Table 4, is strongly affected by the addition of refractory elements; the larger the compositional flux vector changes due to strong R-S bindings, the larger is the interfacial compositional width. Alloys E to J exhibit larger Ni interfacial compositional widths, δ_{Ni} ($t = 256 \text{ h}$), varying from 1.14 nm (alloy G) to 1.52 nm (alloy F), compared with 1.07 nm for the base Ni-Al-Cr alloy [29]. Moreover, we observe that alloys F (with Ta) and H (with W) have larger compositional flux vector changes, and concomitantly they display larger Ni, Al or Cr interfacial compositional widths than do alloys G (with Re) and E (with Ru).
- The refractory elements W, Re, Ru, and Ta are slow diffusing species in the γ -matrix. And the attractive R-Cr binding at the 1st or 2nd NN distance decelerate the solute diffusional fluxes, which implies a decrease of the Ni diffusivity, which in turn hinders the transport of Ni atoms away from the $\gamma(\text{f.c.c.})/\gamma'(L1_2)$ interface. The inhibition effect on the transport of Ni atoms is more significant in alloy F (with Ta) than in alloy E (with Ru).

Acknowledgements

This research was supported by the National Science Foundation, Division of Materials Research (DMR) grant number 1207539, Profs. Diane Farkas and Gary Shiflet, grant monitors. Ms. Yanyan Huang was partially supported by China Scholarship Council (with No. 201206050078). Atom-probe tomography was performed at the Northwestern University Center for Atom-Probe Tomography (NUCAPT), whose LEAP tomograph was purchased and upgraded with funding from NSF-MRI (DMR-0420532) and ONR-DURIP (N00014-0400798, N00014-0610539, N00014-0910781) grants. Instrumentation at NUCAPT was further upgraded by the Initiative for Sustainability and Energy at Northwestern (ISEN). NUCAPT is a Core Facility of Northwestern University and the Materials Research Center of Northwestern University, partially supported by the National Science Foundation's MRSEC program (DMR-1121262). We wish to thank research associate professor Dr. Dieter Isheim for managing NUCAPT. Drs. Georges Martin, Ivan Blum, Jiantang Jiang, Haiming Wen and Sung-II Baik are kindly thanked for helpful discussions. We thank Ms. Elizaveta Y. Plotnikov for some initial help with atom-probe tomography. And we also thank an anonymous reviewer for useful comments and suggestions, which helped us to improve this article.

References

- [1] R.C. Reed, The superalloys: fundamentals and applications, Cambridge University Press, New York, 2006.
- [2] M. Durand-Charre, The Microstructure of Super Alloys, Gordon & Breach Science, Amsterdam, 1997.
- [3] T.M. Pollock, S. Tin, Nickel-based superalloys for advanced turbine engines: chemistry, microstructure and properties, J. Propul. Power. 22 (2006) 361-374.
- [4] K.E. Yoon, R.D. Noebe, O.C. Hellman, D.N. Seidman, Dependence of interfacial excess on the threshold value of the isoconcentration surface, Surf. Interface Anal. 36 (2004) 594-597.
- [5] K.E. Yoon, R.D. Noebe, D.N. Seidman, Effects of rhenium addition on the temporal evolution of the nanostructure and chemistry of a model Ni-Cr-Al superalloy II: Analysis of the coarsening behavior, Acta Mater. 55 (2007) 1159-1169.
- [6] Y. Amouyal, Z. Mao, D.N. Seidman, Segregation of tungsten at $\gamma'(L1_2)/\gamma(fcc)$ interfaces

