On the control of structural/compositional ratio of coherent order-disorder interfaces

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Order-disorder coherent interfaces determine the microstructure and mechanical properties of precipitation-hardened high-temperature alloys. The characteristics of these interfaces can be defined by a compositional width, $\delta$, and structural width, $\delta^*$. The latter, which can be considered as the width of the ordered part of the interface, can play an important role in high-temperature mechanical behavior of precipitation-hardened alloys. This is due to the fact that diffusion in the ordered part of the interface is generally much slower than diffusion in the disordered phase, thus hindering the solid-state diffusion-based phenomena. Here, we investigate the order-disorder interface in a Ni-19Al (at.%$	ext{)}$ alloy as a model alloy for Ni-based superalloys using atomic-resolution scanning transmission electron microscopy and three-dimensional atom probe tomography. Then, we employ thermodynamic modeling to describe the interplay between the structural and compositional interface widths in binary Ni-Al and in ternary Ni-Al-Cr and Co-Al-W systems. We introduce the $\delta^*/\delta$ ratio as a critical parameter that varies significantly in different alloys. Our findings offer a general pathway to control the $\delta^*/\delta$ ratio of interfaces, which in turn affect the high-temperature properties of precipitation-hardened alloys.

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1. Introduction

Solid-solid interfaces play a crucial role in phase transformations of solid materials. This role is especially prominent in nanostructured materials because they have a relatively large volume of interfaces. Among different types of solid-solid interphase boundaries, structurally coherent and chemically diffuse heterophase interfaces have been studied extensively because they can control the formation and coarsening kinetics as well as the morphology of second-phase precipitates in supersaturated solid solutions [1–3]. A continuum description [4] of the diffuse coherent interfaces invokes the gradient energy concept and shows that the interface width $\delta$ is a compromise between the integrated value of theoretical excess interfacial free energy $\Delta G_{\text{rel}}(x)$ and a gradient energy term that is proportional to the square of the concentration gradient: high $\Delta G_{\text{rel}}(x)$ and low gradient energy yields a narrow interface; the opposite circumstance yields a more diffuse interface. However, this hypothesis did not consider the structural differences among phases in coherent interfaces (e.g., order-disorder coherent interfaces) although these differences could influence the structure of interface and the diffusion rate.

A new aspect of diffuse interfaces has recently been advanced by introducing the theory of trans-interface diffusion-controlled (TIDC) particle coarsening [5]. This theory suggests that diffusion through, rather than to, the order-disorder coherent non-sharp interface is the rate-controlling step in coarsening of ordered precipitates. This effect can occur because diffusion coefficients are typically much smaller in partially ordered interfaces than in the disordered matrix. Therefore, $\delta$ is explicitly included in the equations of TIDC theory as it influences the interfacial diffusion and thereby the microstructure stability of precipitation-hardened high-temperature alloys [5–9]. Nevertheless, and despite the importance of interface width in different aspects of materials science, there are still several fundamental unresolved questions.
about the basic definition of interface width between ordered and disordered phases.

The dual nature of order-disorder coherent interfaces was first reported by Srinivasan et al. [10] where the authors studied the interface of γ (A1) and γ′ (L12) phases in the Rene 88DT Ni-based superalloy. Their results have revealed the existence of two different structural and compositional continuous transition zones in the interface of order γ (L12) and disorder γ (A1) phases, in which the compositional gradient (~2.7 nm) is wider than the order-disorder transition zone (~1.3 nm) for the Rene 88DT alloy aged for 50 h at 760 °C. Later, the continuous order-disorder transition was also observed in DD6 and ERBO/1 Ni-based superalloys [11,12]. Shortly after, the structural and compositional interface widths were also measured in Ni-14Al-7Cr and Co-10Al-10 W [13], and in Co-7Al-7W (all content in at.%) [14] alloys and it was discussed that different coarsening behaviors of Co- and Ni-based alloys can be attributable to the different structural widths of their interfaces [13,14]. Despite these observations, the dual nature of order-disorder interfaces has not yet been explained, and the origin of order-disorder transient in the interface is subject to debate. Hence, we studied the γ/γ′ interface in a Ni-Al alloy (as a simple model of Ni-based superalloys) by combining atomic-resolution Z-contrast scanning transmission electron microscopy (STEM) and atom probe tomography (APT). Then, we employed thermodynamic modeling to develop understanding of the phenomenon of order-disorder interfaces in Ni-Al, Ni-Al-Cr, and Co-Al-W basic alloy systems. This paper describes the theory behind structural transition in order-disorder interfaces and shows how this approach can be applied to predict the structural interface width considering the compositional gradient of the interface and temperature effect. On the basis of the developed thermodynamic modeling framework, the interaction between structural and compositional widths of coherent interfaces could be controlled to tailor the high-temperature microstructure stability of precipitation-hardened alloys.