- in a Ni-based superalloy: An atom-probe tomographic and first-principles study, *Appl. Phys. Lett.* 93 (2008) 201905.
- [7] W. Johnson, J. Cahn, Elastically induced shape bifurcations of inclusions, *Acta Metall.* 32 (1984) 1925-1933.
- [8] A.J. Ardell, R.B. Nicholson, On the modulated structure of aged Ni-Al alloys: with an Appendix On the elastic interaction between inclusions by J. D. Eshelby, *Acta Metall.* 14 (1966) 1295-1309.
- [9] A.J. Ardell, An application of the theory of particle coarsening: The γ' precipitate in Ni-Al alloys, *Acta Metall.* 16 (1968) 511-516.
- [10] D.J. Chellman, A.J. Ardell, The coarsening of γ' precipitates at large volume fractions, *Acta Metall.* 22 (1974) 577-588.
- [11] H. Wendt, P. Haasen, Nucleation and growth of γ' -Precipitates in Ni-14 at.% Al, *Acta Metall.* 31 (1983) 1649-1659.
- [12] C. Marsh, H. Chen, An in situ x-ray diffraction study of precipitation from a supersaturated solid solution: The γ' precipitate in a Ni-12.5 at.% Al alloy, *Acta Metall. Mater.* 38 (1990) 2287-2298.
- [13] S.Q. Xiao, P. Haasen, HREM investigation of homogeneous decomposition in a Ni-12 at. % Al Alloy, *Acta Metall. Mater.* 39 (1991) 651-659.
- [14] H.A. Calderon, P.W. Voorhees, J.L. Murray, G. Kostorz, Ostwald ripening in concentrated alloys, *Acta Metall. Mater.* 42 (1994) 991-1000.
- [15] A.J. Ardell, Interfacial free energies and solute diffusivities from data on Ostwald ripening, *Interface Sci.* 3 (1995) 119-125.
- [16] A.J. Ardell, Al-L1₂ interfacial free energies from data on coarsening in five binary Ni alloys, informed by thermodynamic phase diagram assessments, *J. Mater. Sci.* 46 (2011) 4832-4849.
- [17] D.N. Seidman, Three-Dimensional Atom-Probe Tomography: Advances and Applications, *Annu. Rev. Mater. Res.* 37 (2007) 127-158.
- [18] T.F. Kelly, M.K. Miller, Invited Review Article: Atom probe tomography, *Rev. Sci. Instrum.* 78 (2007) 031101-031120.
- [19] M.K. Miller, *Atom probe tomography: analysis at the atomic level*, Kluwer Academic/Plenum Publishers, New York, 2000.
- [20] C. Schmuck, F. Danoix, P. Caron, A. Hauet, D. Blavette, Atomic scale investigation of ordering and precipitation processes in a model Ni-Cr-Al alloy, *Appl. Surf. Sci.* 94 (1996) 273-279.
- [21] C. Schmuck, P. Caron, A. Hauet, D. Blavette, Ordering and precipitation of γ' phase in low supersaturated Ni-Cr-Al model alloy: An atomic scale investigation, *Philos. Mag. A.* 76 (1997) 527-542.
- [22] C. Pareige-Schmuck, F. Soisson, G. Martin, D. Blavette, Ordering and phase separation in Ni-Cr-Al: Monte Carlo simulations vs three-dimensional atom probe, *Acta Mater.* 47 (1999) 1889-1899.
- [23] C. Pareige-Schmuck, F. Soisson, D. Blavette, Ordering and phase separation in low supersaturated Ni-Cr-Al alloys: 3D atom probe and Monte Carlo simulation, *Mater. Sci. Eng. A.* 250 (1998) 99-103.
- [24] C.K. Sudbrack, R.D. Noebe, D.N. Seidman, Compositional pathways and capillary effects during isothermal precipitation in a nondilute Ni-Al-Cr alloy, *Acta Mater.* 55 (2007) 119-130.
- [25] Z. Mao, C. Booth-Morrison, C.K. Sudbrack, G. Martin, D.N. Seidman, Kinetic pathways for phase separation: An atomic-scale study in Ni-Al-Cr alloys, *Acta Mater.* 60 (2012) 1871-1888.
- [26] Z. Mao, C.K. Sudbrack, K.E. Yoon, G. Martin, D.N. Seidman, The mechanism of morphogenesis in a phase-separating concentrated multicomponent alloy, *Nat. Mater.* 6 (2007) 210-216.
- [27] C.K. Sudbrack, K.E. Yoon, R.D. Noebe, D.N. Seidman, Temporal evolution of the nanostructure and phase compositions in a model Ni-Al-Cr alloy, *Acta Mater.* 54 (2006) 3199-3210.
- [28] C. Booth-Morrison, J. Weninger, C.K. Sudbrack, Z. Mao, R.D. Noebe, D.N. Seidman, Effects of solute concentrations on kinetic pathways in Ni-Al-Cr alloys, *Acta Mater.* 56 (2008) 3422-3438.
- [29] C.K. Sudbrack, D. Isheim, R.D. Noebe, N.S. Jacobson, D.N. Seidman, The influence of tungsten on the chemical composition of a temporally evolving nanostructure of a model Ni-Al-Cr superalloy, *Microsc. Microanal.* 10 (2004) 355-365.

- [30] C.K. Sudbrack, T.D. Ziebell, R.D. Noebe, D.N. Seidman, Effects of a tungsten addition on the morphological evolution, spatial correlations and temporal evolution of a model Ni-Al-Cr superalloy, *Acta Mater.* 56 (2008) 448-463.
- [31] K.E. Yoon, R.D. Noebe, D.N. Seidman, Effects of rhenium addition on the temporal evolution of the nanostructure and chemistry of a model Ni-Cr-Al superalloy. I: Experimental observations, *Acta Mater.* 55 (2007) 1145-1157.
- [32] C. Booth-Morrison, R.D. Noebe, D.N. Seidman, Effects of tantalum on the temporal evolution of a model Ni-Al-Cr superalloy during phase decomposition, *Acta Mater.* 57 (2009) 909-920.
- [33] C. Booth-Morrison, R.D. Noebe, D.N. Seidman, Effects of a tantalum addition on the morphological and compositional evolution of a model Ni-Al-Cr superalloy, *Superalloys*. (2008) 73-79.
- [34] Y. Zhou, D. Isheim, G. Hsieh, R.D. Noebe, D.N. Seidman, Effects of ruthenium on phase separation in a model Ni-Al-Cr-Ru superalloy, *Philos. Mag.* 93 (2013) 1326-1350.
- [35] D. Isheim, G. Hsieh, R.D. Noebe, D.N. Seidman, Nanostructural temporal evolution and solute partitioning in model Ni-based superalloys containing ruthenium, rhenium and tungsten, *Solid-Solid Phase Transformations Inorg. Mater.* 2 (2005) 309-314.
- [36] Y-C. Kim, D.N. Seidman, An electrochemical etching procedure for fabricating scanning tunneling microscopy and atom-probe field-ion microscopy tips, *Met. Mater. Int.* 9 (2003) 399-404.
- [37] Y. Zhou, C. Booth-Morrison, D.N. Seidman, On the field evaporation behavior of a model Ni-Al-Cr superalloy studied by picosecond pulsed-laser atom-probe tomography, *Microsc. Microanal.* 14 (2008) 571-580.
- [38] G. Kresse, J. Furthmüller, Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors using a Plane-Wave Basis Set, *Comput. Mater. Sci.* 6 (1996) 15-50.
- [39] G. Kresse, Ab initio molecular dynamics applied to the dynamics of liquid metals and to the metal-nonmetal transition, *J. Non-Cryst. Solids*. 205-207 (1996) 833-840.
- [40] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B Condens. Matter.* 54 (1996) 11169-11186.
- [41] G. Kresse, J. Hafner, Ab initio molecular dynamics of liquid metals, *Phys. Rev. B Condens. Matter.* 47 (1993) 558-561.
- [42] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, *Phys. Rev. B.* 49 (1994) 14251-14269.
- [43] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, *Phys. Rev. B Condens. Matter.* 59 (1999) 1758-1775.
- [44] R.C. Reed, A.C. Yeh, S. Tin, S.S. Babu, M.K. Miller, Identification of the partitioning characteristics of ruthenium in single crystal superalloys using atom probe tomography, *Scripta Mater.* 51 (2004) 327-331.
- [45] M. Xie, R. Helmink, S. Tin, The influence of Ta on the solidification microstructure and segregation behavior of $\gamma(\text{Ni})/\gamma'(\text{Ni}_3\text{Al})-\delta(\text{Ni}_3\text{Nb})$ eutectic Ni-base superalloys, *J. Alloys Compd.* 562 (2013) 11-18.
- [46] C. Jia, K. Ishida, T. Nishizawa, Partition of alloying elements between $\gamma(\text{Al})$, $\gamma'(\text{L}_{12})$, and $\beta(\text{B}_2)$ phases in Ni-Al base systems, *Metall. Mater. Trans. A.* 25 (1994) 473-485.
- [47] L.J. Carroll, Q. Feng, J.F. Mansfield, T.M. Pollock, Elemental partitioning in Ru-containing nickel-base single crystal superalloys, *Mater. Sci. Eng. A.* 457 (2007) 292-299.
- [48] A. Heckl, S. Neumeier, M. Göken, R.F. Singer, The effect of Re and Ru on γ/γ' microstructure, γ -solid solution strengthening and creep strength in nickel-base superalloys, *Mater. Sci. Eng. A.* 528 (2011) 3435-3444.
- [49] A. Heckl, R. Rettig, R.F. Singer, Solidification Characteristics and Segregation Behavior of Nickel-Base Superalloys in Dependence on Different Rhenium and Ruthenium Contents, *Metall. Mater. Trans. A.* 41 (2009) 202-211.
- [50] T. Kitashima, H. Harada, D.H. Ping, T. Kobayashi, Atom Probe Investigation of Ruthenium Distributions around Rhenium, Molybdenum and Tungsten in a Gamma Phase of 5th-Generation