2. Thermodynamic sublattice model

The intrinsic properties of phases and their responses to external stimuli such as temperature, pressure, stress, magnetic field, electric field, and radiation, is articulated as the fundamental notion of materials.

\[
G_{i/j}^{I/y} = \sum_{i,j} \left( y_i y_j \phi_i^{C12} \right) + RT \left[ \frac{3}{4} \sum_i y_i \ln (y_i) + \frac{1}{2} \sum_j y_i \ln (y_i) \right] 
+ \sum_{i,j} \sum_{k} y_i y_j y_k \phi_{i,j,k}^{L12} + \sum_{i,j} \sum_{k,l} y_i y_j y_k y_l \phi_{i,j,k,l}^{L12}
\]

where \( \phi_{i,j,k}^{C12} \) denotes the Gibbs energy of the stoichiometric compound \( i_j \) in the \( L12 \) crystal structure and \( y_i^{(s)} \) is the site fraction of element \( i \) on sublattice \( s \). The colon separates constituents on the same sublattice. \( R \) is the gas constant, and \( T \) is absolute temperature. \( \phi_{i,j,k}^{L12} \) and \( \phi_{i,j,k,l}^{L12} \) are interaction parameters that depend on the fraction of occupation and absolute temperature as

\[
\phi_{i,j,k}^{L12} = \delta \phi_{i,j,k}^{L12} + \phi_{i,j,k}^{L12} \phi_{i,j,k}^{L12} \phi_{i,j,k}^{L12}
\]

and

\[
\delta \phi_{i,j,k}^{L12} = \delta \phi_{i,j,k}^{L12} + \phi_{i,j,k}^{L12} \phi_{i,j,k}^{L12} \phi_{i,j,k}^{L12}
\]

The intrinsic properties of phases and their responses to external stimuli such as temperature, pressure, stress, magnetic field, electric field, and radiation, is articulated as the fundamental notion of materials. The so-called materials genomic database [15] is the key input of techniques for integrated computational materials design (ICMD). Nevertheless, ICMD techniques mostly attempt to estimate interfacial properties by applying an exhaustive process of atomistic modeling or experimental data [15,16]. Therefore, it could be very desirable to be able to determine the properties of the interface between individual phases via CALPHAD (calculation of phase diagrams) genomic databases. In this regard, several attempts have been made to correlate the gradient energy and consequently the interfacial compositional gradient with the thermodynamic properties of individual phases [17–20]. In line with this idea, we use thermodynamic modeling to describe and predict the structural transition across the interface.

It is fairly safe to say that the phenomenological sublattice model (also known as compound energy formalism) can accurately describe and anticipate the thermodynamic behavior of γ and γ′ phases in Ni- and Co-based superalloys. Fig. 1 shows the schematic crystallographic representation of the disordered γ (A1) and ordered γ′ (L12) phases. While there is no site preference for atoms in A1 crystal structure, an order appears between the two sublattices of L12 (Ni3Al-based) structure. Crystallography of these phases inspired a single thermodynamic description for Ni-based superalloys; this description depends on the fractions of elements at different atomic sites [21–23]. The molar Gibbs energies of the γ and γ′ phases are modeled based on a partitioned two-sublattice model (2SL), i.e., \( (A,B,C)_i (A,B,C) \) that uses a single Gibbs energy function [24–26]:
where \( y_{\Gamma_{1}} \) and \( y_{\Gamma_{4}} \) are constant parameters. The mathematical equivalence of the 2SL and four sublattice (4SL) models for L1_2 structure yields a set of constraints (Appendix Table A1) that must be fulfilled to ensure that the L1_2 structure can be disordered [22]. By exploiting a symmetry of the parameters in the 4SL formalism, these relations can be simplified when the Gibbs energy of each stoichiometric compound ABCD is expressed as the sum of the bond energies \( U \):

\[
G_{A,B,C,D} = U_{AB} + U_{AC} + U_{AD} + U_{BC} + U_{BD} + U_{CD} + \alpha_{ABCD}
\]

(5)

In equation (5), the correction parameters \( \alpha_{ABCD} \) have been kept equal to zero for all cases except \( \alpha_{ABCD} \) which has been previously suggested to be +6660 J/mol [25]. Thus, when the correction term \( \alpha_{ABCD} = 0 \), the Gibbs energies of binary and ternary compounds can be deduced as

\[
G_{A,B} = 3U_{AB}
\]

(6)

\[
G_{A,B_3} = 4U_{AB}
\]

(7)

\[
G_{A,B_3} = 3U_{AB}
\]

(8)

\[
G_{A,B_3} = 2U_{AB} + 2U_{AC} + 2U_{BC}
\]

(9)

The bond energies (Appendix Table A2) of the binary Ni-Al and of the ternary Ni-Al-Cr and Co-Al-W alloy systems were used in the current thermodynamic modeling. Calculations of the molar Gibbs energy of pure elements used thermodynamic data were from the SGTE database [27]. Because no absolute values of the Gibbs energy can be defined, the Gibbs energy of the pure element \( i \), \( G_i^{SEK}(T) \), was related to the enthalpy for its stable state at 298.15 K, \( H_i^{SEK}(298.15 \text{ K}) \) and given as a function of temperature as:

\[
\frac{G_i^0}{\gamma_i}(T) = H_i^{SEK}(298.15 \text{ K}) = a + bT + cT\ln(T) + \sum n T^n
\]

(10)

where \( a, b, c \) and \( n \) are coefficients, and \( n \) represents a set of integers, typically taking the values 2, 3, and 1. For some elements like Ni that have a magnetic ordering [27], an additional magnetic contribution \( G_{mag} \) was added to equation (10).