- Nickel-Base Single-Crystal Superalloys, *Mater. Trans.* 48 (2007) 566-569.
- [51] S. Neumeier, F. Pyczak, M. Göken, The influence of Ruthenium and Rhenium on the local properties of the γ - and γ' -phase in Nickel-base superalloys and their consequences for alloy behavior, *Superalloys*. (2008) 109-119.
 - [52] A. Ofori, C. Humphreys, S. Tin, C. Jones, A TEM study of the effect of platinum group metals in advanced single crystal nickel-base superalloys, *Superalloys*. (2004) 787-794.
 - [53] F. Pyczak, S. Neumeier, M. Göken, Temperature dependence of element partitioning in rhenium and ruthenium bearing nickel-base superalloys, *Mater. Sci. Eng. A*. 527 (2010) 7939-7943.
 - [54] J. Rüsing, N. Wanderka, U. Czubyko, V. Naundorf, D. Mukherji, J. Rösler, Rhenium distribution in the matrix and near the particle-matrix interface in a model Ni-Al-Ta-Re superalloy, *Scripta Mater.* 46 (2002) 235-240.
 - [55] L. Viskari, K. Stiller, Atom probe tomography of Ni-base superalloys Allvac 718Plus and Alloy 718, *Ultramicroscopy*. 111 (2011) 652-658.
 - [56] K.E. Yoon, D. Isheim, R.D. Noebe, D.N. Seidman, Nanoscale studies of the chemistry of a René N6 superalloy, *Interface Sci.* 9 (2001) 249-255.
 - [57] Y. Amouyal, Z. Mao, D.N. Seidman, Effects of tantalum on the partitioning of tungsten between the γ - and γ' -phases in nickel-based superalloys: Linking experimental and computational approaches, *Acta Mater.* 58 (2010) 5898-5911.
 - [58] Y. Amouyal, Z. Mao, C. Booth-Morrison, D.N. Seidman, On the interplay between tungsten and tantalum atoms in Ni-based superalloys: An atom-probe tomographic and first-principles study, *Appl. Phys. Lett.* 94 (2009) 041917.
 - [59] T. Miyazaki, H. Imamura, T. Kozakai, The formation of γ precipitate doublets in Ni-Al alloys and their energetic stability, *Mater. Sci. Eng.* 54 (1982) 9-15.
 - [60] P.W. Voorhees, Ostwald ripening of two-phase mixtures, *Annu. Rev. Mater. Sci.* 22 (1992) 197-215.
 - [61] O.C. Hellman, J.A. Vandenbroucke, J. Rüsing, D. Isheim, D.N. Seidman, Analysis of three-dimensional atom-probe data by the proximity histogram, *Microsc. Microanal.* 6 (2000) 437-444.
 - [62] I. Blum, S.-II. Baik, M.G. Kanatzidis, D.N. Seidman, An integral method for the calculation of the reduction in interfacial free energy due to interfacial segregation, *Acta Mater.* submitted.
 - [63] S.-II. Baik, M.J. Olszta, S.M. Bruemmer, D.N. Seidman, Grain-boundary structure and segregation behavior in a nickel-base stainless alloy, *Scripta Mater.* 66 (2012) 809-812.
 - [64] D. Isheim, M.S. Gagliano, M.E. Fine, D.N. Seidman, Interfacial segregation at Cu-rich precipitates in a high-strength low-carbon steel studied on a sub-nanometer scale, *Acta Mater.* 54 (2006) 841-849.
 - [65] M.E. Krug, D.C. Dunand, D.N. Seidman, Effects of Li additions on precipitation-strengthened Al-Sc and Al-Sc-Yb alloys, *Acta Mater.* 59 (2011) 1700-1715.
 - [66] D. Isheim, D.N. Seidman, Nanoscale studies of segregation at coherent heterophase interfaces in α -Fe based systems, *Surf. Interface Anal.* 36 (2004) 569-574.
 - [67] A. Biswas, D.J. Siegel, C. Wolverton, D.N. Seidman, Precipitates in Al-Cu alloys revisited: Atom-probe tomographic experiments and first-principles calculations of compositional evolution and interfacial segregation, *Acta Mater.* 59 (2011) 6187-6204.
 - [68] O.C. Hellman, D.N. Seidman, Measurement of the Gibbsian interfacial excess of solute at an interface of arbitrary geometry using three-dimensional atom probe microscopy, *Mater. Sci. Eng. A*. 327 (2002) 24-28.
 - [69] O.C. Hellman, J.B. Rivage, D.N. Seidman, Efficient sampling for three-dimensional atom probe microscopy data, *Ultramicroscopy*. 95 (2003) 199-205.
 - [70] C.K. Sudbrack, R.D. Noebe, D.N. Seidman, Direct observations of nucleation in a nondilute multicomponent alloy, *Phys. Rev. B*. 73 (2006) 212101.
 - [71] E.Y. Plotnikov, Z. Mao, R.D. Noebe, D.N. Seidman, Temporal evolution of the $\gamma(\text{fcc})/\gamma'(\text{L1}_2)$ interfacial width in binary Ni-Al alloys, *Scripta Mater.* 70 (2014) 51-54.
 - [72] A.J. Ardell, Trans-interface-diffusion-controlled coarsening of γ' precipitates in ternary Ni-Al-Cr

- alloys, *Acta Mater.* 61 (2013) 7828-7840.
- [73] A.J. Ardell, Gradient energy, interfacial energy and interface width, *Scripta Mater.* 66 (2012) 423-426.
- [74] A.J. Ardell, Trans-interface-diffusion-controlled coarsening in ternary alloys, *Acta Mater.* 20 (2013) 7749-7754.
- [75] A.J. Ardell, O. Vidvuds, Trans-interface diffusion-controlled coarsening, *Nat. Mater.* 4 (2005) 309-316.
- [76] G. Van Bakel, K. Hariharan, D.N. Seidman, On the structure and chemistry of Ni_3Al on an atomic scale via atom-probe field-ion microscopy, *Appl. Surf. Sci.* 90 (1995) 95-105.
- [77] C. Booth-Morrison, Z. Mao, R.D. Noebe, D.N. Seidman, Chromium and tantalum site substitution patterns in $\text{Ni}_3\text{Al}(\text{L}_{12})$ γ' -precipitates, *Appl. Phys. Lett.* 93 (2008) 033103.
- [78] Y. Zhou, Z. Mao, C. Booth-Morrison, D.N. Seidman, The partitioning and site preference of rhenium or ruthenium in model nickel-based superalloys: An atom-probe tomographic and first-principles study, *Appl. Phys. Lett.* 93 (2008) 171905.
- [79] Y. Amouyal, Z. Mao, D.N. Seidman, Combined atom probe tomography and first-principles calculations for studying atomistic interactions between tungsten and tantalum in nickel-based alloys, *Acta Mater.* 74 (2014) 296-308.
- [80] E.A. Marquis, D.N. Seidman, M. Asta, C. Woodward, V. Ozoliņš, Mg Segregation at $\text{Al}/\text{Al}_3\text{Sc}$ Heterophase Interfaces on an Atomic Scale: Experiments and Computations, *Phys. Rev. Lett.* 91 (2003) 036101.