To study the ordering across the \( \gamma/\gamma' \) interface, the molar Gibbs energy of the phase, equation (1), is minimized in a custom MATLAB code by mediating \( y_i^{(5)} \) for any given composition \( X_i \) of the interfacial contents. In the disordered part of the interface, the site fractions are identical and \( y_i' = X_i = y_i'' \), whereas in the ordered part, the condition \( y_i'' \rightarrow <X_i < y_i' \) and \( y_i'' > X_i > y_i' \) would be achieved. In order to verify the accuracy of the current thermodynamic calculations, we recalculated the phase boundaries of \( \gamma \) and \( \gamma' \) phases in the binary Ni-Al system (Fig. 2). Furthermore, the Gibbs energy of the FCC phase in different selected Ni-Al-Cr and Co-Al-W alloys was compared with the results of Thermo-Calc software [28] (Fig. 3).

3. Materials and methods

3.1. Specimens preparation

A Ni-19Al (at.% Al) alloy was prepared using high purity Ni and Al pieces in a laboratory-scale vacuum arc melting furnace under Ar gas. Four repetitions of the melting process reduced the macrosegregation and provided an ingot with homogeneous chemical composition. Disks (1 mm thick, 5 mm in diameter) from the remelted ingot were homogenized in a vacuum furnace at 1350 °C for 8 h to remove dendritic segregation and to uniformly disperse the \( \gamma' \) precipitates in the \( \gamma \) matrix. The homogenized samples were first aged at 950 °C for 1 h, then at 715 °C for 100 h. Quenching in iced brine after each heat treatment (homogenization and aging treatments) made it possible to achieve the maximum cooling rate (≈500 °C/s) at 715 °C. The two-step aging treatment results in the formation of relatively large (>200 nm) primary \( \gamma' \) precipitates which are suitable for further interface studies [10]. For STEM investigations, discs of 3-mm diameter were punched out of the aged samples. Thin foils suitable for STEM were prepared using electrolytic jet polishing [36]. For APT analyses, needle-shaped samples with a tip radius ~50 nm were prepared by the lift-out procedure and annular milling using a dual-beam focused ion beam (FIB; Helios Nano-Lab 650i, FEI) [37,38].

3.2. Atomic-resolution STEM analysis

Atomic-resolution STEM bright-field (BF) and high-angle annular dark-field (HAADF) were performed using an aberration-corrected field emission transmission electron microscope electron microscope (JEM-2100F, JEDO™) operated at 200 kV. Coarse cuboidal primary \( \gamma' \) precipitates that had planar \( \gamma'/\gamma' \) interfaces parallel to the electron beam direction, were chosen for analysis. Using a custom MATLAB code, we followed a procedure [14] to calculate the averaged gray level of the columns of the atoms in the high-resolution HAADF-STEM images, to fit the sigmoid functions to the scatter data, and to calculate the structural and compositional interface widths.

3.3. APT analysis

APT data were collected using a local electrode atom probe (LEAP 4000X HR, CAMECA™) under an ultraviolet laser pulsing at a laser energy of 40 pJ. The experimental parameters were set to maintain a 0.5% detection rate and 200-kHz pulse frequency. All measurements were performed at 60 K under ultra-high vacuum (<10⁻⁸ Pa) [37,39]. APT data of two successful measurements, which considered > 10⁷ ions, were analyzed using IVAS software (version 3.6.14). The threshold value of 81 at.% Ni for iso-concentration surfaces could illustrate the \( \gamma'/\gamma' \) interfaces clearly. The compositional gradients across the interfaces were investigated using proximity histogram analyses (Proxigram Panel) in IVAS software. The standard deviation of measured atomic concentration \( C_i \) was calculated as \( (C_i(1-C_i)/N)^{0.5} \), where \( N \) is the total number of atoms in the analyzed volume.
4. Results

4.1. Compositional gradient of order-disorder interface in Ni-Al model alloy

In multi-component Ni-based alloys, $\gamma/\gamma'$ coherent interfaces are chemically diffuse [10,40–44]. In binary Ni-Al alloys, this diffuse interface has been demonstrated experimentally [45] and computationally [5,33,34,46,47]. To investigate the chemical variation across the diffuse $\gamma/\gamma'$ interface in Ni-19Al model alloy, we performed APT analysis on the double-aged samples. The two-step aging treatment provided a typical microstructure of coarse cuboidal $\gamma_0$ precipitates embedded in a $\gamma$ disordered matrix (Fig. 4).