Captions for Figures

Fig. 1. 3D atom-probe tomographic reconstructions for Ni-based superalloys: (a) alloy E, Ni-10.0Al-8.5Cr-2.0Ru; (b) alloy F, Ni-10.0Al-8.5Cr-2.0Ta; (c) alloy G, Ni-10.0Al-8.5Cr-2.0Re; (d) alloy H, Ni-10.0Al-8.5Cr-2.0W; (e) alloy I, Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (f) alloy J, Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%. All the alloys were aged at 1073 K (800 °C) for 256 h. The total number of collected atoms for each alloy ranges from ~70 million (alloy E) to ~85 million (alloy G). Only a fraction of the Al (red), Cr (blue), Ta (magenta), W (purple), Re (dark yellow) and Ru (dark cyan) atoms are displayed, and the Ni atoms are completely omitted for the sake of clarity. The γ -matrix and γ' -precipitates are identified unambiguously, as a result of the strong partitioning of Cr atoms (blue) to the γ -matrix and Al atoms (red) to the γ' -precipitates.

Fig. 2. The elemental concentration profiles of Ni across the γ (f.c.c.)/ γ' (L1₂) interface, with respect to Ni iso-concentration surfaces, for model Ni-based superalloys: (a) alloy E, Ni-10.0Al-8.5Cr-2.0Ru; (b) alloy F, Ni-10.0Al-8.5Cr-2.0Ta; (c) alloy G, Ni-10.0Al-8.5Cr-2.0Re; (d) alloy H, Ni-10.0Al-8.5Cr-2.0W; (e) alloy I, Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (f) alloy J, Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%. All the alloys were aged at 1073 K (800 °C) for 256 h. The solid vertical lines are placed at the inflection points of the Ni concentration profiles, indicating, by definition, the location of the γ (f.c.c.)/ γ' (L1₂) interface. Negative values are into the γ -matrix and positive values are into the γ' -precipitate. The shaded areas in the vicinity of the γ (f.c.c.)/ γ' (L1₂) interface represent the interfacial retention excesses of Ni.

Fig. 3. Refractory-element-centered partial radial distribution function (RDF) vs. radial distance, r , applied to the γ -matrix phase of four quaternary Ni-based superalloys: alloy E, Ni-10.0Al-

8.5Cr-2.0Ru; alloy F, Ni-10.0Al-8.5Cr-2.0Ta; alloy G, Ni-10.0Al-8.5Cr-2.0Re; and alloy H, Ni-10.0Al-8.5Cr-2.0W at.%. All the alloys were aged at 1073 K (800 °C) for 256 h. (a) R-Cr partial RDF and (b) R-Al partial RDF, where R = Ta, Re, W, or Ru. The dashed vertical lines are the 1st through 10th nearest-neighbor (NN) distances. Partial RDF = 1, describes a perfectly random solid-solution distribution, which is denoted by a dashed horizontal line.

Fig. 4. The binding energies (eV atom⁻¹) at 0 K of R-S in Ni as a function of R-S interatomic distance (nm), ranging from the 1st through 6th nearest-neighbor (NN) distance are indicated by the dashed vertical lines. (a) R-Cr binding energy and (b) R-Al binding energy, where R = Ta, Re, W, or Ru. A negative binding energy is attractive and a positive binding energy is repulsive.

Figure 1

Figure 2

Figure 3

Figure 4

Tables

Table 1. The calculated maximum positive accumulation (at.%) on the γ -matrix side and minimum negative depletion (at.%) on the γ' -precipitate side, for the γ (f.c.c.)/ γ' (L1₂) interface of Ni-based superalloys: alloys (E) Ni-10.0Al-8.5Cr-2.0Ru; (F) Ni-10.0Al-8.5Cr-2.Ta; (G) Ni-10.0Al-8.5Cr-2.Re; (H) Ni-10.0Al-8.5Cr-2.W; (I) Ni-10.0Al-8.5Cr-1.Re-1.0Ru; and (J) Ni-10.0Al-8.5Cr-1.W-1.0Re at.% aged at 1073 K (800 °C) for 256 h.

Alloy	Maximum Ni accumulation on the γ -matrix side (at.%)	Minimum Ni depletion on the γ' -precipitate side (at.%)
E	0.50±0.12	0
F	0.49±0.12	-0.65±0.12
G	0.68±0.11	-0.51±0.12
H	0.85±0.12	-0.81±0.14
I	0.67±0.12	0
J	0.41±0.09	-0.53±0.14

Table 2. The calculated Ni (solvent) interfacial excesses Γ_{Ni} (atom nm⁻²) and corresponding local reductions in the Gibbs interfacial free energy $\Delta\sigma_{Ni}$ (mJ m⁻²), by using (a) prior method [1-4] and (b) new integral method [5], for the γ (f.c.c.)/ γ' (L1₂) interface of Ni-based superalloys: (E) Ni-10.0Al-8.5Cr-2.0Ru; (F) Ni-10.0Al-8.5Cr-2.0Ta; (G) Ni-10.0Al-8.5Cr-2.Re; (H) Ni-10.0Al-8.5Cr-2.0W; (I) Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (J) Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%, aged at 1073 K (800 °C) for 256 h.

(a) New integral method

Alloy	Γ_{Ni} (atom nm ⁻²) on the γ -matrix side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) on the γ -matrix side	Γ_{Ni} (atom nm ⁻²) on the γ' -precipitate side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) on the γ' -precipitate side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) in both phases
E	0.65±0.07	-0.05±0.02	0	0	-0.05±0.02
F	0.99±0.13	-0.08±0.03	-0.89±0.12	-0.08±0.03	-0.16±0.06
G	0.99±0.15	-0.09±0.03	-0.30±0.06	-0.02±0.01	-0.11±0.04
H	0.62±0.08	-0.05±0.02	-0.67±0.12	-0.05±0.02	-0.10±0.04
I	0.75±0.09	-0.06±0.02	0	0	-0.06±0.02
J	0.33±0.05	-0.02±0.01	0.48±0.07	-0.04±0.01	-0.06±0.02

(b) Prior method

Alloy	Γ_{Ni} (atom nm ⁻²) on the γ -matrix side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) on the γ -matrix side	Γ_{Ni} (atom nm ⁻²) on the γ' -precipitate side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) on the γ' -precipitate side	$\Delta\sigma_{Ni}$ (mJ m ⁻²) in both phases
E	0.28±0.04	-0.03±0.01	0	0	-0.03±0.01
F	0.65±0.06	-0.06±0.02	-0.67±0.06	-0.08±0.02	-0.14±0.04
G	0.83±0.08	-0.10±0.03	-0.26±0.04	-0.03±0.01	-0.13±0.04
H	0.44±0.04	-0.05±0.02	-0.54±0.04	-0.05±0.02	-0.10±0.04
I	0.63±0.07	-0.07±0.02	0	0	-0.07±0.02
J	0.24±0.03	-0.02±0.01	-0.34±0.04	-0.04±0.01	-0.06±0.02