Fig. 5a displays a 3D reconstruction of an APT analysis of the sample after aging for 100 h at 715 °C. For clear visualization of the $\gamma/\gamma'$ interface, only 3% of the measured Ni atoms and 9% of the measured Al atoms in the analyzed volume are shown. The $\gamma/\gamma'$ interface is represented by an 81 at.% Ni iso-concentration surface (purple), because this value is approximately equal to the average of $\gamma$ and $\gamma'$ equilibrium Ni concentrations. While the $\gamma$ phase in the lower part of the recognized interface appears red because it is rich in Ni, the $\gamma'$...
phase on the top of the image is almost green, due to its higher Al content.

A magnified view (Fig. 5b) of a subsection of the APT volume (Fig. 5a, blue box) distinguishes the atomic layers of Ni and Al; their inter-planar spacing is consistent with the d-spacing of (110) planes of γ and γ′ phases. It is important to note that the pure (220) planes of Ni were not detected as a separate atomic layer during atom probe analysis (Supplementary Fig. 1). This is due to the higher evaporation rate of pure planes in comparison to the mixed atomic planes, which has been previously reported in several atom probe studies of different Ni-based superalloys [48–52]. In view of the above orientation studies, it is verified that the flat γ/γ′ interface in Fig. 5a is parallel to (100) crystallographic plane. For a statistically relevant quantitative analysis of the compositional variation across this interface, a proxigram (proximity histogram) was computed from the 81 at.% Ni isoconcentration surface (Fig. 5c). The proxigram shows a gradual change of Ni and Al concentration across the interface, and thereby confirms the diffuse nature of γ/γ′ interface in the binary Ni-Al alloy.

According to the continuum description of coherent diffuse interfaces [4] and its reformulation [53], a stationary composition profile with minimum interfacial energy σ is achieved when the balance

\[ \Delta G_m(X) = \chi V_m \left( \frac{dX}{dz} \right)^2 \] (11)

between the ΔGm(X) and the composition gradient dX/dz is satisfied for all atoms in the interface, where Vm is the molar volume and ΔGm(X) represents the change in molar free energy by the transformation of the equilibrium mixture of γ and γ′ phases to a material with local composition X. The gradient energy coefficient σ can be related to the material property κ parameter [4] by \( \chi = \kappa N_v \), where \( N_v \) is the number of molecules per unit volume.

The sigmoid function

\[ \frac{X - X_f}{X_f - X_f} = \frac{1}{1 + e^{-\eta \rho}} \] (12)

can fit the concentration profile APT data of γ/γ′ interface excellently [53] (Supplementary Fig. 2); η is a fitting parameter that is related to the compositional interface width as η = 4/δ. Therefore η was then used to calculate δ for the Fig. 5c proxigram (Table 1). The sigmoid description of concentration profile leads to the following relationship between interfacial energy and gradient energy coefficient [53]

\[ \sigma = \frac{\chi \eta \Delta X^2}{3} \] (13)

Therefore, considering the γ/γ′ interfacial energy σ = 19.52 ± 0.90 mJ m⁻² for the binary Ni-Al alloy at 715 °C (calculated from kinetic data on coarsening [7]), \( \chi \) was also calculated (Table 1).

The experimental data [45] on the γ/γ′ interface width for the binary Ni-Al alloy has reported approximately 1.3 and 1.6 nm for the δ of Ni-12.5Al and Ni-13.5Al (at.%) alloys after aging for 256 h at 600 °C. These values have been determined based on 10–90 compositional interface width using a spline fit to the proxigram concentration profile [54,55]. Thus, employing the same approach, we recalculated δ = 1.79 nm for our alloy. The slightly wider compositional interface in our alloy than in the previous two can be attributed to the broadening of the interface as a result of increasing temperature from 600 to 715 °C. Furthermore, first-principles modeling of the γ/γ′ interface in Ni-Al system [34] predicted that δ = 2.1 nm at 727 °C, which is lower than δ = 2.575 nm predicted by Monte Carlo simulations [5,53] at the same temperature, but still is higher than the experimental values.

### 4.2. Structural transition of order-disorder interface in Ni-Al model alloy

We conducted atomic-resolution scanning transmission electron microscopy (STEM) analysis to simultaneously study structural and compositional transition across the γ/γ’ interface (Fig. 6). A bright-field image (Fig. 6a), taken along the [110] zone axis reveals the (100) interface between γ and γ′ phases. The fast Fourier transform (FFT) of Fig. 6a, and FFT patterns of the areas bounded by red and green boxes indicate that ordered γ′ phase occurs to the left of the interface, and disordered γ phases occur to its right (Fig. 6b, h, and 6c). Thus, the periodic alteration in the intensity of atomic layers in the γ‘ side of the interface is also due to the presence of long-range chemical ordering, which decays across the interface over several atomic layers. This is clearer in the composite image of Fig. 6e, obtained by superimposing the inverse FFT images of the fundamental (red) and superlattice (green) spots of Fig. 6b. While all (002) planes are almost identical in the γ side of the interface, the alternating (002) planes of mixed (~50% Ni and ~50% Al) and pure Ni atoms are observable in the ordered L12 structure of the γ’ phase, when viewed along the <110> direction (Fig. 6f).