Table 3. Unit vectors ΔC (at.%) of the base Ni-10.0Al-8.5Cr at.% alloy (calculated from APT data in Ref. [6]) and alloys E to J, and changes of the unit vector of an alloy from the base Ni-Al-Cr alloy, $\Delta\tilde{C} = \Delta C - \Delta C(\text{base})$ (at.%). Alloys E to J are: (E) Ni-10.0Al-8.5Cr-2.0Ru; (F) Ni-10.0Al-8.5Cr-2.0Ta; (G) Ni-10.0Al-8.5Cr-2.0Re; (H) Ni-10.0Al-8.5Cr-2.0W; (I) Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (J) Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%. All the alloys were aged at 1073 K (800 °C) for 256 h.

Alloy	Unit vector, ΔC			Changes of unit vector of an alloy			
	at. %			from the base alloy $\Delta\tilde{C}$, at. %			
	Ni	Al	Cr	Ni	Al	Cr	magnitude
Base alloy	-0.537	0.801	-0.264	0	0	0	0
E	-0.403	0.853	-0.330	0.134	0.052	-0.067	0.16
F	-0.390	0.717	-0.578	0.148	-0.084	-0.314	0.36
G	-0.331	0.850	-0.410	0.206	0.049	-0.146	0.26
H	-0.318	0.774	-0.548	0.219	-0.027	-0.284	0.36
I	-0.380	0.845	-0.376	0.157	0.044	-0.112	0.20
J	-0.342	0.813	-0.471	0.195	0.012	-0.207	0.29

Table 4. The interfacial compositional width, δ_i ($t = 256$ h) (nm), measured from elemental concentration profiles of Ni-based superalloys: base Ni-10.0Al-8.5Cr alloy (calculated from APT data in Ref. [6]); (E) Ni-10.0Al-8.5Cr-2.0Ru; (F) Ni-10.0Al-8.5Cr-2.0Ta; (G) Ni-10.0Al-8.5Cr-2.0Re; (H) Ni-10.0Al-8.5Cr-2.0W; (I) Ni-10.0Al-8.5Cr-1.0Re-1.0Ru; and (J) Ni-10.0Al-8.5Cr-1.0W-1.0Re at.%. All the alloys were aged at 1073 K (800 °C) for 256 h.

Alloy	Ni	Al	Cr	W	Re	Ru	Ta
Base alloy	1.07	1.74	2.02				
E	1.19	1.70	1.66			1.98	
F	1.52	1.81	2.06				1.61
G	1.14	1.54	1.99		2.34		
H	1.28	1.99	2.30	2.11			
I	1.17	1.28	1.65		1.57	2.22	
J	1.22	1.63	2.15	2.43	2.19		

Table 5. R-Cr and R-Al (R = Ta, W, Re, or Ru) binding energies at 0 K for the 1st through 6th nearest- neighbor (NN) distance in Ni as calculated using GGA first-principles calculations (unit: eV atom⁻¹). A negative value implies an attractive binding energy and a positive value implies a repulsive binding energy

(a) R-Cr

	1 NN	2 NN	3NN	4 NN	5 NN	6 NN
Ru-Cr	-0.211	-0.172	0.092	-0.023	0.016	-0.005
Re-Cr	-0.242	-0.154	0.062	-0.028	0.018	-0.004
W-Cr	0.184	-0.186	0.072	-0.043	0.028	-0.006
Ta-Cr	0.292	-0.114	0.079	-0.051	0.025	-0.007

(b) R-Al

	1 NN	2 NN	3NN	4 NN	5 NN	6 NN
Ru-Al	0.372	-0.134	0.064	-0.056	0.023	-0.008
Re-Al	0.281	-0.110	0.052	-0.066	0.019	-0.007
W-Al	0.194	-0.152	0.06	-0.074	0.027	-0.009
Ta-Al	0.156	-0.271	0.083	-0.055	0.016	-0.006

Graphical abstract