To probe the compositional transition from ordered γ’ phase to the disordered γ phase, the corresponding Z-contrast high-angle annular dark-field (HAADF) image was examined in the interfacial region (Supplementary Fig. 3). The γ matrix contains more Ni atoms and has substantially higher mass contrast (Z-contrast) than the γ’ phase, so the γ matrix appears brighter than γ’ phase in HAADF-STEM images. Fig. 6g shows a clipped high-resolution image from the rectangular region perpendicular to the (100) interface (Supplementary Fig. 3, red box). The gray level of atomic columns (representative of (002) planes) were averaged parallel to the interface plane to produce a scatter plot (Fig. 6h). The compositional (Z-contrast) width of this interface was calculated as δ = 2.76 ± 0.29 nm using the sigmoid function to fit the scatter data and following the same procedure used for the APT data. An average δ = 2.80 ± 0.17 nm (based on the error propagation rules) was obtained by estimating δ at several places. Similar to the previous studies [10,12,13], this width of the γ’/γ interface is somewhat higher than the width measured by APT analysis. The difference may occur because the projection nature of TEM-based methods can cause false interface broadening in case of an inclined or ragged interface. However, the structural interface width, δ is also affected by the same projection effect, so this systematic error measurement of interface widths does not affect the δ/δ ratio significantly.

Fig. 6i shows the ratio of the gray level of each atomic column to its next adjacent column as a function of position. The amplitude of oscillation in the progressive gray level ratios (PGLR) represents the long-range chemical ordering of the lattice. The γ’ phase consists of periodic arrangement of mixed and pure atomic planes, so PGLRs alternate between ~0.8 and ~1.2, whereas in the γ solid solution, the Ni and Al atoms are distributed randomly, so PGLR ~1.0. More importantly, a clear transition zone from ordered γ’ to disordered γ occurs; in this zone the long-range order decreases roughly over a

<table>
<thead>
<tr>
<th>Fitting function</th>
<th>η (nm⁻¹)</th>
<th>δ (nm)</th>
<th>χ (m J m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sigmoid</td>
<td>2.46 ± 0.28</td>
<td>1.63 ± 0.19</td>
<td>1.44 ± 0.18</td>
</tr>
</tbody>
</table>

Table 1

Compositional characteristics of γ/γ′ interface at 715 °C for binary Ni-Al alloy. The parameters were determined by analyzing the interface concentration profile in Ni-9Al alloy after aging for 100 h at 715 °C. Errors are 95% confidence limits.
distance of seven atomic {002} planes. The average structural width of the interface was calculated as $d_0 = 1.23 \pm 0.19$ nm, using the same sigmoid fitting procedure for PGRL versus position data at several places. This width is intermediate between previous estimates of $d_0 \sim 0.7$–1.0 nm (4–6 {200} atomic layers) [46] and ~1.8 nm [34], which were obtained by atomistic modeling of the binary Ni-Al system at 427°C and 727°C, respectively.

5. Discussion

5.1. Phenomenology of order-disorder interfaces

According to atomic-resolution STEM results of the Ni-Al model alloy and of other Ni- and Co-based alloys [10–14], the interfacial structural/compositional ratio, $\delta/\delta_0$ may vary dramatically among alloys and affect their long-term high-temperature properties. For instance, although in the present work the $\delta/\delta_0$ ratio was ~0.44 for binary Ni-Al alloy at 715°C, it can be roughly estimated to be ~0.7 in Ni-14Al-7Cr [13], 0.4 in Rene 88DT [10], and 0.8 in Co-7Al-7W [14] alloys. Therefore, to determine the origin of the $\delta/\delta_0$ ratio, we extrapolated the Gibbs energy of ordered and disordered phases to the interfacial region based on the two-sublattice model. Fig. 7a and b shows the Ni-rich part of a typical phase diagram for Ni-based superalloys and its corresponding hypothetical free energy of ordered and disordered phases at $T_1$ temperature (the actual calculated Gibbs energy for the binary Ni-Al system at 715°C can be found in Fig. 8). The common tangent (dashed line) determines the Gibbs energy of an equilibrium mixture of $\gamma$ and $\gamma'$ phases, and the curves in the highlighted region represent the Gibbs energy of interfacial contents. A point in the interfacial region divides this region into two distinct ordered and disordered parts; this observation implies the dual nature of $\gamma/\gamma'$ interfaces in Ni-based alloys.

In Fig. 7c, the Ni concentration profile across the $\gamma/\gamma'$ interface for the binary Ni-Al alloy was reproduced using the sigmoid description of the concentration profile (equation (12)) and compositional interface parameters (Table 1). Thermodynamic two-sublattice modeling enables calculation of the Gibbs energy of interfacial contents in ordered and disordered states (Fig. 7c).
Fig. 7. Thermodynamic description of the order-disorder $\gamma'/\gamma$ interface. (a) Schematic phase diagram (Ni-rich end) of Ni-based superalloys. (b) Corresponding hypothetical free energy of ordered (green curve) and disordered (red curve) phases at T1 temperature. (c) Ni concentration profile across the $\gamma'/\gamma$ interface (reproduced based on the sigmoid description of compositional gradient) and corresponding calculated Gibbs energy of the ordered and disordered phases for binary Ni-19Al alloy at 715 °C, which indicate the structural $\delta$ and compositional $\beta$ widths of the interface. (d) Predicted site fraction of Ni atoms on first ($y_{Ni}^1$) and second ($y_{Ni}^2$) sublattices as a function position in the interface. (e) Computed Ni concentration in successive lattice planes parallel to the interface, showing alternating Ni-rich and Ni-poor (200) planes in ordered across the $\delta$ width. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Although the Gibbs energy is lower in the ordered phase (to the left of the interface) than in the disordered phase, the right side of the interface lacks a driving force to order the interfacial contents; consequently the long-range order disappears from left to right across the interface. This trend is more apparent in Fig. 7d, which shows the site fraction $y_{Ni}^{(1)}$ of Ni atoms on different sublattices. These results explain clearly why the order-disorder transition zone lies completely within the compositional gradient in all experimental studies, including the current work.

Fig. 7e illustrates the Ni concentration in alternating (002) atomic planes, calculated by taking into account the lattice constant of $\gamma'$ phase and $y_{Ni}^{(2)}$ data. The described sigmoid fitting procedure was used for step-up data of Fig. 7e to find the correct end of order-disorder transition and consequently to calculate the structural width of the interface. The calculated $\delta/\beta$ ratio was ~0.58, which is in fair agreement with the observed value of ~0.44. To investigate the effect of alloying elements on the $\delta/\beta$ ratio of $\gamma'/\gamma$ interface, the interfacial properties of Ni-14Al-7Cr [13] and Co-7Al-7W [14] alloys were also assessed employing the same approach. The compositional gradient across the interface was reproduced based on the sigmoid description of the interface and $\beta$ values reported in previous experimental studies. Using the current thermodynamic modeling, the $\delta/\beta$ ratio was calculated as ~0.64 for ternary Ni-14Al-7Cr at 800 °C and as ~0.78 for Co-7Al-7W alloy at 765 °C (Fig. 9).

Considering the results of previous experimental works [13,14], we see the agreement between model and experiment is reasonably good. The higher $\delta/\beta$ ratio in Ni-14Al-7Cr and Co-7Al-7W alloys (even at higher temperatures) compared to binary Ni-19Al alloy implies better intrinsic capability of these ternary alloys to resist against the high-temperature diffusion-based degradation phenomena. It is important to note that we distinguish between the structural and order-disorder transition widths. However, they are almost the same for Ni-19Al (current work), Co-10Al-5W-2Ta [14], and Rene 88DT [10] alloys. They might be unequal in some cases such as Ni-14Al-7Cr [13] at 800 °C, where the structural transition sharply occurs over a few atomic layers at the disorder end of structural interface width. Therefore, we consider the ordered part of the interface as a structural width, because diffusion throughout this ordered part (not only the order-disorder transition zone) may retard diffusion at high temperatures for precipitate coarsening or diffusional deformation at the interface [56,57].

5.2. Coarsening of ordered precipitates

The effect of $\delta'$ on the coarsening of $\gamma'$-type precipitates (Ni$_3$X, X = Al, Ga, Ge, Si, Ti) in the disordered matrix can be described by the TIDC coarsening theory [5]. According to TIDC formulations, two rate equations describe the growth kinetics

$$r^d - r_0^d = k_7 t$$

(14)

of $\gamma'$-type precipitates, and the depletion


**Fig. 9.** Thermodynamic calculations of the order-disorder $\gamma'/\gamma$ interface for two ternary alloys. (a–c) Ni-14Al-7Cr\(^{[13]}\) alloy at 800 °C. (d–f) Co-7Al-7W\(^{[14]}\) alloy at 765 °C. (a,d) Concentration profiles of alloying elements across the $\gamma'/\gamma$ interface (reproduced considering $\delta$-2.5 nm, reported for Ni-14Al-7Cr\(^{[13]}\) alloy at 800 °C and $\delta$-13 nm, reported for Co-7Al-7W\(^{[14]}\) alloy at 765 °C) and corresponding calculated Gibbs energy of the ordered and disordered phases. (b,e) Predicted site fraction of Ni or Co atoms on first and second sublattices as a function position in the interface. (c,f) Computed Ni or Co concentration in successive lattice planes parallel to the interface, indicating the higher values of Al concentrations in the ordered and disordered phases at different temperatures. (a,d) Calculated Gibbs energy of the ordered (green curves) and disordered (red curves) $\gamma'/\gamma$ phases in Co-7Al-7W alloy were estimated based on the experimental phase equilibria data for Co-Al-W system\(^{[58]}\).

\[
X - X_e = (kTt)^{-1/n},
\]

of solute, where $t$ is time, $r$ is the average radius at time $t$, $r_0$ is the average radius at the onset of coarsening, $X$ is the average concentration of solute in the matrix, $X_e$ is the equilibrium concentration of solute in the matrix, and $k_T$ and $k_F$ are rate constants that contain the thermo-physical parameters of the system. In the initial paper\(^{[5]}\) on TIDC theory, a temporal exponent $n = 2$ for equations\(^{[14]}\) and\(^{[15]}\) led to reasonable agreement with data on the coarsening kinetics of Ni$_3$Al precipitate in Ni-Al alloys, but $n = 2.4$ gave the best results when simultaneously fitting experimental particle size distributions (PSDs) and kinetic data.

At $n = 2$, the rate constants of the TIDC coarsening equations obey relationships of the forms $k_T = (D_1/\delta)$ and $k_F = (D_1/\delta)$ and the average chemical diffusion coefficient $D_1$ in the interface can be calculated after measuring $k_T$ and $k_F$ from extant data as

\[
D_1 = \frac{9}{4} \frac{\Delta X_{\gamma'/\gamma} / \delta}{(k_T k_F)^{1/2}},
\]

where $\Delta X_{\gamma'/\gamma} = X_{\gamma'} - X_{\gamma}$ represents the difference between the Al concentrations in the ordered and disordered phases at thermodynamic equilibrium. Therefore, by substituting $\delta$ for $\delta$ in TIDC coarsening equations, the value of $D_1$ will decrease to $D_0$, which is the slower diffusivity value. For instance, using $D_0/\delta = 1.75 \times 10^{-10}$ m s$^{-1}$ (Table 2 of Ardell and Ozolin\(^{[5]}\)) and considering $\delta/\delta = 0.5$ (as roughly measured in this study), the value of the trans-interface chemical diffusion coefficient decreases from $D_1 = 6.26 \times 10^{-18}$ m$^2$s$^{-1}$ to $D_0 = 3.13 \times 10^{-19}$ m$^2$s$^{-1}$. However this $D_1$ still lies between the reported chemical diffusion coefficient of the matrix ($D_{Ni-Al} = 4.16 \times 10^{-18}$ m$^2$s$^{-1}$) and precipitates ($D_{Ni-\gamma} = 9.71 \times 10^{-20}$ m$^2$s$^{-1}$) phases, but nearer to $D_{Ni-Al}$ than to $D_{Ni-\gamma}$. This result may occur because across $\delta$, the long-range chemical ordering fades from ordered $\gamma'$ to disordered $\gamma'$.

Inasmuch as the non-integer temporal exponent in TIDC coarsening, $n$, satisfying $2 \leq n \leq 3$, best fit the PSDs for $\gamma'$ coarsening in different Ni-based alloys, two possible explanation of time-dependence interface width\(^{[6]}\) and concentration-dependent diffusion through the interface\(^{[9]}\) have been recently successfully explored. In both cases, inserting $\delta$ in TIDC coarsening equations does not change their formulation, so $D_1/\delta = D_0/\delta$ equation again can be obtained. However, this redefinition of parameters increases the realism of TIDC coarsening theory, because the $\delta$ can be predicted and controlled using the current thermodynamic modeling framework. Including of the $\delta$ parameter in TIDC coarsening formulation elucidates the importance of manipulating structural interface width in hindering the coarsening of ordered precipitates.

**Fig. 10.** Changes in structural interface width with increasing the temperature. Calculated Gibbs energy of the ordered (green curves) and disordered (red curves) phases for binary Ni-19Al alloy at different temperatures, showing a decrease in $\delta/\delta$ ratio with increasing the temperature. The compositional width is assumed to be constant at different temperatures. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
5.3. Temperature dependence of the $\delta/\delta$ ratio

Knowledge gained in this study indicates that $\sigma$, $\chi$, and $\delta/\delta$ are three phenomenological parameters, which define the interface characteristics of order-disorder coherent interfaces and thereby can determine the TIDC coarsening behavior of $\gamma'$-strengthened superalloys. The $\delta/\delta$ ratio depends on thermodynamic properties of alloy system and may be different for various alloys. This inference suggests the possibility of designing new alloys with higher $\delta/\delta$ ratio than is currently available, and that therefore have superior high-temperature microstructure stability. To achieve this goal, systematic studies of the effects of alloying elements on the $\delta/\delta$ ratio of Ni- and Co-based superalloys are needed. In this regard, combined thermodynamic modeling and experimental investigations of the interface structure in simple Ni-Al-X systems is a good starting point as a bottom-up approach for further modifications and industrial implementation. However, when the $\delta/\delta$ ratios of different alloys are compared, the effect of temperature should also be considered.

Fig. 10 shows the relationship between the $\delta/\delta$ ratios and the temperature for binary Ni-Al alloy system on the basis of current thermodynamic modeling. To simplify comparison, the compositional width of the interface is assumed to be constant at different temperatures, although we know that the $\gamma/\gamma'$ interfaces are more diffuse at higher temperatures. The $\delta/\delta$ ratio decreases as temperature increases from 427 to 1027°C; this trend can be attributed to the increase in the contribution of entropy, which promotes disordering of the interface. These results are important from three perspectives. First, it implies that temperature rise has two effects on the coarsening rate: it both increases the chemical diffusion of elements and increases the $\delta/\delta$ ratio. Second, it clarifies the importance of cooling rate after aging treatment in order to investigate the interface at room temperature. For instance, it is now possible to interpret the only experimental data that reported almost equal structural and compositional widths [11], because the authors investigated the $\gamma/\gamma'$ interface of DD6 Ni-based superalloy after air cooling. Third, it enables use of the current thermodynamic and structural modeling to predict and control $\delta/\delta$, over different temperature ranges. Coupling of this modeling method with $\delta$ calculation methods provides the opportunity to realistically predict and control $\delta$ and thereby to improve the thermal stability of high-temperature materials.

The influence of $\delta$ on the high-temperature properties of precipitation-hardened alloys may also be important in other diffusion-mediated processes such as stress-induced directional coarsening (rafting), dislocation creep, and diffusional creep deformation at the interface. The latter has been recently purported as a responsible creep mechanism for the formation of grooves and ledges at $\gamma/\gamma'$ interface during tertiary creep mode [12,59,60]. Models [56,57] of the effect of interfacial diffusion on the creep behavior of $\gamma'$-strengthened Ni-based superalloys confirm previous findings and indicate that interface width and, as a result, interfacial diffusion has strong influences on the thermo-mechanical properties of these Ni-based alloys. Therefore, interface engineering by manipulating structural interface width on the basis of the current thermodynamic modeling framework, may be a way to control this creep mechanism. The possibility that tailoring $\delta$ will have a beneficial effect on different diffusion-mediated processes and applying these concepts to improve the mechanical properties of commercial alloys is a topic of future works.

6. Conclusions

The $\gamma/\gamma'$ interface was investigated in a precipitation-hardened Ni-19Al model Ni-based alloy after aging at 715°C, using atom probe tomography to map the compositional gradient in the diffuse $\gamma/\gamma'$ interface. The results indicate the compositional width of ~1.6 nm for (100) $\gamma/\gamma'$ interface that is comparable with the reported value in the literature. A thermodynamic modeling framework was developed to study the thermodynamic aspects of the order-disorder interfaces. To achieve this, we defined $\delta$ parameter as the width of the ordered part of the interface, in addition to $\delta$ as the compositional width. The $\delta/\delta$ ratio was measured as -0.44, using the atomic-resolution HAADF-STEM imaging, for binary Ni-Al at 715°C. The following conclusions can be drawn by combining experiments and thermodynamic modeling:

- The structural interface width $\delta$ of order-disorder interfaces can be successfully predicted based on the current thermodynamic modeling and sigmoid description of composition profile. It is interesting that while the $\delta$ always lies within the compositional gradient width, the $\delta/\delta$ ratio varies significantly in different alloys.
- It was shown that the $\delta$ can be inserted explicitly in the TIDC coarsening formulations of $\gamma'$-types precipices and provides more realistic coarsening parameters. These formulations elucidate the importance of $\delta$' in control of the high-temperature stability of precipitation-hardened alloys.
- The modeling results demonstrate that the $\delta/\delta$ ratio is a temperature-dependent parameter that decreases by increasing the temperature. The value measured for Ni-Al at 715°C was found to be lower than the $\delta/\delta$ ratio for Ni-14Al-7Cr and Co-7Al-7W alloys.
- These results clearly indicate that the behavior of order-disorder interfaces and variation of the $\delta/\delta$ ratio in different temperature ranges can be predicted based on the current approach. The thermodynamic and structural model proposed in this work can serve as a foundation for future modeling efforts to design precipitation-hardened alloys with higher interfacial $\delta/\delta$ ratio and thereby more stable ordered precipitates.

Declarations of interest

None.

Acknowledgements

One of the authors (F.F.) would like to thank Prof. Bo Sundman and Dr. Nathalie Dupin for helpful discussions and valuable comments on thermodynamic modeling of Ni-based alloys and using CALPHAD to determine the missing portion of phase diagrams. This work was partially supported by the Center for International Scientific Studies & Collaboration (CISSC).
Appendix

Table A.1
The relations between the parameters of two sublattice (2SL) and four sublattice (4SL) formalism. These constraints must be satisfied during Gibbs energy minimization to allow the phase to disorder. Detailed descriptions of the constraints and conversions of 4SL to 2SL are available in the work of Dupin and Sundman [23].

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<td>$\delta_{10} - \frac{3}{2} \alpha_{AB} + \frac{3}{2} \alpha_{AC} + \frac{3}{2} \alpha_{BC}$</td>
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<td>$\delta_{12} + \frac{3}{2} \alpha_{AB} - \frac{3}{2} \alpha_{AC} + \frac{3}{2} \alpha_{BC}$</td>
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<td>(8)</td>
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<td>$\delta_{42} - \frac{3}{2} \alpha_{BC}$</td>
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Table A.2
Summary of the bond energies and thermodynamic parameters used in the current thermodynamic modeling (J/mo). Temperature (T) is given in Kelvin.

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Table A.2 (continued)

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